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TRU Drum Corrosion Task Team Report

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Published May 1996

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EXECUTIVE SUMMARY

During routine inspections in March 1996, transuranic (TRU) waste drums stored at the Radioactive Waste Management Complex (RWMC) were found with pinholes and leaking fluid. These drums were overpacked, and further inspection discovered over 200 drums with similar corrosion. The director of Waste Operations assigned a task team to investigate the pinhole phenomenon with four specific objectives:

- To identify any other drums in RWMC TRU storage with pinhole corrosion,
- To evaluate the adequacy of the RWMC inspection process,
- To determine the precise mechanism(s) generating the pinhole drum corrosion, and
- To assess the implications of this event for Waste Isolation Pilot Plant (WIPP) certifiability of waste drums.

The task team investigations analyzed the source of the pinholes to be hydrochloric acid-induced localized pitting corrosion. Hydrochloric acid formation is directly related to the polychlorinated hydrocarbon volatile organic compounds (VOCs) in the waste. Most of the drums showing pinhole corrosion are from Content Code-003 (CC-003) because they contain the highest amounts of polychlorinated VOCs as determined by headspace gas analysis. CC-001 drums represent the only other content code with a significant number of pinhole corrosion drums because their headspace gas VOC content, although significantly less than CC-003, is far greater than that of the other content codes. The exact mechanisms of hydrochloric acid formation could not be determined, but radiolytic and reductive dechlorination and direct reduction of halocarbons were analyzed as the likely operable reactions.

With this information, a task team representing a broad cross-section of operations, programs, compliance, and legal conducted a value engineering process to develop a plan for safely managing pinhole corrosion on TRU waste drums. The team considered the entire range of feasible options, ranked and prioritized the alternatives, and recommended the optimal solution that maximizes protection of worker and public safety while minimizing impacts on RWMC and TRU program operations.

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ACRONYMS

AMWTP	Advanced Mixed Waste Treatment Project
ASB	Air Support Building
C&S	Certified and Segregated
CC	content code
CFR	Code of Federal Regulations
CH	contact-handled
DCTT	Drum Corrosion Task Team
DOE	U.S. Department of Energy
DOT	U.S. Department of Transportation
EDF	Engineering Design File
FTIR	Fourier-transform infrared spectroscopy
GC	gas chromatography
GCMS	gas chromatography-mass spectroscopy
GGTS	Gas Generation Testing System
HCl	hydrogen chloride (hydrochloric acid)
HDPE	high-density polyethylene
IC	ion chromatography
ICP-MS	inductively-coupled plasma-mass spectroscopy
IDC	Item Description Code
IH	Industrial Hygiene
INEL	Idaho National Engineering Laboratory
NDA	nondestructive assay
NDE	nondestructive examination
QA	Quality Assurance
QAPP	Quality Assurance Program Plan
QC	Quality Control
RA	radioassay
RADCON	Radiation Contamination
RAT	rapid analytical test
RCRA	Resource Conservation and Recovery Act
RPCIS	RWMC Portable Container Inspection Station
RTR	Real Time Radiography
RWMC	Radioactive Waste Management Complex

SAP	Sampling Analysis Plan
SAR	Safety Analysis Report
SWB	standard waste box
SWEPP	Stored Waste Examination Pilot Plant
TRAMPAC	TRUPACT-II authorized methods for payload control
TRU	transuranic
TRUPACT	Transuranic Package Transporter
TSD	treatment, storage, and disposal
TSR	Technical Safety Report
UT	ultrasonic testing
VOCs	volatile organic compounds
WAC	waste acceptance criteria
WIPP	Waste Isolation Pilot Plant
WSF	Waste Storage Facility

TRU Drum Corrosion Task Team Report

1. INTRODUCTION

On March 11, 1996, during routine drum-moving operations at the Radioactive Waste Management Complex (RWMC) at the Idaho National Engineering Laboratory (INEL), an operator observed small pin-sized holes, rust spots, and a leaking substance on several 55-gallon drums of contact-handled (CH) transuranic (TRU) waste. The drums were being moved from air support buildings into Resource Conservation and Recovery Act (RCRA) Type II-permitted storage modules. The liquid exuding from some of the pinholes tested acidic pH by litmus paper. The majority of the drums contained waste stream Item Description Code (IDC)-003, or Content Code (CC)-003 wastes. These are chlorinated organic wastes such as degreasing agents, lathe coolant, and hydraulic oil. Management and radiation control personnel were alerted. No associated radioactive contamination was detected from any of the drums. All pinhole corrosion drums were overpacked into 83-gallon high-density polyethylene (HDPE)-lined drums.

This discovery initiated a comprehensive technical investigation to identify any other drums in RWMC TRU storage with pinhole corrosion, any characteristics unique to that drum population, the precise mechanism generating the pinhole corrosion, the possibility of pinhole drum-related radioactive contamination, and the adequacy of the drum inspection process.

J. A. VanVliet, INEL Waste Operations Manager, directed K. E. Kooda, Waste Technology Planning and Projects, to form and lead the TRU Drum Corrosion Task Team (DCTT) to conduct the investigation and report the findings. D. P. Zeek was assigned as the technical leader.

As part of the technical investigation, task teams conducted chemical, structural, visual, radioassay, Real Time Radiography (RTR), headspace gas sampling, ultrasonic, theoretical, process, and historical analyses on the drums exhibiting pinhole corrosion, as well as representative drums likely to develop symptoms in the future, to determine the mechanism triggering the pinhole corrosion. A full description of the various analyses, results, and mechanisms for the most probable cause is presented in Section 2.2.

A task team representing personnel with extensive experience from RWMC Operations, the TRU Waste Program, Industrial Hygiene, RWMC Compliance, Radiation Contamination (RADCON), the Stored Waste Examination Pilot Plant (SWEPP), Waste Isolation Pilot Plant (WIPP) requirements, Systems Engineering, Legal, and Project Management conducted a value engineering process to manage pinhole corrosion on drums. Using process knowledge and data from the technical investigation, the team developed a range of scenarios to address the drum pinhole corrosion problem. Each scenario was evaluated for process effectiveness, cost, compliance with the Settlement Agreement with the U.S. Department of Energy (DOE) on Spent Nuclear Fuel (known as the Governor's Agreement), RCRA and other permit compliance, WIPP shipping and waste acceptance considerations, waste retrieval schedule and strategies, employee health and safety, and liability. The team ranked and prioritized the alternatives, and crafted a pinhole drum corrosion management plan that defines a path forward; identifies potential

operational impacts, both short- and long-term; meets compliance commitments; addresses associated risks; and allows incorporation of future data as it is developed. (Section 4 presents the evaluation of the alternative scenarios; Section 5 presents the optimized present and future plan to manage drums with pinhole corrosion at the RWMC.)

During the value engineering process, the team identified significant constraints that will impact *any* plan to manage pinhole drum corrosion at the INEL. Section 3 identifies these constraints in detail.

1.1 Background

The 1992 Consent Order, signed between the State of Idaho and the Department of Energy, stipulates that mixed waste (radioactively-contaminated and hazardous per RCRA definition) stored at the RWMC must be moved to RCRA-compliant storage. Seven fully-permitted Waste Storage Facility (WSF) Type II Storage Modules were built to accommodate this waste, and mixed waste is being moved from the older air-support buildings into these storage modules. Configuration of the waste inside the modules will allow easier inspection of the waste containers. Weekly drum inspections are required under RCRA per Title 40 Code of Federal Regulations (CFR) 270.14 (b)(5).

On March 11, 1996, during the routine weekly container inspection in Air Support Building (ASB)-II, Quality Assurance (QA) personnel observed four drums of TRU waste (Content Code-003, organic setups, oil solids) with rust stains, primarily on the upper one-third of the drums. Closer visual inspection revealed pin-sized holes at the rust spots, with small amounts of liquid exuding from some of the pinholes. No release of radioactive materials was detected. RTR analysis, completed on March 12, 1996, detected no internal liquids.^a

A container with a pinhole (or any deterioration caused by corrosion) is considered by RCRA to be breached, and must be managed per RCRA. Any hazardous constituents coming out of holes must be managed as hazardous waste per the "derived-from rule" (40 CFR 261.3 (c)(2)(I). Regulations under 40 CFR 265.171 state that any breached container holding hazardous waste must be transferred to another container in good condition. The four drums with pinhole corrosion were overpacked into protective U.S. Department of Transportation (DOT) Type 7A UN1A2 83-gal containers, corrosion-resistant, with rotomolded high-density polyethylene lining.

This drum pinhole corrosion event spurred an RWMC investigation to determine if previous similar pinhole corrosion had been observed, and the extent of the current problem. Records disclosed three previous incidents with similar characteristics.

^aLetter from F. P. Hughes to Distribution, "Transmittal of the Radioactive Waste Management Complex (RWMC) Container Integrity Issue Meeting Minutes" - FPH-141-96, April 11, 1996.

In June 1992, viscous material was found under a sludge drum, and the drum was overpacked. No radiological contamination was detected.

In May 1994, a yellow, viscous material was found under a Content Code-001 drum (first-stage sludge). The drum was overpacked; no radiological contamination was detected.^b

In October 1995, paint bubbles with yellow viscous material were found on top of a precertified Content Code-801 (solidified organics) drum. Litmus testing detected a pH between 1 and 0.5. Sample analysis indicated Fe, Cl, and Ca in the liquids.^b

With this information, the investigation expanded to determine how many other TRU drums in storage exhibited the characteristics of pinhole corrosion, and to develop a strategy to predict possible future occurrences.^a

Typical Solidified Organic Waste Packaging Methods After 1972

R96 0209

^bSWEPP Operations logbook.

1.2 Strategy

The objectives of the TRU Drum Corrosion Task Team were:

- To plan and conduct a series of tests to determine the mechanism creating the pinhole corrosion in TRU drums
- To assess the current RWMC TRU drum inspection process and to recommend improvements, short- and long-term, where appropriate
- To develop a management plan for operations that assures detection of pinhole-corroded drums, anticipates future corrosion events, assures mitigation for safe storage or transport, addresses all permit and compliance issues, considers WIPP certifiability, and assures continued health and safety of workers and the environment.

This report presents the Task Team activities, findings, conclusions, and the plans to move forward.

2. FINDINGS

The discovery of Radioactive Waste Management Complex (RWMC) contact-handled (CH) transuranic (TRU) storage drums with pinhole corrosion in March 1996 initiated a comprehensive technical investigation to determine the adequacy of the drum inspection process, the number of drums in RWMC TRU storage with pinhole corrosion, any characteristics unique to that drum population, the precise mechanism generating the pinhole corrosion, and the possibility of pinhole drum-related radioactive contamination. The findings are summarized below.

2.1 Adequacy of the RWMC Drum Inspection Process

Maintaining waste container integrity is essential for any safe and compliant waste management strategy. Title 40 Code of Federal Regulations (CFR) 265.170 through 177 specify precise requirements for managing waste containers. The pinhole drum corrosion discovery prompted the review of the inspection process to accommodate the new information.

A task team was assembled to evaluate the adequacy of the current Stored Waste Examination Pilot Plant (SWEPP) TRU waste container integrity inspection process for drums stored at the RWMC. Through a value engineering process, the team identified short- and long-term impacts of the TRU waste examination, storage, and disposal program. A list of recommendations for process improvement was developed, and it was generally agreed that these process refinements would be beneficial to the TRU waste examination, storage, and disposal program regardless of what plan was chosen to manage the incidence of pinhole drum corrosion.

Any RWMC drum integrity determination process must address the unanticipated future degradation of containers, ensure the safety of workers and the environment, ensure compliance with the Resource Conservation and Recovery Act (RCRA) Part B permit requirements, support meeting the Waste Isolation Pilot Plant (WIPP) waste acceptance criteria (WAC), meet terms of the Governor's Agreement, meet the commitments in the Consent Order, and assure that containers meet Department of Transportation Type A transportation requirements. That is, there are *many* and *potentially incompatible* criteria for RWMC TRU drum integrity.

The categories within the inspection process identified for refinements to augment current techniques include:

- Improve the facility workstation environment (immediate)
- Upgrade inspection techniques and equipment (longer-term)
- Compare waste stream databases for common indicators
- Initiate immediate improved short-term inspection techniques
- Involve all inspection personnel in process evaluations

- Conduct a human factors evaluation for maximum efficiency (methods analysis)
- Increase management involvement in the inspection process
- Challenge the inspection criteria where appropriate (a management issue).

Specific actions that can be accomplished in the short-term include:

- Improve training and operations aids -- provide posters/color photos of actual pinhole drum corrosion at each workstation
- Post container integrity requirements at each workstation
- Increase time spent on actual visual inspection
- Conduct periodic inspector group sessions to review inspection results
- Require two operators during actual visual inspection (synergistic interaction)
- Place the computer terminal nearer the RWMC Portable Container Inspection Station (RPCIS) inspection point
- Evaluate waste streams to anticipate problem drums warranting increased scrutiny
- Increase management awareness of the precise inspection process for informed support of process improvements
- Increase and improve Quality Assurance (QA) and Quality Control (QC)
- Provide improved lighting at inspection stations
- Validate inspection techniques
- Apply a leak-indicator material on drums for early detection
- Establish minimum data input requirements for visual inspection results (software refinement)
- Review the Real Time Radiography (RTR) inspection for possible use as an augmenting technique.

Additional activities that would support improved container integrity include:

- Inspect drum vents for proper operation

- Update Engineering Design File (EDF)-705 “Waste Container Integrity Evaluation for Storage” to describe pinhole characteristics
- Have technical experts review available nondestructive examination (NDE)/nondestructive assay (NDA) inspection techniques and equipment to augment the process
- Catalogue external drum characteristics.

Management issues include:

- Reconsider Transuranic Package Transporter (TRUPACT) authorization to accommodate 83-gal overpack drums
- Challenge the WIPP WAC requirement for demonstrating compliance with Type A requirements
- Review Waste Storage Facility (WSF) criteria in the Technical Safety Report (TSR) for inclusion of pinhole knowledge.

2.2 Mechanism Creating Pinhole Drum Corrosion

The method to identify the drum integrity failure mechanism was to examine and test corroded drums, sample and analyze corroded drums, analyze possible failure mechanisms, and gather and interpret database information.

2.2.1 Examining and Testing Drums

Pinhole corroded drums were examined and tested using visual examination, photographs, litmus paper for pH, x-ray real-time radiography, neutron radioassay (RA) and ultrasonic testing (UT).

Visual examinations were used to characterize the observed failure mechanism. Thirty-one drums were visually examined; 14 of the visual exams were documented with photographs. The 31 drums were sorted by content code for the absence or presence of pinholes, as listed in Table 2-1.

An internal visual drum inspection was attempted using a 6-mm fiber optic video camera, with limited success. The 6-mm probe could not be maneuvered to the outer wall of the drum interior due to the close tolerances between the drum lid and the 90-mil polyethylene liner.

2.2.2 Visual Characteristics of Pinhole Corroded Drums

A few drums had unbroken, roughly circular paint blisters of 2-cm or smaller diameter.

These were located on otherwise pristine areas of clean, painted drum surface, or next to many other broken paint blisters. In most cases, the corrosion appeared as dried, rust-colored streaks emanating from broken paint blisters over pinholes about 2 mm in diameter or smaller. The metal surface under recently-broken paint blisters appeared fresh, with little to no corrosion; the metal surface under older, broken paint blisters exhibited severe surface corrosion (see photos on pages 2-5, 2-7, and 2-9).

The combination of unbroken paint blisters on otherwise pristine drum areas and a fresh metal surface under recently broken blisters indicates that the corrosion originated inside the drum (not outside as generally theorized for drum corrosion).

Table 2-1. Visual examination of 31 drums sorted by content code.

Visual Observation	Item Description Code (IDC)								Totals
	001	003	004	007	336	440	480	481	
Pinholes	0	21	1	1	1	0	0	0	24
No Pinholes	1	1	0	0	0	2	1	1	7
Totals	1	22	1	1	1	2	1	1	31

The drum pinholes appeared predominantly on the sides of the drum above the second roll ring, i.e., the upper one-third of the drum (see Figure 2-1). Some drums had pinholes on the drum lid, and even fewer drums had pinholes on the mid-height region between the bottom two roll rings: still fewer drums had pinholes on the bottom-third sides or on the bottom.

Operations personnel determined pH levels with litmus paper on the wet, rust-colored streaks and broken paint blisters. The pH levels ranged from 0 to 3, indicating that the rust-colored fluid was highly acidic when wet.

X-ray RTR of several IDC-003 drums revealed Type II 90-mil rigid high-density polyethylene (HDPE) liners (see Figure 2-2) and a single polyethylene waste bag inside the liner. As Figure 2-2 illustrates, the liner has a 'milk bottle' shape, where the liner shoulder forms just above the second drum roll ring, also observed by RTR. The drum region above the second roll ring corresponds to the internal drum headspace between the rigid liner and the drum.

RTR is capable of detecting pinholes on the drum and any liquids inside the drum. Liquids were observed inside a few Content Code-003 pinhole corrosion drums, mostly between the waste bag and the rigid drum liner. In one drum, RTR examination revealed small pinholes after visual inspection of the drum had revealed none. Upon further examination of the drum (barcode 021919, IDC-003) by the designated technical lead, he reported readily observable small paint blisters, but without associated rust-colored streaks. However, it required the trained RTR operator to identify faint white spots on the RTR display as small pinholes.

P96 0233

Figure 2-1. Schematic of TRU waste drum.

Figure 2-2. Type II storage liner schematic.

Neutron RA of a sample of these drums determined that they had little to no fissile material content, as expected. Hand-held UT was performed on two pinhole corrosion drums (IDC-003, barcodes 0212919 & 030949). The first drum was the same drum that exhibited small pinholes with RTR. The second drum had numerous pinholes with associated rust-colored streaks. The one-half-inch diameter probe distinguished no differences in drum wall thickness around or directly over pinholes.

2.3 Pinhole Corrosion Drum Sampling and Analysis

Two liquid samples were collected. A small sample (~5 microliters) was collected from three Content Code-003 drums (barcodes 029696, 029716 and 029748). Due to the small sample volume, only anion analysis by ion chromatography (IC) was performed.^a It detected a strong chloride presence, with a trace (four orders of magnitude lower) of nitrate. The second liquid sample was also from a Content Code-003 drum (barcode 029757). Cation analysis by inductively-coupled plasma-mass spectroscopy (ICP-MS) showed a high iron and sodium content, with some boron. Anion analysis by IC also identified a strong chloride presence.

An atypical solid sample was collected from the bottom of a Content Code-001 drum (barcode 030099), and separated into chunky white solids and darker granular solids for analysis. Cation analysis by ICP-MS showed sodium, iron and some boron for both solids. X-ray diffraction analysis showed that both solids were primarily sodium nitrate, with possible sodium borate hydrates. The white chunky solid also contained sodium silicate, and the dark granular solid had a small amount of goethite [FeO(OH)]. These solids could be related to clay absorbent, which consists of alumina silicates.

Gas samples were collected from the headspace of a number of drums. Gas chromatography (GC) was used to determine the volume concentration of hydrogen, methane, alcohols and ketones. Gas chromatography-mass spectroscopy (GCMS) was used to determine the volume concentration of volatile organic compounds (VOCs) such as carbon tetrachloride, chloroform, methylene chloride, trichloroethene, trichloroethane, toluene, trichlorotrifluoroethane (Freon), etc.^b These analyses detected little hydrogen or methane in any of the drums, and indicated that the Content Code-003 pinhole corrosion drums were high in VOCs and contained some acetone. Additional analysis for hydrogen chloride (HCl) by silver chloride titration was inconclusive. It was suspected that any HCl would interact with the stainless steel of the gas sample canisters. A gas sample from a Content Code-003 pinhole corrosion drum (barcode 029757) was collected in a plastic bag and analyzed by silver chloride titration; the response was positive for HCl.

Additional Content Code-003 pinhole corrosion drum headspace gas sample analyses

^aICPP Analytical Laboratory conducted the liquid, solid, and HCl gas sample analyses.

^bThe Environmental Chemistry Laboratory conducted the GC and GCMS gas sample analyses.

with another MS system and by Fourier-transform infrared (FTIR) spectroscopy showed limited success. The Gas Generation Testing System (GGTS)-MS analysis^c of a sample from a stainless steel canister showed a small HCl response. FTIR analyses^d of samples from both stainless steel canisters and plastic bags did not detect HCl, but did yield results similar to those by GCMS for the VOCs. The FTIR system was unable to detect HCl directly introduced into the system because it operates at 110°C with stainless steel.

Headspace gas was also tested with chromatographic tubes for HCl and moisture responses.^e Headspace gas was drawn through the drum vent and the chromatographic tubes via a teflon fitting with the aid of a calibrated pump. The tubes have a graduated scale in ppmv and contain a substance that changes color in response to HCl for one type of tube and in response to moisture for another type of tube. The previously-described gas sampling and analyses used gas samples collected with the aid of a needle through the filter and into the headspace of the drum, and therefore did not have to pass through the drum filter. A correction factor for barometric pressure via the ideal gas law was applied to the responses to calculate the volume concentration in ppmv. No correction factor for temperature was applied, although a physical effect is suspected. Tests performed in a heated building showed higher responses, in general, than did those in unheated buildings. Tube tests for HCl are summarized in Table 2-2 and Figure 2-3.¹⁻⁴ Positive HCl responses were observed primarily in Content Code-003 drums, and the greatest proportion of these, as in the overall testing, were seen in drums with pinholes. The moisture-sensitive chromatographic tubes indicated the presence of moisture or water vapor in the few drums tested at levels near or slightly higher than that of the ambient air.^{4,5}

Table 2-2. Summary of tube tests for the presence of HCl.

Chromatographic Tube Tests	IDC													Total
	001	003	004	007	336	337	339	374	440	442	480	481	900	
Total tested	9	17	1	1	2	5	3	1	4	1	1	1	1	47
Pinhole drums	1	7	1	0	1	0	0	0	0	0	0	0	0	10
Positive HCl	1	7	0		1									9
Negative HCl	0	0	1		0									1
No pinhole drums	8	10	0	1	1	5	3	1	4	1	1	1	1	37
Positive HCl	2	7		0	0	0	0	0	0	0	0	0	0	9
Negative HCl	6	3		1	1	5	3	1	4	1	1	1	1	28

^c J. E. Owens and C. R. Edinborough conducted the GGTS-MS testing. J. E. Owens, W. F. Bauer and D. L. Miller analyzed the GGTS-MS results.

^d W. F. Bauer conducted the FTIR analyses.

^e J. G. Jolley and K. J. Galloway conducted the chromatographic tube testing.

2.4 Pinhole Drum Corrosion Failure Mechanism Analysis

Calculations were conducted for radiolytic dechlorination, analysis of possible corrosion mechanisms, and analysis of pitting corrosion as the mechanism in pinhole formation. The precise mechanism(s) for HCl formation cannot be determined without further experimentation.

Calculations for radiolytic dechlorination were performed using a conservatively-assumed gas generation rate for chloride from the Content Code-003 waste.⁶ This yielded calculated pHs similar to those measured by litmus paper for time periods ranging from 1 to 6 years. The actual gas generation rate is likely lower than that conservatively assumed. Therefore, the time period required to reach the appropriate pHs would also be longer. This analysis is not refuted by the current problem because most of the accessible Content Code-003 drums have package dates ranging from 1980 through 1983.

