Accident Investigation Report

Sulfuric Acid Spill and Resulting Injury at 200 Area Effluent Treatment Facility

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ACRONYMS

ACGIH	American Conference of Governmental Industrial Hygienists
AJHA	Automated Job Hazard Analysis
ANSI	American National Standards Institute
ASME	American Society of Mechanical Engineers
BED	Building Emergency Director
CPVC	Chlorinated polyvinyl chloride
CRO	Control Room Operator
EAL	Emergency Action Level
EP	Emergency Preparedness
ETF	Effluent Treatment Facility
FC	Foot Candle
HASP	Health and Safety Plan
HAZCOM	Hazard Communication
HAZMAT	Hazardous Material
HFD	Hanford Fire Department
HFD-BC	Hanford Fire Department-Battalion Chief
HFF	Hanford Fire Department
LWPF	Liquid Waste Processing Facility
MSDS	Material System Data Sheet
MTT	Main Treatment Train
NCO	Nuclear Chemical Operator
NIOSH	National Institute of Occupational Safety and Health
ONC	Occurrence Notification Center
OSHA	Occupational Safety and Health Administration
PPE	Personal Protective Equipment
PFDF	Polyvinylidene Fluoride
RBA	Radiological Buffer Area
SOM	Shift Operations Manager
SRTC	Savannah River Technology Center
STT	Secondary Treatment Train
SWRT	Secondary Waste Receiving Tank
TEDF	Treated Effluent Disposal Facility
TLV	Threshold Limiting Value
UV/OX	Ultraviolet/Oxidation

1.0 SCOPE OF INVESTIGATION

In response to a spill and spraying of sulfuric acid on a NCO at the 200 Area Effluent Treatment Facility (ETF) on Friday, October 15, 1999, an investigation team, as directed by the LWPF Manager, was commissioned. The team was charged with reviewing the accident, developing a root cause and contributing causes, good practices and recommendations for prevention of recurrence. A formal investigation was performed using Accident Methodology per DOE 5484.1, *Environmental Protection, Safety, and Health Protection Information Reporting Requirements,* as a guide. The scope of the team's investigation was to conduct and perform analysis of the circumstances surrounding the spill, the spraying of an individual and the cleanup of the sulfuric acid.

The team consisted of six exempt and three bargaining unit employees. Representatives were from Fluor Daniel Hanford and Waste Management Federal Services Hanford. Brief resumes are included in the report. The team convened and began its investigation on Monday, October 18, 1999.

The investigation involved the following steps:

- Develop a timeline of the event.
- Review logs, written statements and work packages.
- Interview involved personnel to fully understand the event.
- View the accident scene.
- Conduct tests on the equipment to determine possible modes of failure.
- Analyze the event to determine causes.
- Propose corrective opportunities.
- Recognize positive aspects of event

Specific findings are included in Section 5 of this report, along with conclusions and judgements of need.

2.0 EXECUTIVE SUMMARY

2.1 Event Sequence

During the early morning of October 15, 1999, a NCO was conducting housekeeping in the chemical berm area of the 200 Area ETF. While performing housekeeping near the 92% sulfuric acid pump, the pump case drain line failed and the employee was sprayed with 92% acid. The operator evacuated to a safety shower, exited the safety shower briefly to call the control room and then recommenced showering. The HFD responded to the emergency call and subsequently took the individual to Kadlec Medical Center in Richland, Washington. Due to the uncertainty of the extent of tissue damage, the operator was flown to Harborview Medical Center in Seattle, Washington for further evaluation.

2.2 Emergency Response

The call to 911 was immediate and facilitated a quick response from emergency personnel. The HFD and HAZMAT crew arrived on the scene within 10 minutes of notification. Trained facility personnel provided the appropriate immediate medical care to the injured operator while others stood ready to direct the HFD to the location of the injured person. The injured employee was provided on-scene treatment by HFD and was in transit to Kadlec Medical Center in Richland, Washington within 11 minutes of the HFD arriving.

Facility and company management was informed in a timely manner. Although the event occurred in the early morning hours, a relief shift manager and others were on the scene within 2 hours. External contacts to the Employee Health Advocate and the Hanford Environmental Health Foundation staff were made in a timely manner.

2.3 Facility Response

The immediate facility response to the injury and all activities necessary to ensure facility stabilization occurred within 30 minutes of the event. A recovery team was established to assess the situation by 0630. Two individuals entered the accident scene to take pictures and preserve the area for the accident investigation team. A recovery plan was written which included the following three phases:

- Phase 1 - remove concentrated acid from the chemical berm area.
- Phase 2 - verify valve positions to ensure that the chemical system is isolated, gather pictures, and install lockouts and tagouts.
- Phase 3 – rinse down area and equipment and apply neutralizer on piping system.

All three phases of the recovery plan were completed by October 17, 1999.

2.4 Securing the Scene and Evidence

In an effort to secure the scene for the accident investigation team, a trained investigator was called out to assist in the effort. Detailed photographs and a video were taken of the scene. The area was restricted to authorized personnel only. Written statements were taken from all involved individuals with the exception of the injured NCO. Additionally, the facility performed an “as found” valve line-up and made copies of all operating logs used during and immediately after the event. This timely isolation of the area and obtaining of facts helped greatly in the investigation process.

2.5 Conclusions and Judgement of Need

2.5.1 Root Cause

The cause of the accident, the one element that if not present would have prevented the accident, is the less than adequate protection of the pump case drain line that would have prevented it breaking from an inadvertent application of an external force. The 200 area ETF Management should evaluate systems containing hazardous materials to ensure they have protection i.e., covers, vertical or horizontal supports, which would prevent inadvertent application of excessive force. Every attempt should be made to develop and provide lessons learned to potential users of this type of chemical system to prevent recurrence of similar types of events throughout the DOE complex.

2.5.2

The investigation resulted in identifying several other opportunities for improvement that, if addressed, may not have alone prevented the accident, but could have reduced the severity of the injury and improved facility operations. These conclusions and the corresponding judgements of need are presented below.

Conclusions:

1. *The pump case drain line was chemically degraded as a result of the chemical system operating conditions i.e., chemical constituents, operating temperature.*

   Judgement of Need: The 200 area ETF management should ensure that an evaluation is conducted to ensure that the existing CPVC piping is appropriate for a given application.

2. *The chemical berm area is difficult to access and to perform work in due to various systems, structures, and components.*

   Judgement of Need: The 200 area ETF management should ensure, where practical, systems, structures and components are relocated to facilitate personnel working in the area. Additionally, a human factor performance evaluation task analysis should be conducted to identify and resolve potential operability and work environment problems.

3. *The adequacy of the illumination in the berm area may have contributed to inadvertent contact with the pump casing drain.*

   Judgement of Need: Illumination levels in the area surrounding the 92% acid pump ranged from 3.5- 4.8 fc, which is less than the suggested 5-fc level. Management should conduct a more detailed survey of the facility illumination levels, evaluating the type of task being performed and the need for accuracy or risk. The survey results should be utilized to develop feasible remedies to identified weaknesses. The use of temporary task lighting should be encouraged to mitigate low light problem areas until actions that are more permanent are taken.

4. *The use of long sleeve shirts and full-length trousers or long sleeve, full-length coveralls may have reduced the amount of material which contacted the employee's skin and the severity of the resultant burns.*

   Judgment of Need*:* Long sleeve shirts and full-length trousers or long sleeve coveralls should be required for routine access to the process area and other bulk chemical storage areas in the facility, i.e., air compressor room. Laboratory coats may be an acceptable alternative.

5. *The use of standard PPE in areas posing a higher risk due to the configuration of equipment, or activities being performed, is not adequate to prevent injury to personnel in the event of an accident.*

   Judgement of Need*:* Areas such as the acid/caustic pumping berm and the hydrogen peroxide berm should be designated as special areas. These areas should be distinctly marked, and posted, with additional PPE required for entry. Specifically, chemical goggles instead of safety glasses should be required for any entry.

6. *Timely alerting of the other operation's personnel to the event and the need for assistance were delayed due to the lack of a shower activation alarm.*

   Judgement of Need*:* Flow activation alarms should be installed on all safety showers. The alarms should provide for both audible and visual local and remote indication, in a normally manned location, i.e. ETF Control Room.

7. *The use of cold water for safety showers is extremely uncomfortable and may result in employees not rinsing the affected area with large quantities of water. Additionally, the cold water may make emergency medical treatment more difficult especially in the event the injured employee goes into shock.*

   Judgement of Need*:* Water tempering device(s) should be installed on facility safety showers to prevent additional injury to employees due to the use of cold water.

8. *The location of the safety shower resulted in the mixing of rinse water with liquid spilled in the berm area. This posed a hazard to employees due to the possible generation of an aerosol mist from local boiling and the potential for the employee to actually step or fall back into the berm area.*

   Judgement of Need*:* Relocate the acid/caustic berm shower to block ready access to the berm. Install a fixed or moveable curtain on the shower adjacent to the process area acid/caustic berm to prevent entry of water into the berm and any resultant interaction with spilled chemicals. Other shower locations should be evaluated for similar problems.

9. *The 92% sulfuric acid system was routinely operated above the alarm setpoint. Alarm response procedures were carried out and although the temperature remained above the alarm setpoint, no further actions were taken.*

   Judgement of Need: Review facility alarm response procedures for adequacy in mitigating the alarmed condition. Ensure appropriate actions are taken if operating above an alarm setpoint. Evaluate the basis for the 92% Sulfuric Acid System high temperature alarm setpoint. Take the appropriate actions to ensure that future normal system operation is below the alarm setpoint.

10. *An employee was working alone in an area in which a higher risk for potential injury existed in the event of a system failure resulting in an acid or caustic release.*

    Judgement of Need: The facility should evaluate the use of the AJHA to analyze the hazards and risks of routine operations, i.e., housekeeping and surveillance activities within the facility. This process should focus on the location of the work activity as well as the hazards associated with the actual work.

11. *The BED was not clear regarding which emergency procedure (major or minor spill) applied to the accident.*

    Judgement of Need: Facility management should reinforce the expectation to review all applicable procedures as time permits and event stabilization has occurred. Additionally, the site needs to review and, if necessary, revise spill criteria to ensure it is appropriate yet not too restrictive to facilitate commensurate emergency response.

12. *The standing AJHA developed for work in the chemical berm area did not adequately identify all of the hazards in that slipping and tripping hazards were not identified.*

    Judgement of Need: Facility management should review EL-104, the standing AJHA for work in the acid berm area, to ensure hazards are adequately identified.

2.5.3 Additional Observations

In addition to the root and contributing causes to the accident and injury, the team noted some opportunities for improvement in event response:

A. Considerations for having a telephone close to each safety shower.

B. Training should include activating the fire pull-box to alert emergency response personnel.

C. Fill/grout void space in the pump mounting bases to eliminate climbing/stepping on the support framework for the pumps.

D. Ensure HAZMAT team is in proper PPE for initial response.

E. Install new spray guards on flanges in acid and caustic systems within the berm area, in order to detect and mitigate leaks.

2.5.4 Good Practices

The following good practices were noted throughout the event:

A. Drills helped prepare the shift for the emergency. Facility personnel responded in a timely manner. All shift workers knew exactly what to do.

B. Outstanding response by the Hanford Fire Department

C. Timely notification of facility, company and DOE management

D. Good teamwork displayed in starting the recovery. Although the event occurred during a normal non-work day, a large contingent of staff and bargaining unit personnel came in to assist in recovery actions.

3.0 FACTS

3.1 Plant Conditions Prior to Event

On the night of October 14, 1999 through the morning of October 15, 1999, the night crew at the 200 ETF was assigned to perform preparation work for startup of the MTT, startup the ETF evaporator and conduct surveillance and housekeeping activities.

At 1830 on October 14, 1999, "C" shift attended the shift turnover briefing from the previous shift. The following items were discussed regarding equipment status:

- The ETF Evaporator was in "Start-up/Heatup" mode of operation.
- All other facility systems, excluding utilities, were in "Shut-down" mode of operation. The facility chemical feed system is considered utilities; thus, the 92% and 4% acid pumps were operating.

Following shift turnover, the SOM assigned the following duties:

- Continue with start-up of the ETF Evaporator (two operators – one in the control room and one on the process floor).
- Three hours after startup of the ETF evaporator – start-up the MTT (two operators – one in the control room and one on the process floor).
- One operator was assigned to perform housekeeping duties. The operator was instructed to work off the list provided and look for other areas that needed housekeeping. (See Appendix A)
- One operator was assigned TEDF activities.
- The control room operator was instructed to transfer verification tank "C" contents to the State Approved Land Disposal Site. The TEDF Operator was told to drive down the transfer line and inspect it for leaks during the transfer of liquid. The MTT Operator needed to manipulate the applicable valves to facilitate the transfer.

At 2000, the MTT operator performed the facility surveillance rounds of the MTT. This surveillance included an inspection of the 4% sulfuric acid chemical berm located in the ETF process area. One leak was noted on the ETF MTT round sheet, however, no leaks were found near the 92% sulfuric acid pump. (See Appendix B)

At 2245, the ETF Evaporator was placed in the "Run" mode while the miscellaneous operator continued housekeeping duties.

At 0200 on October 15, 1999, the SOM gave direction to provide status of the SWRT level in preparation for start-up of MTT, to ensure that the SWRT volume would support MTT operation. After reviewing the SWRT status information, the SOM instructed operations personnel to wait one more hour before starting MTT. This would allow additional time to run the ETF Evaporator, thus decreasing the SWRT volume.

At 0215, the SOM was in the ETF control room to review process memos and procedures for MTT start-up with the MTT operator. Subsequently, the MTT operator initiated the valve line-up sequence to support start-up of the MTT operation per plant procedures POP-60-002 and POP-60-006.

3.2 Event Sequence

NOTE: The 200 ETF operations crew was assigned as follows (See Appendix C):

- *1 MTT operator was at Reverse Osmosis*
- *1 STT operator and the SOM had just left the ETF control room*
- *2 operators were in the ETF control room (TEDF and CRO)*
- *1 miscellaneous operator was performing housekeeping duties*
- *1 HPT was in the HPT office*
- *1 operator was at the 242-A evaporator (shutdown surveillance)*

At approximately 0228, the miscellaneous operator assigned housekeeping duties (See Appendix D) entered the 4% and 92% sulfuric acid berm area to commence cleanup of an assigned space. When the operator bent down to pick up some debris, the 92% sulfuric acid pump case drain line failed spraying the NCO's right leg and arm with acid (See Appendix E). Upon feeling the wet pant leg, the NCO immediately fled the berm and headed straight for the safety shower. While attempting to exit, the NCO tripped and fell but quickly recovered and left the area. The operator stood under the safety shower for approximately five minutes and after removing the blue coveralls, exited to call the control room on the PAX phone located on the west wall. The operator then returned to the shower and continued the washdown.

At 0230, while descending the stairway from the control room to inspect the settings on the UV/OX system, the STT operator and SOM heard water running through the sanitary water system, which supplies water to the facility safety showers. They thought that because of the recent cold weather that a sanitary water pipe had broken outside. Because they were close to the exit door, the STT operator and SOM checked the safety shower located outside and finding no indication of leakage, they returned to inspect the process area.

At 0233, the ETF control room operator received a call over the PAX phone from the miscellaneous operator who had been conducting housekeeping activities. The miscellaneous operator stated "I need help and to shut the pump down". The control room operator immediately called 911. (See Appendix F) Simultaneously, the STT operator entered the process area and proceeded to the chemical berm area. Seeing the operator in the safety shower with coveralls removed, the STT operator immediately called the CRO to request that the acid pumps be shutdown. The TEDF operator, who was in the control room, shut down the 4% and 92% sulfuric acid and 4% and 50% sodium hydroxide pumps. Realizing it was 92% sulfuric acid coming from the pump in a 180-degree pattern (See Appendix G), the STT operator exited the process area via the normal egress route, and closed the supply valve from the 92% sulfuric acid storage tank. The STT operator then re-entered the process area via the personnel door located on the south side of the ETF building.

The miscellaneous operator in the safety shower told the STT operator that she had been sprayed with acid. The STT operator opened the rollup door by the safety shower about 2 feet, to allow air to remove the chemical fumes. The SOM also called the control room and instructed them to call 911 and to shutdown, the chemical feed system. The control room operator told the SOM that he was in contact with the HFD and they were on the way. The SOM also told the control room operator that approximately 15-20 gallons of 92% sulfuric acid had spilled into the chemical berm area. The control room operator informed the HFD of this finding. The SOM requested the TEDF operator to come to the process area to assist the injured operator.

At approximately 0238, the TEDF operator arrived on the process floor to provide additional assistance to the injured employee. The MTT operator was assigned by the SOM to meet the emergency response personnel and provide them with directions to the accident scene. The SOM notified the control room operator and directed him to make a public address system announcement stating that the process floor was off limits due to the presence of chemical fumes. The TEDF operator talked to and comforted the injured employee while flushing continued.

At 0240, the SOM left the process area and went to the ETF control room to initiate BED activities. The SOM evaluated whether or not the facility had reached an EAL and concluded that it had not. The SOM then categorized the acid spill as minor because spilled material was contained within the facility (secondary containment) and the volume of material spilled was 15-20 gallons.

Note: Facility spill procedure categorizes spill volumes <60-gallon uncontained and >60 gallons contained as minor.

At 0243, the HFD arrived at the accident scene. The HFD-BC instructed all personnel to leave the process area because of the presence of chemical fumes in the area. The roll-up door was then opened fully. The building ventilation was subsequently lost due to low building differential pressure thus shutting down the ETF Evaporator. The SOM met with the HFD-BC to conduct a turnover of the incident command post describing the area and hazards present near the event scene. HFD personnel, without respiratory protection, entered the accident scene to provide initial aid to the injured operator. The SOM also identified several employees that may have been exposed to chemical fumes during the initial emergency response. The SOM and HPT briefly discussed set-up of a temporary RBA from the process area to the ambulance for transporting the injured employee.

Operators posted the entrance doors to the ETF process area as “Danger No Entry” due to the presence of chemical fumes. Following initial treatment, response personnel moved the injured employee to the ambulance. At the ambulance, the injured employee was surveyed by an HPT with no contamination found. Additionally, a survey was conducted at the hospital with negative results.

At 0253, the ambulance left for Kadlec Hospital with the injured operator. The TEDF operator was also sent to provide support to the injured employee and doctor. The HAZMAT response team suited up in PPE, including respiratory protection, entered the accident area to assess the spill, perform air sampling and test absorbent on the spill area. The HAZMAT team completed a preliminary evaluation of the event scene and determined that either 1500 lbs. of Soda-ash for acid neutralization or sump pumps to pump the liquid out of the berm into drums would be needed to clean-up the spilled acid. The HFD-Industrial Hygienist stated that initial air sample data results were within limits for sulfuric acid within the process area.

At 0310, the ONC was notified (See Appendix H). Incident command turnover was completed from the SOM to the HFD-BC. The HAZMAT team was requested by the SOM to perform spill clean up due to the lack of operations’ resources at the facility. The SOM at that point categorized the spill as a major spill due to a reevaluation of the need for outside assistance and lack of on-scene Operations resources to clean up the spill. The day shift manager arrived on the scene to assist the SOM. The SOM stated that he wanted to complete an evaluation of the potential reaction prior to using Soda ash to neutralize the acid.

3.3 Recovery and Cleanup

At 0400, due to the magnitude of the accident, additional NCOs were called out to support the cleanup effort.

At 0500, the HFD-BC reported to the SOM that the materials needed to clean up the spilled acid could not be found. The SOM, following an evaluation of the scene, resource availability and discussions with the day shift manager, determined that the ETF facility personnel were capable of spill clean up without further assistance from the HFD. The HFD-BC turned the incident scene back over to the SOM.

Following emergency treatment, the Kadlec Hospital doctors decided to transport the injured employee to Harborview Burn Center in Seattle, WA. This decision was based primarily on the patient’s lack of pain as a result of the 1st and 2nd degree chemical burns received, and a concern that nerve damage may have occurred. The operator was burned on the left side of the face, right arm and left leg.

At 0615, shift turnover was completed with the following plant status:

- ETF was in the shutdown mode.

- The facility ventilation system was shutdown.
- The ETF Evaporator was shutdown due to loss of ventilation.
- The facility seal water system was in operation.
- The cooling water system was in operation.
- The instrument air compressors were online.

The on-duty shift manager took control of plant activities while the day shift manager took charge of recovery actions. The emergency response status was turned over to the on coming shift personnel. The on coming shift was informed of the need to develop a recovery plan for re-entry into the process area. BED responsibilities were turned over to the on coming SOM. The SOM also identified a need to preserve the accident scene for subsequent inspection. The SOM relayed that an occurrence had not been declared because the initial reports and information did not indicate that a clearly categorized event had occurred.

The seven persons, four operations personnel from 200 ETF and three members of the HFD, involved with the emergency response to this event were directed to report to HEHF for evaluation as a precautionary measure due to possible exposure to sulfuric acid fumes. These individuals received a pulmonary test, a blood test, a blood pressure test, a urine test, and a doctor's examination. Following the examination, all employees were released with no work restrictions.

At 0630, the day shift manager and 200 ETF safety representative entered the accident scene to document the area via still photography and digital recording. (See Appendix I) They, along with additional personnel, began preparing a recovery plan including the development of an AJHA.

Because a distinct chemical odor was present within the process area, it was decided that for employee comfort, the initial phases of the recovery action would be completed using respiratory protection. The event scene was limited to the process berm area and the area immediately adjacent. Personnel preparing the AJHA and work plan, including operators, HPTs, and supervisors, toured the scene but did not enter the barricaded area until work plans and protective measures were established and in place.

The recovery plan was written and implemented in three separate phases:

- Phase 1 - remove concentrated acid from the chemical berm area.
- Phase 2 - verify valve positions to ensure that the chemical system is isolated, gather pictures, and install lockouts and tagouts.
- Phase 3 – rinse down area and equipment and apply neutralizer on piping system.

All three phases of the recovery plan were completed by October 17, 1999.

At 0834, on October 15, 1999, the event was categorized as an Off-Normal Group 3A, ON (1), "Any occupational illness or injury resulting in in-patient hospitalization."

4.0 ANALYSIS

4.1 Conduct of Operations

The procedural guidance outlining good conduct of operations at the ETF is found in WMH-200, Section 2, *Conduct of Operations*. The requirements and practices found in this procedure are built into the plant operations and emergency response procedures used to operate the ETF. After reviewing all procedures and responses performed by the on-shift crews, no procedural violations were noted. However, it was discovered that the "92% H_2SO_4 Tank Temperature High" alarm was activated for approximately eight and one half days. Additionally, it was in alarm status for 201 days out of the past 12 months. This alarm's set point is 110^{o}F. Further investigation showed that temperatures had exceeded

110°F and reached a high of 148°F within the past 12 months. All required actions per the alarm response procedure (ARP-65C-001) were taken. ARP-65C-001 requires the operator to check the heat trace system and turn it off if it is on. Although this alarm response was performed, it did not decrease the system temperature below the alarm set point. Additionally, although engineering personnel understood that operating the acid system pump was the cause of the alarm, no action was taken to raise the alarm setpoint. This system has routinely been operated above the 110°F-alarm setpoint.

4.2 Safety

4.2.1 Chemical Safety Practices

The basis for safety practices and controls for 200 LWPF is found in Appendix D. This document identifies the various chemical hazards and controls, including PPE, to be utilized during activities in the facility. This procedure, along with the facilities HazCom program, provides the framework for training of employees in the identification and control of chemical hazards.

Storage tanks, piping systems and components are designed to meet the applicable ASME specification for their intended service. In accordance with facility permits, EP instructions, HazCom requirements and Conduct of Operations guidelines, the tanks and systems containing process chemicals are marked and employees are trained to recognize the hazards associated with each.

Chemical handling practices within the facility were developed from information provided by the chemical manufacturers, general industry practices, federal OSHA standards, and other sources including NIOSH.

The hazards and protective measures to be employed during each chemical use operation are identified in either a facility operating procedure, or work documents prepared specifically for the application. The primary tool being used for work activity hazard identification and mitigation is the AJHA, which is developed by a work group with the assistance of subject matter experts including Industrial Hygiene and Safety professionals.

Though chemicals normally do not require "contact" handling by employees, the facility has found it necessary to utilize significant quantities of certain ones (sulfuric acid) to perform bulk additions and adjustments to the process system. These operations consisted of barrel pumping acid into process system tanks using temporary hose systems. The operations were carried out in accordance with a procedure, using the PPE defined in the HASP. To reduce employee exposure during these operations, a more permanent system was installed using primarily rigid plastic piping, a fixed pump, and large acid totes. This system provided easier access, remote pump operation and improved containment, reducing the potential for release and exposure. The need for bulk chemical additions was further reduced or eliminated with changes in operational chemistry and the installation of mixers in the STT concentrate tanks. Other improvements involving the 4% acid system piping replacement with lined carbon steel piping, and the relocation of the Surge Tank chemical metering pumps from the top of the tank, outside, to a location in the process area, are in-progress to further reduce exposure potential.

Safety showers are maintained and located strategically throughout the facility. The showers are flushed and tested weekly in accordance with the requirements of ANSI Z358.1-1998 governing Emergency Eyewash and Shower Equipment. However, the facility does not have flow or activation alarms on the equipment, or water tempering equipment to maintain a tepid water temperature during operation. Both of these are advocated in the most recent revision of the ANSI standard. The lack of activation alarms is especially significant given the length of time and the manner in which the control room and SOM were made aware of the problem. Comments raised by employees and discussion with medical personnel at HEHF indicated that the use of tepid water might help to prevent an injured person from going into shock or from exacerbating the problem should one occur. Additionally, the location of the acid/caustic safety shower may have contributed to the release of vapors, primarily water vapor, due to the addition of water to the berm while the employee used the shower.

Discussions with Engineering and Safety staff from various chemical manufacturers and users indicate that the practices with regards to process area access and routine operations are very similar to those in use in the general industry. However, some specific recommendations with regards to posting, signage and personnel attire are included in section 5.0 based on those discussions and industry practices.

4.2.2 Personal Protective Equipment

The HASP provides information regarding the type of activities involving chemical handling and the PPE required. The procedure establishes requirements for eye, face, skin and respiratory protection and provides information on the resistance of various materials to exposure to the process chemicals.

Normal access to the process area requires; full-length trousers, long or short sleeve (covers shoulder and upper arm) shirt, or coveralls, substantial footwear, safety glasses with side shields and hard hat. The injured employee was wearing all of the required PPE, plus earplugs (See Appendix D).

Discussions with various chemical manufacturers and users, including two process water treatment operators, indicate that similar attire is required for routine access to the general process areas in their facilities. However, long sleeve shirts or coveralls were the choice of the majority of the facilities, and special areas, similar to the acid/caustic pumping berm, specifically required some additional level of protection i.e., chemical goggles, for access.

PPE material specifications are included in the HASP. The material requirements are based on the recommendations provided in the various chemical MSDSs, information provided by protective clothing manufacturers, OSHA, and NIOSH.

The facility's emergency procedures and operator training required the use of a self-contained breathing apparatus, which is inspected monthly, when entering areas of unknown airborne hazards or above established limits. The manner in which the spill was found, and the nature of the spill does not necessarily indicate that respirator use was necessary. The principle hazards associated with sulfuric acid are acute: burning of the skin, eyes and mucous membranes. ACGIH and NIOSH criteria documents concerning the basis for the TLV 1 mg/m_3, indicate that exposure to levels at or above the TLV would have been irritating to the pulmonary system and have been very evident. Exposure levels in the range of 1.1 to 2.4 mg/m_3 will result in eye irritation to 40% of the exposed population. None of the exposed personnel mentioned eye irritation and only some had any pulmonary irritation other than a mild sore throat, which cleared after exiting the area.

4.2.3 Lighting

The ANSI/EIS-RP-7-1991 standard "Industrial Lighting," was reviewed and used as the basis for an illumination survey of the accident scene. The illumination levels in the berm area were compared with the recommended lighting levels for "pump rows" and "operating platforms" in the petroleum, chemical, and petrochemical industry. The standard level was 5 foot-candles (fc). The levels in the area adjacent to the 92% acid pump ranged from 3.5 - 4.8 fc. Note that 1 fc is the suggested minimum in the general process area at ground level, and is related to the ability to discern obstructions in an employee’s path of travel. Although average lighting levels in the berm appeared consistent with suggested values, the routing of piping, cable trays, conduits and other equipment in the overhead area below the installed luminaries, results in shadowing in many areas.

4.3 Emergency Response

4.3.1 Facility Response

The miscellaneous operator performing housekeeping activities in the chemical berm area made the first notification to the control room. The Control room operator called 911, staying on line to give all pertinent information to the emergency responders. The operator working in the chemical berm had to leave the safety shower to make notification to the control room of the accident. The telephones in the process area could have been used to call 911. Alternatively, the fire pull box, located about 20 feet from the safety shower, could have been used. Facility personnel responding to the scene were trained first aid providers and provided valuable assistance to the victim until the HFD arrived. Facility personnel were dispatched to meet the emergency responders and guide them to the event scene. The operators responding to the event scene did an excellent job in attending to the injured person. The operators made sure the injured employee stayed in the safety shower until the fire department arrived.

The facility HASP establishes the criteria to be used in the classification of spills, ranking them as either incidental, minor, or major. Although by using these guidelines and the facility emergency procedures, the spill could have been classified as incidental, the SOM initially classified this as a minor spill, based on the spill size and location (completely contained within the berm). Subsequently, the spill was reclassified as major due to a reevaluation of the need for outside assistance and lack of on-scene operations resources to clean up the spill. The HFD turned over to Operations personnel the follow-up response and spill clean-up/neutralization.

The miscellaneous operator was working alone in an area where a greater risk of incident could occur. If there was a second operator present, notification and response could have been quicker. Overall, facility response was immediate and outstanding.

4.3.2 Emergency Medical Personnel Response

The HFD and HAZMAT teams were dispatched and arrived at the scene within 10 minutes of notification. The teams experienced no delays in locating the patient due to plant personnel meeting the responders. The HFD then entered the accident scene to care for the injured operator and requested that all personnel leave the immediate area. During this entry, the HFD did not don respiratory protection. The operator was then moved to the ambulance and contamination surveys were performed, with no detectable contamination. The injured person was transported to Kadlec Hospital for proper care. The response and care at Kadlec Emergency Room by hospital personnel was very good. The FDH Health Advocate, LWPF line management and WMH senior management were available at the hospital and provided excellent support to the employee and the employee’s family members.

4.4 Training

Each ETF position has specific training requirements. The positions are Main Treatment Train (MTT), Secondary Treatment Train (STT), Control Room Operator (CRO), Treated Effluent Disposal Facility (TEDF), and Shift Operations Manager (SOM). Training requirements for each of these positions are outlined in the training matrix for ETF. All shift personnel assigned duties on October 15 were current on plant certifications and training requirements, which included response to chemical spills (See Appendix C). On shift personnel responded in a timely and effective manner. Finally, as noted by two operators on shift during the event, including the injured operator, “Drills paid off.”

4.5 Engineering (Including SRTC Conclusions)

4.5.1 As Found Material Condition

This engineering analysis is provided to identify the source of the fugitive 92% sulfuric acid, as well as assess the operational integrity and material condition of the failed component within this system. A simple system schematic is shown in Figure 1.

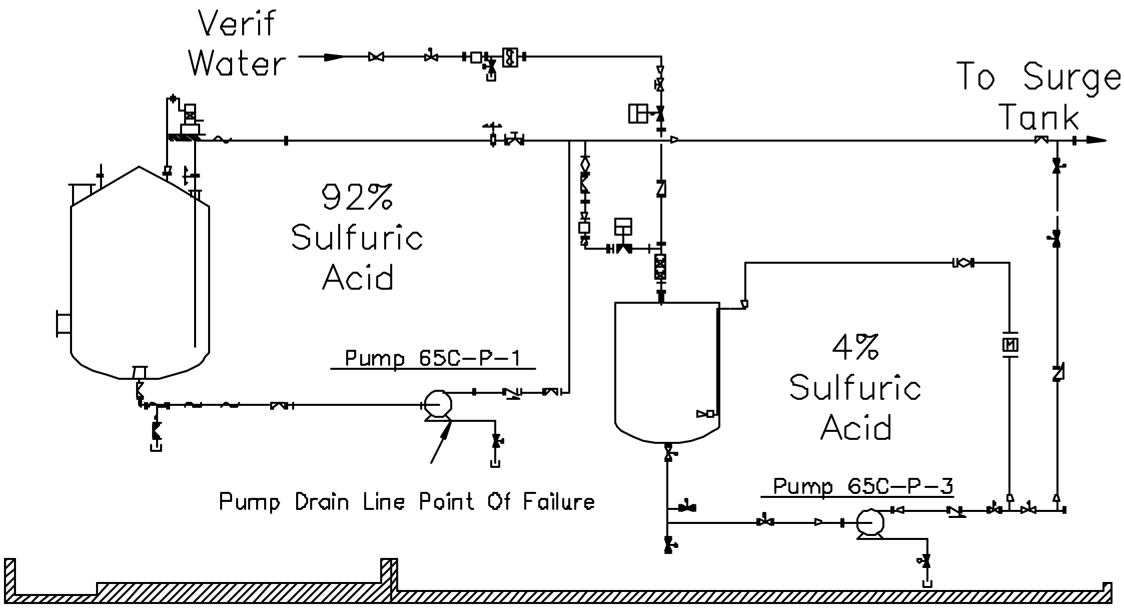

Figure 1. ½ inch diameter drain line off of the Centrifugal Pump, 65C-P-1.