A literature review was conducted for analysis on possible corrosion mechanisms (see Appendix A). Due to the limited evaluation period, only the readily-available literature was reviewed, but the analyst concluded that no further significant understanding (neither content nor accuracy) would be achieved without fairly extensive experimentation. Topics for literature review were adsorption phenomena on iron surfaces, corrosion mechanisms, electrochemical reactions, and halocarbon interactions with reducing agents.

2.5 Hypothesis

A four-phase process hypothesis was developed for the observed pinhole corrosion. In the first phase, the inner drum surface is partially corroded in fabrication. The surface corrosion consists of a mixture of iron oxides and hydrated iron oxides with intermittent surface discontinuities. In the second phase, water, oxygen, halocarbons and hydrochloric acid attack the exposed iron and oxo-iron surfaces at discontinuities and other areas such as stress points. This attack results in localized corrosion, the formation of soluble corrosion by-products, and corrosion products that can participate in further corrosive reactions. The third phase involves several reactions directly causing corrosion or generating corrosive by-products. The number of reactions and the vigor in which they proceed increase dramatically. The fourth phase represents pit penetration into the drum wall, and continues until it penetrates the entire drum wall thickness and blisters the exterior paint.

The reactions suspected as initially operable in the CH-TRU waste drums (second phase) are: radiolysis, direct reduction of halocarbons, and reductive dehalogenation. A number of other possible reactions were investigated, but they were deemed not as likely as the above three reactions. All the reactions investigated are well-documented and quite real, but their rates and competitiveness with other reactions cannot be predicted with any certainty.

Finally, pitting corrosion was analyzed as the source of the drum pinhole formation (see Section 2-4). Pitting is localized corrosion of a metal surface, confined to a point or small area, taking the form of cavities. The pitting process initiates changes in the internal chemistry of the pit as compared to the bulk solution chemistry such that pitting corrosion rates can be orders of

magnitude higher than the general corrosion rate. The analyst concluded that photographs of the leaking drums showed pitting corrosion that initiated on the drum interior. Also, the chemical analysis of the corrosion product identified aggressive anions and acidic pH, which is characteristic of active pitting corrosion.

2.6 Database Analysis

Information from a few databases was examined to determine any correlations with the overpacked pinhole corrosion drums. The examined databases contain information from waste generators, container inspections, drum venting, and headspace gas analysis. The overwhelming majority of overpacked pinhole corrosion drums contain organic setups, designated as Content Code-003 (or IDC-003). The only other significant number of pinhole corrosion drums was in Content Code-001, the inorganic sludge waste. Table 2-3 lists drums overpacked from March 11, 1996, through May 17, 1996. The headspace gas analysis data for limited numbers of drums (without pinholes) in each content code showed that Content Code-003s had high amounts of VOCs. Content code-001 drums also had amounts of selected VOCs significantly higher than other content codes but significantly lower than the amounts for the selected VOCs in Content Code-003.

One must note that there is an element of fallibility in the container inspection database comment field requesting the reason for a drum overpack. The operators' comments were not always consistent for a certain type of defect such as pinhole corrosion. For instance, comments such as 'acid,' 'acid drum,' 'drum has pinholes,' and 'possible acid,' were all used for pinhole corrosion drums. The references to 'acid' were used after the leaking fluid was determined acidic by litmus paper. It is not known whether pinhole corrosion drums were seen or were overpacked using other ambiguous comments such as 'rust' prior to March 11, 1996. With the current awareness, the operators have been sensitized to the characteristics of pinhole corrosion, and the more recent container inspection comments use words such as 'pinhole corrosion.' The comment 'liquid between liner and drum' is entered for a drum based on the RTR examination. When such a drum goes through the container inspection system, it is automatically flagged for overpacking and no further comment (input) on container condition is permitted for the operators. There is a considerable number (at least 76) of Content Code-003 drums overpacked with this comment. It is highly probable that a fair percentage of these have pinhole corrosion, but there is no way to count these as pinhole corrosion drums short of opening overpacks and inspecting drums. The number of pinhole corrosion drums in Table 2-3 was determined by counting drums in the database noting either 'acid' or 'hole' in their comment field.

When lists of overpacked drums were compiled, a large portion of the drums had package dates from 1980 through 1983. There was suspicion that the drum pinhole corrosion problem was related to something that happened in this time frame. The analysis on the database showed that there was no correlation to the package date. Most of the overpacked pinhole corrosion drums had package dates from 1980 through 1983 because most of the accessible drums from content codes that exhibited this problem are from this same time frame. The only database field to show a correlation to the overpacked pinhole corrosion drums, other than the high VOC levels in the Content Codes-003 and -001 headspace gas data, was 'matrix category.' This field simply

Table 2-3. Summary of drums overpacked from March 11, 1996, through May 17, 1996.

Content Code	Pinhole Drums	Other Drums	Total Overpacks
0	0	1	1
1	43	63	106
2	2	7	9
3	215	95	310
4	7	4	11
7	3	11	14
292	1	3	4
300	2	3	5
303	0	1	1
320	1	1	2
330	1	30	31
335	0	2	2
336	4	36	40
337	9	13	22
338	0	2	2
339	1	3	4
371	0	2	2
374	3	3	6
376	3	0	3
393	1	0	1
432	0	2	2
440	6	5	11
441	1	1	2
442	6	4	10
480	4	8	12
481	3	1	4
800	0	1	1
801	0	2	2
807	0	4	4
822	0	1	1
900	0	1	1
960	0	5	5
Totals	316	315	631

contains a code representing absorbed organic liquids for the overpacked pinhole corrosion drums. This is reasonable because the absorbed organic liquids are the VOCs.

2.7 Conclusions

- The pinholes are localized pitting corrosion caused by hydrochloric acid, which occurs predominately in the headspace of the drums.

- Hydrochloric acid formation is directly related to the polychlorinated hydrocarbon volatile organic compounds (VOCs) in the waste.
- Most of the pinhole/pitting corrosion drums are from Content Code-003 (IDC-003) because they contain the highest amount of polychlorinated VOCs as determined by headspace gas analysis. Content Code-001 (IDC-001) drums are the only other content code with a significant number of pinhole corrosion drums because their headspace gas VOC content, although significantly lower than that of Content Code-003, is still far greater than that of the other content codes.
- The exact mechanism(s) of hydrochloric acid formation could not be determined, but radiolytic and reductive dechlorination and direct reduction of halocarbons were analyzed as the likely operable reactions.

Identifying the precise pinhole drum mechanism(s) further would require extensive experimentation and yield marginal benefits. The drums can be managed sufficiently knowing that the event corresponds directly to the VOC content of the waste.

Specific activities, however, will contribute useful data to the ongoing pinhole drum corrosion solution.

- Chromatographic tube testing should be developed as a tool to identify potential problem drums.
- A preemptory plan of action for boxes could avert a similar problem. Currently, there is no equivalent overpack for boxes corresponding to the HDPE-lined 83-gal overpack for drums.
- The current standard for reporting off-normal events is at the point of origin, in the field, through verbal communication only. Valuable information could be retained by sensitizing operations personnel to document what, when, where, the extent, and by whom, and avoid later backtracking.
- Database design should incorporate the users' needs as well as the owner/operator concerns (as is being designed into the integrated information management system). When RTR examination indicates 'liquid between liner and drum,' the container inspection database (RWMC Portable Container Inspection System-RPCIS) should require comment in the container condition data field.
- Before a valid correlation analysis could be performed, multiple listings of drums in the database were deleted or modified. Several comment fields lead drums to be listed more than once. The RPCIS database should be modified to eliminate multiple-listed drums.

2.8 References

(Letters are included in Appendix C to this report)

1. J. G. Jolley and K. J. Galloway letter to D. P. Zeek and M. J. Sherick, Vapor Phase HCl Concentration Data for Over Packed Drums, JGJ-18-96, April 29, 1996.
2. J. G. Jolley and K. J. Galloway letter to D. P. Zeek and M. J. Sherick, Vapor Phase HCl Concentration Data for Over Packed Drums, JGJ-19-96, April 29, 1996.
3. J. G. Jolley and K. J. Galloway letter to D. P. Zeek and M. J. Sherick, Vapor Phase HCl Concentration Data for Over Packed Drums, JGJ-20-96, April 29, 1996.
4. J. G. Jolley and K. J. Galloway letter to D. P. Zeek and M. J. Sherick, Vapor Phase HCl and Water Concentration Data for Drums, JGJ-22-96, May 13, 1996.
5. J. G. Jolley and K. J. Galloway letter to D. P. Zeek and M. J. Sherick, Vapor Phase Water Concentration Data for Drums, JGJ-21-96, May 1, 1996.
6. B. J. Mincher letter to K. E. Kooda, HCl Generation Calculations, BJM-08-96, April 25, 1996.

3. CURRENT RWMC OPERATING CONSTRAINTS ON PINHOLE-CORRODED DRUM MANAGEMENT

Any strategy to manage containers with pinholes must accomodate all of the operating constraints on the Radioactive Waste Management Complex (RWMC) and the Waste Storage Facility (WSF). These constraints are mandated by the U.S. Code of Federal Regulations (CFRs); U.S. Department of Energy (DOE) Orders; the State of Idaho permits; Treatment, Storage, and Disposal (TSD) operating permits; and the Waste Isolation Pilot Plant (WIPP) waste acceptance criteria (WAC) and Quality Assurance Program Plan (QAPP), to list only some. The "best" management plan for these containers will be the one that provides for maximum public protection (minimizing the real threat to public safety) and minimal impacts on the existing RWMC operating constraints. It is essential to understand the complexity of the operating restrictions placed on the facility before the management plan can be developed. Following is a brief description of the major operating constraints currently in place at the RWMC and the WSF.

- Notice of Noncompliance Consent Order dated April 1992 in which the State of Idaho requires movement of ALL waste containers from the Certified and Segregated (C&S) and Air Support Building (ASB)-II buildings by January 1, 1998.
 - Non-negotiable requirements mandate the schedule
- RWMC Hazardous Waste Management Act (HWMA) Resource Conservation and Recovery Act (RCRA) permit, which details:
 - Container segregation requirements
 - Container stacking requirements
 - Container inspection/monitoring requirements
 - Container integrity requirements
 - WSF operational requirements
- RWMC WSF Safety Analysis Report (SAR) provides the safety basis for operations and:
 - Specifies fissile material management requirements
 - Requires verification of container physical integrity
 - Specifies waste container inventory limits
 - Specifies waste container physical configuration
- WIPP WAC/QAPP/TRAMPAC specifies the configuration of waste destined for WIPP; in particular:
 - TRUPACT does not accommodate 83-gal overpacks
 - WIPP must approve standard waste box (SWB) load configurations
 - WIPP WAC and QAPP are "moving targets" (continuously modified)
 - Varied and potentially incompatible criteria for drum integrity

- Settlement Agreement with the Department of Energy on Spent Nuclear Fuel (the "Governor's Agreement")
 - The first TRU waste must be shipped out of the State of Idaho by April 30, 1999
 - 15,000 drum-equivalents of TRU waste must be shipped out of the State of Idaho by Dec 31, 2002
 - A three-year running average of 2000 m³/yr of TRU waste must be shipped out of the State of Idaho after January 1, 2003

The ultimate and overarching operational constraint is the need to provide a safe working environment for the RWMC employees, where hazards are immediately identified and mitigated.

It is within this context that the TRU Drum Corrosion Task Team constructed a functional container management plan. The team prioritized and weighted each of the constraints on operations (Table 4-5). It is important to note that no single management solution would satisfy all the constraints that bear on this issue. There is no "conservative" or "safe" management plan; all solutions require tradeoffs and a balancing of impacts. The recommended management plan is most accurately characterized as the "optimal" rather than the "best" solution.

4. EVALUATION OF PINHOLE DRUM CORROSION MANAGEMENT OPTIONS

4.1 Method

Information from the specialized investigations was compiled and used to formulate management strategies for the corroded drums, as recounted below.

The Radioactive Waste Management Complex (RWMC) transuranic (TRU) drum inspection process was assessed through value engineering techniques, and a set of cost-effective revisions and process improvements were developed to aggressively detect drums with pinhole corrosion, to incorporate drum headspace sampling analyses for improved data gathering, and to correlate waste stream characteristics to anticipate future drum corrosion.

Specialized task teams conducted extensive chemical, structural, visual, radioassay, Real Time Radiography (RTR), headspace gas sampling, ultrasonic, theoretical, process, and historical analyses to determine the precise pinhole drum corrosion population, the unique characteristics, any possible radioactive contamination, and the corrosion mechanism (or a combination of possible mechanisms). As presented in Section 2, analyses indicate that the most likely mechanism is radiolytic and reductive dechlorination resulting from polychlorinated hydrocarbon volatile organic compounds (VOCs) in the waste form (primarily organic sludges) reacting with moisture in the headspace between the drum and poly liner. This action creates hydrogen chloride (HCl) in the headspace, which corrodes the upper one-third of the steel drum from the inside-out, eventually creating exterior pinholes, paint blisters, and rust.

With this information, a task team representing personnel with extensive experience from RWMC Operations, the TRU Waste Program, Industrial Hygiene, RWMC Compliance, Radiation Contamination (RADCON), the Stored Waste Examination Pilot Plant (SWEPP), Waste Isolation Pilot Plant (WIPP) requirements, Systems Engineering, Legal, and Project Management conducted a value engineering process to develop solutions for safely managing pinhole corrosion on drums.

The team goal was to develop a plan to manage RWMC TRU drums with pinhole corrosion, immediately and over the RWMC storage life of the drums. Objectives were to identify potential operational impacts, short- and long-term, and to identify potential impacts to WIPP certifiability for the affected waste streams. The technique was to develop alternative management scenarios and attendant consequences, and to evaluate and prioritize the alternatives.

Using process knowledge and data from the technical investigation, the team developed a range of scenarios to address the drum pinhole corrosion problem. Each scenario was evaluated for process effectiveness; cost; compliance with the Consent Order on RWMC drum storage, the Settlement Agreement with the Department of Energy on Spent Nuclear Fuel (the Governor's Agreement), the Resource Conservation and Recovery Act (RCRA), and other permits; WIPP shipping and waste acceptance considerations; waste retrieval schedule and strategies; employee

health and safety; and liability.

The team ranked and prioritized the alternatives, and crafted a pinhole drum corrosion management plan that defines a path forward; identifies potential operational and regulatory impacts, both short- and long-term; meets compliance commitments; addresses associated risks; and allows incorporation of future data as it is developed. The team also identified additional technical issues awaiting resolution.

4.2 Operational and Regulatory Impacts

The team acknowledged that there is a considerable range of possible impacts for *any* plan to manage the corroded drums. They include the following:

- Drum inspection (improvements)
- Permits (changes)
- Compliance commitments, including the Governor's Agreement, the Consent Order, and current permits
- Budget
- Resources, including staffing, facilities, and equipment
- Schedule
- Interpretations of mitigation versus treatment
- Employee health and safety
- Retrieval from waste storage
- Certification for WIPP
- Revised Safety Analysis Report (SAR) (RWMC and Waste Storage Facility)
- State's perception of the Idaho National Engineering Laboratory's ability to manage waste
- Workers' perceptions of the safety and health risks
- Personal and company liability

The team conducted a paired comparison analysis of these areas of impact in order to mathematically apply them in evaluating the management scenarios. For purposes of evaluation,

selected impact areas (personnel safety and the SAR) were eliminated because they were accommodated equally (they were equally important) in all scenarios.

4.3 Assumptions

Drawing on technical and operations process understanding, the team clarified a set of working assumptions used to conduct evaluations and make decisions for any pinhole drum corrosion management plan.

- Pinhole drum corrosion is caused from a vapor-phased chloride mechanism.
- HCl is detected in a very high percentage of pinhole drums identified to date.
- High levels of chlorinated VOCs are present in pinhole drums with corrosion.
- All identified pinhole corrosion could be detected visually.
- No radioactive contamination has been detected on the pinhole corrosion areas.
- Pinholes are not restricted to mechanically-vented drums. (There was one pinhole drum without a mechanical vent, Content Code-801.)
- Every drum in storage can possibly contain moisture.
- Production operations to characterize containers for shipment to WIPP will begin July 1997.
- WIPP will open on schedule.
- The Advanced Mixed Waste Treatment Project will begin operation in 2002.

4.4 Development and Evaluation of the Management Options

Initially, in order to establish the extreme parameters for the solution, the team composed eight scenarios for managing the pinhole drum corrosion problem. The range of alternatives spanned a continuum from essentially continuing as is, i.e., overpack pinhole-corroded drums as they are found (with the improved inspection process recommended by the task team), estimated at approximately 1,100 containers, to overpacking all content code drums with high chlorinated VOCs (approximately 11,000-12,000 containers).

Four management scenarios were refined from the original eight. The four are described below, including a pro-con analysis for each scenario (see Tables 4-1 through 4-4).

4.4.1 Management Scenario #1

Proceed essentially with the current process:

- Overpack drums with pinholes when identified
- Do not increase inspections
- Implement improved visual inspection process, and training and management involvement (included in all scenarios)
- No rework
- Continue to characterize and overpack drums after establishing certifiability, as scheduled

Table 4-1. Analysis of Management Scenario #1.

PRO	CON
- Meets the Consent Order	- Increased fines/liability over container integrity issues
- Meets the schedule for the Governor's Agreement	- No method to detect leakers; no method to predict leakers
- Meets the <i>current</i> requirements of the RCRA Part B permit	- Potential for rework/contamination in the out-years
- Meets the baseline budget (without inspection improvements)	- Could call into question the entire dense-pack storage strategy
- Does not force early retrieval	- State may perceive a RCRA violation, lowering State confidence in INEL processes
	- May not appear sufficiently aggressive; may be politically unpopular

4.4.2 Management Scenario #2

Current process with the following modifications:

Use quantitative verification for drums going to the storage modules (WSF)

- Determine the presence of HCl in the headspace with a rapid analytical test (RAT)
- 3-5 min. for each drum
- Develop and conduct a sampling plan for suspect content codes in the storage modules by sampling drums before transfer into the storage modules.
- No rework unless driven by sampling results
- Modify segregation and storage requirement for high HCl drums to allow increased inspection

Table 4-2. Analysis of Management Scenario #2.

PRO	CON
- Can meet terms of the Consent Order	- Requires a RCRA Part B permit notification/modification
- Enhances the probability of meeting the Governor's Agreement	- Requires more resources (SWEPP technicians)
- Reduces potential risk of radiation contamination	- Decreased throughput at inspection
- Reduces the risk of fines/liabilities	- More complicated
- Requires fewer overpacks than Options #3 and #4	- Potential for change in stacking configuration in storage module
- Makes more drums certifiable for WIPP	
- Least likely option to force early retrieval	
- Minimizes rework	
- Less likely to impact modified densepack storage configuration	
- Politically acceptable to stakeholders	
- Good public relations	

4.4.3 Management Scenario #3

Current process **plus** overpack **all** Content Code-003 only (2,643 drums above-ground)

- Implement improved visual inspection process, training, and management involvement
- No additional analysis for Content Code-003
- Use quantitative verification for other high-risk drums (a statistical sample of those drums remaining in the C&S and ASB-II)

Table 4-3. Analysis of Management Scenario #3:

PRO	CON
- Meets the Consent Order	- Requires significantly more resources
- Meets current RCRA Part B permit	- Increases facility radiation exposure (rework)
- Reduces rad and HCl releases	- Requires significantly more budget (\$1M minimum)
- Reduces the risks of fines/penalties	- Must start retrieval early
- Increases State confidence in INEL processes	- Puts Governor's Agreement commitments at risk
- Sufficiently aggressive; politically acceptable to stakeholders	- Increases inspection time for reconfiguration
	- Sets a questionable precedent with the State (may require commensurate action on future problems)
	- Does not address potential corrosion issues for other waste streams (i.e., CC-001)

4.4.4 Management Scenario #4

Current process **plus:**

- Overpack all content code drums with high VOCs
 - Includes Content Codes 1, 2, 3, 336, 337, 339, 801, and 900
 - Totals approximately 11,000-12,000 drums
- Implement improved visual inspection process, training, and management involvement

Table 4-4. Analysis of Management Scenario #4.

PRO	CON
- Low regulatory risk	- Significantly increased costs (\$4M minimum)
- Increased State confidence in INEL processes	- Requires early retrieval
- Reduced risk of fines/penalties	- Additional storage modules required to support early retrieval
- Decreased risk of radiological release in the out-years	- Does not meet commitments of the Governor's Agreement
- Politically acceptable to stakeholders	- May jeopardize the Consent Order
- Perceived as an aggressive approach; good public relations	- Increases facility radiation exposure (rework)

Table 4-5 illustrates the Scenario Evaluation Matrix. Each scenario was rated against the individual impacts, where the lowest impact = 1 and the highest impact = 10. The scenario with the lowest total is considered the most favorable (least impact) on operations and regulatory requirements.

Section 5 describes the TRU drum pinhole corrosion management plan developed around Scenario #2, judged to be the optimal choice considering overall impact and acceptability within the operating constraints that prevail for any RWMC drum management plan, as explained in Section 3.

Table 4-5. Scenario evaluation matrix.

Rating 1-10

1 = Lowest Impact

10 = Highest Impact

Impact	Wt	Option 1	Option 2	Option 3	Option 4
Personnel Safety	20	5 100	5 100	5 100	5 100
Consent Order Liability	17	2 34	3 51	5 85	9 153
Personal/Company Liability (Container Integrity)	17	10 170	7 119	3 51	1 17
SAR - Public Safety	17	3 51	2 34	5 85	8 136
RCRA Part B Permit (endangers densepack configuration)	16	9 144	6 96	3 48	1 16
Consent Order	12	1 12	2 24	3 36	6 72
Budget	5	1 5	2 10	5 25	10 50
Governor's Agreement	4	3 12	1 4	5 20	10 40
Resources	3	1 3	2 6	5 15	10 30
Retrieval	2	2 4	2 4	5 10	10 20
Schedule	2	3 6	4 8	7 10	10 20
WIPP Certifiability	2	3 6	1 2	5 10	10 20
State Confidence	0	8 0	3 0	5 0	1 0
TOTAL		547	458	495	674

Option #1: As documented in letter to the State.

Option #2 Use quantitative verification for HCl; sample suspect drums.

Option #3: Overpack all Content Code-003; use quantitative verification for other high-risk drums.

Option #4 Overpack all content code drums with high chlorinated VOCs.

5. PINHOLE DRUM MANAGEMENT PLAN

The Transuranic (TRU) Drum Corrosion Task Team selected Scenario #2, the Rapid Analytical Test, as the optimal management plan for pinhole-corroded containers. This scenario had the minimum impact on existing Radioactive Waste Management Complex (RWMC) operating constraints and met all of the significant concerns for public and employee safety. Figure 5-1 illustrates the process flow of this scenario. The process incorporates three significant modifications to the existing drum movement process to anticipate and test headspace gas for hydrogen chloride (HCl) levels in selected content codes. Candidate drums for pinhole corrosion will then be identified and segregated as appropriate.