Once the accident scene was sufficiently cleaned to enable a thorough visual inspection of the system hardware, personnel discovered that the ½ inch diameter drain line off of the centrifugal pump, 65C-P-1, had been breached. Although this breached drain line could have been the single source of the fugitive acid, additional testing was conducted to ensure that no additional system leaks were present. Based on the acid leak spray pattern, which discolored the coating on the adjacent wall, and actual operator accounts of where the leak was observed, a specific section of the system was identified for further leak testing.

Following removal of the broken drain line and plugging of the drain connection, the suspect portion of the system was pressurized to 70 psig, which corresponds to maximum possible system operating pressure. The results of this test confirmed that no additional system leaks existed.

Since the leak testing confirmed that the fugitive acid had been released from the failed pump drain line, the evaluation focused on how the drain line may have failed. The possible failure mechanisms for breaching this drain line are:

- operation of the 92% Sulfuric Acid System beyond material design capability, or
- external force applied to the piping system.

4.5.2 Operation of Acid System With Respect to Material Design Capability

The 92% Sulfuric Acid System is composed of a 7500 gallon, polyvinylidene fluoride (PVDF) lined carbon steel storage tank, a Carpenter 20 centrifugal pump, and PVDF lined carbon steel piping. The pump drain line was manufactured from chlorinated polyvinyl chloride (CPVC). The ETF 92% Sulfuric Acid System was designed to operate within a temperature band of –15 degrees F to +120 degrees F. The lower temperature limit represents the freezing point of 92% sulfuric acid and the upper limit was established to promote long term system integrity. Although the construction materials were capable of accommodating a greater temperature range, corrosion and chemical attack typically accelerate as system temperature increases. The 92% Sulfuric Acid System low and high temperature software alarms were set to activate at –15 degrees F and +110 degrees F, respectively.

Although system components would experience better service life if continuously operated within the system design temperature range, components other than the CPVC drain line have mechanical and chemical capabilities well beyond those experienced or anticipated.

Additionally, all pressurized components are capable of withstanding an internal pressure of at least 150 psig. Therefore, the scope of this evaluation will focus on the design capabilities of the CPVC drain line.

While CPVC has excellent resistance to highly concentrated sulfuric acid at ambient temperatures, the actual recommended temperature ratings vary depending upon a number of factors including resin quality, chlorine content, degree of fusion/gelation, applied/internal stresses, and manufacturing technique (extruded pipe versus injection-molded fittings). Each Supplier/Manufacturer provides unique technical data prescribing recommended operating conditions for their product.

The failed CPVC drain line fitting in the ETF 92% Sulfuric Acid System was supplied by the Spears Company, who purchases raw material from the B. F. Goodrich Company. B. F. Goodrich publishes an Engineering Design Manual that includes technical information one should utilize when specifying and installing Corzan™ CPVC material. This Engineering Design Manual contains chemical resistance data that indicates Corzan™ CPVC is recommended for applications in 92% sulfuric acid at temperatures less than 145 degrees F.

A review of system operating history over the last twelve months indicates that system-operating temperatures varied from 70 degrees F to 148 degrees F. Although the system was operated in excess of the 145 degree F temperature recommendation provided by the B. F. Goodrich Company for approximately 7 days, B. F. Goodrich does not indicate that operation at 148 degrees F is unacceptable. B. F. Goodrich classifies use between 145 degrees F and 155 degrees F as a "caution" zone, which indicates that customers should exercise additional caution if expecting routine operation in this temperature band. The B. F. Goodrich Design Manual indicates that use of Corzan™ CPVC material above 155 degrees F is not recommended.

Laboratory testing performed by the B.F. Goodrich Company on CPVC material, which was held at a constant temperature of 150 degrees F, indicated that the material could experience some blackening and embrittlement within a few months. No published test data was available for expected operating life or the potential failure mode.

Although the technical information used to procure the CPVC drain line material was believed to indicate that the material should have been compatible with the ETF 92% sulfuric acid system application, visual inspection of the failed CPVC fitting indicated that the material had experienced some chemical degradation. For this reason, the failed component was sent offsite for a more sophisticated material failure analysis.

4.5.3 Operation of Acid System With Respect to Material Design Capability

The Westinghouse Savannah River Company has a Savannah River Technology Center (SRTC) that employs professionals who are considered experts in thermoplastics. This organization was contracted to perform a detailed analysis of the failed CPVC pipe fitting to determine whether the acid environment had significantly degraded the base material and to identify the likely cause of the fitting failure.

The SRTC Report includes significant details on the physical properties of CPVC. Although the report author acknowledged that the B. F. Goodrich Company technical information seems to indicate that the Corzan™ temperature criteria could be interpreted as applicable to LWPF drain line design, he identified that temperature ratings for the base material are not directly applicable to molded pipe fittings. He also identified that the B. F. Goodrich Company technical information provided a poor representation of the critical relationship between pressure, temperature, and concentration of sulfuric acid. The report recommends not utilizing CPVC in 92% sulfuric acid applications that involve operating temperatures greater than 120 degrees F.

The Failure Analysis section of the report provides details on the various techniques utilized to analyze the failed fitting. These techniques include magnified photography, Scanning Electron

Microscopy (SEM), Fourier-Transform Infrared (FT-IR) Spectroscopy, and mechanical testing. The pertinent report conclusions are provided below:

- Published generic B.F. Goodrich data indicates that Corzan® CPVC was suitable for the drain line application up to 145°F. Published disclaimers indicate that the full hydrostatic pressure rating of the pipe may not apply to the "Recommended" range and that determining compatibility is the end-user's responsibility. Previous and recent discussions with B.F. Goodrich technical representatives indicated that service life would be reduced to 12-24 months upon continuous exposure at 150°F, but this is not indicated in the published data. Infrequent, short-term excursions approaching 150°F was not adequately addressed, and possible variation in resistance of injection-molding and extrusion compounds to this service environment was not specifically indicated.

- With a few exceptions, CPVC materials are typically rated as satisfactory or recommended for 93% sulfuric acid at room temperature to 100°F, with some references indicating acceptability at 120°F. Temperatures of 140-150°F are typically considered to be the maximum continuous use temperature range for 93 wt% sulfuric acid, with service life sometimes acknowledged to be limited, particularly for stressed or pressurized applications. Although the Hanford CPVC drain line was infrequently operating at the upper bound of the recommended range, such periods were of limited duration and normal service temperatures never exceeded 150°F.

- Failure of the CPVC fitting is attributed to a combination of environmental degradation and probable impact or bending stresses. Based on the extent of degradation observed, any inadvertent contact with the piping would have likely resulted in failure. Inherent failure in the absence of external forces would have also been expected at some point in service, particularly in metal-to-plastic joints (threads) and/or solvent-cement joints.

Note: Amplifying information from Section 5.0 discussion in WSRC-TR-99-00484 December 1999 states that "Fracture of the fitting is believed to have occurred in the thread root as indicated in Section 4.3, towards the top orientation of the piping, which would correspond with the region under the highest tensile stress if force was applied in a downward direction. There is also matching evidence of nearly through-wall oxidation and cracking at the same location. **.** Whether failure occurred primarily as a result of internal pressure, vibration, pressure surges, etc. in absence of external forces cannot be conclusively determined. However, the extent of degradation in the fitting was significant**.**"

- Variation in appearance between the failed fitting and adjoined piping is attributed to several possible causes, including but not limited to: thermal expansion, variation in chemical composition, processing parameters, residual stresses, morphology, degree of fusion, and possible presence of solvent cement on fitting interior. Such variation may be lot or batch-specific or could be inherent between molded and extruded components. Although the effects of such variation are expected to be insignificant in most service environments, they may have been specifically targeted or enhanced by this particular application. Additional investigation would be necessary to determine the individual contribution of such effects and is strongly recommended.

- Structural integrity of the failed fitting was significantly reduced as indicated by mechanical test results. It is acknowledged that such testing was performed using non-standard techniques due to limited material and part geometry. Additional tests and material characterization can be performed if necessary.

- As with many thermoplastics, CPVC is notch-sensitive and exhibits low fracture toughness. Threaded fittings are therefore the most susceptible to failure, in the absence of major defects or poor joining techniques. For this reason and the generally lower strength of thermoplastics compared to metals, additional support and/or shielding is commonly recommended for thermoplastic piping particularly in areas where contact is possible or for pressurized applications.

- Observations from previous CPVC components in the same application seemed to indicate some degree of degradation occurring, particularly in the threaded fitting. Although this component did not fail after approximately 2 years of service, such observed degradation is considered insightful. The cracking pattern and degraded appearance was similar to that observed in the failed fitting, but was less extensive and the exact service conditions to which the previous assembly was exposed are not known.

- Generic chemical resistance ratings are typically based on short-term immersion tests and nominal mechanical properties of laboratory-prepared samples. Although useful for general comparison, such ratings are not adequate to evaluate the long-term performance of as-fabricated components under actual service conditions. Testing by the end-user is recommended if only for product liability reasons, but should be performed particularly if degradation has been previously observed or if material performance is questionable under the expected service conditions.

- Excess solvent-cement on thermoplastic surfaces should be avoided and/or removed during application, particularly if components will subjected to potentially aggressive chemical exposures. Solvent-joints may be resin poor and more susceptible to chemical attack.

4.5.3 Evaluation of Externally Applied Forces

The physical configuration of the pump case drain line was evaluated to determine whether an external force could have been applied which exceeded the strength of the piping system. The failed component was a schedule 80, CPVC male adapter. This fitting facilitated the transition from socket type (bonded) schedule 80 piping to a ½ inch threaded drain opening in the pump casing. The piping dimensions are identified in Figure 2.

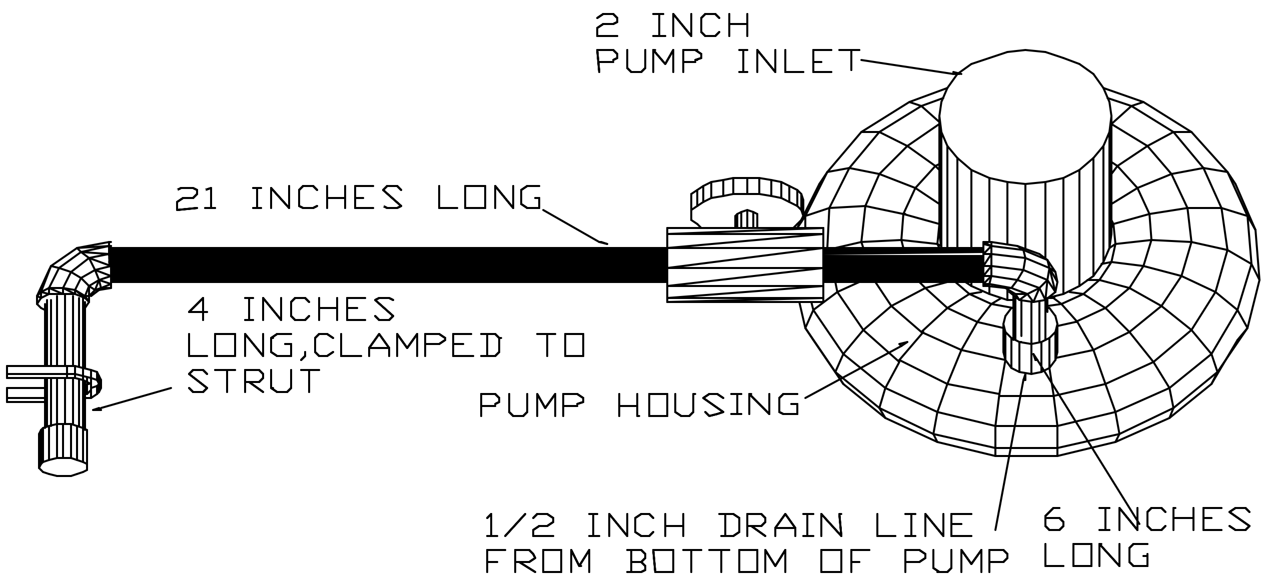

Figure 2. Drain Line Dimensional Layout

The drain line was supported at the pump casing and adjacent to the drain cap. This support configuration was designed to support the pipe and its contents only. No provisions were made to accommodate externally applied forces.

Rough engineering calculations indicate that the material, when originally installed, was capable of withstanding a vertically applied force of between 35 – 50 lbs. This drain line was susceptible to an externally applied force and should have been better protected and/or supported based on its location.

Much of the CPVC piping installed in the Chemical Addition System throughout the Effluent Treatment Facility, constructed under Project C-018H, was identified for replacement in 1998 because of the potential for failure due to personnel inadvertently bumping or grabbing it to prevent a fall. The facility prioritized the areas for replacement based on perceived hazard. Almost all of the 4% Sulfuric Acid System CPVC piping within the Chemical Berm had been replaced with lined carbon steel piping within the previous 6 months.

Finally, during this work on the 4% acid system, maintenance workers worked near the 92% sulfuric acid pump. However, interviews indicate that the 92% acid pump drain line was not damaged during this work.

4.5.4 Engineering Conclusion

The cause of failure of the CPVC fitting was a combination of environmental degradation and application of an external force. Based on the appearance of the fracture surface and post-failure orientation of the assembly, the probability of external force initiating failure is considered high. Considering the physical condition of the fitting, any inadvertent contact with the piping, particularly at mechanically advantaged locations, would have likely resulted in failure. Finally, weighing the many factors discussed above, failure in the absence of external forces would have eventually occurred.

4.6 Causal Analysis

The root cause analysis methodology used for determining the causes of this accident was an events and causal factor analysis utilizing REASON computer based software. An analysis of the sulfuric acid spill and resultant injury at 200 ETF on October 15, 1999 was conducted. REASON is an electronic program that uses a point analysis step-by-step process. It requires orderly input of event information to determine the factors that came together to produce an unwanted event. REASON creates a model of these factors that enable analysis of quantified data and option comparisons to simplify and encourage decision making for corrective action. REASON does not provide a single solution rather it guides one through a process that helps the analyst to discover causal factors. Principles are applied in REASON that recognizes management does only four things organizationally to establish control over any activity or process: command (policy/procedure), apply, monitor, and enforce. Effective organization controls require action at three functional levels: management, supervisory and worker. When there is lack of control, the REASON process will drive the analyst to one or more of these levels with a less than adequate application of one or more of the principles. To begin, a problem statement must be established from which a questioning technique is then applied to develop the REASON.

The problem statement, "an employee was sprayed with 92% sulfuric acid at the 200 Area ETF," is the unwanted event that by using the REASON process will identify corrective opportunities that will prevent its happening again in the future. The analyst asks why this occurred looking at all the factors that came together to produce the unwanted event. Refer to Appendix J to see the REASON Event Model for this accident.

The event model is comprised of causal factors that join together into sets (those factors that explain the preceding factor). Referring to the model the reader will notice that each chain is terminated with either a NC (non-correctable), CO (correctable opportunity) or ID (insufficient data). Another feature of the REASON program is the narrative. REASON takes the information contained in each factor and writes a narrative of the event that provides a check for logic and order of the related facts.

5.0 CONCLUSIONS AND JUDGEMENTS OF NEED

5.1 Root Cause

The cause of the accident, the one element that if not present would have prevented the accident, is the less than adequate protection of the pump case drain line that would have prevented it breaking from an inadvertent application of an external force. The 200 area ETF Management should evaluate systems containing hazardous materials to ensure they have protection i.e., covers, vertical or horizontal supports, which would prevent inadvertent application of excessive force. Every attempt should be made to develop and provide lessons learned to potential users of this type of chemical system to prevent recurrence of similar types of events throughout the DOE complex.