The first change will require operators to conduct a rapid analytical test for headspace HCl as a indicator of potential drum pinhole corrosion. The test (now being finalized) will use Dreager Colorimetric tubes for a 3-5 minute go/no-go test on each drum entering inspection. The test will be implemented by a sampling analysis plan (SAP) to confirm the relationship between HCl in the headspace and the formation of pinholes. The test will distinguish those drums with a high probability of developing pinholes and allow aggressive management of those drums. The SAP will apply to the container inventory still in the Certified and Segregated (C&S) and Air Support Building (ASB)-II buildings and provide data to support the continued use of the modified densepack storage configuration in the Waste Storage Facility (WSF) for containers without high HCl levels. Drums with Content Codes-001 and -003 should be 100% tested until a statistically-significant database is created for evaluation. The SAP will determine the number of other containers from each waste population requiring sample analyses.

The second major change will be revision of Engineering Design File (EDF)-705, "Waste Container Integrity Evaluation for Storage," the drum inspection procedure used to verify container integrity. The EDF will be modified to require overpacking of any drum posing an immediate threat (i.e., a leaker or a drum with a pinhole) prior to the end of shift. This change will address the Resource Conservation and Recovery Act (RCRA) concerns of imminent threat to health and public safety. The remainder of the EDF-705 inspection will evaluate the drum's suitability for storage in the WSF. In any case, a drum which fails EDF-705 **MUST BE OVERPACKED PRIOR TO SHIPMENT TO THE WSF** (per Safety Analysis Report requirement). If SWEPP capacity is available and if TRU programs can develop a Waste Isolation Pilot Plant (WIPP)-acceptable method to assemble a load in standard waste boxes, the drums failing EDF-705 could be overpacked into standard waste boxes (SWBs), shipped to the WSF, and be available for transport to WIPP.

The third major change is that drums high in HCl and assumed to have a high potential for developing pinholes but pass the EDF-705 criteria will be shipped to the WSF and segregated into a configuration that allows more complete and frequent inspection from the isles (i.e., 4x4x2). This modification will support meeting the Consent Order milestone and allow greater vigilance on those containers suspected of developing pinholes.

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Figure 5-1. Recommended Pinhole Drum Corrosion Management Plan "Rapid Analytical Testing."

The rapid analytical testing and modified segregation requirements will be limited to those containers in the C&S and ASB-II until sampling results indicate a need to alter the present management strategy. Any rework in the WSF to reconfigure specific content codes should be carefully weighed against the additional required worker radiation exposure.

Implementing the Rapid Analytical Test management plan will aggressively manage those drums with the highest potential for developing pinholes while maintaining the largest possible population of drums available for shipment to WIPP. This plan supports the Consent Order, the RCRA permit, and the Governor's Agreement, and maintains employee and public safety.

6. CONCLUSIONS

The Task Team has completed its objectives of identifying the mechanism and developing the optimal management plan for the pinhole containers. A significant amount of work still remains to bring the plan to fruition. These tasks include:

- Finalize the exact HCl test and procedures for use in conducting the rapid analytical test.
- Develop the Sampling Analysis Plan to specify the exact number and content codes of the drums needed to produce a statistically significant database.
- Continue the Waste Isolation Pilot Plant (WIPP) sampling program to fully characterize sludge drums.
- Revise Engineering Design File (EDF)-705 to select imminent threat drums for immediate overpacking and to allow for segregation of high HCl drums in the WSF.
- Revise the Radioactive Waste Management Complex (RWMC) Waste Storage Facility (WSF) Configuration Management Plan to implement the modified waste process flow.

It is important to note that the management of these containers is new scope and will require additional funding to implement the plan. The optimal plan was developed with due consideration of the funding and resource limitations and is the lowest-cost option.

APPENDIX A
Literature Review

INTERDEPARTMENTAL COMMUNICATION

Date: May 13, 1996

To: D. P. Zeek MS 2424 6-7728

From: S. K. Janikowski *SKJ* MS 2208 6-0265

Subject: LETTER REPORT CONCERNING CORROSION IN RWMC WASTE
DRUMS, SKJ-48-96

A summary of the literature review I conducted, evaluating the role of halocarbons in corrosive degradation of the RWMC waste drums, is contained in the enclosed letter report. The literature does not indicate an exclusive mechanism for the observed corrosion but does provide a wealth of information describing all of the reactions that will proceed under the conditions reported inside the drums. The report is my assessment of which reactions are important, and how they contribute to the observed corrosion.

A more complete description could be generated from evaluating additional literature since there is substantially more information available. I do believe, however, that no significant increase in content or accuracy could be achieved in the general description provided, the description of the mechanism of corrosion, or in your ability to predict reaction/corrosion rates unless some fairly extensive experimentation were involved. From our past conversations, it is my understanding that you do not want to get that involved, but rather, you would like to know if there is a way to stop the corrosion that is occurring or prevent new corrosion from occurring in drums that are not currently compromised.

There are several conceivable actions that you could take to change the situation. The viability of these actions is, of course, up to your discretion, based upon cost, timeliness, suitability, regulatory compliance, etc. The situation could be changed by: 1) slowing the corrosion reactions, 2) repairing the containers, 3) transferring the contents, or 4) providing additional containment.

Slowing the corrosion reactions can be achieved by three potentially suitable means. First, the drums could be evacuated periodically to remove halocarbons, HCl, water, hydrogen, and oxygen, then back-filled with an inert gas. Under these conditions, the corrosion would still occur, but would likely not be as extensive nor localized. Second, the drums could be evacuated and filled with an active material to corrode sacrificially. This would be a lower maintenance method to retard further degradation of the drums. Third, the drums could be evacuated and then filled with a solidifying, non-permeable plastic to provide a protective barrier on the inside of the drums.

D. P. Zeek
May 13, 1996
SKJ-48-96
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If you need additional material or clarification of that already provided, please contact me at your convenience. What's more, if you want to conduct any experiments to further elucidate some aspects of the corrosion, or if you would like assistance in evaluating some of the analytical data in your possession, please feel free to contact me.

I appreciate the opportunity to have worked with you and hope that my contribution is valuable to the successful completion of this program.

Enclosures:
As Stated (1)

cc: C. A. Allen, MS 2208
D. A. Miller, MS 2208
S. K. Janikowski Letter File

CORROSION OF RWMC WASTE DRUMS: LITERATURE REPORT

revised and submitted by Stuart K. Janikowski
May 16, 1996

This letter report summarizes my literature investigation of the possible reactions of iron and halocarbons in stored waste containers at the RWMC. The emphasis is on reactions which lead to corrosion of the steel drums, support observations of the drum conditions, are consistent with drum contents and head gas analyses, and not on those reactions causing the formation of other products. No experiments were conducted, and due to the short evaluation period and limited quantitative data in the literature that is directly transferable, no exact mechanism for the corrosion, nor prediction of the corrosion rate is presented. Rather, a brief overview of the literature searched is presented up front; followed by a phenomenological description of the most likely mechanism for the observed corrosion in the body of this letter, and finally a description of suspect corrosion causing reactions is presented in the attachments.

Several journal articles, Federal publications, and books were reviewed and provide the basis for the description of corrosion presented in the body of this report. No source of experimental data, replicating the conditions of the RWMC waste drums, was found, and therefore, the contents herein are somewhat speculative. The reactions presented are well documented and very real, but their rates and competitiveness with other reactions are impossible to predict with any certainty.

The literature review covered several relevant topics. They are presented briefly before going on to the description of corrosion in the RWMC waste drums. Generally the phenomena described were obtained from studies conducted in aqueous environments.

Adsorption Phenomena On Iron Surfaces: Two reviews in the literature were consulted for presenting a realistic perspective on the interactions of water with iron surfaces,¹ and halogen adsorption phenomena on iron surfaces.² These reviews provide the theoretical and experimental foundation for presenting several reactions listed in the Attachments. Essentially, they describe the 1) mechanisms of adsorption of the respective compounds on iron surfaces, followed by 2) mechanisms of dissociation (homolytic radical formation as well as ion formation) and recombination, and 3) mechanisms for oxidation of the iron surfaces by water, air, or halocarbons.

Corrosion Mechanisms: The mechanism of iron oxidation,³ the nature and composition of oxo-iron layers,^{3,4,5} and physical⁶ and mathematical⁷ models describing pitting corrosion were reviewed. The model has oxygen and water adsorbing onto the iron surface, whereafter, a limited number of reaction occurs creating an ordered oxo-iron (hydroxylated) surface. The mechanism involves direct reduction of water and oxygen by the iron or can be described more fully by the more complex mechanism of anodic dissolution and passivation.⁸ The role of

anions in pitting^{9,10,11} is more fully described in other references.¹² The role of anions in various environments is also described in great detail^{13,14,15} and also in the presence of various inhibitors.^{16,17} Other articles of interest dealt with general mechanisms for reduction at metal surfaces¹⁸ and corrosion performance of various materials in nuclear environments.¹⁹

Electrochemical Reactions: The various electrochemical half-cell reactions and standard potentials were obtained in some instance from articles, but primarily from the CRC Handbook.²⁰ The thermodynamic equations were taken from a standard textbook.²¹

Halocarbon Interactions With Reducing Agents: The remaining articles reviewed, dealt specifically with dehalogenation reactions under various conditions. The bulk were relatively recent and examined reactions of halocarbons with various environmental reductants,²² or under anaerobic conditions,²³ including various environments containing elemental iron.²⁴⁻²⁸ Other articles dealt with the kinetics and mechanism²⁹ involved for a variety of metals.^{30, 31} Reductive electrolytic conditions were also examined as a means to elucidate simple mechanisms for simple systems³² and complex reactions with soils and clay.³³

The last set of articles reviewed had particular information relative to materials commonly present in DOE wastes. The article³⁴ examines the transformations of carbon tetrachloride in the presence of hydrochloric acid and hydrogen sulfide over sheet silicate minerals containing small amounts of oxidized iron. This is of particular interest since the reaction mixture and conditions are similar to those inside the RWMC waste drums. Although not specifically analyzed for, H₂S and sulfide species are likely compounds in the waste drums since sulfur and other hetero-atomic species are frequently part of hydraulic oils, cutting fluids, and lubricants. These compounds decompose with use and are readily degraded under the radiolytic conditions inside the drums. If sulfur is in fact present in the drums, the mechanism for corrosion will be even more complex than what is presented in this letter. In any event, it appears that the silicate minerals behave as catalytic surfaces for halocarbon transformations.

Last, a report³⁵ issued by Rocky Flats in 1976 demonstrates that halocarbons in the presence of radionuclides undergo multiple reactions in the absence of iron. The types of products and product distributions appear to be heavily dependent on the initial halocarbon present and not on the source of ionizing radiation. Of particular interest is the fact that significant amounts of hydrogen are generated in the reactions. This presumably is the result of radiation induced homolytic dissociation to produce reactive free radical hydrogen atom intermediates, followed by recombination of the radicals to produce hydrogen gas. The same radiation induced reactions will occur with halocarbons to yield reactive free radical halides that can recombine with hydrogen radicals to produce hydrochloric acid. The study did not analyze for HCl, however, the likelihood of its presence is overwhelming.

Phenomenological Description Of Corrosion In RWMC Waste Drums

Overview

The RWMC waste drums are fabricated from low alloy steels and are naturally susceptible to corrosion under relatively mild environmental conditions. I have seen no evidence in the literature to indicate that the presence of halocarbons alone will cause the extent of corrosion observed. However, the presence of oxygen, water, and ionizing radiation are sufficient to cause the observed corrosion. These other factors, plus the presence of halocarbons, can create an environment that is highly corrosive to low alloy steels and produces the observed mixture of products identified in drum samples.

The complexity and specific mechanism of the corrosion is far too sophisticated to extract from the literature or determine experimentally in a short period of time. However, enough is known about the corrosion of iron and interactions between iron and halocarbons to piece together a reasonable scenario.

It is assumed that the waste drums contain carbon tetrachloride, trichloroethane, polyvinyl chloride (PVC), other halocarbons, oils, greases, drying agents, and calcium silicate as intentional contents. [NOTE: The hazardous components of wastes are typically singled out as the main source of problems during all stages of processing, treatment, and storage, while seemingly inert materials used as filler or for containment are assumed to play a passive role in the chemistry of the bulk. This isn't so for most organic based materials in the presence of ionizing radiation. A significant component in this study is the source of hydrogen, which must be available for acid generation and for reductive dehalogenation to occur. It is also necessary for catalytic dehalogenation to occur, which becomes more favorable as hydrogen concentration increases. The presence of hydrogen in the drums indicates that a hydrogen source (other than water) is being continually acted upon to release hydrogen, because hydrogen leaks through the smallest of openings and can further escape the drums through quantum mechanical tunneling. PVC, where present with radiation sources, will be a source of mobile hydrogen and chlorine. The radiolytic decomposition of PVC can double the pressure inside a drum and result in greater than 50% hydrogen composition of the head gas.³⁵ Other "inert" materials will have a similar effect. Plexiglas®, polyethylene, oils, etc. lead to similar hydrogen compositions in the headgas over radioactive materials.] Oxygen and water are also present. Some of these chemicals are volatile and will establish equilibrium within the drum, thereby being exposed to the drum surface. Others of these are non-volatile, but may decompose radiolytically to produce hydrogen, hydrochloric acid, carbon monoxide, and various substituted halocarbons. These, in turn, are volatile and will reach an equilibrium distribution throughout the drums, thereby also contacting the drum. The combination of these chemicals and the known reactions they undergo are more than sufficient to explain the observed corrosion, and reasonably inclusive so that no other source of corrosion need be suspect.

I believe the corrosion leading to the pin-holes and ultimate containment failure occurs through four progressive phases. They are described briefly here, and in more detail in the following section. In the first phase, the drum is partially

corroded in the normal fabrication process, and also made susceptible to further corrosion through the same process. The surface corrosion is a mixture of iron oxides and hydrated iron oxides with discontinuities in chemical environments intermittent over the entire surface. This layer is very thin and may not be observable to the unaided eye. In the second phase, water, oxygen, halocarbons, and hydrochloric acid directly attack the exposed iron and oxo-iron surface at discontinuities and other areas susceptible to attack. Other areas may include physical stress points in the drum, or areas subject to changing temperatures or moisture. This attack results in localized corrosion, the formation of soluble corrosion by-products, and corrosion products that can participate in further harmful reactions. Visible blemishes appear on the inside surface of the drum walls. The third phase involves several reactions directly causing corrosion or generating corrosive by-products. The number of reactions and the vigor at which they proceed increases dramatically. Large pits and areas of deep corrosion penetration into the iron drum walls becomes evident. The hygroscopic corrosion products begin to absorb water, creating a better localized environment for the production and concentration of hydrochloric acid. This latter situation further escalates the corrosion. The fourth phase is relatively unexciting without much new going on. Rather it reflects a steady-state situation within the "pits" where the reactions becomes rate limited at each site because of limited mass transfer of corrosion products away from the corrosion front. The corrosion continues virtually unnoticed until it has penetrated the entire thickness of the drum wall and causes the exterior paint to blister.

Phenomenological Description

Phase I:

The steel drums develop a mill scale covering of hydrated iron oxides while they are being fabricated. This scale serves to protect the underlying iron from aggressive attack by other chemicals by providing a barrier shield. The mill scale does not completely close off the iron surface from attack, however, because it has three primary falabilities.

- 1) First, the oxo-iron scale is less dense than the underlying iron and therefore only covers a portion of the surface, allowing aggressive chemicals to access the iron through cavities, cracks, and channels. Furthermore, as the oxo-iron layer thickens, the compounds tend to further oxidize, dry out, and expand, resulting in less adherent "rust" coatings that fall away from the surface and expose the underlying iron.
- 2) Second, the scale has interruptions, anomalies, and other discontinuities that change the chemical potential of the iron surface in different regions, i.e., the iron becomes a low voltage battery. The relatively large surface covered by the scale behaves as the cathode, while the small exposed regions around the discontinuities behave as anodes. Oxidative attack at the anode can be quite intense since it has a relatively small size when compared to the cathode. The large amount of oxygen reaching the large cathodic area will usually permit fairly high currents to flow if coupled with a similarly unrestricted anode. In the specific case of a large cathodic iron surface with several small anodic

sites, the current will be concentrated at the small anodic sites, and severe pitting will occur.

3) Third, the oxo-iron species are susceptible to oxygen displacement by other anions; whose reactions occur in the solid state as well as when contacted by a liquid. Chloride, for example, will displace oxygen in oxo-iron compounds, with two deleterious effects.

- i) Iron chlorides are more soluble than oxo-iron species so they are easily washed away from the surface; leaving exposed iron to react.
- ii) The crystal lattice of iron chlorides, originating from oxygen displacement from oxo-iron compounds, has major defects because of displacing divalent O^{2-} from the lattice and replacing it with mono-valent Cl^{-1} . The lattice becomes porous and permeable, and facilitates the inward migration of chloride ions and other disruptive species, while also facilitating the outward migration of oxygen ions. The cumulative effect is a thickening corrosion layer in which the front moves progressively deeper into the basis metal and will not stop.

Phase II:

Considering these falabilities of an iron surface, it does not require a very aggressive environment to induce further corrosion, or to continue its propagation.

There are several reactions that are likely to initiate the corrosion of waste drums. Some representative examples of various reactions are shown below.

1) Direct reduction of halocarbons on exposed iron surfaces.

2) Surface oxo-iron degradation resulting from attack on the surface oxo-iron species by hydrochloric acid. The HCl was initially formed from radiolysis reactions between the radionuclides and halocarbons present in the waste forms, or through free radical recombinations on the iron surface. The iron chloride species are soluble products that are washed away from the immediate area, leaving exposed iron to further corrode. (Examples shown)

3) Reductive dehalogenation on exposed iron surfaces.

4) Aerobic oxidation of the iron.

5) Acid assisted aerobic oxidation of the iron.

There is no way of telling which reactions are most involved in the early or late stages of initiating the corrosion, however, I suspect that Rxs 7, 9, 29, and 18 are largely operable in the early stages, while Rxs 33, 5, and 17 are responsible for the accelerated corrosion leading into Phase III. Further explanation is offered below.

[Explanation: If the corrosion inside the drums was both local and active, the onset of exterior blisters would occur within weeks or months after packing. This means that the corrosion occurring is both uniform and slow, initially. Rx 7 will occur readily over active iron surfaces and even through a thin mill scale. It is not highly aggressive, nor will it contribute to thick corrosion deposits. It does result in salt formation over the drum surface, however, but is not further active in degrading the metal. When the salt becomes wet, it becomes an active electrolyte and will create conditions that promote further corrosion. I assume that initially the water inside the drums is bound by the drying agents and silicates, thereby holding the environment to one in which localized aggressive corrosion is minimal. The effects of Rx 7 are consequential, although seemingly not very destructive to the drum. The net affect is to change the thickness and composition of the scale over much of the drum surface, thereby creating stress in the scale (which causes fractures and openings) and differing surface potentials, i.e., the surface becomes a stronger battery.

Rx 9 begins as soon as the contents are placed together and continues at a relatively constant rate until all of the hydrocarbon reactants are consumed. The product ($\text{Cl}_3\text{C}-\text{CHCl}_2$) shown is probably a minor one, but illustrates one mechanism of HCl formation. The point is that all hydrocarbons subject to ionizing radiation generate hydrogen, quite conclusively, through the recombination of free radical intermediates. The major products observed are H_2 , CO_2 & CO (when oxygen is also present), and low molecular weight hydrocarbons. In past studies, HCl was not observed because it was either not analyzed for, or because it has high adsorptivity on many surfaces, e.g., iron, silicates, drying agents, etc., and does not maintain a significant vapor pressure in the presence of suitable surfaces. The fact clearly remains, however, that HCl will be formed in these reactions. Its affect on corrosion will not be immediate, however, because it is generated in the interior of the wastes where most of it will be adsorbed, and only a small amount will migrate out to interact with the drum. Even then, the attack will not be very aggressive in the absence of water, which is similarly

bound up in the interior of the waste or being formed slowly on the drum surface. The net effect is this: Early stages - HCl is formed via Rx 9 at an appreciable rate, but appears to be of little consequence. Later - HCl is still formed at a rate close to initial, but achieves breakthrough. Now the drum "sees" a sudden upsurge in HCl, whereby the HCl starts reacting with the iron. The HCl begins to react with the iron, corrosion products, water, etc., and targets anodic sites. Hence, localized corrosion begins. The formation of HCl through this mechanism is not to be considered as important in the early stages only, rather, it is important in the early stages and throughout the corrosion process. In latter stages, there are so many competing reactions that radiolysis to form HCl appears to be of lesser importance, but it is not.

Rx 29 is similar to Rx 7 in that it requires a reasonably clean surface, i.e., active iron surface, thin mill scale, etc., to occur. The reaction does not occur on iron oxides and there are no other obvious surfaces in the drum contents that would host this reaction. The reaction will occur over most of the drum surface with very little initial preference for sites. Halogens are known to adsorb onto iron surfaces in concentrations as high as 9×10^{14} atoms/cm², under ambient conditions (ref. 2 and references cited within). The adsorption/homolytic dissociation is known to clean surfaces, activate surfaces, preserve active surfaces, promote surface transport phenomena, etc., as well as create conditions suitable for recombination with other radicals. Most studies showing high adsorptivity have been conducted under gaseous conditions with other studies conducted under aqueous conditions indicating lower halogen adsorption and differences in the preferred reactions. The bottom line description is this: In the early stages (or history of the drum), the iron surfaces are relatively dry and have only a thin scale. These are the "best" conditions that will ever be realized in the drum for Rx 29 to occur. The reaction will occur, but I can't estimate its rate. For a period of time preceding the build-up of corrosion products and scale in the drum, the rate is likely to increase as localized corrosion begins to take place. The likelihood is due to the increasing potential differences developing between anodic and cathodic sites on the drum. The changing conditions within the drum will, however, cause this reaction to decrease in rate as the scale thickens and as water and other species compete for available adsorption sites. The reaction will continue indefinitely, but with ever decreasing rate.

Rx 18 is the reaction responsible for creating the initial mill scale. Atmospheric oxygen and water readily attack exposed iron and cause a thin semi-permeable scale to develop. Under mild conditions, the scale will thwart deep corrosion and flaky less adherent "rust" deposits. Under wet conditions with no restrictions to atmospheric oxygen, however, this reaction will cause the complete consumption of iron in a relatively short time (weeks to months). After the initial formation of the scale, the reaction proceeds only slowly over the average surface of the drum, yet will become quite aggressive at freshly exposed iron in developing cracks. The reaction will ultimately decrease in rate as the drum atmosphere becomes more reducing, i.e., as hydrogen builds up, or when acid concentrations become sufficient to promote the more aggressive competing reaction, Rx 17.

Rx 33 is a common metathesis reaction that involves simple replacement of oxo-hydroxy ions from iron. The reaction proceeds readily at room temperature and

yields soluble iron compounds that are easily washed away. The reaction under room temperature is the basis for pickling steel prior to electroplating and cleaning metals prior to etching or soldering. It is necessarily not a reaction that can proceed during the early stages of corrosion since no appreciable amount of acid is present at that time. Yet when acid and water are present, the reaction is quite facile.

Rx 5 (reductive dehalogenation) occurs readily in aqueous environments. There is considerable data in the literature to demonstrate that the reaction proceeds at an appreciable rate. The kinetic studies²⁹ I've seen, however, stop short of expressing the rate. Rather they assert that iron is a "good" reductant, the reaction is pseudo-first order in halocarbon, and they present data showing active reductive dehalogenation occurring in solutions containing halocarbon passed over iron metal. They further conclude that the apparent reaction is reductive dehalogenation of the halocarbon accompanied by oxidative dissolution of the iron.

Rx 17 is commonly known as the most facile method to dissolve iron. In fact, the only way to dissolve iron more quickly is to replace the HCl with an oxidizing acid. I could find no data in the literature indicating the actual rate of this reaction, however, without any doubt, this reaction will have the highest rate and contribute more to the corrosion than any other reaction occurring in the drums.]

Phase III:

Once active corrosion sites have become established in Phase II, the number of corrosion products creates an environment that facilitates further corrosion. The corrosion products have relatively lower density and provide easy access for corrosive agents through their bulk to the iron surface. Many of the corrosion products are hygroscopic and absorb moisture and acid out of the atmosphere and concentrate them in the area of the corrosion. Reactions between the corrosion products and the water and acid transform the original corrosion products into soluble compounds that migrate away from the iron/corrosion interface. This latter phenomenon occurs largely because of concentration gradients within the developing pit. By the same mechanism, concentration gradients facilitate the transport of oxygen, halocarbons, acid, and water into the pit and up against the exposed iron surface.

Special attention to Rx 33 should provide insight into what appears to be a catalytic transport mechanism, although no such term has ever been coined. The reaction:

proceeds from left-to-right as written, in the interior of the corrosion pit, solubilizing the rust (FeO(OH)) and facilitating its transport to the outer surface of the corrosion. However, once the FeCl₃ has reached the outer surface of the pit, the environment around it changes. The FeCl₃ is now in a relatively drier environment surrounded by other oxo-iron compounds, including hydroxides. This environment initiates the reverse of reaction 33, generating rust on the

corrosion surface while releasing 3HCl's to migrate back into the depths of the pit. This mechanism of facilitated transport becomes operable in this phase and lasts through the duration of the corrosion.

The reactions prevalent during the latter stages of Phase II remain active in phase III. Additional reactions (too many to mention, and not all of them known) occur also, however, the most prevalent ones are those that produce or release HCl, and those corrosion reactions using HCl.

[Explanation: The determination for assertions made in the above paragraph are based upon the belief that Rx 17 (aerobic, acid, iron oxidation) is the reaction primarily responsible for the localized, deep penetrating corrosion observed in the drums. Although Rx 17 consumes HCl, and therefore should result in a decreased rate of corrosion, it remains the most widely known iron corrosion reaction, it has the highest conceivable rate for reaction of those possible, and is the most commonly accepted means of corrosion for iron. The fact that the "soup" released through paint blisters is highly acidic provides basis for asserting that HCl is continually being generated.]

Phase IV:

Phase IV isn't so much distinct from Phase III in the nature of the reactions occurring. Rather it is the phase of corrosion where steady state conditions prevail and the corrosion front moves through the iron at a more-or-less constant rate. Again, those reactions over the entirety of the drum producing HCl and those consuming HCl within the corrosion pit are the most important.

[Explanation: In the earlier phases of corrosion, several reactions are occurring at competitive overall rates, i.e., the specific rates differ, but the overall effect of the different rates is insignificant. This is due in part to the fact that the corrosion occurring in the early stages is dispersed over the entire drum surface and does not compromise the drum significantly. The rate of corrosion is really only significant when it becomes localized. There is a period of time (in phase III) where localized corrosion becomes noticeable. There are many competing reactions occurring at the site and the corrosion rate is dependent upon the supply of reactants to the site and on the individual reaction rates. Once the localized site builds a sufficient covering of corrosion by-products and scale, the rates of the individual reactions decrease in importance because they are faster than the rate of transport. At this point (phase IV), the corrosion of concern (in the pits) is rate limited by transport phenomena inside the pit and not the actual rates of the respective reactions occurring in the pits. Other reactions occurring on the drum surface, and the atmospheric conditions inside the drum affect the corrosion insofar as to provide reactants to the pit, but are not the actual corrosion reactions of interest.]

The steady state conditions and the reactions operable under those conditions, proceed until the corrosion front meets the paint barrier. At this point, the forward progress of the corrosive "solution" stops and the solution begins to etch a path between the paint and the iron, radially. The lower density (expansive) corrosion products build up bulk in the path of the radially moving corrosion

front, all the while drawing water, acid, and oxygen into close proximity to the front. The build-up of material causes the paint to blister. The corrosion will continue in this manner until some condition changes. Frequently, the paint blister will burst and release the "soupy" corroding mixture to flow down the side of the drum. Once the water, acid, and salts (good electrolyte medium) are removed from the corrosion front, the rate of corrosion drops to a significantly lower level. It will not stop, however, because acidic and hygroscopic salt residues remain in the corroded area, and are capable of continuing the dynamics already discussed.

ATTACHMENT 1

Halocarbon Reactions

The following nine (9) reactions of halocarbons are possible in the environment inside the RWMC waste containers. R represents an organic group or hydrogen. All of the reactions directly cause corrosion, or produce other agents that are corrosive to iron. All of the reactions are possible, and proceed to some degree, however, I suspect that only three of the 9 listed reactions proceed with an appreciable rate. Specifically, Rx's 5, 7, and 9 represent those most likely to occur; or will occur to a degree overwhelming other competing reactions.

- 1) Nucleophilic Substitution: by water, hydroxide, or other nucleophiles.

Example: alkyl chloride with base or water to yield an alcohol and chloride or hydrochloric acid, respectively. [Note: This reaction is not likely to occur under the ambient temperatures experienced in the drums, or on the solid hydroxide surfaces of the rust. Laboratory reactions require reflux to achieve an appreciable rate.]

- 2) Dehydrohalogenation (or β -elimination): base catalyzed.

Example: 1,1,1-trichloroethane with base to yield 1,1-dichloroethene and hydrochloric acid. [Conditions for this reaction are very suitable, since they usually require heat under aqueous conditions, or metals more active than iron in organic solvents under ambient temperatures.]

- 3) Gem Elimination (or α -elimination): strong base required.

Example: chloroform with an alkoxide to yield a reactive carbene, alcohol, and chloride ion. [This reaction requires a base stronger than hydroxide and the presence of a metal more active than iron.]

- 4) Reductive Elimination (vicinal dehalogenation): active metal required.

Example: tetrachloroethane with active metal to yield dichloroethene and metal chloride. [Usually reflux conditions and the presence of a metal more active than iron are required to promote this reaction.]

- 5) Reductive Dehalogenation.

Example: Carbon tetrachloride with active metal to yield chloroform and metal chloride. [Literature sources indicate that this reaction is responsible for most of the halocarbon conversion observed in aerated aqueous solutions. The reaction is pH dependent and proceeds at measurable rates, even when conducted over short experimental times.]

6) Catalytic Reductive Dehalogenation.

Example: Carbon tetrachloride on a catalytic surface to yield chloroform and hydrochloric acid. [This reaction usually requires a noble or precious metal catalyst (from the iron group) and an over-pressure of hydrogen to proceed measurably at temperatures well above ambient. To my knowledge, this reaction has never been observed on iron.]

7) Direct Reduction.

Example: Carbon tetrachloride on an iron surface (in the presence of H₂ or a hydrocarbon) to yield hexachloroethane and ferrous chloride. [This reaction does occur under anaerobic conditions in aqueous solutions and is competitive with Rx 5. Literature reports indicate that its rate is about the same order of magnitude as Rx 5 under anaerobic conditions, but considerably less under aerobic conditions, or in the presence of acid.]

8) Oxidation.

Example: carbon tetrachloride with ferric oxide to yield carbon dioxide and ferric chloride. [This reaction occurs readily at elevated temperatures but not under ambient conditions.]

9) Radiolysis (homolytic dissociation/free radical recombination).

Example: chloroform with ionizing radiation to yield hydrochloric acid and pentachloroethane. [This reaction proceeds readily and can be a major source of HCl. The rate is dependent upon the power of the radiation source and the concentration of the halocarbon.]

Summary of Halocarbon Reactions

Reaction 5 (Reductive Dehalogenation) will occur at an appreciable rate in the presence of acid. Assuming HCl is formed by radiolysis and surface recombination reactions of free radicals, this will be a corrosion initiating reaction, and will increase corrosion once other reactions produce additional acidic by-products.

Reaction 7 (Direct Reduction) will occur any time halocarbons are contacted with the iron surface. This can occur 1) by direct contact of the halocarbon with exposed iron surfaces, 2) at surfaces that are covered with a liquid barrier, in which case the halocarbon dissolves into the liquid and contacts unreacted iron, or 3) at dry corroded surfaces protected by a passivation layer of corrosion products, in which the halocarbon diffuses through cracks and voids in the barrier to reach the underlying iron.

Reaction 9 (Radiolysis) will occur until the radionuclides expend themselves, or until the possibility of generating volatile radicals is exhausted. The radioactivity is not directly responsible for the corrosion. Rather the ionizing radiation generates free radical species that are reactive toward iron, or recombine to form molecules that are reactive toward iron. This reaction will decrease as time increases and other more competitive reactions take precedence.

ATTACHMENT 2

Electrochemical Reactions

There are several reactions that may occur, in the RWMC waste drums, which lead to corrosion based on the innate tendency of certain atomic and molecular species present, to undergo reduction/oxidation reactions. Several half reactions are shown below to illustrate this point. The significance originates in the thermodynamic relationship:

$$\Delta G = \Delta H - T\Delta S \text{ (for constant temperature process).} \quad \text{Eq 1}$$

A reaction proceeds spontaneously from left to right when $\Delta G < 0$. ΔG is further related to the electrode potential for a given reduction/oxidation couple by:

$$\Delta G = -n\mathcal{F}\mathcal{E} \quad \text{Eq 2}$$

where n is the number of electrons involved in the reaction, $\mathcal{F}$ is Faraday's constant, and $\mathcal{E}$ is the Reduction Potential. When $\mathcal{E}$ is positive for a given reaction, the reaction proceeds spontaneously. The innate driving force for a reaction is greater as $\mathcal{E}$ becomes larger. I have written the reactions shown below in a form that indicates their forward (left to right) progress is spontaneous under standard conditions. This is not conventional, since the term "reduction potential" refers to the reactions written as reductions under standard conditions. Therefore, the $\mathcal{E}^\circ$ values should be referred to as electrode potentials. Further, the driving force ($\mathcal{E}$) implied by the $\mathcal{E}^\circ$ values changes with the activity (a) of the reactants and products according to the Nernst equation:

$$\mathcal{E} = \mathcal{E}^\circ - \frac{RT}{n\mathcal{F}} \ln \frac{[\text{Products}]_a}{[\text{Reactants}]_a} \quad \text{Eq 3}$$

where $\mathcal{E}$ is the driving force of the reaction under the actual conditions, R is the ideal gas constant, T is the absolute temperature, and the other terms have been explained.

Some species tend to give up electrons in redox reactions and are thus oxidized. Some examples for species in the RWMC waste drums include:

Other species tend to accept electrons in redox reactions and are thus reduced. Some examples for species in the RWMC waste drums include:

To summarize these reactions, it is clear that:

- 1) Iron metal is a good source of electrons and is readily oxidized in the presence of: i) oxygen and water, ii) oxygen and acid, and iii) halocarbons and acid.
- 2) Iron(III) is a strong oxidizing agent and can: i) cause corrosion of iron metal when in a suitable electrolyte (water), and ii) cause the direct oxidation of halocarbons.
- 3) The combination of oxygen and acid create a very strong oxidizing environment, capable of: i) directly oxidizing iron metal, or ii) directly oxidizing halocarbons when in the presence of a catalyst. Iron(III) is a good catalyst for this latter reaction.

Summary Of Electrochemical Reactions

When you take various binary combinations of Reactions 10 through 16 to make whole reactions, and add real reactants (i.e., Fe^0 for 2e^- , HCl for H^+ , etc.), it becomes clear that iron is easily corroded by the contents present in the RWMC waste drums.

Aerobic corrosion

Anaerobic corrosion

Dehalogenation (aerobic or anaerobic)

ATTACHMENT 3

Surface Adsorption, Dissociation, & Recombination Reactions

The reactions shown here illustrate that a "clean" iron surface is not really clean when in the presence of moisture (Rx 23 through 28) or halocarbons (Rx 29). In fact, from temperatures below freezing (relative to water) to well above room temperature, many molecules adsorb (Rx 23) onto iron metal and undergo dissociative type reactions. The dissociative reactions produce reactive free radicals (Rx 24 & 29) that may undergo reduction (as shown in Attachment 2), disproportionation (Rx 25, & 26), and recombination (Rx 27, 28, 30, & 31).

The reactions shown here will not be prevalent over the surface of the steel drums, because they require a clean and active iron surface (something the drums haven't had since a few minutes after their fabrication). However, when the iron surface becomes clean and active, all of the above reactions, plus others shown on Attachments 1 & 2, will proceed. The iron surface will become clean and active in microscopic regions under a variety of conditions. A couple sets of conditions are shown below.

1) When iron is initially corroded by oxygen and water, several oxo-iron species are formed. They include $\text{FeO}(\text{OH})$, Fe_2O_3 , $\text{Fe}(\text{OH})_2$, $\text{Fe}(\text{OH})_3$, Fe_3O_4 and others. These species form a passive layer on the iron surface and slow down further corrosion. The passive layer is less dense than the underlying iron and so, does not effectively keep other corroding agents from gaining access to the underlying iron. Consequently, when the passive layer is either wet (water or halocarbon) or dry, chemicals still have access to active iron beneath the corroded surface. The

corrosion induced under these circumstances will not generally be localized or very deep unless some condition aggravates it. Two such conditions are illustrated below.

- i) If water or some other "rust" solubilizing agent (acid) is present, the corrosion products will leach away from the area, causing the passive layer to thin, and allowing corrosive agents deeper penetration into the iron. The resulting corrosion will appear in localized regions.
- ii) If halogen ions (Cl^- , F^- , etc.) or other ions (SO_4^{2-} , NO_3^- , etc.) contact the oxo-iron species, they will displace the oxygen component, e.g.,

making the iron compounds more soluble. Contact with moisture will then facilitate the leaching of corrosion products away from the area and expose fresh iron surface, which will be highly susceptible to corrosion.

2) When HCl is present, it can function to clean away corrosion products and "pickle" or activate the iron. This is a common practice in the electroplating industry. The HCl can further attack the surface directly as in 1) above, or it can be reduced as in Rx 20 or it can facilitate the oxidation of iron, as in Rx 18.

3) When free radicals, formed by radiolysis, contact the drum surface, they can recombine as acid (Rx 30), water (Rx 25), or react with surface corrosion products and reduce them electrochemically (similar to Rx 20). In each case, the surface is made more susceptible to further corrosion.

REFERENCES

1. "The Interaction Of Water With Solid Surfaces: Fundamental Aspects" P.A. Thiel and T.E. Madey, *Surface Science Reports* **7** (1987) 211-385,.
2. "A Review Of Halocarbon And Halogen Adsorption With Particular Reference To Iron Surfaces" M. Grunze and P.A. Dowben, *Applications Of Surface Science* **10** (1982) 209-239.
3. "Sequential Oxidation Of Fe(100) By Water Adsorption: Formation Of An Ordered Hydroxylated Surface" W.H. Hung, J. Schwartz, and S.L. Bernasek, *Surface Science* **248** (1991) 332-342.
4. "InSitu Vibrational Spectra Of The Passive Film On Iron In Buffered Borate Solution" J. Gui and T.M. Devine, *Corrosion Science*, Vol. 32, No. 10, pp. 1105-1124, 1991.
5. "On The Breakdown Of Passivity Of Iron By Thiocyanate" C.A. Melendres, J. Acho, and R.L. Knight, *J. Electrochem. Soc.*, Vol. 138, No. 3, pp. 877-878, 1991.
6. "A Mathematical Model Of Crevice And Pitting Corrosion - I. The Physical Model" S.M. Sharland and P.W. Tasker, *Corrosion Science*, Vol. 28, No. 6, pp. 603-620, 1988.
7. "A Mathematical Model Of Crevice And Pitting Corrosion - II. The Mathematical Solution" S.M. Sharland, *Corrosion Science*, Vol. 28, No. 6, pp. 621-630, 1988.
8. "Mechanism Of Anodic Dissolution And Passivation Of Iron - I. Behavior In Neutral Acetate Buffer Solution" K. Takahashi, J.A. Bardwell, B. McDougall, and M.J. Graham, *Electrochimica Acta*, Vol. 37, No. 3, pp. 477-487, 1992.
9. "Role Of Anions On Iron Pitting Kinetics In Aqueous Solution" Y.I. Kunznetsov and I.A. Valuev, *Elektrokhimiya*, Vol. 20, No. 3, pp. 424-427, 1984. (and references cited within)
10. "Study Of The Cl⁻-Induced Breakdown Of The Passive Layer On Steel" J.F. Marco, J.R. Grancedo, W. Meisel, P. Greisbach, and P. Gutlich, *Corrosion*, Vol. 47, No. 7, pp. 498-500, 1991.
11. "Corrosion, Passivity, And Pitting Of Carbon Steel In Aqueous Solutions Of HCO₃⁻, CO₂, and Cl⁻" K. Videm and A.M. Koren, *Corrosion Science*, Vol. 49, No. 9, pp. 746-754, 1993.
12. *Corrosion Handbook*, H.H. Uhlig, Ed., Wiley, 1948.

13. "The Corrosion Of Carbon Steel In A Chloride Environment Due To Periodic Voltage Modulation: Part II" S.B. Lalvani and G. Zhang, *Corrosion Science*, Vol. 37, No. 10, pp. 1583-1598, 1995.
14. "The Measurement Of Pitting Corrosion Currents Of Steel In Neutral Aqueous Solutions" S.M. Sayed and H.A. El Shayeb, *Corrosion Science*, Vol. 28, No. 2, pp. 153-162, 1988.
15. "Electrochemical Noise Measurements On Mild And 12% Cr Steel In Chloride Solution" M.S. Sherratt, F.P.A. Robinson, M. Tullmin, and A.N. Rothwell, *British Corrosion Journal*, 1994, Vol. 29, No. 1, pp. 33-37.
16. "Pitting Potential And Protection Potential Of Carbon Steel For Chloride Ion And The Effectiveness Of Different Inhibiting Anions" M. Ergun and A.Y. Turan, *Corrosion Science*, Vol. 32, No. 10, pp. 1137-1142, 1991.
17. "Temporary Inhibitors Of Corrosion In Wet Atmosphere: Electrochemical Investigations Of The Mechanism And Efficiency" K. Saurbrier, J.W. Schultze, and J. Geke, *Electrochimica Acta*, Vol. 39, No. 8/9, pp. 1171-1178, 1994.
18. "Mechanisms Of Reductions At Metal Surface. I. A General Working Hypothesis" J.H. Brewster, *Mechanisms Of Reductions At Metal Surfaces*, Vol. 76, pp. 6361-6363, 1954.
19. "Materials Used And Their Corrosion Performance In The Field Of Spent Nuclear Fuel Reprocessing And High-Level Waste Treatment/Disposal" S. Takeda and H. Ishikawa, *Corrosion Engineering* 43, 433-447 (1994).
20. Handbook Of Chemistry And Physics, 57th. ed., CRC Press, pp. D-141-146, 1977.
21. Principles Of Instrumental Analysis, D.A. Skoog and D.M. West, 2nd ed., Saunders, 1980.
22. "Abiotic Reductive Dechlorination Of Carbon Tetrachloride And Hexachloroethane By Environmental Reductants" M. Reinhard, G.P. Curtis, and M.R. Kriegman, Report# EPA/600/2-90/040, 1990. (40 pages)
23. "Abiotic Reduction Reactions Of Anthropogenic Organic Chemicals In Anaerobic Systems: A Critical Review" D.L. MacAlady, P.G. Tratnyek, and T.J. Grundl, *Journal Of Contaminant Hydrology*, 1, (1986) 1-28.
24. "Dehalogenation Of Chlorinated Solvents In Groundwater Under Reductive Conditions" M.L. McCullough, J. Hill, S. Mills, and J. V. Dagdigan, Proceeding from the SUPERFUND XIV Conference and Exhibition, Nov. 30 - Dec. 1, 1993, pp. 1156-1161.
25. "Reductive Dehalogenation Of Chlorinated Methanes By Iron Metal" L.J. Matheson and P.G. Tratnyek, *Environ. Sci. Technol.* 1994, 28, 2045-2053.

26. "Reductive Dechlorination Of Carbon Tetrachloride With Elemental Iron" B.R. Helland,, P.J.J. Alvarez, and J.L. Schnoor, *Journal of Hazardous Materials* 41 (1995) 205-216.
27. "Processes Affecting The Reductive Dechlorination Of Chlorinated Solvents By Zero-Valent Iron" L.J. Matheson and P.G. Tratnyek, Preprint Extended Abstract, Division of Environmental Chemistry, American Chemical Society Meeting, March 28-April 2, 1993.
28. "Enhanced Degradation Of Halogenated Aliphatics By Zero-Valent Iron" R.W. Gillham and S.F. O'Hannesin, *GROUND WATER*, Vol. 32, No. 6, pp. 958-967, 1994.
29. "Kinetics And Mechanism Of Reductive Dehalogenation Of Carbon Tetrachloride Using Zero-Valence Metals" K.D. Warren, R.G. Arnold, T.L. Bishop, L.C. Lindholm, and E.A. Betterton, *Journal of Hazardous Materials* 41 (1995) 217-227.
30. "Destruction Of Organohalides In Water Using Metal Particles: Carbon Tetrachloride/Water Reactions With Magnesium, tin, and Zinc" T. Boranina and K.J. Klabunde, *Environ. Sci. Technol.* 1995, 29, 1511-1517.
31. "Reactivity Of Carbon Tetrachloride With A series Of Metals" W.L. Archer and M.K. Harter, *Corrosion*, Vol. 34, No. 5, pp. 159-162, 1978.
32. "Electrolytic Model System For Reductive Dehalogenation In Aqueous Environments" C.S. Criddle and P.L. McCarty, *Environ. Sci. Technol.*, Vol. 25, No. 5, pp. 973-978, 1991.
33. "Dechlorination Of Polychlorinated Biphenyls On Soils And Clay By Electrolysis in A Bicontinuous Microemulsion" S. Zhang and J.F. Rusling, *Environ. Sci. Technol.* 1995, 29, 1195-1199, 1195.
34. "Transformation Of Carbon Tetrachloride In The Presence Of Sulfide, Biotite, And Vermiculite" M.R. Kriegman-King and M. Reinhard, *Environ. Sci. Technol.* 1992, 26, 2198-2206.
35. "Radiolytic Gas Generation In Plutonium Contaminated Waste Materials" A. R. Kazanjian, Report RFP, UC-70 Nuclear Waste Management, TID-4500-R64, 1976.

APPENDIX B

Corrosion Pitting In Metals

INTERDEPARTMENTAL COMMUNICATION

Date: May 9, 1996

To: D.P. Zeek MS 2424 6-7728

From: R.E. Mizia MS 3210 6-3352

Subject: Pitting Corrosion (REM-03-96)

Per your verbal request, I have put together a short letter report on the corrosion pitting of metals. The request is based on the observed pits and leakage of corrosion products from a few hundred drums located at the RWMC.