5.2 Contributing Causes

The investigation resulted in identifying several other opportunities for improvement that, if addressed, may not have alone prevented the accident, but could have reduced the severity of the injury and improved facility operations. These conclusions and the corresponding judgements of need are presented below:

Conclusions:

1. *The pump case drain line was chemically degraded as a result of the chemical system operating conditions i.e., chemical constituents, operating temperature.*

   Judgement of Need: The 200 area ETF management should ensure that an evaluation is conducted to ensure that the existing CPVC piping is appropriate for a given application.

2. *The chemical berm area is difficult to access and to perform work in due to various systems, structures, and components.*

   Judgement of Need: The 200 area ETF management should ensure, where practical, systems, structures and components are relocated to facilitate personnel working in the area. Additionally, a human factor performance evaluation task analysis should be conducted to identify and resolve potential operability and work environment problems

3. *The adequacy of the illumination in the berm area may have contributed to inadvertent contact with the pump casing drain.*

   Judgement of Need: Illumination levels in the area surrounding the 92% acid pump ranged from 3.5- 4.8 fc, which is less than the suggested 5-fc level. Management should conduct a more detailed survey of the facility illumination levels, evaluating the type of task being performed and the need for accuracy or risk. The survey results should be utilized to develop feasible remedies to identified weaknesses. The use of temporary task lighting should be encouraged to mitigate low light problem areas until actions that are more permanent are taken.

4. *The use of long sleeve shirts and full-length trousers or long sleeve, full-length coveralls may have reduced the amount of material which contacted the employee's skin and the severity of the resultant burns.*

   Judgment of Need*:* Long sleeve shirts and full-length trousers or long sleeve coveralls should be required for routine access to the process area and other bulk chemical storage areas in the facility, i.e., air compressor room. Laboratory coats may be an acceptable alternative.

5. *The use of standard PPE in areas posing a higher risk due to the configuration of equipment, or activities being performed, is not adequate to prevent injury to personnel in the event of an accident.*

   Judgement of Need*:* Areas such as the acid/caustic pumping berm and the hydrogen peroxide berm should be designated as special areas. These areas should be distinctly marked, and posted, with additional PPE required for entry. Specifically, chemical goggles instead of safety glasses should be required for any entry.

6. *Timely alerting of the other operation's personnel to the event and the need for assistance were delayed due to the lack of a shower activation alarm.*

   Judgement of Need*:* Flow activation alarms should be installed on all safety showers. The alarms should provide for both audible and visual local and remote indication, in a normally manned location, i.e. ETF Control Room.

7. *The use of cold water for safety showers is extremely uncomfortable and may result in employees not rinsing the affected area with large quantities of water. Additionally, the cold water may make emergency medical treatment more difficult especially in the event the injured employee goes into shock.*

   Judgement of Need*:* Water tempering device(s) should be installed on facility safety showers to prevent additional injury to employees due to the use of cold water.

8. *The location of the safety shower resulted in the mixing of rinse water with liquid spilled in the berm area. This posed a hazard to employees due to the possible generation of an aerosol mist from local boiling and the potential for the employee to actually step or fall back into the berm area.*

   Judgement of Need*:* Relocate the acid/caustic berm shower to block ready access to the berm. Install a fixed or moveable curtain on the shower adjacent to the process area acid/caustic berm to prevent entry of water into the berm and any resultant interaction with spilled chemicals. Other shower locations should be evaluated for similar problems.

9. *The 92% sulfuric acid system was routinely operated above the alarm setpoint. Alarm response procedures were carried out and although the temperature remained above the alarm setpoint, no further actions were taken.*

   Judgement of Need: Review facility alarm response procedures for adequacy in mitigating the alarmed condition. Ensure appropriate actions are taken if operating above an alarm setpoint. Evaluate the basis for the 92% Sulfuric Acid System high temperature alarm setpoint. Take the appropriate actions to ensure that future normal system operation is below the alarm setpoint.

10. *An employee was working alone in an area in which a higher risk for potential injury existed in the event of a system failure resulting in an acid or caustic release.*

    Judgement of Need: The facility should evaluate the use of the AJHA to analyze the hazards and risks of routine operations, i.e., housekeeping and surveillance activities within the facility. This process should focus on the location of the work activity as well as the hazards associated with the actual work.

11. *The BED was not clear regarding which emergency procedure (major or minor spill) applied to the accident.*

    Judgement of Need: Facility management should reinforce the expectation to review all applicable procedures as time permits and event stabilization has occurred. Additionally, the site needs to review and, if necessary, revise spill criteria to ensure it is appropriate yet not too restrictive to facilitate commensurate emergency response.

12. *The standing AJHA developed for work in the chemical berm area did not adequately identify all of the hazards in that slipping and tripping hazards were not identified.*

    Judgement of Need: Facility management should review EL-104, the standing AJHA for work in the acid berm area, to ensure hazards are adequately identified.

5.3 Additional Observations

In addition to the root and contributing causes to the accident and injury, the team noted some opportunities for improvement in event response:

A. Considerations for having a telephone close to each safety shower.

B. Training should include activating the fire pull-box to alert emergency response personnel.

C. Fill/grout void space in the pump mounting bases to eliminate climbing/stepping on the support framework for the pumps.

D. Ensure HAZMAT team is in proper PPE for initial response.

E. Install new spray guards on flanges in acid and caustic systems within the berm area, in order to detect and mitigate leaks.

5.4 Good Practices

The following good practices were noted throughout the event:

A. Drills helped prepare the shift for the emergency. Facility personnel responded in a timely manner. All shift workers knew exactly what to do.

B. Outstanding response by the Hanford Fire Department

C. Timely notification of facility, company and DOE management

D. Good teamwork displayed in starting the recovery. Although the event occurred during a normal non-work day, a large contingent of staff and bargaining unit personnel came in to assist in recovery actions.

SIGNATURE PAGE

W. H. Meader, Chairman
Project Support, Operations
Consultant, Fluor Hanford
2/22/00
Date

E. D. Beck, Safety Representative
Fluor Hanford
02/23/2000
Date

R. L. Brooks, Health Physicist
Fluor Hanford
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Date

M. W. Clayton, Safety Representative
Fluor Hanford
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Date

T. W. Dallas, Shift Manager
Fluor Hanford
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Date

W. R. Schneider, Building Steward
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H. A. Showalter
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N. J. Sullivan, Engineering Team Lead
LWPF Engineering
Fluor Hanford
2-24-00
Date

T. L. Woodford, Assessor
Assessment Management
Fluor Hanford
2-25-2000
Date

INVESTIGATIVE TEAM RESUME BRIEFS

William H. Meader, Fluor Hanford, Chairman
Mr. Meader holds BS in Marine Engineering from the U.S. Naval Academy. He served on three different nuclear submarines in various capacities including operations and weapons officer. He is qualified in the operation of a naval nuclear propulsion plant. He has an extensive background as an operations and maintenance manager in various facilities working on diverse projects such as pumping waste from nuclear storage tanks. Additionally, he served for two years on the Facility Evaluation Board conducting 13 assessments. His areas of expertise were operations, maintenance and engineering. He also served as a team member on two contractor Startup Reviews. He is currently the site maintenance technical authority and is trained in root cause analysis.

E. D. Beck, Fluor Hanford
Mr. Beck has 18 plus years of experience in industrial hygiene and safety with eight years in the private sector and 10 years at the Hanford Site. He has done work in all Hanford facilities in the last 10 years. The American Board of Industrial Hygiene certifies him in the Comprehensive Practice of Industrial Hygiene. He has also assisted in numerous accident investigations in the private sector, as well as several Type C and B DOE accident/exposure investigations at Hanford. Mr. Beck has completed the Root Cause Analysis training and two 16 hour accident investigation courses sponsored by the American Industrial Hygiene Association.

Richard L. Brooks, Fluor Hanford
Mr. Brooks is a Health Physics Technician with over 23 years of experience. He has participated on numerous safety councils including working with VPP. He is the chairman of the LEF Safety Council. Additionally, he is a coordinator for the Hammer ICWU Hazardous Waste Training.

Michael W. Clayton, Fluor Hanford
Mr. Clayton has seven years at Hanford performing oversight and field activities involving Nuclear Safety and Occupational Safety and Health. He has completed DOE sponsored training in accident investigation, root cause analysis, and corrective action verification. He has also completed training and performed duties as team leader and team member for nuclear facility Integrated Annual Appraisals at various Hanford facilities. Mr. Clayton has six years with the Naval Reactors Representative's Office, Puget Sound Naval Shipyard, performing oversight duties involving event investigation, root cause evaluation and corrective action follow-up.

Timothy W. Dallas, Fluor Hanford
Mr. Dallas has 18 years experience in operations at Hanford at various facilities. He is currently the 242A/ETF Operations Manager at 200 Area ETF. He has worked at N-Reactor and was qualified as Shift Operations Manager for reactor operations. Mr. Dallas has been the lead for many site related task teams including PFP Conduct of Operations upgrades and implementation, PFP plant restart/recovery team from 1993-work stand down, and re-engineering team for ETF re-engineering.

William R. Schneider, Fluor Hanford
Mr. Schneider has been a nuclear chemical operator for over 21 years. He has participated on numerous accident councils and safety committees. He is qualified on the 242-A Evaporator and is the present vice-chair of the LWPF Safety Council. He has been a Union steward for 18 years.

Hans A. Showalter, Fluor Hanford
Mr. Showalter has an Associates Degree in nuclear technology. He has over 16 years experience as a Health Physics Technician working at various facilities on the Hanford site. He is currently the Union steward for Solid Waste and the HAMTC safety representative for Waste Management Hanford. He has participated in accident investigations and many work related injury cases.

Neal J. Sullivan, Fluor Hanford
Mr. Sullivan holds a B.S. in Mechanical Engineering from Washington State University. He is currently the Operations Support Engineering Lead at the 200 Area Liquid Waste Processing Facilities. He has over 17 years of practical experience in the commercial nuclear power industry and Department of Energy (DOE) Complex. His career responsibilities encompass all phases of engineering including; design, construction, startup, operation, in-service inspection/testing, regulatory compliance, and maintenance. He has over ten years experience in supervision of engineering personnel. Mr. Sullivan's specific areas of expertise are plant/process engineering, mechanical design, and project management. He has extensive training and experience in the application of root cause analysis techniques.

Terry L. Woodford, Fluor Hanford
Mr. Woodford has been involved with accident investigations for approximately six years. In his current position, he is the team leader for conducting critique meetings, evaluating/preparing ORPS reports, and Price Anderson Amendment Act nuclear safety compliance officer evaluation/reporting for Waste Management Hanford. He is trained and qualified to conduct accident investigations and root cause analysis.

APPENDIX A

Housekeeping List date October 15, 1999

2 pages including cover sheet

LEF's Housekeeping Wish List

	Location	Description of Wish
omplete [initials] 10/14/99	Room #122 (PCM/Decon)	Area needs swept & mopped. Grease-like tar on floor needs to be scrubbed clean.
OK 10/17/99	Room #125A (Clean SWP Hard Hat Area)	SWP's need restocking/straighten up. Remove large cardboard box with funky shoe covers.
Done 10-14-99	Lab	General Area clean-up / straighten up.
	~~Process Area (@Chem. Berm)~~	~~Floor area needs to be mopped - chemicals have been spilled, getting tracked all over Plant.~~
	Behind Evap. Boiler	Insulation stuffed in corner - Needs taken care of. Put on or put away!!
Done 10/17/99 →	Between CTA/CTB & Wall between Swrt Tks & Concentrate Tanks	Chemical spill - On flooring and support beams Needs to be cleaned up.
10/16/99 addressed. [initials] →	N. of the New Vidmar RMA	Rubber matting - ugly mess.
	T.F.D.R.	Entire floor & horizontal surfaces need to be Mopped / wiped. 20,000dpm on flooring by exit door - it's just waiting to escape to the airlock.
omplete [initials] 10/14/99	T.F.D.R./Airlock	A plethora of dead icky bugs! And dust bunnies.
unable to get waste conveyed out; Done 10-14	Drum Load-out Area	Wooden pallets, pallets, pallets, plastic wrap, etc.
	Drum Storage Area (exterior exit door)	Needs brooming, mopping & de-bugging. Comp 10/14

APPENDIX B

POP-30-001, *"ETF Control Room, MTT, STT, Outside Operator Rounds"*

2 pages including cover sheet

LIQUID WASTE PROCESSING FACIL...IES

ETF CONTROL ROOM, MTT, STT, OUTSIDE OPERATOR ROUNDS

POP-30-001

REV/CHANGE NO. 2-1 | Printed: August 9, 1999, 3:44pm | PAGE 41 of 104 | EFFECTIVE DATE 8/9/99

ATTACHMENT 2 - ETF MTT ROUNDS

DATE:	10-11-99		10-12-99		10-13-99		10-14-99		10-15-99		10-16-99		10-17-99	
DAY	MON		TUES		WED		THUR		FRI		SAT		SUN	
PARAMETER	D	N	D	N	D	N	D	N	D	N	D	N	D	N
SURGE PUMPS AND INFLUENT FILTERS														
Inspect filters 60B-FL-1A, -1B, -1C (influent filters) and process system(s) for integrity and signs of corrosion. (No leakage from vessels, piping, valves, flanges, cabinets, ETC. No rust buildup) RCRA	(1)	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
CHEMICAL FEED SYSTEM														
Inspect tanks 65C-TK-3 and 4 and process systems for integrity and signs of corrosion. (No leakage from vessels, piping, valves, flanges, cabinets, ETC. No rust buildup)	✓	✓	(2)	Remark (2)	Remark (2)	Remark (2)	Remark (2)	Remark (2)	EDL 1,2 (3)	EDL 1,2 (3)	EDL 1,2 (2)	EDL 1,2 (3)	EDL 1,2 (3)	EDL 1,2 (3)

EDL #	(1) 99-MT-045	REMARKS: (1) valve 60B-118 has a small Leak. – EV-99-1166
EDL #	(2) 99-MT-004	(2) small Drip from valve RET-65C212-4. Bucket in Place. JT-99-2[illegible]
EDL #	(3)	Has Been written. (3) Leak on 93% H_2SO_4 pump or Line. Area
EDL #	(4)	Roped off. SOM already notifed.

APPENDIX C

LWPF Watchstanders List

2 pages including cover sheet

LWPF QUALIFIED WATCHSTANDERS LIST

Operator	Lock & Tag AW 003034	Lock & Tag CO 003036	Waste Generator 705020	Evap Bot SU Oper 350400	Evap Oper Exam 350401	Evap Cntrl Oper 350402	LWPF Outside Operator 705120	ETF Primary Operator 705125	ETF Secondary Operator 705130	ETF Ctrl Room Operator 705135	Aerial Lift 042720	Fork Lift 044470	Sample Transport 020077
Crew C													
Burt Andor OJT	2/12/00	2/09/00	1/12/00				4/18/01	3/6/00	3/6/00	06/13/00	6/03/02	5/5/01	10/22/01
Steve Burt OJT/OJE		2/09/00	1/12/00	10/11/00	10/10/00	10/11/00	8/07/01	5/15/01	11/28/00	5/16/01	6/18/02	4/08/02	10/22/01
Bob Caffland OJT	2/12/00	2/09/00	1/12/00				4/18/01	10/03/01	4/24/01	10/02/01	11/19/00	5/06/02	12/17/00
Tina Gomey OJT	2/12/00	2/09/00	1/12/00				4/18/01	9/17/01	2/23/00	11/23/00		6/3/00	12/17/00
Sharron Vermeulen OJT	2/12/00	2/09/00	1/12/00				8/27/01	9/07/01	9/07/01	2/24/00		[illegible]	10/22/01
Fran Wolfe OJT		2/09/00	1/12/00				4/18/01	9/17/01	[illegible]	[illegible]			10/22/01

Procedure used for MTT Line up was POP-60-006 MTT Line up Config 1
POP-60-002 MTT Startup Config 1.