Problem Description:

The RWMC Facility is currently transferring radioactive waste storage drums from the Air Storage Buildings to the Storage Modules. During this operation, a few hundred drums have been identified with severe localized corrosion degradation on the top and sides that causes the paint to bubble and spall off with a release of a corrosion product containing liquid extrudate. These drums contain Content Code 3 material (solidified organic wastes placed inside plastic bags) which contain significant amounts of carbon tetrachloride and Trichloroethane. An examination of the provided photographs (Figure 8) identify this degradation as pitting that is initiated from the inside of the drum.

Corrosion Product Sampling:

The corrosion products from the drums were sampled in November, 1995 and March/April, 1996. The results from the November, 1995 sample identified high iron and chloride content with acidic pH levels from 1 to 3.5. Other elements identified were sulfate, phosphate, and nitrate. The microbial samples were positive but the origin of the microbes (inside or outside) was not positively established.^{1,2} The microbial isolation showed that both acid producing organisms as well as organic carbon utilizers were found in the extrudate that was sampled on the outside of the barrel.³ During the sampling process, the liquid sampled from under the blisters on the top of the barrel would run back into the barrel through a small hole when the sample needle penetrated the paint blister. The samples taken in March/April 1996 show high chloride levels with nitrate present. These results show that phosphate and sulfate were not detected. There was no iron result reported.

Pitting:

In searching the literature, the following two definitions or descriptions seemed the most

appropriate:

Pitting is localized corrosion of a metal surface, confined to a point or small area, that takes the form of cavities.⁴

or

"It is well known from many investigations that pitting corrosion occurs on passivated metal surfaces which are protected by a thin poreless oxide layer. These passive layers usually have a thickness of 10 Angstroms. Some metals are only covered with a monolayer. Under the influence of aggressive anions, such as chloride ions, a strong localized attack takes place causing the formation of hemispherical or, occasionally, polygonal holes called pits. These pits may grow to diameters of 1 mm and more, and they are often filled with solid reaction products."⁵ (This definition is supported by 17 literature citations)

The pitting process causes changes in the chemistry inside the pit as compared to the bulk solution chemistry. Specifically, the pit chemistry acidifies and becomes the anodic site where the corrosion occurs. A classic diagram of the general case of pitting is shown below where the metal ions (M^+) formed from the corrosion process are migrating out of the pit and Cl^- ions are migrating into the pit. If we take the case of carbon steel pitting, the corrosion reaction (anodic site) within the pit for iron is: $Fe \rightarrow Fe^{++} + 2e^-$. If we assume that there is oxygen present in the solution, the reaction that occurs outside of the pit (cathodic site) is as follows: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$. The metal iron ions then hydrolyze (raising the local acidity within the pit) according to the following typical reaction: $3Fe^{++} + 4H_2O \rightarrow Fe_3O_4 + 8H^+ + 2e^-$. The end result in this case is the formation of hydrochloric acid in the bottom of the pit from the Cl^- ion migration from the bulk environment into the pit and acidification due to hydrolysis.

Figure 3-19 Autocatalytic processes occurring in a corrosion pit.

*U. R. Evans, *Corrosion*, 7:238 (1951).

The problem with localized corrosion such as pitting is that the rate of growth of a pit may cause unexpected perforation of a container wall in comparison to general corrosion of the same container. The corrosion rate of pitting can be hundreds of thousands of times higher than general corrosion.

The aggressive anions that can start pitting in metals commonly used at the INEL are listed in Table 1 which is excerpted from Reference 6.

Table 1

Metal	Aggressive Anion
Aluminum	Cl^- , Br^- , I^- , ClO_4^- , NO_3^- , SCN^-
Iron	Cl^- , Br^- , ClO_4^- , $\text{SO}_4^{=}$
Stainless Steel	Cl^- , Br^- , SCN^-

Microbial Mediated Phenomenon:

Microbiologically Influenced Corrosion (MIC) is not a new form of corrosion but can be defined as the influence of living organisms (microbial metabolism) on well characterized chemical and electrochemical reactions that occur on a surface of a metal. This type of corrosion usually occurs as a result of a biofilm being formed on the surface of the metal. Most all metals and their alloys have been shown to undergo MIC. As a general rule, MIC will manifest itself as localized corrosion (pitting or crevice).

Microbial metabolism is extremely diversified. For instance, some organisms can degrade complex synthetic molecules, e.g., polymers, multi ring compounds, insecticides, etc. Additional organisms can degrade single carbon compounds, e.g., methane, chloroform, while others can degrade petroleum components and halogenated compounds. Still other organisms can cause the oxidation and reduction of metallic and nonmetallic atoms, e.g., iron, manganese, uranyl ions, selenium, sulfur, phosphorous, nitrogen, etc. The microbial world is also very adaptable and living processes can be maintained under a wide range of environmental conditions, e.g., pH 1-13, 0- 100°C, high salinity, anaerobic, high radiation fields, etc.

The complexity of this microbial activity is further extended by the fact that attachment to surfaces occurs. This attachment results in the formation of a biofilm. The attached cells produce exocellular components that form a film and cause microenvironments to form at the interface of the substratum and the biofilm. The bulk media can be aerobic but under the micron thick biofilm, the environment can be anaerobic or be very different in ionic strengths and pH values. This is the case that is occurring in many of the older sewer systems in the world. Sewer

deterioration is not occurring under the liquid layer but in the crown area as a result of biofilm formation. Also gas production of both non and explosive mixtures can be generated as a result of microbial activities. This attachment phenomenon could also occur on the lids and sides of the RWMC drums.

Pitting Evaluation/Case Histories:

Pitting on a metal surface can be evaluated on a macroscopic basis per the requirements of ASTM G 46. Figures 1 and 2 show various geometric evaluation data for pitting⁷. This type of evaluation must be enhanced by sampling of any corrosion product for chemistry to identify aggressive anions and to look for the presence of microbes that could influence the corrosion reaction.

The INEL has had problems with pitting corrosion of different metals. The following examples show that aluminum and carbon steel can be susceptible to pitting clean water environments with low levels of halides.

Figure 3 shows the cross section of an aluminum (Type 6061) Fermi Fuel Canister mockup that has been stored in the FAST Fuel Basin (CPP 666) for four years. The typical water quality for this fuel storage area is as follows: pH - 6.0, Chloride - 0.2 ppm, Conductivity - 1.5 μ MHOs/cm, Temperature - 60 to 75 °F.⁸

Figure 4 shows pitting of a carbon steel sample exposed in the PBF Fuel Pool for one year. The typical water quality reported for this fuel pool during 1995 are: pH - 5.7, Chloride - <0.1ppm, Conductivity - 1.2 μ MHOs/cm, Temperature - not reported.⁹ To give a better understanding of the size, shape, and depth of these pits, the sample has been characterized by interferometry. The scans were conducted on an area of 426.7 x 574.4 μ m located below the hole in the middle of the sample. The surface data plot (Fig.5), shows the surface area of the pits and their depth where the blue color delineates the pits, the bar chart shows the peak amplitude of +33.725 to -46.765 μ m, and R_T give the maximum peak to valley height (80.49 μ m). The area shown in Figure 5 is replotted as a three dimensional image in Figure 6. The blue color outlines the inside surface of the pits. Figure 7 shows a plot of the surface profile along the designated lines in the x and y directions. The maximum value of R_T shown for these plots (55.7 μ m) is less than the maximum shown in Figure 5 for the whole surface.

Conclusions:

1. Visual inspection of the photographs provided of the leaking drums show pitting corrosion that initiated on the drum interior.
2. The chemical analysis of the corrosion product identified aggressive anions and acidic pH that is characteristic of active pitting corrosion.
3. The microbes identified in the samples may contribute to the corrosion process.

Recommendation:

1. LITCO should assemble a team with the proper technical and operations skills to develop an inspection plan for these drums.
2. All of the drums that have Content Code 3 or equivalent material in them should be inspected even if there is no external evidence of corrosion.

References:

1. Sampling Narrative, "RWMC Drum", Analytical Log Number: 95 - 1034, dated 10/19/95
- 2.. Interim Analytical Report, Analytical Log Number: 96 - 040113, dated 04/01/96
3. Note, J.H. Wolfram to P. Marusha, "Samples from the leaking RWMC drum", dated 11/20/95
4. Metals Handbook, Ninth Edition, Volume 13, "Corrosion", ASM International, September, 1987 (from "Glossary of Terms")
5. K.J. Vetter and H.H. Strehblow, "Pitting Corrosion in an Early Stage and its Theoretical Implications", Localized Corrosion, National Association of Corrosion Engineers, December, 1971
6. J.R. Galvele, "Pitting Corrosion", in Treatise on Materials Science and Technology, Volume 23, Corrosion: Aqueous Processes and Passive Films, edited by J.C. Scully, Academic Press, 1983
7. "Standard Recommended Practice for Examination and Evaluation of Pitting Corrosion", ASTM G 46, Annual Book of ASTM Standards, American Society for Testing and Materials
8. CPP - 666 BASIN WATER TREATMENT FACT SHEET, obtained from LITCO - Nuclear Fuel Operations, May, 1996
9. LITCO Form PBF - 221.12, "CANAL SYSTEM CHEMISTRY LOG", January, April, July, 1995

References:

1. Sampling Narrative, "RWMC Drum", Analytical Log Number: 95 - 1034, dated 10/19/95
- 2.. Interim Analytical Report, Analytical Log Number: 96 - 040113, dated 04/01/96
3. Note, J.H. Wolfram to P. Marusha, "Samples from the leaking RWMC drum", dated 11/20/95
4. Metals Handbook, Ninth Edition, Volume 13, "Corrosion", ASM International, September, 1987 (from "Glossary of Terms")
5. K.J. Vetter and H.H. Strehblow, "Pitting Corrosion in an Early Stage and its Theoretical Implications", Localized Corrosion, National Association of Corrosion Engineers, December, 1971
6. J.R. Galvele, "Pitting Corrosion", in Treatise on Materials Science and Technology, Volume 23, Corrosion: Aqueous Processes and Passive Films, edited by J.C. Scully, Academic Press, 1983
7. "Standard Recommended Practice for Examination and Evaluation of Pitting Corrosion", ASTM G 46, Annual Book of ASTM Standards, American Society for Testing and Materials
8. CPP - 666 BASIN WATER TREATMENT FACT SHEET, obtained from LITCO - Nuclear Fuel Operations, May, 1996
9. LITCO Form PBF - 221.12, "CANAL SYSTEM CHEMISTRY LOG", January, April, July, 1995

FIG. 1 Variations in the Cross-Sectional Shape of Pits

	<u>A</u> DENSITY	<u>B</u> SIZE	<u>C</u> DEPTH
1	$2.5 \times 10^3 / m^2$	0.5 mm^2	0.4 mm
2	$1 \times 10^4 / m^2$	2.0 mm^2	0.8 mm
3	$5 \times 10^4 / m^2$	8.0 mm^2	1.6 mm
4	$1 \times 10^5 / m^2$	12.5 mm^2	3.2 mm
5	$5 \times 10^5 / m^2$	24.5 mm^2	6.4 mm

FIG. 2 Standard Rating Charts for Pits

INEL-LITCO

DATE:07/27/95
SAMPLE:4yr #1
CALIBRATION:4.608
MAGNIFICATION: 50X

PIT #1 FROM THE FERMI MOCKUP FUEL CANISTER
EXPOSED FOR FOUR YEARS

Length (um)
562.21
858.57

ALL MEASUREMENTS ARE IN
MICRONS

FIGURE 3

DATE

NAME

FIGURE 4

Mag: 10.9 X

Mode: VSI

Surface Data

Date: 05/09/96

Time: 14:13:1

Surface Statistics:

Ra: 14.40 um

Rq: 16.92 um

Rz: 74.08 um

Rt: 80.49 um

Set-up Parameters:

Size: 368 X 236

Sampling: 1.57 um

Processed Options:

Terms Removed:

Tilt

Filtering:

None

426.7 um

300.0

200.0

100.0

0.0

0.0

100.0

200.0

300.0

400.0

574.4

um

33.725

20.000

5.000

-10.000

-25.000

-46.765

um

Title: PBF C.S. Coupon

Note: # side lower portion

FIGURE 5

Mag: 10.9 X

Mode: VSI

3-D Plot

Date: 05/09/96

Time: 14:13:1

Surface Statistics:

Ra: 14.40 μm

Rq: 16.92 μm

Rz: 74.08 μm

Rt: 80.49 μm

Set-up Parameters:

Size: 368 X 236

Sampling: 1.57 μm

Processed Options:

Terms Removed:

Tilt

Filtering:

None

Title: PBF C.S. Coupon

Note: # side lower portion

FIGURE 6

Mode: VSI
Mag: 10.9 X

2D Profiles X-Profile / 2 Pt / Radial

05/05/98
14:13:10

Size: 368 X 236

Title: PBF C.S. Coupon
Note: # side lower portion

I: 183,117

Rq: 16.01 um
Ra: 14.19 um
Rt: 55.70 um
Rp: 19.27 um
Rv: -36.43 um

L: 0.00 um -3.14 um
R: 574.44 um 3.41 um
D: 574.44 um 6.55 um
Angle: 0.65°
Curve: 7.50 mm
Terms: None
AvgHt: -5.26 um
Area: -3020.39 um²

Y-Profile / Circular

Rq: 14.17 um
Ra: 12.38 um
Rt: 46.09 um
Rp: 21.46 um
Rv: -24.64 um

L: 0.00 um 20.79 um
R: 426.68 um 0.97 um
D: 426.68 um -19.82 um
Angle: -2.66°
Curve: 1.44 mm
Terms: None
AvgHt: 2.77 um
Area: 1180.61 um²

FIGURE 7

APPENDIX C

Letter Reports

Lockheed Idaho Technologies Company

INTERDEPARTMENTAL COMMUNICATION

Date: April 25, 1996

To: K. E. Kooda MS 2414 6-8505

From: B. J. Mincher *BJM* MS 7111 3-4449

Subject: HCl GENERATION CALCULATIONS - BJM-08-96

Based upon the information you sent me I ran some HCl generation calculations. The general conclusion is that it is unlikely that HCl is your problem, but not impossible.

One has to assume a G-value for Cl⁻ production from the halogenated hydrocarbons in your system. The G value depends on both the species being irradiated and the matrix that it is in. Only aqueous G values are available in references. Knowing nothing about your matrix I used a typical G_{Cl} of 5.5 molecules per 100 eV per gram. I also repeated the calculation at G = 550.

The other assumptions were:

- 1) sludge mass = 464 lbs = 210,470 g
- 2) activity = 0.44 Ci based on drum D45117
- 3) every decay deposits 5 MeV.

Therefore:

$$\frac{0.44 \text{ Ci}}{210,470 \text{ g}} \times \frac{3.7E10 \text{ dps}}{\text{Ci}} \times \frac{5 \text{ MeV}}{d} = 3.8E11 \text{ eV/g} = 3.8E9 \text{ 100 eV/g}$$

$$3.89E9 \text{ 100 eV/g} \times \frac{5.5 \text{ Cl}^-}{100 \text{ eV}} = 2.1E10 \text{ atoms Cl}^-/\text{g/sec}$$

$$2.1E10 \times \frac{\text{mole}}{6.02E23 \text{ atoms}}$$

$$\begin{aligned} &= 3.47E-14 \text{ moles HCl/g/sec} \\ &= 1.1E-6 \text{ moles/yr/g} \\ &= 1.1E-3 \text{ moles/yr/L.} \end{aligned}$$

K. E. Kooda
April 25, 1996
BJM-08-96
Page 2

After 1 year in the drum the pH = 3, after 2 years pH = 2.7, after 6 years pH = 2.2. This is probably not sufficient to cause the problems you are seeing. This calculation is conservative for several reasons: 1) the actual G_{Cl} is probably lower than 5.5 in your system; 2) the Cl^- generated in your system may not end up as HCl , it depends on sludge chemistry; 3) I used the activity value for your most radioactive drum, many showed values much lower than this.

Next, I assumed that some strange set of circumstances in the chemistry of your sludge was allowing a chain reaction dechlorination to occur. Using a $G_{Cl} = 550$, the pH's become: 1 yr = 0.96, 2 yr = 0.66, 6 yr = 0.18. However, only a chain reaction dechlorination could result in this.

Some ideas you should consider are the corrosivity of the sludge itself, (I don't know what it's made of) or radiolysis products of the sludge itself. Please call me at any time, 3-4449.

jd

cc: J. W. Mandler, MS 2114
B. J. Mincher File
File Code 415

Lockheed Idaho Technologies Company

INTERDEPARTMENTAL COMMUNICATION

Date: April 29, 1996

To:	Doug P. Zeek	MS 2424	6-7728
	Mark J. Sherick	MS 4202	6-4212

From:	John G. Jolley <i>g~</i>	MS 2208	6-8036
	Kelly J. Galloway <i>KJG</i>	MS 3953	6-8255

Subject: VAPOR PHASE HCl CONCENTRATION DATA FOR OVER PACKED DRUMS-JGJ-18-96

Enclosed please find one table containing vapor phase HCl concentration data for 14 over packed drums that were located in the SWEPP High Bay on 04/17/96. Sensidyne Colormetric Gastec Detector Tubes (No. 14L, 0.2 - 40 ppm) and pump (Sensidyne Gastec Model 800) were used for the determinations. Teflon® interfaces were installed directly onto the drum vent filters. After both tube ends were broken off, the tube inlets were installed into the Teflon® interfaces and the pump was installed onto the tube outlets. Aliquots were drawn into the tubes with the pump. Two to five pump cycles were used (maximum of five) according to vendor specifications. Data were corrected for barometric pressure (measured by a micrometeorological station in WMF-629) as follows:

$$\frac{\text{tube reading}}{\text{no. pump cycles}} \times \frac{29.92'' \text{ Hg}_{STP}}{24.65'' \text{ Hg}_{\text{measured}}} = \text{corrected concentration}$$

HCl (0.2 to 7.3 ppm) was detected in Content Code 1, 3, and 336 drums. HCl was not detected (minimum detection limit of 0.2 ppm) in the Content Code 4, 7, 440, 480, and 481 drums.

If you have any questions or comments, please do not hesitate to give us a call or PROFS (6-8255/KG3 for Galloway or 6-8036/JJY for Jolley). Have a good day.

jgj

Enclosed:
As Stated

cc: K. J. Galloway, MS-3953
D. L. Miller, MS-2208 *DLM*
J. G. Jolley (Letter File)

Drum ID Number	Content Code	Location	Test Start Date/Time	Test End Date/Time	Number Pump Cycles	HCl Tube Response (ppm)	HCl Concentration (ppm)
IDRFOP1200578	IDC 1	SWEPP	4/17/96 14:39	4/17/96 14:42	5	1.5	0.4
IDRFOP4315939	IDC 3	SWEPP	4/17/96 14:11	4/17/96 14:14	3	7.0	2.8
IDRFOP4315275	IDC 3	SWEPP	4/17/96 14:20	4/17/96 14:23	3	5.5	2.2
IDRFOP4314979	IDC 3	SWEPP	4/17/96 14:32	4/17/96 14:33	2	6.0	3.6
IDRFOP4315257	IDC 3	SWEPP	4/17/96 14:49	4/17/96 14:52	5	1.0	0.2
IDRFOP4314980	IDC 3	SWEPP	4/17/96 14:53	4/17/96 14:55	2	12.0	7.3
IDRFOP4315945	IDC 3	SWEPP	4/17/96 15:02	4/17/96 15:03	3	10.0	4.0
IDRFOP4402384	IDC 4	SWEPP	4/17/96 14:44	4/17/96 14:47	5	<0.2	<0.2
IDRFOP4700907	IDC 7	SWEPP	4/17/96 14:25	4/17/96 14:26	5	<0.2	<0.2
IDRFOP2500134	IDC 336	SWEPP	4/17/96 14:28	4/17/96 14:29	2	8.0	4.9
IDRFOP3701981	IDC 440	SWEPP	4/17/96 14:16	4/17/96 14:18	5	<0.2	<0.2
IDRFOP2900435	IDC 440	SWEPP	4/17/96 14:58	4/17/96 15:00	5	<0.2	<0.2
IDRFOP0234626	IDC 480	SWEPP	4/17/96 14:35	4/17/96 14:37	5	<0.2	<0.2
IDRFOP1901560	IDC 481	SWEPP	4/17/96 15:05	4/17/96 15:07	5	<0.2	<0.2

Lockheed Idaho Technologies Company

INTERDEPARTMENTAL COMMUNICATION

Date: April 29, 1996

To:	Doug P. Zeek	MS 2424	6-7728
	Mark J. Sherick	MS 4202	6-4212

From:	John G. Jolley <i>JGJ</i>	MS 2208	6-8036
	Kelly J. Galloway <i>KJG</i>	MS 3953	6-8255

Subject: VAPOR PHASE HCl CONCENTRATION DATA FOR OVER PACKED DRUMS-JGJ-19-96

Enclosed please find one table containing vapor phase HCl concentration data for two and six drums that were located in the SWEPP Paint Room and C&S Building, respectively on 04/18/96. Sensidyne Colormetric Gastec Detector Tubes (No. 14L, 0.2 - 40 ppm) and pump (Sensidyne Gastec Model 800) were used for the determinations. Teflon® interfaces were installed directly onto the drum vent filters. After both tube ends were broken off, the tube inlets were installed into the Teflon® interfaces and the pump was installed onto the tube outlets. Aliquots were drawn into the tubes with the pump. Five pump cycles were used according to vendor specifications. Data were corrected for barometric pressure (measured by a micrometeorological station in WMF-629) as follows:

$$\frac{\text{tube reading}}{\text{no. pump cycles}} \times \frac{29.92'' \text{ Hg}_{STP}}{24.66'' \text{ Hg}_{measured}} = \text{corrected concentration}$$

The temperature (3.5°C in WMF-629) was not taken into account in the corrected concentrations. HCl (0.7 to 1.4 ppm) was detected in Content Code 3 drums. HCl was not detected (minimum detection limit of 0.2 ppm) in the Content Code 1, 337, and 440 drums.