Printed: October 8, 1999

Page 5 of 8

NOTE: This list is **NOT VALID** after the 12th of November, 1999

APPENDIX D

WHM-331, ***200 Area LWPF Health and Safety Plan (HASP),*** Section 4.4

5 pages including cover sheet

Table 6.3-1 LWPF Chemical Exposure Limits Table

Chemical	TLV - TWA	TLV - STEL	PEL - TWA	PEL - STEL
Sulfuric Acid	1 mg/m^3	3 mg/m^3	1 mg/m^3	NA
Sodium Hydroxide	2 mg/m^{3}C*	NA	2 mg/m^3	NA
Hydrogen Peroxide	1 ppm	NA	1 ppm	NA
Ammonia	25 ppm	35 ppm	50 ppm	NA

TLV-TWA	**= Threshold Limit Value - Time Weighted Average (8 Hours)**
TLV-STEL	**= Threshold Limit Value - Short Term Exposure Limit (15 minutes)**
PEL-TWA	**= Permissible Exposure Limit - Time Weighted Average (8 Hours)**
PEL-STEL	**= Permissible Exposure Limit - Short Term Exposure Limit (15 minutes)**
C*	**= Ceiling Limit (Never to be exceeded)**
NA	**= Not Applicable**
mg/m^3	**= milligrams per cubic meter**
ppm	**= parts per million**

6.4 Personal Protective Equipment Programs

(HNF-PRO-083)

Several operations or tasks performed by LWPF personnel create potential exposures to hazardous chemicals, excessive noise levels, high temperature surfaces, electricity and/or ionizing or non-ionizing radiation. A variety of PPE is used in conjunction with Engineering and Administrative Controls to eliminate and/or minimize these hazards. All personnel will ensure that PPE is inspected, decontaminated and maintained in a state of readiness prior to use.

If PPE is lost or unable to be removed from a controlled area, then the worker will obtain replacement PPE or exit the area as soon as possible.

1. Protective Headwear

   (HNF-PRO-083) - Protective headwear or hard hats will not be routinely required inside ETF support areas or at the 242-A Evaporator. At ETF, hard hats will be required when working in the process area, thin film dryer room, drum handling areas, and in other areas during construction or maintenance activities that present head injury risks.

All Hard Hat Areas will be posted as appropriate. Examples of these activities and/or areas include:

a. Working below areas where workers above on elevated surfaces are using tools or materials which might fall onto workers below. This includes work with liquids which could drip onto workers below.

b. Working in close proximity to exposed overhead electrical conductors.

c. Working in areas with low headroom (bumping hazard).

d. Working in construction areas.

Only ANSI Z-89.1 listed Class B Hard hats approved for protection from impact from falling objects and exposed high voltage conductors are to be used by LWPF personnel.

2. Eye and Face Protection

HNF-PRO-083, *Eye and/or Face Protection* will be required for a variety of operations performed by LWPF personnel. All eye and face PPE must meet ANSI approval specifications (ANSI Z87.1, *Practice for Occupational and Educational Eye and Face Protection*). All areas requiring eye protection will be posted with appropriate warning signs.

Tasks requiring eye protection and the appropriate PPE are listed in the following sections based on the potential for chemical exposure, foreign body/impact hazards or non-ionizing radiation exposure.

a. Chemical Splash Protection

1) Chemical goggles, safety glasses, or face shields are required for the following operations.

a) Sample collection of corrosives or use of sample jars with corrosive preservatives.

b) Addition of, or transfer of, water treatment chemicals from small containers (jars, 1 gallon or less containers).

c) Handling or transfer of small quantities of corrosive chemicals in the laboratory.

d) Other similar operations where only small quantities of corrosive or eye-contact hazardous chemicals are used.

e) For access inside the ETF process area.

2) Chemical goggles <u>and</u> face shields are required for the following operations.

a) Unloading of bulk chemicals from tanker trucks.

b) Adjustment of corrosive chemical pumps, valves or lines while pumps are in operation or lines are under pressure.

c) External inspection of corrosive storage tanks through the open manhole (internal inspections are conducted in accordance with the confined space program).

d) Tasks where large quantities or pressurized eye-contact hazard chemicals are used.

b. Foreign Body/Impact Protection

Safety glasses, goggles, or face shields are required for the following operations.

1) Operation of saws, drills, grinders, chippers or other chip and dust producing equipment.

2) Operation of explosive-actuated fastening tools.

3) Use of compressed air for cleaning.

4) Welding and cutting/scarfing operations.

5) Other similar chip, dust or projectile producing work.

c. Non-Ionizing Radiation Protection

HNF-PRO-582 - Safety glasses, goggles or welding hoods with appropriate filter lenses are required for the following operations.

1) Welding, torch or plasma arc cutting, brazing, soldering and scarfing operations.

The UV oxidizers in the ETF treatment train are enclosed with shielding and system interlocks to prevent accidental exposures during operation. Viewing ports are installed on the UV Oxidizers but exposure levels are below the requirements restricting access. The enclosures are also appropriately labeled.

3. Foot Protection

(HNF-PRO-083) - Standard work shoes or boots of substantial construction should be worn during work in the facility and are adequate for most routine operations performed by LWPF operations personnel. A work boot/shoe which provide a well defined heel, a steel shank, good ankle support, and a slip resistant sole are the preferred/recommended form of footwear. Boots or shoes meeting the requirements above and with toe protection meeting ANSI Z41.4 specifications are required for personnel directly involved in material handling operations such as movement of waste drums in the ETF drum fill and storage area, and movement of heavy tools and equipment/components.

Footwear protection for chemical spills is addressed in Section 6.4.4 in this document.

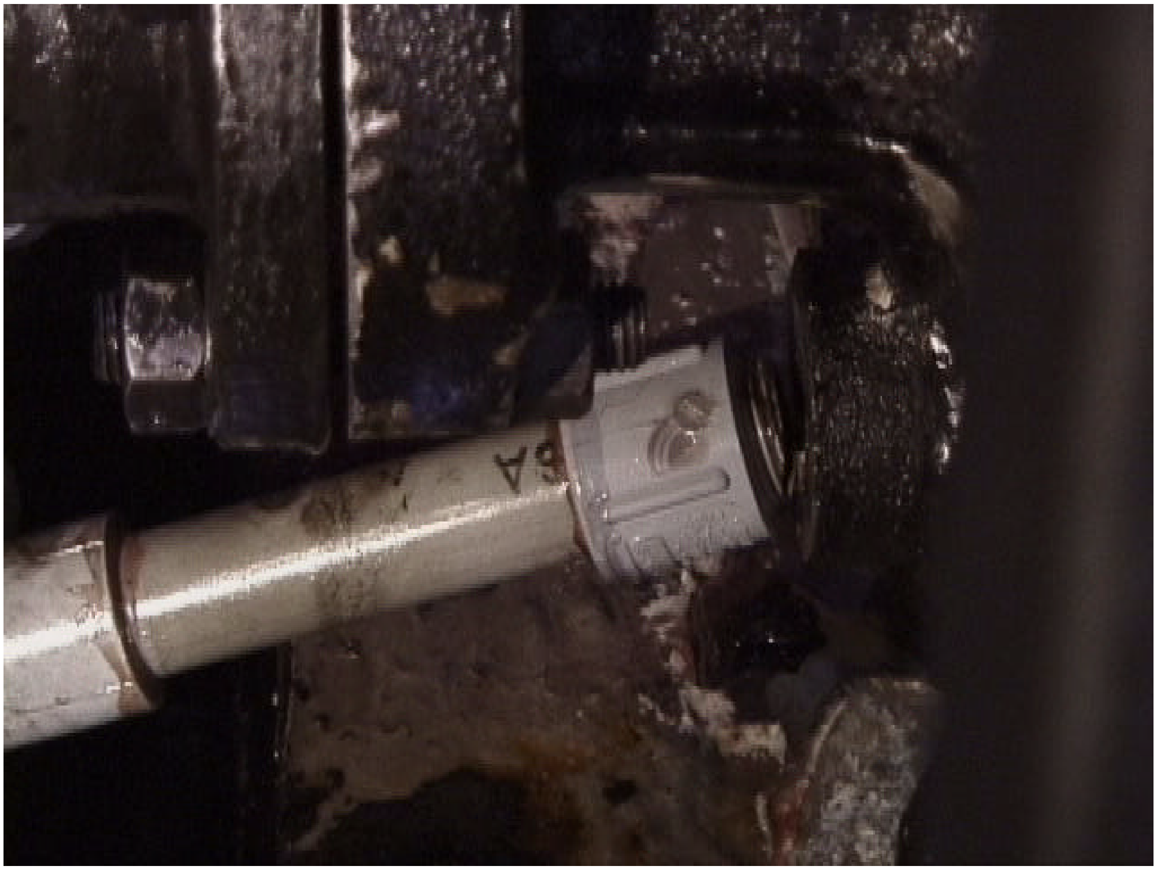
4. Chemical Protective Apparel

(HNF-PRO-083) - Corrosive and toxic materials in both solid and liquid forms will be handled by LWPF personnel. During routine operations, LWPF personnel involved in work activities in the process, waste handling and load out, and chemical storage areas at ETF and 242A equipment rooms (Condenser, Evaporator, AMU, and raw/process water building, shall wear full length pants and shirts with sleeves which cover the shoulder and upper arm, or full length coveralls. Full length trousers, and long sleeve shirts or coveralls should be worn during all chemicals handling operations. Special chemical protective apparel is discussed below.

APPENDIX E

Picture - Fractured drain line

2 pages including cover sheet



Fractured drain line. Notice line still connected by 20% of lower section.

APPENDIX F

Hanford Fire Department Incident Report 99000920, dated October 15, 1999

4 pages including cover sheet

Hanford Fire Department
INCIDENT REPORT
99000920-000

GENERAL SECTION	
INCIDENT DATE	FRIDAY, OCTOBER 15, 1999
ALARM TIME	0234
DISPATCH TIME	0234
ARRIVAL TIME	0242
END TIME	0635
RESPONSE (IN MIN)	8
PROPERTY MANAGEMENT	PRIVATE TAX-PAYING PROPERTY (1)
MUTUAL AID	NO AUTOMATIC/MUTUAL AID OR NOT REPORTED (0)
METHOD OF ALARM	TELEPHONE TIE-LINE TO FIRE DEPARTMENT (7)
SITUATION(S) FOUND	HAZARDOUS CONDITION UNABLE TO CLASSIFY FURTHER (40)
ACTION(S) TAKEN	RESCUE, REMOVE FROM HARM (31)
WEATHER	CLEAR (1)
TEMPERATURE	50
ADDRESS/LOCATION	2025-E CANTON & 12TH AVENUE
UNIT/APT #	WMH
NUMBER OF PERSONNEL	
PAID	18
NUMBER OF APPARATUS	
ENGINE	2
COMMAND	1
EMS	3
HAZMAT	1
OTHER	1
GENERAL PROPERTY USE	POWER, ENERGY PRODUCTION/DISTRIBUTION (61)
SPECIFIC PROPERTY USE	WATER SUPPLY SYSTEM (647)
BUILDING CODE TYPE	OCCUPANCY WITH HEALTH HAZARD (H7)
STRUCTURE STATUS	IN USE WITH FURNISHINGS IN PLACE, ROUTINELY USED (2)
OCCUPIED	YES (1)
ALARM TYPE	Other/Not Reported (9)
ZONE	200 East Area (200E)
STATION	Fire Station 92 (92)
SHIFT	C
HAZMAT SECTION	
ORIGIN OF RELEASE	
AREA	MACHINERY ROOM, AREA (61)
LEVEL	GRADE OR FIRST FLOOR (A01)
RELEASE FACTOR(S)	OTHER PART FAILURE, LEAK, BREAK (54)
NUMBER OF CHEMICALS	1
EQUIPMENT INVOLVED	SEPARATE PUMP, COMPRESSOR (65)
ACTION(S) TAKEN	RESCUE, REMOVE FROM HARM (31) INVESTIGATE (71)
DISPOSITION	INCIDENT SCENE RELEASED TO PROPERTY OWNER/MANAGER (8)
IDENTIFICATION SOURCES	MATERIAL SAFETY DATA SHEET (MSDS) (73) RESPONSIBLE OWNER, MANAGER (32) HAZARDOUS MATERIALS TEAM PERSONNEL (11) HAZMAT SPECIALIST (43)
NON-FIRE SERVICE INJURIES	1
CHEMICAL SECTION	
Sulfuric Acid	
CAS NO	7664-93-9
DOT NO	1830
DOT CLASS	CORROSIVES
PHYSICAL STATE	LIQUID

Page 6

Hanford Fire Department
INCIDENT REPORT
99000920–000

QUANTITY RELEASED	55 GALLONS
EXTENT OF RELEASE	CONFINED TO SPECIFIC PROPERTY USE OF ORIGIN
CONTAMINATION	NO ENVIRONMENTAL IMPACT
CONTAINER	
TYPE	PIPE
MATERIAL	IRON, STEEL AND OTHER IRON ALLOYS
DESCRIPTION	FIXED USE
FEATURE	PRESSURIZED
CAPACITY	0

APPARATUS RESPONDING

	CODE	MILES	HOURS	DISP	ROLL	ARRIV	LEFT	FACIL	BACK	END	REACT	ENRTE
BC91	8	4.00	0234	0237	0242			0635	0635	3	5	
MED92	80	2.50	0234	0237	0243	0253	0323	0408	0510	3	6	
AID91	16	2.50	0234	0237	0244			0503	0511	3	7	
HM92	8	3.70	0237	0240	0246			0615	0623	3	6	
ENG92	8	3.70	0234	0237	0246			0615	0623	3	9	
ENG942	24	4.10	0240	0243	0308			0510	0646	3	25	
MED94	24	4.20	0240	0244	0303			0623	0654	4	19	
UTL931	38	3.80	0245	0248	0310			0612	0640	3	22	

PERSONNEL RESPONDING

CODE AMOUNT1 AMOUNT2

Bumgarner, Gary
Wolfe, Gregory B
Knight, William M
Adams, Lynn R
Aardal, Douglas D
Castona, John A
Cope, Mark A
Lane, Edward F
Marcotte, Virgil N
Williams, Lee W
Whitney, William S
Barajas, Sean J
Thier, William B
Kiichle Karl C
McQuown, James G
Simard, Scott P
Shrum, Hubert A
Zable, Michael L

SUMMARY
Sulfuric Acid leak from a flange sprayed onto patient. Leak contained in dike. Patient transported to KMC and then onto Harbowview in Seattle.

REPORTED BY
Adams, Lynn R

OFFICER IN CHARGE
Knight, William M

INCIDENT NARRATIVE
At 0234 hours on Friday, October 15, 1999 (C-Shift), we were dispatched to a hazardous condition. Eight units were assigned to this incident. Eighteen personnel responded. We arrived on scene at 0242 hours and cleared at 0635 hours. The incident was reported to the fire department by a telephone tie-line. No automatic or mutual aid was provided or received. The weather was clear. Th temperature was 50 degrees.

The incident occurred at 2025-E CANYON & 12TH AVENUE #WMH. This location is a water treatment facility. The local zone is 200 (200 East Area). The local station is 92 (Fire Station 92).

The primary task(s) performed by responding personnel was rescue, removal from harm. One patie was found under an emergency shower who had been sprayed with Sulfuric acid. The patient was transported to KMC in Medic 92. Two other employees who were in the area were checked by Medic 94 at the scene and sent later to HEHF for further testing. 3 Firefighters were also checked at HEHF as a precaution.

Hanford Fire Department
INCIDENT REPORT

99000920-000

NCIDENT NARRATIVE

"Machinery room or area" best describes the primary use of the room or space where the hazardous materials incident originated. The incident occurred on the first floor or at grade level. "Other part failure, leak, break" best describes the factor present at the time and place of the incident that caused, or contributed to, the release or threatened release of the material. One chemical released or presented a hazard. A flange failed while working properly, allowed the release of the material.

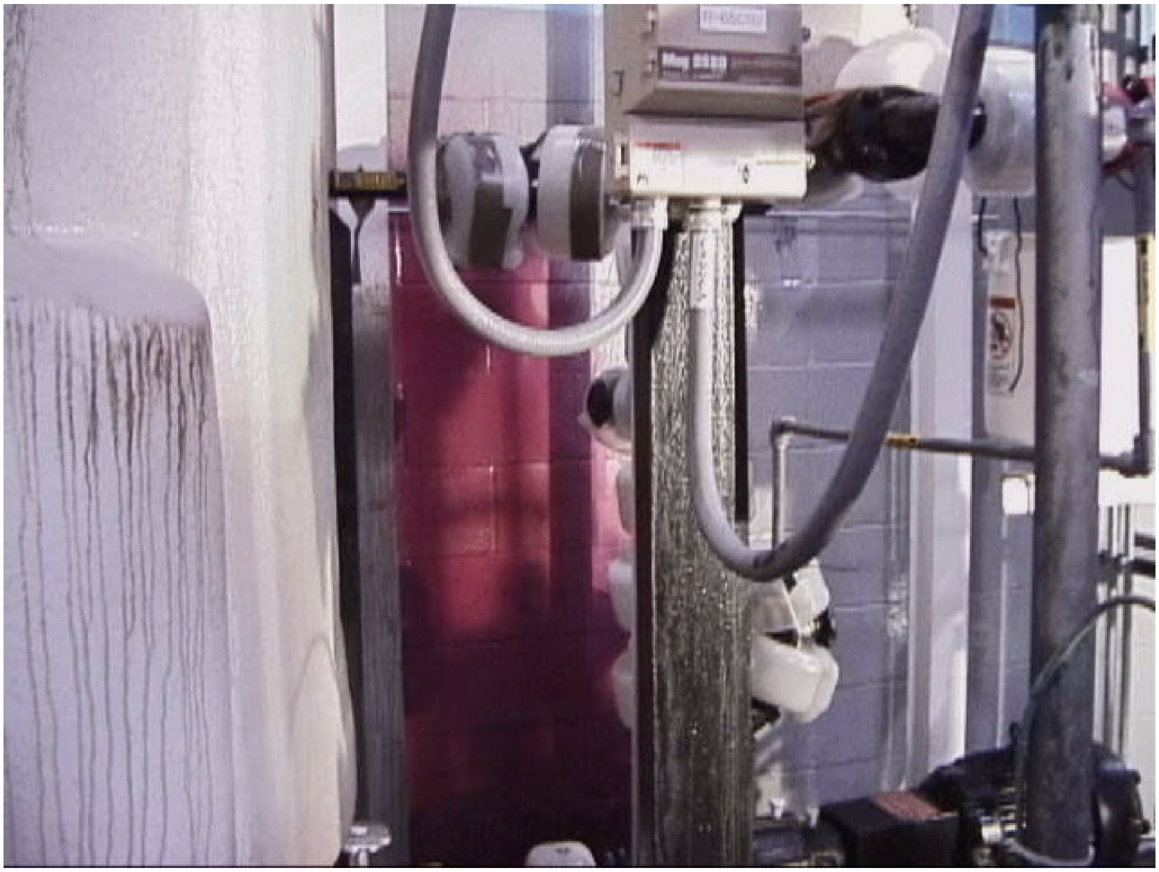
The Haz-Mat team was called in and upon their arrival a primary team, back up team and de contamination team were assembled. The team went into the building to examine the extent of the spill. It was found that all of the spill had been contained inside the diked area. No further spill was occurring and the scene was stable. Building personnel had shut off the tank and pumps when the leak was found. Plan A was to try to pump the acid from the dike to a container. No suitable pump could be found and Plan B was to neutralize the acid with Soda Ash. Not enough Soda Ash could be found on the site (approx 1500 pounds was needed) to start this effort. After further contact with the building personnel it was decided to wait for the day shift crew who knew where the pump was and who were trained in clean up to do the job. The scene was released for disposition to the property owner or manager. The sources of information used to identify the hazardous material released or involved in the incident were "Material safety data sheet (MSDS)", "Responsible owner, manager", "Hazardous materials team personnel", "Hazmat specialist".

Alarm number 99000920 has been assigned to this incident.

APPENDIX G

Picture - Chemical Berm Area

2 pages including cover sheet



Chemical berm area. Pump located behind unistrut support in center of picture. Notice spray pattern on wall.

APPENDIX H

ONC Communications Log dated October 15, 1999

6 pages including cover sheet

HANFORD SITE
OCCURRENCE NOTIFICATION CENTER
COMMUNICATIONS LOG

DATE	TIME	DUTY OFFICER	CONTACT		REMARKS
			TO	FROM	
10-14-99	1504	SGR	LMHC	ONC	Contacted Bill Parnell and inquired if their ONO was an environmental issue. He said it is because it is tracking whatever plume is going into the ground water & vadose zone. He will notify his own oncall person, Phil Miller
	1509	SGB	FDH	ONC	Returned VM call to Dennis Axel which he left at 1504. 2E/ON2 Waste water transfers not covered by NOC
	1524	SGB	Comm	ONC	Craig Kuhlman notified of ONO
	1528	SGB	ONC	LMHC	Pete Galotis – 2 events to be rolled-up to RP-LMHC-TANKFARM-1999-0002. 1) contaminated RR tie 2) Two specks of contamination outside ER151
	1745	SGB	ONC	BWHC	Lynn Nye – They just held a critique for the UO they had earlier this week, RL-PHMC-327FAC-1999-0008, and they determined that they need to notify WDOH. They will update their U.O. with this new information and add category 2E/ON2.
	2100	[illegible]	ONC	–	ON DUTY
10/15/99	0238	[illegible]	ONC	POC	Akers reported HFD responding an ambulance to 2025E for person sprayed with sulphuric acid.

HANFORD SITE
OCCURRENCE NOTIFICATION CENTER
COMMUNICATIONS LOG

DATE	TIME	DUTY OFFICER	CONTACT TO	CONTACT FROM	REMARKS
					(373-9000)
10/15/99	0307	KW	2025E	ONC	Called the IEP for the sulphuric acid incident. Spoke with the on scene manager (Roger Wanlquist). He said that he estimates approximately 10 to 15 gallons of acid spilled, but is within secondary containment. He also said that he had notified the Facility Manager (Ken Smith) and their safety rep. (Mike Clayton). Also left a message for their RL rep. Roger Quintero. He said that he will call the ONC when immediate actions are complete and he has had time to assess the severity and extent of the incident.
	0319	KW	EDO	ONC	Updated EDO with above information.
	0328	KW	Comm	ONC	Gave Comm. (Kuhlman) a heads up on info so far.
	0330	KW	EDO	ONC	Asked EDO whether or not RL Senior management had been brought into the loop yet. He said that he would follow-up with the exec oncall (Olguin) to make sure appropriate contacts have been made.
	0340	KW	ONC	EDO	EDO said that RL Senior Management (Augustenburg) is aware of the situation.

HANFORD SITE
OCCURRENCE NOTIFICATION CENTER
COMMUNICATIONS LOG

DATE	TIME	DUTY OFFICER	CONTACT TO	CONTACT FROM	REMARKS
10/15/99	0349	[illegible]	ONC	EHA	McCauley reported that the individual does not not appear to have any serious injuries. Some minor burns to arms & legs, but no internal exposure or eye problems. He does not anticipate any inpatient hospitalization, but will let us know something more definitive later.
	0350	[illegible]	EDO	ONC	Updated EDO with above info.
	0404	[illegible]	ACC. ENV.	ONC	Notified L. G. Mason of incident (including 0406 info below) Accident Investigation Support
	0406	[illegible]	ONC	EHA	McCauley said that the individual is being transported by helicopter to Harborview for further treatment.
	0408	[illegible]	ONC	Comm	Kuhlman said that there will most likely be some sort of press release, but not until later in the morning.
	0426	[illegible]	ONC	POC	Three other people were in the area of the acid spill and will be evaluated at HEHF later this morning (~0700 hrs). They are: Tim Gosney, Bob Coffland, and Sharon Vermeullen.
	0500	[illegible]	Comm	ONC	Craig Kuhlman said that he will contact the ONC later this morning with a determination as to whether or not a press release concerning the event.

HANFORD SITE
OCCURRENCE NOTIFICATION CENTER
COMMUNICATIONS LOG

DATE	TIME	DUTY OFFICER	CONTACT TO	CONTACT FROM	REMARKS
10/15/99	0500	RHS	—	—	ON DUTY
	0510	RHS	ONC	HealthAd	McCauley report transport to HarborView taking place & 5 individuals were to be evaluated in AM at HEHF – when opened
	521	RHS	ONC	mgmt.	Becky Austin called and wanted to know if the ONC had done an Abnormal Event notification due to patient being transported in a helicopter – informed her that criteria didn't apply and we were waiting on "press release" declaration – She requested information about when they (Comm) was notifying
	538	RHS	ONC	POC	Ackers (Bacs) reported information on – 4th individual W. W. Clifford was going to be evaluated by HEHF when they opened this morning – information was provided by HFD to POC
	544	RHS	ONC	POC	Ackers reported a request from Brent Ander at the Command Post for 1200–1500 lbs. of sodash for clean-up
	547	RHS	EDO	ONC	Notified L. Campbell of request & provided phone #s for his use.
	600	RHS	ONC	EDO	Campbell reported the facility was going to pump the material rather than absorbing after neutralization
	607	RHS	Radio	Trans	ICP was disbanded/terminated
	620	RHS	ONC	Bin.	M. Dallas inquired about EDO being involved – stated the individual received some to the face as well,
	745	RHS	HFD	ONC	Request HFD info for ES Mgm report – info provided by Kevin Miller
	834	RHS	ONC	Public Comm.	Mr. Gerber reported "No Press (or) Release" – person in "Stable" condition – "serious" would have prompted PR

HANFORD SITE
OCCURRENCE NOTIFICATION CENTER
COMMUNICATIONS LOG

DATE	TIME	DUTY OFFICER	CONTACT		REMARKS
			TO	FROM	
10-15-99	0838	RHL	ONC	2025E	Brian VonBergen reported OffNormal 3A ON(1) for Sulfuric acid incident (Recommended the USE 3A UO(4), but the facility didn't feel it qualified). Brian also indicated they would call Culmer
	0912	RHL	ONC	Envir. PDH	Culmer returned page and was notified of event. POC previously notified him ~3am but the facility had not.
	1114	RHS	ONC	Ecology	Steve Moore requested the occurrence report from Sulfuric Acid incident last night the facility told him they had submitted it.
	1255	[illegible]	ONC	T. Woodford	T. Woodford requests copy of DAR for 200LWP Acid incident
10/15/99	1300	[illegible]	ONC	–	ON DUTY
	1500	[illegible]	ONC	–	Checked ORPS GUI for occurrence report submitted by 200LWP not on system yet. Steve Moore request.
	1649	[illegible]	ONC	PNNL	ONO 26 ON2, APEL, Richland - pH requirements exceeded.
10/16/99	0900	[illegible]	ONC	–	ON DUTY
	2100	[illegible]	ONC	–	ON DUTY
10/17/99	0900	[illegible]	ONC	–	ON DUTY
10/17/99	2100	[illegible]		–	on Duty
10/18/99	0900	SGB	ONC	–	On Duty

APPENDIX I

Picture – Chemical Berm Area during Cleanup

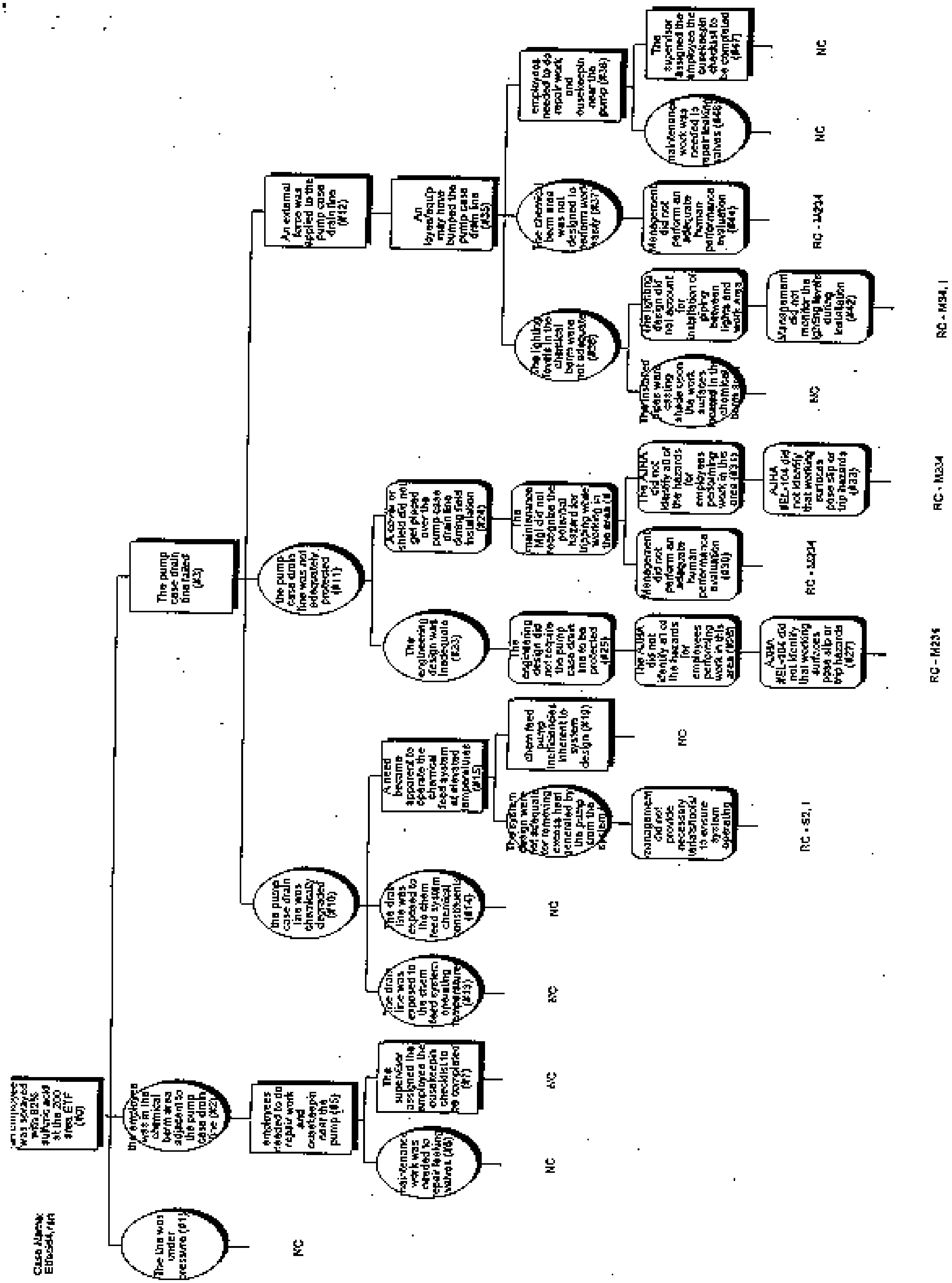
2 Pages including cover sheet

Chemical Berm Area during Cleanup

APPENDIX J

REASON ANALYSIS

5 pages including cover sheet


Case Name: Effacid4.rtn
The line was under pressure (#1)
The pump case drain line failed (#3)
An external force was applied to the pump case drain line (#12)
The pump case drain line was chemically degraded (#10)
The pump case drain line was not adequately protected (#11)
The engineering design was inadequate (#23)
A need became apparent to operate the chemical feed system at elevated temperatures (#15)
chem feed pump inefficiencies inherent to system design (#19)
Management did not perform an adequate human performance evaluation (#30)
Management did not perform an adequate human performance evaluation (#44)
employees needed to do repair work and housekeeping near the pump (#5)
employees needed to do repair work and housekeeping near the pump (#38)
The supervisor assigned the employee the housekeeping checklist to be completed (#7)
The supervisor assigned the employees the housekeeping checklist to be completed (#47)
Management did not monitor the lighting levels during installation (#42)
NC
RC - S2, I
RC - M234
RC - M34, I

Root Cause Analysis Report

Title: Sulfuric Acid Spill and Resulting Injury at 200 Area ETF

Problem #: Occurrence Report RL–PHMC-200LWP-1999-0010

Est. Loss: $200,000.00

Author: Terry L. Woodford

REASON Narrative

As maintenance work was needed to repair leaking valves, and because the supervisor assigned the employee the housekeeping checklist to be completed, employees needed to do repair work and housekeeping near the pump. So, the employee was in the chemical berm area adjacent to the pump case drain line.

In addition, because management did not provide necessary materials/tools/etc. to ensure system operating temp was met, the system design were not adequate for removing excess heat generated by the pump from the system. Thus, because chem feed pump inefficiencies inherent to system design, a need became apparent to operate the chemical feed system at elevated temperatures. Then, as the drain line was exposed to the chem feed system operating temperatures, and as the drain line was exposed to the chem feed system chemical constituents, the pump case drain line was chemically degraded.

Furthermore, because AJHA #EL-104 did not identify that working surfaces pose slip or trip hazards, the AJHA did not identify all of the hazards for employees performing work in this area. After this, because the engineering design did not require the pump case drain line to be protected, the engineering design was inadequate.