If you have any questions or comments, please do not hesitate to give us a call or PROFS (6-8255/KG3 for Galloway or 6-8036/JJY for Jolley). Have a good day.

jgj

Enclosed:
As Statedcc: K. J. Galloway, MS-3953
D. L. Miller, MS-2208 *DLM*
J. G. Jolley (Letter File)

Drum ID Number	Bar Code	Content Code	Location	Test Start Date/Time	Test End Date/Time	Number Pump Cycles	HCl Tube Response (ppm)	HCl Concentration (ppm)
741-12875	10228	1	C&S	4/18/96 15:40	4/18/96 15:44	5	<0.2	<0.2
RF741202658		1	C&S	4/18/96 15:47	4/18/96 15:49	5	<0.2	<0.2
RF074317423		3	SWEPP Paint Room	4/18/96 14:38	4/18/96 14:40	5	3.0	0.7
743-11567	15857	3	C&S	4/18/96 15:27	4/18/96 15:30	5	5.8	1.4
743-11598	15920	3	C&S	4/18/96 15:33	4/18/96 15:37	5	3.1	0.8
RF074403840		337	SWEPP Paint Room	4/18/96 13:59	4/18/96 14:05	5	<0.2	<0.2
28-00171	30268	440	C&S	4/18/96 15:14	4/18/96 15:16	5	<0.2	<0.2
RF0302401	9592	440	C&S	4/18/96 15:22	4/18/96 15:25	5	<0.2	<0.2

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Lockheed Idaho Technologies Company

INTERDEPARTMENTAL COMMUNICATION

Date: April 29, 1996**To:** Doug P. Zeek MS 2424 6-7728
Mark J. Sherick MS 4202 6-4212**From:** John G. Jolley *JGJ* MS 2208 6-8036
Kelly J. Galloway *KJG* MS 3953 6-8255**Subject:** VAPOR PHASE HCl CONCENTRATION DATA FOR OVER PACKED DRUMS-
JGJ-20-96

Enclosed please find one table containing vapor phase HCl concentration data for 23 drums and ambient air located in the C&S Building, respectively on 04/24/96. Sensidyne Colormetric Gastec Detector Tubes (No. 14L, 0.2 - 40 ppm) and pump (Sensidyne Gastec Model 800) were used for the determinations. Teflon® interfaces were installed directly onto the drum vent filters. After both tube ends were broken off, the tube inlets were installed into the Teflon® interfaces and the pump was installed onto the tube outlets. Aliquots were drawn into the tubes with the pump. Five pump cycles were used according to vendor specifications. Data were corrected for barometric pressure (measured by a micrometeorological station in WMF-629) as follows:

$$\frac{\text{tube reading}}{\text{no. pump cycles}} \times \frac{29.92'' \text{ Hg}_{STP}}{24.71'' \text{ Hg}_{\text{measured}}} = \text{corrected concentration}$$

The temperature (7.0°C in WMF-629) was not taken into account in the corrected concentrations. HCl (0.2 to 2.1 ppm) was detected in some of the Content Code 3 drums. HCl was not detected (minimum detection limit of 0.2 ppm) in the Content Code 1, some 3, 336, 337, 339, 374, 442, and 900 drums. Ambient air HCl concentration was <0.2 ppm.

If you have any questions or comments, please do not hesitate to give us a call or PROFS (6-8255/KG3 for Galloway or 6-8036/JJY for Jolley). Have a good day.

jgj

Enclosed:
As Stated

cc: K. J. Galloway, MS-3953
D. L. Miller, MS-2208 *DL Miller*
J. G. Jolley (Letter File)

Drum Bar Code	Content Code	Location	Test Start Date/Time	Test End Date/Time	Number Pump Cycles	HCl Tube Response (ppm)	HCl Concentration (ppm)
32288	1	C&S	4/24/96 10:45	4/24/96 10:48	5	<0.2	<0.2
32672	1	C&S	4/24/96 11:05	4/24/96 11:08	5	<0.2	<0.2
32675	1	C&S	4/24/96 10:40	4/24/96 10:43	5	<0.2	<0.2
32702	1	C&S	4/24/96 10:34	4/24/96 10:37	5	1.0	0.2
32979	1	C&S	4/24/96 10:56	4/24/96 10:58	5	<0.2	<0.2
12049	3	C&S	4/24/96 11:10	4/24/96 11:13	5	1.1	0.3
12054	3	C&S	4/24/96 10:23	4/24/96 10:25	2	3.4	2.1
21375	3	C&S	4/24/96 11:16	4/24/96 11:19	5	<0.2	<0.2
21385	3	C&S	4/24/96 11:25	4/24/96 11:29	5	<0.2	<0.2
22362	3	C&S	4/24/96 11:20	4/24/96 11:23	5	<0.2	<0.2
22985	3	C&S	4/24/96 10:51	4/24/96 10:53	3	2.1	0.8
23967	3	C&S	4/24/96 10:28	4/24/96 10:31	3	1.6	0.6
13558	336	C&S	4/24/96 09:16	4/24/96 09:19	5	<0.2	<0.2
10726	337	C&S	4/24/96 09:26	4/24/96 09:28	5	<0.2	<0.2
32423	337	C&S	4/24/96 10:16	4/24/96 10:19	5	<0.2	<0.2
32512	337	C&S	4/24/96 09:33	4/24/96 09:36	5	<0.2	<0.2
32759	337	C&S	4/24/96 08:54	4/24/96 08:56	5	<0.2	<0.2
32527	339	C&S	4/24/96 09:09	4/24/96 09:12	5	<0.2	<0.2
32575	339	C&S	4/24/96 08:59	4/24/96 09:02	5	<0.2	<0.2
32760	339	C&S	4/24/96 09:57	4/24/96 10:01	5	<0.2	<0.2
11313	374	C&S	4/24/96 10:11	4/24/96 10:14	5	<0.2	<0.2
9054	442	C&S	4/24/96 09:04	4/24/96 09:07	5	<0.2	<0.2
10530	900	C&S	4/24/96 10:05	4/24/96 10:08	5	<0.2	<0.2
Ambient Air	n.a.	C&S	4/24/96 11:31	4/24/96 11:33	5	<0.2	<0.2

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Lockheed Idaho Technologies Company

INTERDEPARTMENTAL COMMUNICATION

Date: May 1, 1996

To:	Doug P. Zeek	MS 2424	6-7728
	Mark J. Sherick	MS 4202	6-4212
From:	John G. Jolley	MS 2208	6-8036
	Kelly J. Galloway	MS 3953	6-8255

Subject: VAPOR PHASE WATER CONCENTRATION DATA FOR DRUMS- JGJ-21-96

Enclosed please find two tables containing vapor phase water concentration data. The first table lists data for eight drums located in the SWEPP Paint Room, C&S Building, WMF-628 and WMF-629 during 04/22-23/96. Sensidyne Colormetric Gastec Detector Tubes (No. 6, 0.5 - 32 mg/L) were used for the determinations. Teflon® interfaces were installed directly onto the drum vent filters. After both tube ends were broken off, the tubes were inverted and the outlets installed into the Teflon® interfaces. The tube inlets were exposed to the ambient air. This configuration would allow for a measured detection of the H₂O entering into the drum. It is also important to note that the volume of air was not measured and that this test is only qualitative (i.e., indicative and comparative only). The temperature and barometric pressure (7.2°C and 25.00 "Hg in WMF-629) were not taken into account also.

The colormetric water vapor tube's original virgin color is green. As the tube material is exposed to water vapor, the tube changes color from green to purple. The more water that's drawn into the colormetric tube, the greater the purple zone produced. All eight drums tested indicated that the water vapor tended to move into and out of the drum during the test period. Drum RF074403840 in the SWEPP Paint Room showed evidence of approximately equal amounts of water vapor being drawn into the drum and expelled from the drum. The other seven drums showed evidence that more water was moving into the drums than out. This, however, may be a function of test timing (barometric pressure and temperature trend at the time). Table 1 outlines the qualitative data and observations made during this series of water vapor tests.

Table 2 lists the data collected from one drum and the ambient air located in the SWEPP Paint Room on 04/23/96. Sensidyne Colormetric Gastec Detector Tubes (No. 6, 0.5 - 32 mg/L) and pump (Sensidyne Gastec Model 800) were used for the determinations. One Teflon® interface was installed directly onto the drum vent filter. After both tube ends were broken off, the tube inlet was installed into the Teflon® interface and the pump was installed onto the tube outlet. An aliquot was drawn into the tube with the pump. Only one pump cycle was used according to vendor specifications. Data were corrected for barometric pressure (measured by a micrometeorological station in WMF-629) as follows:

Doug P. Zeek
May 1, 1996
JGJ-16-96
Page 2

$$\frac{\text{tube reading}}{\text{no. pump cycles}} \times \frac{29.92'' \text{ Hg}_{STP}}{25.00'' \text{ Hg}_{\text{measured}}} = \text{corrected concentration}$$

H₂O was detected in drum RF074403840 at 5.4 mg/L. Ambient air H₂O concentration was 3.8 mg/L.

In summary, the tests showed vapor phase water as following:

- Vapor phase water was present in the drums tested.
- Ambient air vapor phase water did move into the drums tested.
- Vapor phase water did move out of the drums tested.
- During this testing period, in general, more vapor phase water moved into the drums tested than out of the drums.

If you have any questions or comments, please do not hesitate to give us a call or PROFS (6-8255/KG3 for Galloway or 6-8036/JJY for Jolley). Have a good day.

jgj

Enclosed:
As Stated

cc: K. J. Galloway, MS-3953
D. L. Miller, MS-2208
J. G. Jolley (Letter File)

Table 1.

Drum ID Number	RF074403840	RF074317423	74315888	RF0302401	RF074701719	RF04315995	RF074403624	RF001901477
Content Code	337	3	3	440	7	3	337	339
Location	SWEPP Paint Room	SWEPP Paint Room	C&S	C&S	WMF-628	WMF-628	WMF-629	WMF-629
Filter ID	NFT-N	NFT-M	NFT-P	NFT-L	NFT-J	NFT-H	NFT-M	NFT-L
Test Start Date/Time	4/22/96 13:55	4/22/96 13:56	4/22/96 14:11	4/22/96 14:10	4/22/96 14:26	4/22/96 14:29	4/22/96 14:55	4/22/96 14:56
First Observation	Purple indications at both ends.	Purple indications at both ends.	Purple indication at bottom. None at top.	Slight purple indication at bottom. None at top.	Purple indication at bottom. None at top.	Purple indication at bottom. None at top.	Purple indications at both ends.	Purple indications at both ends.
Water Vapor Concentration (mg/L)	<1	1	<1	<1	<1	<1	<1	<1
Date/Time	4/22/96 15:06	4/22/96 15:06	4/22/96	4/22/96	4/22/96 15:40	4/22/96 15:41	4/22/96 15:46	4/22/96 15:46
Second Observation	~ Equal length purple zones at both ends.	Purple zone at top. Slight purple indication at bottom.	Purple zone at top. Slight purple indication at bottom.	Purple zone at top. Slight purple indication at bottom.	Purple zone at top. Very slight purple indication at bottom.	Purple zone at top. Very slight purple indication at bottom.	Purple zone at top. Slight purple indication at bottom.	Purple zone at top. Slight purple indication at bottom.
Water Vapor Concentration (mg/L)	10	18	>18	>18	18	>18	>18	16
Date/Time	4/23/96 08:05	4/23/96 08:06	4/23/96 08:13	4/23/96 08:20	4/23/96 08:31	4/23/96 08:32	4/23/96 08:38	4/23/96 08:39
Final Observation	Totally purple	Purple zone at top. 0.6 cm purple zone at bottom.	Top and bottom purple zones were 3.3 and 1.1 cm long, respectively.	2.8 cm long purple zone at top. Slight purple indication at bottom.	2.7 cm long purple zone at top. Slight purple indication at bottom.	2.8 cm long purple zone at top. Slight purple indication at bottom.	Top and bottom purple zones were 3.9 and 0.9 cm long, respectively.	Purple zone at top. Slight purple indication at bottom.
Water Vapor Concentration (mg/L)	>10	>18	>18	>18	>18	>18	>18	18
Date/Time	4/23/96 13:10	4/23/96 13:14	4/23/96 13:24	4/23/96 13:28	4/23/96 13:40	4/23/96 13:45	4/23/96 13:54	4/23/96 13:52

Table 2.

Drum ID Number	Content Code	Location	Test Start Date/Time	Test End Date/Time	Number Pump Cycles	H ₂ O Tube Response (mg/L)	H ₂ O Concentration (mg/L)
RF074403840	IDC 337	SWEPP Paint Room	4/23/96 14:31	4/23/96 14:33	1	4.5	5.4
Ambient Air	n.a.	SWEPP Paint Room	4/23/96 14:36	4/23/96 14:38	1	3.2	3.8

Lockheed Idaho Technologies Company

INTERDEPARTMENTAL COMMUNICATION

Date: May 13, 1996**To:** Doug P. Zeek MS 2424 6-7728
Mark J. Sherick MS 4202 6-4212**From:** John G. Jolley ² MS 2208 6-8036
Kelly J. Galloway *KJG* MS 3953 6-8255**Subject:** VAPOR PHASE HCl AND WATER CONCENTRATION DATA FOR DRUMS-
IGJ-22-96

Enclosed please find two tables containing vapor phase HCl and water concentration data for two over packed drums that were located in the SWEPP High Bay. Sensidyne Colormetric Gastec Detector Tubes (No. 14L, 0.2 - 40 ppm for HCl and No. 6, 0.5 - 32 mg/L for water) and pump (Sensidyne Gastec Model 800) were used for the determinations. One Teflon® interface was installed directly onto the drum vent filter. After both tube ends were broken off, the tube inlet was installed into the Teflon® interface and the pump was installed onto the tube outlet. An aliquot was drawn into the tube with the pump. One to five pump cycles were used (maximum of five) according to vendor specifications. Data were corrected for barometric pressure (measured by a micrometeorological station in WMF-629) as follows:

$$\frac{\text{tube reading}}{\text{no. pump cycles}} \times \frac{29.92'' \text{ Hg}_{STP}}{24.85'' \text{ Hg}_{\text{measured}}} = \text{corrected concentration}$$

HCl was detected in drums IDRFOP4315011 and IDRFOP1200878 at 4.2 and 0.2 ppm, respectively. H₂O was detected in drums IDRFOP4315011 and IDRFOP1200878 at 5.4 and 4.8 mg/L, respectively. Ambient air H₂O concentration was not measured.

If you have any questions or comments, please do not hesitate to give us a call or PROFS (6-8255/KG3 for Galloway or 6-8036/JJY for Jolley). Have a good day.

jgi

Enclosed:
As Stated

cc: K. J. Galloway, MS-3953
D. L. Miller, MS-2208 *DLM*
J. G. Jolley (Letter File)

Table 1.

Drum ID Number	Content Code	Location	Test Start Date/Time	Test End Date/Time	Number Pump Cycles	HCl Tube Response (ppm)	HCl Concentration (ppm)
IDRFOP4315011	3	SWEPP High Bay	5/8/96 13:39	5/8/96 13:40	1	3.5	4.2
IDRFOP1200878	1	SWEPP High Bay	5/8/96 13:54	5/8/96 13:57	5	1.0	0.2

Table 2.

Drum ID Number	Content Code	Location	Test Start Date/Time	Test End Date/Time	Number Pump Cycles	H ₂ O Tube Response (mg/L)	H ₂ O Concentration (mg/L)
IDRFOP4315011	3	SWEPP High Bay	5/8/96 13:43	5/8/96 13:44	1	4.5	5.4
IDRFOP1200878	1	SWEPP High Bay	5/8/96 13:59	5/8/96 14:00	1	4.0	4.8

LOCKHEED MARTIN

Lockheed Idaho Technologies Company
P. O. Box 1625 Idaho Falls, ID 83415

May 8, 1996

Mr. G. L. Beausoleil
U.S. Department Energy
Idaho Operations Office
850 Energy Drive, MS 4201
Idaho Falls, ID 83401-1563

RESPONSE TO THE REQUEST FROM THE IDAHO DEPARTMENT OF HEALTH AND
WELFARE, DIVISION OF ENVIRONMENTAL QUALITY (DEQ), PERMITTING BUREAU
FOR INFORMATION CONCERNING PINHOLES IN WASTE DRUMS AT THE RADIOACTIVE
WASTE MANAGEMENT COMPLEX (RWMC) - FPH-190-96

Dear Mr. Beausoleil:

The Idaho National Engineering Laboratory (INEL)/Operating Permits Bureau (OPB) Quarterly Meeting was held on April 25, 1996, with the Department of Environmental Quality (DEQ) OPB personnel. During this meeting a concern was expressed by Mr. Randall W. Steger, Manager, OPB, regarding perceived violations of the Radioactive Waste Management Complex (RWMC) Hazardous Waste Management Act (HWMA) Resource Conservation and Recovery Act (RCRA) Permit as a result of the pinhole corrosion problem occurring in some of the mixed-waste drums currently in storage at the RWMC. This letter addresses these concerns and describes the corrective actions taken by the RWMC as requested by Mr. Steger.

During routine weekly RCRA inspections (in accordance with the RWMC HWMA/RCRA Permit, Attachment 4, titled Inspections) of the mixed wastes located in Building Numbers WMF-628 and WMF-629, an apparent "pinhole corrosion" problem was detected on several waste drums. As required by the RWMC HWMA/RCRA Permit, [Attachment 1.B., Section D-1b(2)(1) (page D-66, lines 22-30), which references Section D-1a(2)(1) (page D-41, lines 17-22) and; the Final Permit Section, Permit Conditions II.C. titled Condition of Containers and II.E.4.], the containers with questionable integrity were overpacked into 83-gallon drums. As of May 6, 1996, all of the containers in Building Numbers WMF-628 and WMF-629 suspected of having corrosion pinholes have been overpacked. The RWMC is now overpacking drums in the Air-Support Weather Shield (ASWS) suspected of having pinhole corrosion, in accordance with Title 40 of the Code of Federal Regulations (CFR), Section 265.171. As the drums are removed from the stack and inspected, the drums which fail the inspection criteria, including suspect pinholes, are overpacked. These containers may then be moved into one of the fully-permitted Waste Storage Facility (WSF) Type II Storage Modules.

G. L. Beausoleil
May 8, 1996
FPH-190-96
Page 2

A Transuranic (TRU) Drum Corrosion Task Team was formed April 10, 1996 to investigate the mixed waste-drum pinhole corrosion problem.

This task team has four main objectives:

1. Identify the pinhole corrosion mechanism
2. Identify the short-and long-term operational impacts
3. Identify impacts to the Waste Isolation Pilot Plant (WIPP) certifiability
4. Review the container integrity evaluation process.

This task team has used Real Time Radiography (RTR), radioassay, headspace gas sampling and analysis, and ultrasonic testing to evaluate the mechanism of the pinhole corrosion problem.

The preliminary investigation of the pinhole corrosion problem has resulted in the following conclusions:

- No releases of radiological contamination have been detected from any of the drums to date
- The waste in the drums is contained within a 90-mil polyethylene liner and has not been detected outside of the waste drums
- Minute amounts of a secondary liquid (assumed to be condensate-related) have "oozed" from some of the pinholes.
 - The liquid is not radioactive or radiologically contaminated and is not mixed waste
 - The largest amount collected for a sample was approximately 0.5 milliliter
 - The liquid is acidic (pH 2), apparently caused by chlorine released from the chlorinated hydrocarbons within the waste, reacting with moist air, drawn through the drum vent and forming an acidic solution. The solution appears to condense on the inside of the drum and corrode the carbon steel, creating pinholes.

Additionally, professional engineers have performed a preliminary structural analysis of the storage drums and stacks. Conservative calculations show that over 50 percent of the drum thickness could corrode away around the entire circumference before structural failure of the drum occurs. Ultrasonic testing of the pinhole areas indicates very little thinning of the drum walls. The failure mechanism would be a slow deformation, leading to a shortening of the drum by a maximum of 2.5 inches at the rib. Existing operational procedures limit drums heavier than 700 lbs to the bottom of the stack, which limits the axial load on the bottom drum. Analyses of the stack stability shows a stack could tilt 33° without a drum toppling off the top row. This tilt would require two or more ribs to completely fail in one stack of drums without being noticed during routine weekly HWMA/RCRA inspections. The drums located on the bottom outside corners of the drum stacks are the most critical to stack stability and these drums are the most accessible and easily inspected for corrosion.

As a result of these preliminary findings, it has been determined that a radioactive release has not occurred and threat of a release to the environment has a low probability of occurring. If a drum is determined to have questionable integrity, the drum is overpacked as a routine operation, in accordance with the applicable sections of the RWMC HWMA/RCRA Permit as indicated above.

Title 29 of the CFR, Section 1910.120 (p), requires that employers conducting operations at a treatment, storage and disposal facility provide and implement a safety and health program. This program is designed to identify, evaluate, and control safety and health hazards for the purpose of employee protection. In accordance with the established RWMC Safety and Health Program, Industrial Hygiene is conducting ongoing monitoring in the storage facilities. Potential employee exposure to the acidic material on drum surfaces has also been evaluated. The Industrial Hygienist reports that the only route for worker exposure to the acidic material on drum surfaces is through direct contact. Personnel handling these containers have been briefed on the safety concerns and the appropriate safe-work practices associated with the handling of these drums have been implemented.

Mixed-waste containers stored at the RWMC are vented to prevent a buildup of radiolytic hydrogen. Volatile organic compounds (VOCs) in these containers are also incidentally vented from the containers into the atmosphere inside the buildings. Routine VOC air monitoring activities have not detected any increased levels in VOC emissions due to the pinhole corrosion problem. Monitoring results indicate that employee exposures to VOCs have been below established regulatory limits to date. All buildings at the RWMC handling mixed wastes are continuously monitored for releases of contamination. Personnel exposure to radiation and hazardous materials is also monitored.

G. L. Beausoleil
May 8, 1996
FPH-190-96
Page 4

Based on our original and continuing analysis of the issue, it has been determined that the pinhole corrosion problem does not constitute an emergency condition and no release of materials which could threaten human health or the environment has occurred. Upon discovery of the problem, immediate corrective action in accordance with the permit was taken to overpack the suspect drums. The DEQ has been informed of the situation, and LITCO/DOE has also provided the DEQ with up-to-date information on the status of our corrective actions and investigations of the cause of the problem. The expected rate of corrosion is too slow to warrant increased inspection frequency and the attendant increase in worker radiation exposure. The final TRU Drum Corrosion Task Team report is scheduled for completion in June 1996 and any recommended changes in the facility operation will be evaluated at that time.

The RWMC discovered this pinhole corrosion problem during the routine HWMA/RCRA-required weekly inspections performed in accordance with the RWMC HWMA/RCRA permit and 40 CFR 265. The RWMC will continue to operate safely and within the conditions established in the RWMC HWMA/RCRA permit and no changes in operations or permit conditions are needed at this time.

If you have questions or require additional information, please call me at 526-8916.

Sincerely,

F. P. Hughes, Manager
Radioactive Waste Management Complex

KEK:mp

cc: DOE-ID

J. D. Depperschmidt, MS 1146
J. N. Perry, MS 4201
D. N. Rasch, MS 1146
J. R. Wade, MS 4201

LITCO

D. L. Forsberg, MS 4201
P. B. Gray, MS 3428
J. M. Jackson, MS 4201
K. E. Kooda, MS 2414
J. C. Kvanne, MS 4201
J. R. Mitchell, MS 3428
C. L. Tellez, MS 3428
J. A. Van Vliet, MS 3940
F. P. Hughes File

LOCKHEED MARTIN

Lockheed Idaho Technologies Company
P. O. Box 1625 Idaho Falls, ID 83415

May 22, 1996

Mr. Randal W. Steger, Manager
Operating and Permits Bureau
1410 N. Hilton
Boise, ID 83706-1255

bcc: P. B. Gray, MS 3428
F. P. Hughes, MS 4201
J. M. Jackson, MS 4201
K. E. Kooda, MS 2414
C. R. Koshuta, MS 3428
J. C. Kvamme, MS 4201
C. L. Tellez, MS 3428
J. R. Mitchell File

PINHOLE DRUMS AT RWMC - JRM-171-96

Dear Mr. Steger:

The Idaho National Engineering Laboratory (INEL)/Operating Permits Bureau (OPB) Quarterly Meeting was held on April 25, 1996, with the Department of Environmental Quality (DEQ) OPB personnel. During this meeting a concern was expressed by Mr. Randal W. Steger, Manager, OPB, regarding perceived violations of the Radioactive Waste management Complex (RWMC), Hazardous Waste Management Act (HWMA), Resource Conservation and Recovery Act (RCRA) Permit as a result of the pinhole corrosion problem occurring in some of the mixed-waste drums currently in storage at the RWMC. This letter addresses these concerns and describes the corrective actions taken by the RWMC as requested by Mr. Steger.