Then, because Management did not perform an adequate human performance evaluation, and the AJHA did not identify all of the hazards for employees performing work in this area, the maintenance Mgt did not recognize the potential hazard for tripping while working in the area. So, a cover or shield did not get placed over the pump case drain line during field installation. Since the engineering design was inadequate, and because a cover or shield did not get placed over the pump case drain line during field installation, the pump case drain line was not adequately protected.

Meantime, because Management did not monitor the lighting levels during installation, the lighting design did not account for installation of piping between lights and work area. Consequently, as the installed pipes were casting shade upon the work surfaces located in the chemical berm area; the lighting levels in the chemical berm were not adequate.

Additionally, because Management did not perform an adequate human performance evaluation, the chemical berm area was not designed to perform work easily. Since the lighting levels in the chemical berm were not adequate, and since the chemical berm area was not designed to perform work easily, and because employees needed to do repair work and housekeeping near the pump, an employee/equipment may have bumped the pump case drain line. So, an external force was applied to the pump case drain line. Since the pump case drain line was chemically degraded, and since the pump case drain line was not adequately protected, and because an external force was applied to the pump case drain line, the pump case drain line failed. As the line was under pressure, and since the employee was in the chemical berm area adjacent to the pump case drain line, and because the pump case drain line failed, an employee was sprayed with 92% sulfuric acid at the 200 area ETF.

REASON Interpretation

Analysis of this investigation shows that it is valid to compare the identified Corrective Opportunities to each other, given a calculated Reliability of 100%. This event contains a typical mix of both conditions and actions.

MANAGEMENT DID NOT PROVIDE NECESSARY MATERIALS/TOOLS/ETC. TO ENSURE SYSTEM OPERATING TEMP WAS MET

In terms of preventing this problem, this is the 4th best option, removing 21% of this model. Of the options in this model, this Corrective Opportunity will produce the 4th broadest prevention effect.

AJHA #EL-104 DID NOT IDENTIFY THAT WORKING SURFACES POSE SLIP OR TRIP HAZARDS

This is the 2nd best prevention option. It eliminates 33% of this problem. When compared to the other options in this model, action on this root cause will have the broadest prevention impact.

MANAGEMENT DID NOT PERFORM AN ADEQUATE HUMAN PERFORMANCE EVALUATION

Preventing this root cause is the best option, and will deal with 36% of the causes that produced this problem. Preventing this root cause will have the 2nd broadest impact within the organization, compared to the other identified options.

MANAGEMENT DID NOT MONITOR THE LIGHTING LEVELS DURING INSTALLATION

This action, the 3rd best option, will remove 26% of this problem. Eliminating this root cause will provide the 3rd broadest prevention impact.

REASON Summary Sheet

The Model is:	Closed
Quantification Reliability:	100.0%
Total Relative Causal Stress:	17.9500
Total Proper Causal Stress:	55
Causal Stress TTP:	3.2636
Total Relative Generating Causality:	12.4667
Total Proper Generating Causality:	42

REFERENCES

HNF-IP-0858, Section 2-L, *Emergency Response Duties, Abnormal Event Notifications*

HNF-PRO-077, *Reporting, Investigating, and Managing Events*

DOE Order 225.1A, *Accident Investigations*

MSDS 041765, Sulfuric Acid, 77-100%

POP-85B-001, *Sulfuric Acid/Acidic Water Spill Cleanup*

Critique Meeting Report for 92% Acid Spray Burned a Chemical Operator at 200 LWPF" held on 10/15/99

Occurrence Report, RL--PHMC-200LWP-1999-0010, "92% Sulfuric Acid Spill"

Patrol Daily Status Report, dated 10/15/99

Spill and Release Checklists dated 10/15/99 for Sulfuric Acid Spill

ETF Control Room Operator's Log 10/15/99

Failure Analysis of CPVC Piping in 93% Sulfuric Acid at The Hanford Effluent Treatment Facility (U) SR Report #: WSRC-TR-99-00484 December 1999

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FAILURE ANALYSIS OF CPVC PIPING IN 93% SULFURIC ACID AT THE HANFORD EFFLUENT TREATMENT FACILITY (U)

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Westinghouse Savannah River Company
Savannah River Technology Center
Materials Technology Section
Materials Consultation Group

December 1999

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Westinghouse Savannah River Company
Savannah River Site
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TITLE: FAILURE ANALYSIS OF CPVC PIPING IN 93% SULFURIC ACID AT THE HANFORD EFFLUENT TREATMENT FACILITY (U)

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LIST OF ACRONYMS, TRADENAMES, AND ABBREVIATIONS

ADS	Analytical Development Section of WSRC/SRTC
ASTM	American Society for Testing and Materials
Corzan®	B.F. Goodrich CPVC resin
CPVC	Chlorinated Polyvinyl Chloride
DMA	Dynamic Mechanical Analysis
EDS	Energy-Dispersive X-Ray Spectroscopy (also EDX)
ETF	Effluent Treatment Facility
FlowGold®	B.F. Goodrich tradename for CPVC hot/cold water piping
FT-IR	Fourier-Transform InfraRed spectroscopy or photospectrometry
Kynar ®	Pennwalt tradename for PVDF fluoropolymer resin
LWPF	Liquid Waste Processing Facility
MCG	Materials Consultation Group of MTS/SRTC
MTS	Materials Technology Section
PDCE	Polydichloroethylene
PVC	Polyvinyl chloride
PVDC	polyvinylidene chloride
PVDF	polyvinylidene fluoride
Saran®	Dow chemical's tradename for polyvinyidene chloride (PVDC) copolymers
SEM	Scanning Electron Microscopy
Solef®	Solvay tradename for PVDF resin
SRTC	Savannah River Technology Center
Sygef®	George Fischer tradename for PVDF piping
TempRite®	B.F.Goodrich tradename for CPVC resin
Tg	Glass transition temperature
WSRC	Westinghouse Savannah River Company

1.0 SUMMARY

Waste Management Federal Services of Hanford, Inc. contracted the Materials Technology Section of the Westinghouse Savannah River Co. (WSRC) Savannah River Technology Center (SRTC) to perform a failure analysis on ½" diameter Schedule 80 piping fabricated from chlorinated polyvinyl chloride (CPVC). The CPVC piping section was installed in the Hanford Effluent Treatment Facility (ETF) as a drain line for an acid transfer pump handling 93% sulfuric acid (H_2SO_4). On October 15, 1999, failure occurred in the threads of a male adapter fitting connected directly to the pump casing and resulted in an operator injury.

Based upon physical examination, evaluation of material properties, and review of chemical resistance data, the primary contributing causes of the CPVC fitting failure are listed below. It should be noted that several of these factors are believed to have synergistically contributed to failure.

- Chemical degradation, accelerated by brief pump temperature excursions to nearly 150°F
- Probable bending stresses and impact loading
- Stress-concentration in fitting threads due to thermal expansion effects
- Variation in chemical resistance between injection-molded fittings and extruded piping
- Notch sensitivity of CPVC piping and threaded fitting components
- Lack of physical barriers and adequate support to prevent damage or incidental contact

Generic data published by B.F. Goodrich (base resin manufacturer) indicates that Corzan® CPVC is suitable for the rated service temperature of this application (120°F). This data also indicates that the borderline temperature between the "Recommended" and "Caution" regions for 93% sulfuric acid is approximately 145°F. General disclaimers identify the possible reduction in pressure ratings in the "Recommended" region and end-user responsibility to determine chemical resistance, but no specific variation in resistance between fittings and piping in this service was indicated. It should also be noted that although previous and recent discussions with B.F. Goodrich technical representatives indicated that service life could be reduced in this application, such effects are not clearly represented in the published data.

Although the majority of references consulted indicate that CPVC is compatible with 93% sulfuric acid to 120°F, SRTC/Materials Technology found several notable exceptions to the contrary. Slight contradictions in ratings were also noted between suppliers of CPVC fittings and piping, even for those based on B.F. Goodrich's Corzan® material. This report describes the failure analysis performed, summarizes the results, and provides conclusions as to the root cause(s) of the failure. In addition, a brief review of the resistance of CPVC to 93wt% sulfuric acid is provided.

2.0 BACKGROUND

Waste Management Federal Services of Hanford, Inc. contracted the Materials Technology Section of the Westinghouse Savannah River Co. (WSRC) Savannah River Technology Center (SRTC) to perform a failure analysis on a ½" diameter Sch. 80 piping section fabricated from chlorinated polyvinyl chloride (CPVC). The piping section was installed in the Hanford Effluent Treatment Facility (ETF) as a drain line for a magnetically-coupled pump handling 93% sulfuric acid (H_2SO_4). The ETF is an indoor processing facility; therefore materials and components are not subject to significant aging or UV exposure, with the exception of overhead lighting.

On October 15, 1999, failure of a male adapter fitting occurred, releasing acid under pressure and causing injury to an operator. Photographs supplied by the customer of the general failure location and the drain line prior to removal are shown in Figures 1-3 respectively. Service conditions for the drain line were specified as a maximum pressure of 100 PSI at 120°F per ETF piping code P155 [1]. The pump is assumed to have been operating smoothly prior to failure with no pressure surges or significant vibration. According to the customer, the injured operator was in the pump vicinity prior to failure but was not performing tasks related directly to pump operation [2].

Configuration of the piping is shown in Figures 4 and 5. The drain line is essentially a 31" section of pipe containing two 90° elbows, a CPVC ball valve, and an end cap to allow pump drainage. The drain line is supported at the pump by the fitting threads and by a clamp on the drain end. It is assumed that only Teflon tape was used on fitting threads during installation.

The drain line is located approximately 12-18 inches above ground level, with no specific protection or physical obstacles to prevent incidental contact or damage. At the time of failure, it is assumed that the valve was closed and the end cap was installed to prevent drainage during pump operation. Per customer-supplied data and information, the drain line was operated at approximately 50 PSI [2].

The manufacturer of the 1/2" Sch. 80 CPVC fitting which failed is Spears Manufacturing Co., Sylmar, CA (part#836-005C). These fittings are fabricated (injection-molded) per ASTM F439 [3] from Corzan® CPVC resin, which is manufactured by B.F. Goodrich. The piping solvent-cemented to the Spears fitting has no markings distinguishing the piping manufacturer or supplier, other than "SA" between the elbow and failed fitting and "CPVC 4120" between the elbow and valve fitting.

The "SA" designation is unknown (possibly "USA"), but the "4120" designation correlates to ASTM D1784 which classifies CPVC piping by cell type and mechanical properties [4]. CPVC 4120 correlates to a Type IV(4), Class I(1) compound with a design stress of 2000 PSI (in units of 100). It is also assumed that the piping to fitting joints were made with CPVC solvent cement in accordance with ASTM F493 [5]. Per the customer, the design drawing for this system only specifies generic CPVC, with no specific resin or supplier identified.

Figure 1. General location of CPVC acid piping failure, Effluent Treatment Facility
(Courtesy of Waste Management Federal Services of Hanford, Inc.)
(acid pump is located to the right and beyond the employee in the containment dike)

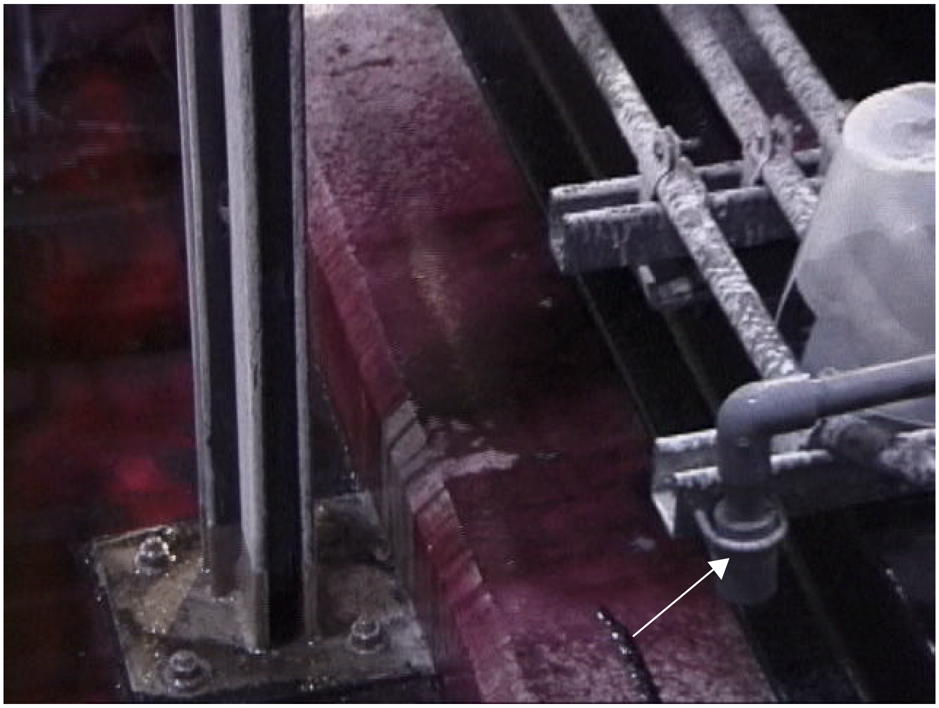


Figure 2. End of CPVC acid pump drain line and support clamp
(Courtesy of Waste Management Federal Services of Hanford, Inc.)

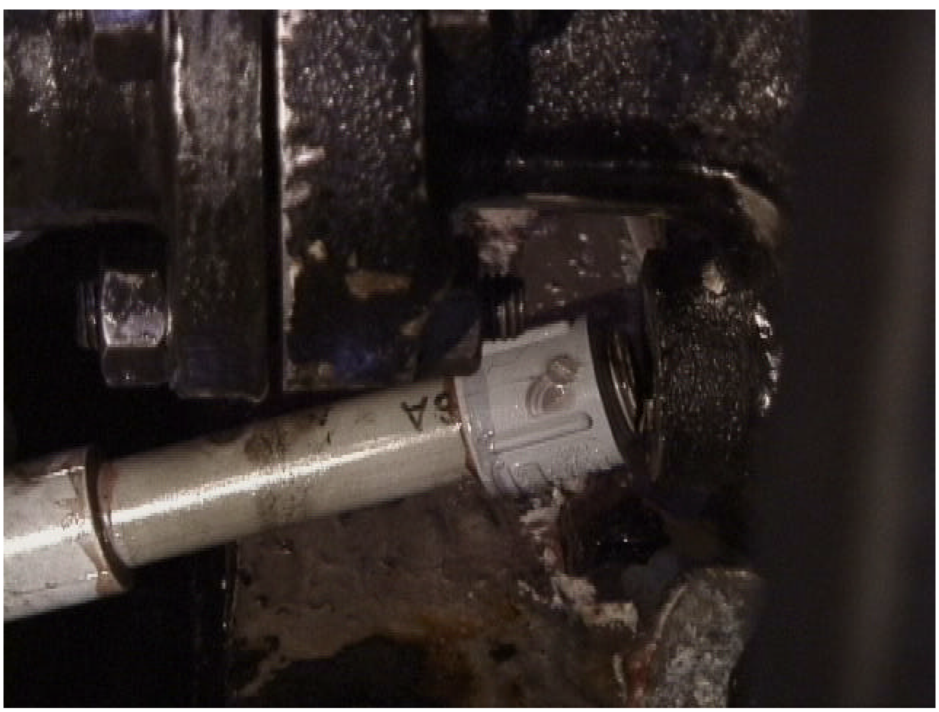


Figure 3. Failed CPVC drain line before removal from pump
(Courtesy of Waste Management Federal Services of Hanford, Inc.)