During routine weekly RCRA inspections (in accordance with the RWMC HWMA/RCRA Permit, Attachment 4, titled Inspections) of the mixed wastes located in buildings WMF-628 and WMF-629, an apparent "pinhole corrosion" problem was detected on several waste drums. As required by the RWMC HWMA/RCRA Permit, [Attachment 1.b., Section D-1b(2)(1) (page D-66, lines 22-30), which references Section D-1a(2)(1) (page D-41, lines 17-22) and; the Final Permit Section, Permit Conditions II.C. titled Condition of Containers and II.E.4.], the containers with questionable integrity were overpacked into 83-gallon drums. As of May 6, 1996, all of the containers in buildings WMF-628 and WMF-629 suspected of having corrosion pinholes have been overpacked. The RWMC is now overpacking drums in the Air-Support Weather Shield (ASWS) suspected of having pinhole corrosion, in accordance with Title 40 of the Code of Federal Regulations (CFR), Section 265.171. As the drums are removed from the stack and inspected, the drums which fail the inspection criteria, including suspect pinholes, are overpacked. These containers may then be moved into one of the fully-permitted Waste Storage Facility (WSF) Type II Storage Modules.

A Transuranic (TRU) Drum Corrosion Task Team was formed April 10, 1996, to investigate the mixed waste-drum pinhole corrosion problem.

This task team has four main objectives:

1. Identify the pinhole corrosion mechanism
2. Identify the short- and long-term operational impacts
3. Identify impacts to the Waste Isolation Pilot Plant (WIPP) certifiability
4. Review the container integrity evaluation process.

This task team has used Real Time Radiography (RTR), radioassay, headspace gas sampling and analysis, and ultrasonic testing to evaluate the mechanism of the pinhole corrosion problem.

The preliminary investigation of the pinhole corrosion problem has resulted in the following conclusions:

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 - The liquid is not radioactive or radiologically contaminated and is not mixed waste
 - The largest amount collected for a sample was approximately 0.5 milliliter
 - The liquid is acidic (pH 2), apparently caused by chlorine released from the chlorinated hydrocarbons within the waste, reacting with moist air, drawn through the drum vent and forming an acidic solution. The solution appears to condense on the inside of the drum and corrode the carbon steel, creating pinholes.

Mr. Randal W. Steger
May 22, 1996
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Additionally, professional engineers have performed a preliminary structural analysis of the storage drums and stacks. Conservative calculations show that over 50 percent of the drum thickness could corrode away around the entire circumference before structural failure of the drum occurs. Ultrasonic testing of the pinhole areas indicates very little thinning of the drum walls. The failure mechanism would be a slow deformation, leading to a shortening of the drum by a maximum of 2.5 inches at the rib. Existing operational procedures limit drums heavier than 700 lbs to the bottom of the stack, which limits the axial load on the bottom drum. Analyses of the stack stability show a stack could tilt 33° without a drum toppling off the top row. This tilt would require two or more ribs to completely fill in one stack of drums without being noticed during routine weekly HWMA/RCRA inspections. The drums located on the bottom outside corners of the drum stacks are the most critical to stack stability and these drums are the most accessible and easily inspected for corrosion.

The Waste Storage Facility Safety Analysis Report (WSF SAR) hazard/accident analysis (maximum credible) for the breached container assumes that the container is a waste box and 10 percent of its contents are lost due to a breach. The assumptions in this analysis would be equivalent to 150 waste drums breaching and losing 10 percent of their contents. A drum toppling scenario due to corrosion that exceeds the box spill in the (WSF SAR) has been evaluated and determined to be incredible (less than 1 in 10⁶) by Department of Energy Safety Analysis guidelines. The WSF SAR completely bounds the potential risk of a drum toppling event and existing Technical Safety Requirements assures that this potential risk is limited by inspection and overpacking.

As a result of these preliminary findings, it has been determined that a radioactive release has not occurred and threat of a release to the environment has a low probability of occurring. If a drum is determined to have questionable integrity, the drum is overpacked as a routine operation, in accordance with the applicable sections of the RWMC HWMA/RCRA Permit as indicated above.

Title 29 of the CFR, Section 1910.120 (p), requires that employers conducting operations at a treatment, storage and disposal facility provide and implement a safety and health program. This program is designed to identify, evaluate, and control safety and health hazards for the purpose of employee protection. In accordance with the established RWMC Safety and Health Program, Industrial Hygiene is conducting ongoing monitoring in the storage facilities. Potential employee exposure to the acidic material on drum surfaces has also been evaluated. The Industrial Hygienist reports that the only route for worker exposure to the acidic material on drum surfaces is through direct contact. Personnel handling these containers have been briefed on the safety concerns and the appropriate safe-work practices associated with the handling of these drums have been implemented.

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Mixed-waste containers stored at the RWMC are vented to prevent a buildup of radiolytic hydrogen. Volatile organic compounds (VOCs) in these containers are also incidentally vented from the containers into the atmosphere inside the buildings. Routine VOC air monitoring activities have not detected any increased levels in VOC emissions due to the pinhole corrosion problem. Monitoring results indicate that employee exposures to VOCs have been below established regulatory limits to date. All buildings at the RWMC handling mixed wastes are continuously monitored for releases of contamination. Personnel exposure to radiation and hazardous materials is also monitored.

Based on our original and continuing analysis of the issue, it has been determined that the pinhole corrosion problem does not constitute an emergency condition and no release of materials which could threaten human health or the environment has occurred. Upon discovery of the problem, immediate corrective action in accordance with the permit was taken to overpack the suspect drums. The DEQ has been informed of the situation, and LITCO/DOE-ID has also provided the DEQ with up-to-date information on the status of our corrective actions and investigations of the cause of the problem. The expected rate of corrosion is too slow to warrant increased inspection frequency and the attendant increase in worker radiation exposure. The final TRU Drum Corrosion Task Team report will be sent to the OPB by June 28, 1996.

The RWMC discovered this pinhole corrosion problem during the routine HWMA/RCRA-required weekly inspections performed in accordance with the RWMC HWMA/RCRA Permit and 40 CFR 265. The RWMC will continue to operate safely and within the conditions established in the RWMC HWMA/RCRA Permit and no changes in operations or permit conditions are needed at this time.

The INEL recognizes concerns over the aging TRU waste containers and is aggressively pursuing treatment and disposal options. The Waste Isolation Pilot Plant is due to open in April 1998 and a contract award for the Advanced Mixed Waste Treatment Facility is scheduled for September 1996. Until these facilities open and accept TRU waste the containers will be managed safely in accordance with the RWMC HWMA/RCRA Permit.

Additionally, enclosed are photographs taken of the drums during the OPB walkthrough on April 24, 1996.

Mr. Randal W. Steger
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If you have any questions or require further information, please call Phillip Gray of my staff at (208) 526-7934.

Sincerely,

A handwritten signature in cursive script that reads "Jay R. Mitchell". The signature is written in dark ink and is positioned above the typed name and title.

Jay R. Mitchell, Manager
NEPA/Permitting Department

PBG:cl

cc: G. L. Beausoleil, DOE-ID, MS 4201
R. C. Cullison, DOE-ID, MS 1146
J. D. Depperschmidt, DOE-ID, MS 1146
D. N. Rasch, DOE-ID, MS 1146
J. R. Wade, DOE-ID, MS 4201

SAFETY EVALUATION SCREEN

Nuclear Facility or Activity: Radioactive Waste Management Complex (RWMC)Safety Evaluation Number: SE-RWMC-96-016
Facility-Year-NumberRevision No.: 0

1.	Title of Proposed Change or New Information:
	Indicate which type: Proposed Change _____ New Information <u>X</u>
	Probability of Drum Corrosion and Resulting Perforations Causing Stack Collapse and Multiple Drum Breaches.
2.	Describe the Proposed Change or New Information:
	Waste containers (55 gallon drums) have been identified that have small holes (perforations) in the outer steel container. The presences of the perforations in the drums indicate a corrosion problem that could degrade their structural integrity and increase the probability of a drum stack collapse during routine operations or during a design basis earthquake.
3.	Describe the purpose of the Proposed Change or New Information:
	Does not apply.
4.	Describe the direct and/or indirect effects of the Proposed Change or New Information:
	The occurrence of drum corrosion raises the question of the adequacy of the WSF Safety Analysis Report in addressing the possible risks associated with stack stability and multiple waste container breaches caused by collapsing drum stacks during normal operations and during the design basis earthquake.
5.	List the reference location of each safety requirement in the authorization basis or any Technical Safety Requirement (TSR) related to the Proposed Change or New Information:
	The WSF SAR has analysis for a breach and associated spill of waste (WSF SAR, sec. 11.2.1). The analysis results in consequences (dose to the worker) that do not require any extra safety requirements beyond those already practiced in the Radiological Protection Program. The WSF TSR has requirements for waste container integrity (TSR 3/4.2.2) that requires the physical integrity of waste containers to be verified and that containers with holes, punctures or cracks be overpacked within 7 days. The requirement to overpack within 7 days is an arbitrary time limit and is not driven by any risk presented in the SAR hazard/accident analysis. The WSF TSR also has an Administrative Control requiring waste container stack stability which is ensured by implementing weight segregation and the use of retaining spacers. This last requirement is based on a probable earthquake occurring and the waste stacks not collapsing through the use of steel pallets, retaining spacers and the assumption that the stacked drums are structurally sound.

SAFETY EVALUATION SCREEN

Nuclear Facility or Activity: Radioactive Waste Management Complex (RWMC)Safety Evaluation Number: SE-RWMC-96-016
Facility-Year-NumberRevision No.: 0

6. Does the New Information or Proposed Change indicate a potential inadequacy in a safety analysis or a possible reduction in margin of safety in a TSR?
Yes _____ No X Explain:

The WSF SAR hazard/accident analysis for the breached container assumes that the container is a waste box and 10 percent of its contents are lost due to a breach. The breached waste box material at risk is equivalent to 150 waste drums breaching and losing 10 percent of their contents. The consequence of a breach of this magnitude would be a 4 Rem dose to a worker exposed to the airborne radiological hazard for 5 minutes and a negligible dose to a person offsite. The SAR accident analysis would be inadequate if the corrosion of the waste drums would result in probable consequences that would exceed the breaching of 150 drums.

There are two accidents to consider, a single stack collapse during normal operations and multiple stacks collapsing during the design basis earthquake. These two scenarios will not cause more than 150 waste drums to breach because of the waste stack inspection requirements and the probability of a significant number of drums corroding to the point that only 30% of the drum wall remained.

The probability of a single stack collapse during normal operations would require that at least 4 first layer drums corrode unnoticed to the point that they become structurally unsound (about 30% of the drum wall remaining). The value of 30% of the drum wall is recommended by RWMC EDF-0530 as the minimum remaining drum wall that will support a 5 high drum column before collapsing. The best estimate of the probability of the single stack collapse is the product of the corrosion failure of 4 adjacent drums, that these drums are located in the bottom corner of a row and inspection fails to detect the corrosion. Using 1.0×10^{-4} for failure of 4 adjacent drums, 1.0×10^{-2} for the failed drums being located in the bottom corner of the stack and 1.0×10^{-2} for failure to detect corrosion results in an overall probability of 1.0×10^{-8} (not credible). The value of 1.0×10^{-8} does not consider the probability of the stack collapse causing the drums to breach or the fact that an end stack collapse would only involve 40 drums.

The multiple stack collapse during a design basis earthquake is also not credible when one considers that the probability of the earthquake is only $2.0 \times 10^{-6}/\text{yr}$ (reference WSF SAR Appendix C) and multiple bottom corner drums on each stack must have corroded to the minimum drum wall thickness.

The WSF TSRs do not contain a margin of safety (no safety limit) therefore a margin of safety is not affected by the consequences of drum corrosion.

SAFETY EVALUATION SCREEN

Nuclear Facility or Activity: Radioactive Waste Management Complex (RWMC)Safety Evaluation Number: SE-RWMC-96-016
Facility-Year-NumberRevision No.: 0

7.	Does the Proposed Change or New Information involve a change or modification to the nuclear facility or activity described in the authorization basis or a TSR? Yes _____ No <u>X</u> Explain:
Does not apply, the new information is for a condition that currently exists with the waste containers stored in WSF.	
8.	Does the Proposed Change or New Information involve a temporary or permanent change to a procedure described by or defined in the authorization basis or a TSR? Yes _____ No <u>X</u> Explain:
Current procedures for examination and overpacking of the waste containers adequately implement the requirements of the TSR and are sufficient to resolve any risk associated with the waste containers that appear to have corroded/perforated drums.	
9.	Does the Proposed Change involve a test or experiment not described and considered or clearly enveloped in the authorization basis? Yes _____ No <u>X</u> Explain:
The existing condition with the waste drums is not part of or the result of a test or an experiment.	
10.	Must an Unreviewed Safety Question Determination form be completed? Yes _____ No <u>X</u> Explain:
All of the key questions have a No answer, therefore a USQ does not exist and a USQ determination form need not be completed. The WSF SAR addresses an accident (breach and leak of a waste box) that bounds any postulated risk associated with the apparent corrosion/perforation of the waste drums. Also it should be noted that no radiological contamination has been detected as a result of the perforations and the drums are overpacked within 7 days which assures that there is never any significant number of drums that have a potential to leak or become structurally unsound.	

SAFETY EVALUATION SCREEN

Nuclear Facility or Activity: Radioactive Waste Management Complex (RWMC)

Safety Evaluation Number: SE-RWMC-96-016
Facility-Year-Number

Revision No.: 0

Paul R. Neppner 3230
Preparer Signature/Organization

5-23-96
Date

Amadeo Rans. 3170
Independent Review Certified USQ Evaluator Signature

5/23/96.
Date

Shannon for F. Hughes
Approval Signature/Manager of the Nuclear Facility or Activity

5/23/96.
Date

ENGINEERING DESIGN FILE

PROJECT FILE NO. _____

EDF SERIAL NO. _____

0530

FUNCTIONAL FILE NO. _____

RWMCPROJECT/TASK **RWMC Drum Storage Evaluation**DATE **May 2, 1996**SUBTASK **Corrosion Failure Modes**EDF PAGE NO. **1** OF **16****SUBJECT****55 Gallon Storage Drum Structural Failure Due to Corrosion****ABSTRACT**

The EDF documents several analyses of 55 gallons drums which were purchased to comply with Department of Transportation (DOT) 17C requirements. The drum dimensions used in the analyses were a diameter of 22-1/2 inches, a height of about 34-3/4 inches and a drum body nominal thickness of 0.0598 inches (16 gage). The body thickness was varied to determine the thickness at which the stresses produced by a 4000 lb axial load would exceed either the material yield stress or the buckling stress.

Several computer models were used to analyze the drums. The finite element program COSMOS/M was used for the majority of the work. IDEAS and hand calculations were done to verify that no major errors were made in the models. The models included a straight walled cylindrical model with top and bottom, a cylindrical model with ribs at approximately the 1/3 points of the height and simple supports at the top and bottom, and a model of about one-quarter of a drum with one rib. The IDEAS model used to verify results was a cylindrical model with ribs. The geometry and fineness of the mesh of the ribs had significant effects on the stress. The quarter model used for most of the drum rib analyses had rib geometry taken from a tracing of a section of a drum.

Several previous EDFs were reviewed as part of the work of this EDF. They are included in the References. RWMC EDF 406 predicted failure due to buckling at a thickness of 0.006 inches. It recommended that a thickness of 0.018 inches be used to ensure adequate safety factor. The straight cylinder wall model results were similar to the results of this EDF. The following are the approximate thicknesses at which failure occurred for each of the models analyzed:

Model	Wall Thickness at Failure	% of Original Wall Thickness	Failure Type
Hand Calculations	0.006"	10%	Buckling
Straight Wall Cylinder	0.006"	10%	Buckling
Straight Wall Cylinder w/ 4 holes	0.008"	13%	Buckling
21% of Circumference Hole	0.0478"	80%	Yielding
Quarter Drum with Rib	0.037"	62%	Yielding*
Axisymmetric, 3 Rib, 4 kip Load	0.036"	60%	Yielding*
Axisymmetric, 3 Rib, 2.8 kip Load	0.029"	49%	Yielding*

KEYWORDS (e.g. area, structure no., general subject matter, etc.)

RWMC, drums, evaluation, corrosion

AUTHOR/P. E. STAMP

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EDF file, K. Kooda, D. Wilkinson, RWMC files

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LITCO APPROVAL

DATE

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PROJECT FILE NO. _____

EDF SERIAL NO. 0530

FUNCTIONAL FILE NO. RWMC

PROJECT/TASK RWMC Drum Storage Evaluation

DATE May 2, 1996

SUBTASK Corrosion Failure Modes

EDF PAGE NO. 2 OF 16

ABSTRACT (Continued)

*This causes collapse of the rib resulting in shortening of the drum at the rib.

Buckling stresses were calculated using the buckling equation for a simply supported cylinder with an axial load. See Reference 3. Buckling stresses were checked by performing buckling analyses for some of the thicknesses. The results were similar to the results from the equation. The attached graphs show plots of the Von Mises stress from the analyses versus thickness of the body of the drum. The failure stress (the lower of buckling or yield stress) is also plotted on most of the graphs.

A short calculation of the stability of stack under vertical loading was performed. It assumed that one of the ribs had failed on a bottom drum. This may result in a maximum drum stack shortening of about 2-1/2 inches. The calculations show that a single drum is stable if sliding is prevented until it tilts about 33 degrees. This is equivalent to a shortening on one side of about 12 inches. If the nesting pallets perform as they are intended, failure of one rib should not cause a drum to fall. Failure of two or more ribs may cause a drum to fall depending on the extent and location of the failure.

Buckling of the drum during handling may be a problem at a drum body thickness of 0.014 inches. This should be investigated further.

Assumptions:

1. Drums are a mild steel with minimum yield stress of 36,000 psi.
2. The worst case load on the drums is 4,000 lbs. Four, 1,000 lbs drums on top of the drum being analyzed. This is a conservative assumption since the average drum weight is about 500 lbs. Information received after most of the analyses were performed indicates that the maximum weight for a drum above the bottom layer is 700 lbs. This means that the maximum stresses in the bottom drum would be about 70% of the stress obtained from these analyses.
3. Failure of a drum is defined as exceeding the assumed yield stress or the theoretical buckling stress. Failure of a stack is falling of one or more drums.
4. Seismic loads were not included in this EDF.
5. The nesting pallet (XUREX indexing fixture) will hold the drums in place during failure of 1 drum rib.
6. The METTON polymer used for the "XUREX" nesting pallet has a tensile modulus of 287 ksi, a flexural modulus of 284 ksi, a flexural strength at 5% strain of 10.2 ksi, and a tensile strength at yield of 6.5 ksi.

Color plots of stress obtained from the analyses will be placed in the EDF file. However, they are not included in this EDF. Copies of the plot may be obtained by contacting Scott Jensen at 526-0544.

References:

1. COSMOS/M 1.70-A, STRUCTURAL RESEARCH AND ANALYSIS CORPORATION
2. IDEAS
3. Buckling of Bars, Plates and Shells, by Don O. Brush and Bo O. Almorth
4. RWMC EDF 406, Pad A Drum Wall Thickness Calculation
5. INEL Drawing Number 446756, 55 Gallon Drum "Eight Pack" Nesting Pallet

Other related EDFs that were reviewed but not used:

1. AMG-01-94, Seismic Stability and Pallet Stress Analysis
2. RWMC EDF 405, Drum Stack Stability Evaluation

Critical buckling stress for a cylinder under axial load

Reference: Buckling of Bars, Plates, and Shells by Brush and Almroth

Modulus of Elasticity (E) = 29,000 ksi
 Radius (a) = 11.25 in
 Thickness (h) = 0.0598 in
 Poisson's ratio (u) = 0.30
 Yield Stress (Y) = 36 ksi

55 Gallon Drum

COSMOS Stress Analysis

2-May-96

Axisymmetric Model with 3 Ribs

Buckling stress from the theoretical equation for buckling of a simply supported axially loaded cylinder.

(in) Thickness	(ksi) Critical Buckling Stress	Von Mises Stress (ksi)	
		4 kip load	2.8 kip load
0.0030	4.7		
0.0060	9.4		
0.0120	18.7		
0.0231	36.0		46.8
0.0299	36.0	46.2	33.2
0.0349	36.0	37.4	26.9
0.0399	36.0	30.9	22.2
0.0478	36.0	23.8	17.1
0.0598	36.0	17.1	12.2

Stress Graph

Critical buckling stress for a cylinder under axial load

Reference: Buckling of Bars, Plates, and Shells by Brush and Almroth

Modulus of Elasticity (E) = 29,000 ksi
 Radius (a) = 11.25 in
 Thickness (h) = 0.0598 in
 Poisson's ratio (u) = 0.30
 Yield Stress (Y) = 36 ksi

(in)	(ksi)	(ksi)
Thickness	Critical Buckling Stress	Von Mises Stress
0.0030	4.68	
0.0060	9.36	
0.0120	18.72	
0.0231	36.00	
0.0299	36.00	46.70
0.0399	36.00	31.40
0.0478	36.00	24.20
0.0598	36.00	17.40

Stress Graph

55 Gallon Drum
 COSMOS Stress Analysis

Quarter Model with Ribs
 4 kips Load

2-May-96

Buckling stress from the theoretical equation for buckling of a simply supported axially loaded cylinder.

DRUM STABILITY CALCULATIONS:

Drum Dimensions:

Diameter - $D := 22.5 \cdot \text{in}$ Height - $H := 34.75 \cdot \text{in}$
 Assumed height of center of gravity of each drum - $\text{cg} := 17 \cdot \text{in}$
 Height of drum and nesting fixter - $H1 := 35 \cdot \text{in}$

See the attached drum and stack dimensional sketch.

Drums are unstable when the center of gravity is beyond the bottom of the drum. The following calculations determine the tipping angle at which one drum and stacks of 2, 3, and 4 drums become unstable. The vertical dimension (d) corresponding to the angles is also calculated.

One drum - $\theta_1 := \text{atan}\left(\frac{11.25 \cdot \text{in}}{17 \cdot \text{in}}\right)$ $\theta_1 = 33.495 \cdot \text{deg}$

$d_1 := D \cdot \sin(\theta_1)$ $d_1 = 12.417 \cdot \text{in}$

Two drum stack - $\theta_2 := \text{atan}\left(\frac{11.25 \cdot \text{in}}{35 \cdot \text{in}}\right)$ $\theta_2 = 17.819 \cdot \text{deg}$

$d_2 := D \cdot \sin(\theta_2)$ $d_2 = 6.885 \cdot \text{in}$

Three drum stack - $\theta_3 := \text{atan}\left(\frac{11.25 \cdot \text{in}}{52 \cdot \text{in}}\right)$ $\theta_3 = 12.208 \cdot \text{deg}$

$d_3 := D \cdot \sin(\theta_3)$ $d_3 = 4.758 \cdot \text{in}$

Four drum stack - $\theta_4 := \text{atan}\left(\frac{11.25 \cdot \text{in}}{70 \cdot \text{in}}\right)$ $\theta_4 = 9.13 \cdot \text{deg}$

$d_4 := D \cdot \sin(\theta_4)$ $d_4 = 3.57 \cdot \text{in}$

See the drum stability sketch for an illustration of the above.

Collapse of the drum rolling ribs may cause tipping of the drums. However, the "XUREX" nesting pallet between the drum will restrain sliding and tipping to some extent. This nesting pallet is shown on INEL Drawing No. 446756. The nesting pallet is located between the drum layers. The following calculations as an estimate of the movement of the drums with collapse of a rib and restraint from the nesting pallet.

Outside diameter of the nesting pallet restraining rib - $Dr := 22.20 \cdot \text{in}$

$D - Dr = 0.3 \cdot \text{in}$ Angle if slippage is difference in diameters -

$\phi := \text{atan}\left(\frac{0.03 \cdot \text{in}}{17 \cdot \text{in}}\right)$ $\phi = 0.101 \cdot \text{deg}$

Calculate angle if one rolling rib collapses on one side of drum -

$$\alpha := \text{atan}\left(\frac{2.5 \cdot \text{in}}{22.5 \cdot \text{in}}\right) \quad \alpha = 6.34 \cdot \text{deg}$$

Calculate the distance the nesting pallet would have to stretch in order for a drum to tip to the above angle -

$$\text{For one drum -} \quad s1 := 17.5 \cdot \text{in} \cdot \sin(\alpha) \quad s1 = 1.933 \cdot \text{in}$$

Estimate the stretching of the nesting pallet -

Area of nesting pallet that is stretching -

$$A := \frac{1}{4} \cdot \text{in} \cdot 24 \cdot \text{in} \quad A = 6 \cdot \text{in}^2$$

Assume 24" x 1/4"

Assume length being stretched -

$$ln := 2 \cdot \text{in}$$

The maximum force will be less than the weight. Assume -

$$P_{\max} := 700 \cdot \text{lbf}$$

$$\text{For METTON polymer material -} \quad Et := 287000 \cdot \frac{\text{lbf}}{\text{in}^2}$$

$$sn := \frac{P_{\max} \cdot ln}{A \cdot Et} \quad sn = 8.13 \cdot 10^{-4} \cdot \text{in} \quad \frac{sn}{s1} = 4.207 \cdot 10^{-4}$$

Angle of tipping based on stretching and slipping -

$$\beta := \text{atan}\left(\frac{sn}{35 \cdot \text{in}}\right) \quad \beta = 0.001 \cdot \text{deg}$$

$$\beta + \phi = 0.102 \cdot \text{deg}$$

CONCLUSIONS:

1. If the nesting pallet did not provide any restraint, collapse of one rib will not cause instability. Collapse of two ribs may cause instability.
2. The nesting pallets provide extra safety factor since they restrain the horizontal movement of the drums. This restraint should limit the tipping angles to less than 1 degree.
3. Based on the other conclusions the likely rib failure will be a uniform collapse of a rolling rib rather than a failure that tips the drums.

TYPICAL DRUM

TYPICAL STACK

DRUM STABILITY
ANGLES & VERTICAL
MOVEMENT DIMENSIONS

STACK WITH COLLAPSE
OF ONE ROLLING RIB
ON THE BOTTOM DRUM
AND RESTRAINT BY THE
NESTING PALLET

Critical buckling stress for a cylinder under axial load

Reference: Buckling of Bars, Plates, and Shells by Brush and Almroth

Modulus of Elasticity (E) = 29,000 ksi
 Radius (a) = 11.25 in
 Thickness (h) = 0.0478 in
 Poisson's ratio (u) = 0.30
 Yield Stress (Y) = 36 ksi
 Load (P) = 4.00 kips

Stress Graph

(in) Thickness	(ksi) Critical Buckling Stress	(ksi) Actual Stress
0.0015	2.33	37.88
0.0030	4.66	18.94
0.0060	9.32	9.47
0.0090	13.98	6.31
0.0120	18.64	4.74
0.0149	23.30	3.79
0.0179	27.97	3.16
0.0209	32.63	2.71
0.0239	36.00	2.37
0.0269	36.00	2.10
0.0299	36.00	1.89
0.0329	36.00	1.72
0.0359	36.00	1.58
0.0388	36.00	1.46
0.0418	36.00	1.35
0.0448	36.00	1.26
0.0478	36.00	1.18

55 Gallon Drum
 Approximate Stress Analysis

Hand Calculations

2-May-96

Stress = P/A

Straight Cylinder

Critical buckling stress for a cylinder under axial load

Reference: Buckling of Bars, Plates, and Shells by Brush and Almroth

Modulus of Elasticity (E) = 29,000 ksi
Radius (a) = 11.25 in
Thickness (h) = 0.0478 in
Poisson's ratio (ν) = 0.30
Yield Stress (Y) = 36 ksi

(in) Thickness	(ksi) Critical Buckling Stress	(ksi) Von Mises Stress
0.0030	4.68	
0.0060	9.36	9.80
0.0120	18.72	4.90
0.0239	36.00	2.47
0.0478	36.00	1.24

Stress Graph

**55 Gallon Drum
COSMOS Stress Analysis**

Straight Cylinder Model

2-May-96

Buckling stress from the theoretical equation for buckling of a simply supported axially loaded cylinder.

4 kip Load

Critical buckling stress for a cylinder under axial load

Reference: Buckling of Bars, Plates, and Shells by Brush and Almroth

Modulus of Elasticity (E) = 29,000 ksi
Radius (a) = 11.25 in
Thickness (h) = 0.0478 in
Poisson's ratio (ν) = 0.30
Yield Stress (Y) = 36 ksi

(in) Thickness	(ksi) Critical Buckling Stress	(ksi) Von Mises Stress
0.0030	4.68	
0.0060	9.36	18.20
0.0120	18.72	8.65
0.0239	36.00	4.06
0.0359	36.00	2.72
0.0478	36.00	2.03

Stress Graph

55 Gallon Drum
COSMOS Stress Analysis

Straight Cylinder Model

2-May-96

4 holes with spaces between
12.5% of circumference
missing

4 kip Load

RWMC Drum Stability
Stress with continuous holes around the circumference

Size of hole expressed as a percent of the circumference which is missing

Hole Size Circum. %	(ksi) Von Mises Stress
3%	1.97
6%	3.63
13%	10.90
16%	17.30
19%	26.50
22%	39.20

55 Gallon Drum
COSMOS Stress Analysis

Straight Cylinder Model

Thickness = 0.0478

2-May-96

4 kip Load

Buckling stress during drum lifting
Taken from COSMOS/M model

Modulus of Elasticity (E) = 29,000 ksi
 Radius (a) = 11.25 in
 Yield Stress (Y) = 36 ksi

(in) Thickness	(ksi) Critical Buckling Stress	(ksi) Von Mises Stress
0.0060	12.04	30.10
0.0150	20.81	15.30
0.0299		9.25
0.0478		6.18
0.0598		5.02

Stress Graph

55 Gallon Drum
COSMOS Stress Analysis

Straight Cylinder Model

2-May-96

1 kip vertical load

500 lb crushing load (horiz)

Estimated
Dimensions

Traced
Dimensions

ENGINEERING DESIGN FILE

PROJECT FILE NO. _____

EDF SERIAL NO. 0530

FUNCTIONAL FILE NO. RWMC

DATE May 2, 1996

PROJECT/TASK RWMC Drum Storage Evaluation

SUBTASK Corrosion Failure Modes

EDF PAGE NO. 1 OF 16

SUBJECT **55 Gallon Storage Drum Structural Failure Due to Corrosion**

ABSTRACT

The EDF documents several analyses of 55 gallons drums which were purchased to comply with Department of Transportation (DOT) 17C requirements. The drum dimensions used in the analyses were a diameter of 22-1/2 inches, a height of about 34-3/4 inches and a drum body nominal thickness of 0.0598 inches (16 gage). The body thickness was varied to determine the thickness at which the stresses produced by a 4000 lb axial load would exceed either the material yield stress or the buckling stress.

Several computer models were used to analyze the drums. The finite element program COSMOS/M was used for the majority of the work. IDEAS and hand calculations were done to verify that no major errors were made in the models. The models included a straight walled cylindrical model with top and bottom, a cylindrical model with ribs at approximately the 1/3 points of the height and simple supports at the top and bottom, and a model of about one-quarter of a drum with one rib. The IDEAS model used to verify results was a cylindrical model with ribs. The geometry and fineness of the mesh of the ribs had significant effects on the stress. The quarter model used for most of the drum rib analyses had rib geometry taken from a tracing of a section of a drum.

Several previous EDFs were reviewed as part of the work of this EDF. They are included in the References. RWMC EDF 406 predicted failure due to buckling at a thickness of 0.006 inches. It recommended that a thickness of 0.018 inches be used to ensure adequate safety factor. The straight cylinder wall model results were similar to the results of this EDF. The following are the approximate thicknesses at which failure occurred for each of the models analyzed:

Model	Wall Thickness at Failure	% of Original Wall Thickness	Failure Type
Hand Calculations	0.006"	10%	Buckling
Straight Wall Cylinder	0.006"	10%	Buckling
Straight Wall Cylinder w/ 4 holes	0.008"	13%	Buckling
21% of Circumference Hole	0.0478"	80%	Yielding
Quarter Drum with Rib	0.037"	62%	Yielding*
Axisymmetric, 3 Rib, 4 kip Load	0.036"	60%	Yielding*
Axisymmetric, 3 Rib, 2.8 kip Load	0.029"	49%	Yielding*

KEYWORDS (e.g. area, structure no., general subject matter, etc.)

RWMC, drums, evaluation, corrosion

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EDF file, K. Kooda, D. Wilkinson, RWMC files

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ENGINEERING DESIGN FILE

PROJECT FILE NO. _____

EDF SERIAL NO. 0530FUNCTIONAL FILE NO. RWMCDATE May 2, 1996PROJECT/TASK RWMC Drum Storage EvaluationSUBTASK Corrosion Failure ModesEDF PAGE NO. 2 OF 16

ABSTRACT (Continued)

*This causes collapse of the rib resulting in shortening of the drum at the rib.

Buckling stresses were calculated using the buckling equation for a simply supported cylinder with an axial load. See Reference 3. Buckling stresses were checked by performing buckling analyses for some of the thicknesses. The results were similar to the results from the equation. The attached graphs show plots of the Von Mises stress from the analyses versus thickness of the body of the drum. The failure stress (the lower of buckling or yield stress) is also plotted on most of the graphs.

A short calculation of the stability of stack under vertical loading was performed. It assumed that one of the ribs had failed on a bottom drum. This may result in a maximum drum stack shortening of about 2-1/2 inches. The calculations show that a single drum is stable if sliding is prevented until it tilts about 33 degrees. This is equivalent to a shortening on one side of about 12 inches. If the nesting pallets perform as they are intended, failure of one rib should not cause a drum to fall. Failure of two or more ribs may cause a drum to fall depending on the extent and location of the failure.

Buckling of the drum during handling may be a problem at a drum body thickness of 0.014 inches. This should be investigated further.

Assumptions:

1. Drums are a mild steel with minimum yield stress of 36,000 psi.
2. The worst case load on the drums is 4,000 lbs. Four, 1,000 lbs drums on top of the drum being analyzed. This is a conservative assumption since the average drum weight is about 500 lbs. Information received after most of the analyses were performed indicates that the maximum weight for a drum above the bottom layer is 700 lbs. This means that the maximum stresses in the bottom drum would be about 70% of the stress obtained from these analyses.
3. Failure of a drum is defined as exceeding the assumed yield stress or the theoretical buckling stress. Failure of a stack is falling of one or more drums.
4. Seismic loads were not included in this EDF.
5. The nesting pallet (XUREX indexing fixture) will hold the drums in place during failure of 1 drum rib.
6. The METTON polymer used for the "XUREX" nesting pallet has a tensile modulus of 287 ksi, a flexural modulus of 284 ksi, a flexural strength at 5% strain of 10.2 ksi, and a tensile strength at yield of 6.5 ksi.

Color plots of stress obtained from the analyses will be placed in the EDF file. However, they are not included in this EDF. Copies of the plot may be obtained by contacting Scott Jensen at 526-0544.

References:

1. COSMOS/M 1.70-A, STRUCTURAL RESEARCH AND ANALYSIS CORPORATION
2. IDEAS
3. Buckling of Bars, Plates and Shells, by Don O. Brush and Bo O. Almorth
4. RWMC EDF 406, Pad A Drum Wall Thickness Calculation
5. INEL Drawing Number 446756, 55 Gallon Drum "Eight Pack" Nesting Pallet

Other related EDFs that were reviewed but not used:

1. AMG-01-94, Seismic Stability and Pallet Stress Analysis
2. RWMC EDF 405, Drum Stack Stability Evaluation

Critical buckling stress for a cylinder under axial load

Reference: Buckling of Bars, Plates, and Shells by Brush and Almroth

Modulus of Elasticity (E) = 29,000 ksi
Radius (a) = 11.25 in
Thickness (h) = 0.0598 in
Poisson's ratio (ν) = 0.30
Yield Stress (Y) = 36 ksi

55 Gallon Drum
COSMOS Stress Analysis

2-May-96

Axisymmetric Model with 3 Ribs

Buckling stress from the theoretical
equation for buckling of a simply
supported axially loaded cylinder.

(in) Thickness	(ksi) Critical Buckling Stress	Von Mises Stress (ksi)	
		4 kip load	2.8 kip load
0.0030	4.7		
0.0060	9.4		
0.0120	18.7		
0.0231	36.0		46.8
0.0299	36.0	46.2	33.2
0.0349	36.0	37.4	26.9
0.0399	36.0	30.9	22.2
0.0478	36.0	23.8	17.1
0.0598	36.0	17.1	12.2

Stress Graph

— Failure Stress —◆— 4 K Load —△— 2.8 K Load

Critical buckling stress for a cylinder under axial load

Reference: Buckling of Bars, Plates, and Shells by Brush and Almroth

Modulus of Elasticity (E) = 29,000 ksi
Radius (a) = 11.25 in
Thickness (h) = 0.0598 in
Poisson's ratio (ν) = 0.30
Yield Stress (Y) = 36 ksi

(in) Thickness	(ksi) Critical Buckling Stress	(ksi) Von Mises Stress
0.0030	4.68	
0.0060	9.36	
0.0120	18.72	
0.0231	36.00	
0.0299	36.00	46.70
0.0399	36.00	31.40
0.0478	36.00	24.20
0.0598	36.00	17.40

Stress Graph

55 Gallon Drum
COSMOS Stress Analysis

Quarter Model with Ribs
4 kips Load

2-May-96

Buckling stress from the theoretical equation for buckling of a simply supported axially loaded cylinder.

DRUM STABILITY CALCULATIONS:

Drum Dimensions:

Diameter - $D := 22.5 \cdot \text{in}$ Height - $H := 34.75 \cdot \text{in}$
 Assumed height of center of gravity of each drum - $cg := 17 \cdot \text{in}$
 Height of drum and nesting fixter - $H1 := 35 \cdot \text{in}$

See the attached drum and stack dimensional sketch.

Drums are unstable when the center of gravity is beyond the bottom of the drum. The following calculations determine the tipping angle at which one drum and stacks of 2, 3, and 4 drums become unstable. The vertical dimension (d) corresponding to the angles is also calculated.

One drum - $\theta_1 := \text{atan}\left(\frac{11.25 \cdot \text{in}}{17 \cdot \text{in}}\right)$ $\theta_1 = 33.495 \cdot \text{deg}$

$d_1 := D \cdot \sin(\theta_1)$ $d_1 = 12.417 \cdot \text{in}$

Two drum stack - $\theta_2 := \text{atan}\left(\frac{11.25 \cdot \text{in}}{35 \cdot \text{in}}\right)$ $\theta_2 = 17.819 \cdot \text{deg}$

$d_2 := D \cdot \sin(\theta_2)$ $d_2 = 6.885 \cdot \text{in}$

Three drum stack - $\theta_3 := \text{atan}\left(\frac{11.25 \cdot \text{in}}{52 \cdot \text{in}}\right)$ $\theta_3 = 12.208 \cdot \text{deg}$

$d_3 := D \cdot \sin(\theta_3)$ $d_3 = 4.758 \cdot \text{in}$

Four drum stack - $\theta_4 := \text{atan}\left(\frac{11.25 \cdot \text{in}}{70 \cdot \text{in}}\right)$ $\theta_4 = 9.13 \cdot \text{deg}$

$d_4 := D \cdot \sin(\theta_4)$ $d_4 = 3.57 \cdot \text{in}$

See the drum stability sketch for an illustration of the above.

Collapse of the drum rolling ribs may cause tipping of the drums. However, the "XUREX" nesting pallet between the drum will restrain sliding and tipping to some extent. This nesting pallet is shown on INEL Drawing No. 446756. The nesting pallet is located between the drum layers. The following calculations as an estimate of the movement of the drums with collapse of a rib and restraint from the nesting pallet.

Outside diameter of the nesting pallet restraining rib - $Dr := 22.20 \cdot \text{in}$

$D - Dr = 0.3 \cdot \text{in}$ Angle if slippage is difference in diameters -

$\phi := \text{atan}\left(\frac{0.03 \cdot \text{in}}{17 \cdot \text{in}}\right)$ $\phi = 0.101 \cdot \text{deg}$

Calculate angle if one rolling rib collapses on one side of drum -

$$\alpha := \operatorname{atan}\left(\frac{2.5 \cdot \text{in}}{22.5 \cdot \text{in}}\right) \quad \alpha = 6.34^\circ$$

Calculate the distance the nesting pallet would have to stretch in order for a drum to tip to the above angle -

$$\text{For one drum -} \quad s1 := 17.5 \cdot \text{in} \cdot \sin(\alpha) \quad s1 = 1.933 \cdot \text{in}$$

Estimate the stretching of the nesting pallet -

Area of nesting pallet that is stretching -

$$A := \frac{1}{4} \cdot \text{in} \cdot 24 \cdot \text{in} \quad A = 6 \cdot \text{in}^2$$

Assume 24" x 1/4"

Assume length being stretched -

$$l_n := 2 \cdot \text{in}$$

The maximum force will be less than the weight. Assume -

$$P_{\max} := 700 \cdot \text{lbf}$$

For METTON polymer material -

$$E_t := 287000 \cdot \frac{\text{lbf}}{\text{in}^2}$$

$$s_n := \frac{P_{\max} \cdot l_n}{A \cdot E_t}$$

$$s_n = 8.13 \cdot 10^{-4} \cdot \text{in}$$

$$\frac{s_n}{s1} = 4.207 \cdot 10^{-4}$$

Angle of tipping based on stretching and slipping -

$$\beta := \operatorname{atan}\left(\frac{s_n}{35 \cdot \text{in}}\right)$$

$$\beta = 0.001^\circ$$

$$\beta + \phi = 0.102^\circ$$

CONCLUSIONS:

1. If the nesting pallet did not provide any restraint, collapse of one rib will not cause instability. Collapse of two ribs may cause instability.
2. The nesting pallets provide extra safety factor since they restrain the horizontal movement of the drums. This restraint should limit the tipping angles to less than 1 degree.
3. Based on the other conclusions the likely rib failure will be a uniform collapse of a rolling rib rather than a failure that tips the drums.

TYPICAL DRUM

TYPICAL STACK

DRUM STABILITY
ANGLES & VERTICAL
MOVEMENT DIMENSIONS

STACK WITH COLLAPSE
OF ONE ROLLING RIB
ON THE BOTTOM DRUM
AND RESTRAINT BY THE
NESTING PALLET

Critical buckling stress for a cylinder under axial load

Reference: Buckling of Bars, Plates, and Shells by Brush and Almroth

Modulus of Elasticity (E) = 29,000 ksi
 Radius (a) = 11.25 in
 Thickness (h) = 0.0478 in
 Poisson's ratio (u) = 0.30
 Yield Stress (Y) = 36 ksi
 Load (P) = 4.00 kips

Stress Graph

(in) Thickness	(ksi) Critical Buckling Stress	(ksi) Actual Stress
0.0015	2.33	37.88
0.0030	4.66	18.94
0.0060	9.32	9.47
0.0090	13.98	6.31
0.0120	18.64	4.74
0.0149	23.30	3.79
0.0179	27.97	3.16
0.0209	32.63	2.71
0.0239	36.00	2.37
0.0269	36.00	2.10
0.0299	36.00	1.89
0.0329	36.00	1.72
0.0359	36.00	1.58
0.0388	36.00	1.46
0.0418	36.00	1.35
0.0448	36.00	1.26
0.0478	36.00	1.18

55 Gallon Drum
 Approximate Stress Analysis

Hand Calculations

2-May-96

Stress = P/A

Straight Cylinder

Critical buckling stress for a cylinder under axial load

Reference: Buckling of Bars, Plates, and Shells by Brush and Almroth

Modulus of Elasticity (E) = 29,000 ksi
 Radius (a) = 11.25 in
 Thickness (h) = 0.0478 in
 Poisson's ratio (u) = 0.30
 Yield Stress (Y) = 36 ksi

(in) Thickness	(ksi) Critical Buckling Stress	(ksi) Von Mises Stress
0.0030	4.68	
0.0060	9.36	9.80
0.0120	18.72	4.90
0.0239	36.00	2.47
0.0478	36.00	1.24

Stress Graph

55 Gallon Drum COSMOS Stress Analysis

Straight Cylinder Model

2-May-96

Buckling stress from the theoretical equation for buckling of a simply supported axially loaded cylinder.

4 kip Load

Critical buckling stress for a cylinder under axial load

Reference: Buckling of Bars, Plates, and Shells by Brush and Almroth

Modulus of Elasticity (E) = 29,000 ksi
Radius (a) = 11.25 in
Thickness (h) = 0.0478 in
Poisson's ratio (ν) = 0.30
Yield Stress (Y) = 36 ksi

(in) Thickness	(ksi) Critical Buckling Stress	(ksi) Von Mises Stress
0.0030	4.68	
0.0060	9.36	18.20
0.0120	18.72	8.65
0.0239	36.00	4.06
0.0359	36.00	2.72
0.0478	36.00	2.03

Stress Graph

**55 Gallon Drum
COSMOS Stress Analysis**

Straight Cylinder Model

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**4 holes with spaces between
12.5% of circumference
missing**

4 kip Load

RWMC Drum Stability

Stress with continuous holes around the circumference

Size of hole expressed as a percent of the circumference which is missing

Maximum Stress

Hole Size Circum. %	(ksi) Von Mises Stress
3%	1.97
6%	3.63
13%	10.90
16%	17.30
19%	26.50
22%	39.20

55 Gallon Drum
COSMOS Stress Analysis

Straight Cylinder Model

Thickness = 0.0478

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4 kip Load

Buckling stress during drum lifting
Taken from COSMOS/M model

Modulus of Elasticity (E) = 29,000 ksi
 Radius (a) = 11.25 in
 Yield Stress (Y) = 36 ksi

(in) Thickness	(ksi) Critical Buckling Stress	(ksi) Von Mises Stress
0.0060	12.04	30.10
0.0150	20.81	15.30
0.0299		9.25
0.0478		6.18
0.0598		5.02

Stress Graph

55 Gallon Drum
COSMOS Stress Analysis

Straight Cylinder Model

2-May-96

1 kip vertical load

500 lb crushing load (horiz)

Estimated
Dimensions

Traced
Dimensions