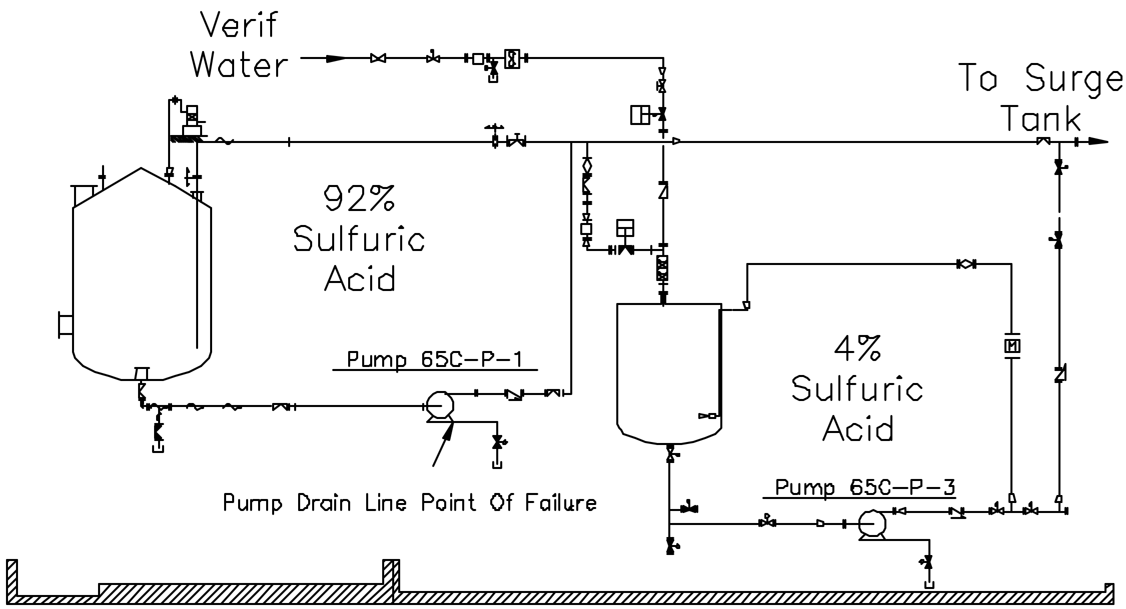


Figure 4. Section of P&ID drawing showing pump/drain line configuration
(Courtesy of Waste Management Federal Services of Hanford, Inc.)

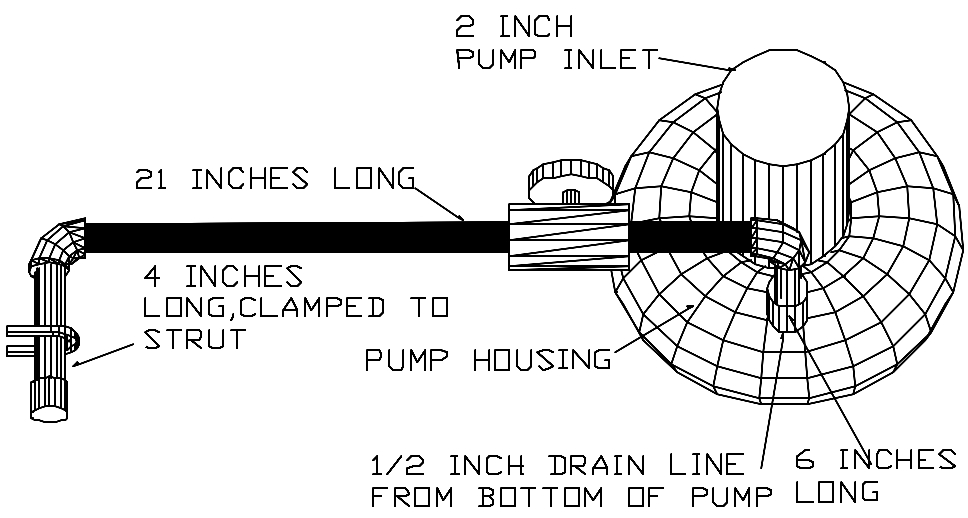


Figure 5. AutoCad 3D drawing of CPVC piping configuration
(Courtesy of Waste Management Federal Services of Hanford, Inc.)

Pump temperatures and pressures are continuously monitored, with data taken every 90 seconds in a programmable loop controller system. Data supplied by the customer indicates that the pump operated at temperatures >120°F on several occasions within the last 12 months, including temperatures >140°F for approximately 15 days, Figures 6 and 7 [6]. Temperatures and pressures are monitored on the inlet side of the pump and are assumed to be representative of those at the fitting/failure location. Per the customer, fluid temperature excursions are believed to be due to pump inefficiency and thermal stratification.

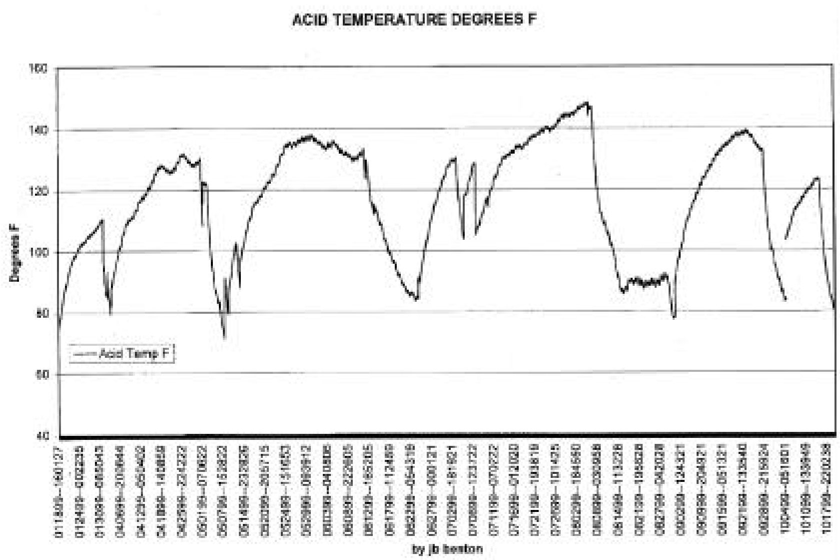


Figure 6. Temperature data for 93% sulfuric acid pump

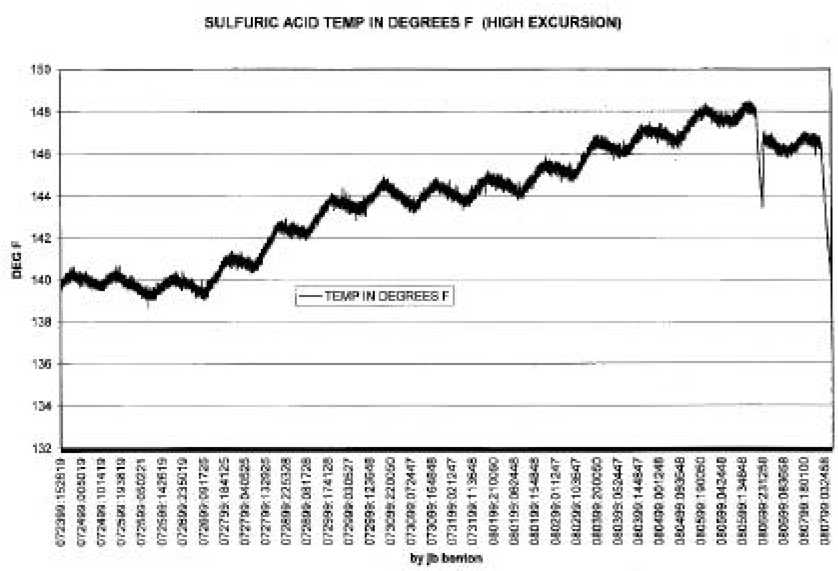


Figure 7. Abbreviated temperature excursion data for 93% sulfuric acid pump (7/23/99-8/7/99)

According to the customer, a section of similar CPVC piping had been previously removed from this service in September 1997, Figure 8 [2]. This particular piping assembly was removed to facilitate pump repair and not because of failure. Therefore, the effect of service environment upon material properties of this component were not investigated. However, note the cracking pattern and the greater depth of blackening observed along the interior surface of the threaded male adapter fitting as compared to the adjacent extruded piping.

Although this component was in service for nearly 2 years and did not fail, the appearance clearly indicates degradation and possible variation in chemical resistance between the fitting and piping in this environment. Such behavior could be due to many factors, including variation in composition, morphology, processing, and/or localized service conditions. It must also be noted that although the inner surfaces are blackened, the depth of oxidation and degradation is significantly less than that observed in the more recently failed fitting.

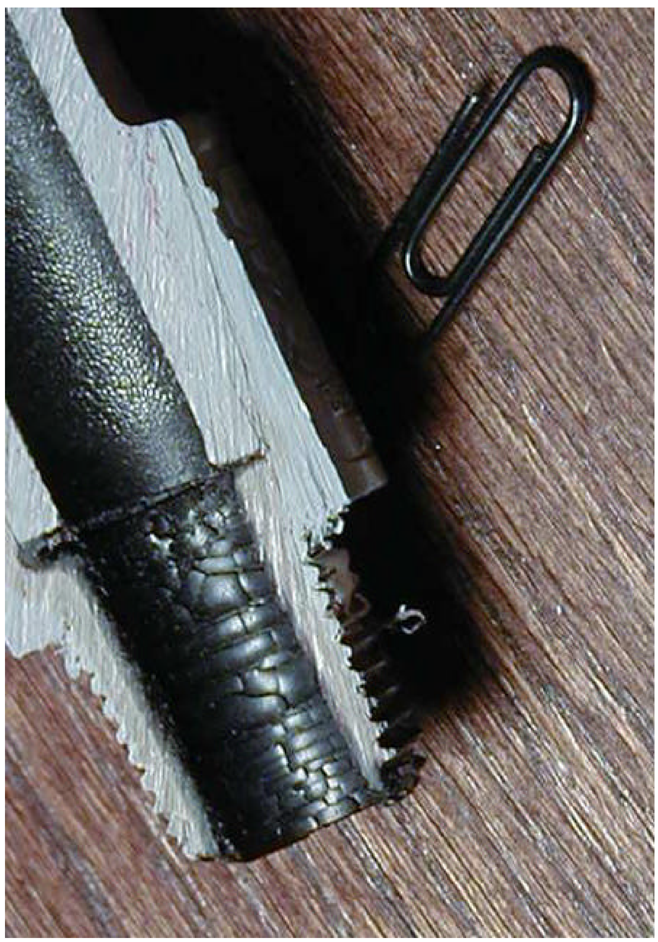


Figure 8. Degraded CPVC piping section, removed from same service in 9/97.
(Courtesy of Waste Management Federal Services of Hanford, Inc.)

3.0 CHLORINATED POLYVINYL CHLORIDE

3.1 General

Chlorinated polyvinyl chloride (CPVC), also known as after-chlorinated or post-chlorinated polyvinyl chloride, was first produced in Germany in the late 1930's to improve thermal properties of PVC compounds, primarily by increasing the glass transition temperature (Tg). CPVC is typically processed by treating dispersions of PVC in the presence of chlorinated hydrocarbons such as chloroform, catalyzed by heat or UV light. Although thermal properties are superior, the mechanical and chemical resistance properties of CPVC polymers are generally similar to those of rigid, unplasticized PVC (Type I) with some exceptions [4-7].

The general chemical structures of relevant vinyl polymers are shown in Figure 9 [4, 7]. In PVC, one hydrogen atom on alternating carbon atoms is replaced with a chlorine atom. In CPVC, additional chlorination takes place at the CH_2 group (1,2-chlorinated). Note that complete chlorination does not occur as in 1,2 polydichloroethylene (PDCE) homopolymer. CPVC is also similar in molecular structure to PVDC homopolymer (polyvinylidene chloride, Saran® – Dow Chemical), differing only in the location and orientation of the chloride ions. Although PVC and CPVC polymers contain some regions of crystallinity, they are primarily amorphous. The chlorine content of the base polymer is typically 50-60wt% for PVC and 65-70% for CPVC [4].

PVC —CH_2—CHCl—CH_2—CHCl—

CPVC —CHCl—CHCl—CH_2—CHCl—

PDCE —CHCl—CHCl—CHCl—CHCl—

PVDC —CH_2—CCl_2—CH_2—CCl_2—

Figure 9. Chemical structures of vinyl polymers [4, 7].

Due to higher density, glass transition temperature, melt viscosity, and lower sensitivity of melt viscosity to temperature, CPVC typically requires much higher processing temperatures and lubrication (both internal and external) than most PVC compounds [4-7]. CPVC is primarily used in place of PVC for elevated temperature service (chemicals and hot water) and is marketed by B.F. Goodrich under several tradenames such as TempRite®, Corzan®, and FlowGold®. Although B.F. Goodrich is the leading U.S. supplier, CPVC compounds are also available from other manufacturers.

3.2 Resistance of CPVC to Sulfuric Acid

Sulfuric acid (H_2SO_4) is one of the most common industrial chemicals, used extensively in chemical processing, wastewater treatment, neutralization processes, electroplating operations, electrolytic cell (battery) production, etc. [10]. It is also one of the most aggressive towards many metals and non-metals, with aggressiveness heavily dependent upon concentration, temperature, and the specific material involved. Sulfuric acid can act as either an oxidizing or reducing agent and is therefore one of the more complex acids to evaluate in terms of corrosion resistance [10-12]. Corrosion resistance of some materials, particularly carbon steel, is also dependent upon flow rate and presence of oxygen [10-12].

As a result of previously-observed degradation and known pump thermal excursions, Hanford ETF personnel reviewed published chemical resistance data and consulted with B.F. Goodrich technical representatives [2, 13, 14]. Published B.F. Goodrich data generically rates Corzan® CPVC as "Recommended" in 93 wt% sulfuric acid up to approximately 145°F (Figure 10). Published disclaimers also state that pressure ratings may not apply throughout the recommended range and that determining chemical compatibility of as-fabricated components is the responsibility of the end-user.

In recent discussions with SRTC/Materials Technology, B.F. Goodrich technical representatives indicated that service life would be reduced to 12-24 months by continuous exposure at 150°F, depending upon actual nature of application [11]. Although consistent with previous discussion with Hanford ETF personnel, such effects are not represented in the published data and do not address short-term, infrequent exposure to temperatures between 120-150°F. Neither the customer nor SRTC/Materials Technology knows the extent to which certain factors such as infrequent temperature excursions, service life reduction, and previously observed degradation were discussed at the time of previous inquiry.

SRTC/Materials Technology reviewed several references regarding the chemical resistance of CPVC materials to concentrated sulfuric acid [10-25]. SRTC/Materials Technology also discussed the chemical resistance data for Corzan® CPVC with B.F. Goodrich and Spears Mfg. representatives. From this review, several general observations and conclusions are summarized:

- Most references indicate that CPVC is compatible with 93 wt% sulfuric acid to at least 100°F, with some indicating compatibility to 120°F. One notable exception to this is Schweitzer's Chemical Resistance Tables, which rates generic CPVC as "U" (unsatisfactory) for both 90 and 95 wt% H_2SO_4, regardless of temperature [15]. A second noteworthy exception is the NACE Corrosion Data Survey [16], which rates CPVC as "Not Recommended" above 70°F for 93wt%.

- In many cases, ratings are only provided for either room temperature or 180°F, which is consistently rated as not recommended or unsatisfactory. Most references with data between these temperatures indicate that CPVC is not recommended for 93 wt% sulfuric acid above 140-150°F. It should also be noted that CPVC is often rated less resistant than rigid, unplasticized PVC for 93wt% sulfuric acid.

- Most references provide only general chemical resistance ratings (satisfactory, not recommended, etc.), without specifying effects on properties or pressure-retention capability. Chemical resistance data is usually based on short-term (90 days or less), well-controlled laboratory tests on specimens of specific composition and compression-molded under ideal conditions. Components fabricated by different techniques or from different compositions may vary in chemical resistance. Therefore, the effects of additives and processing parameters in a specific environment are often unknown.

- Data published by B.F. Goodrich is typically generic and provides only standard mechanical properties such as tensile strength and elongation following a 90-day immersion exposure at temperature. Other properties such as impact strength, bending strength, etc. vs. acid exposure are not known, nor is the pressure-retention capability of specific as-fabricated products. As typical of most resin suppliers, B.F. Goodrich does recommend testing of as-fabricated products by the end-user, but the possibility of variation in performance is not well emphasized from an end-user point of view.

- Spears Mfg. bases the chemical resistance of their CPVC fittings on B.F. Goodrich Corzan® data and does not publish independent test data. According to Spears Mfg., CPVC piping made by Harvel Plastics, Inc. (Easton, PA) is typically recommended for use with Spears CPVC fittings. It should be noted that Harvel Plastics CPVC pipe is rated as "Not Recommended" for 93 wt% sulfuric acid at 140°F [17]. This slightly contradicts the "Recommended" rating of Corzan® up to 145°F, especially since both are based on Corzan® CPVC base resin. The specific formulations for extrusion and injection-molding compounds could not be obtained (proprietary), but all companies contacted acknowledge possible slight differences for processing purposes. It was also consistently stated that significant variation in chemical resistance would not be expected for most service environments, but the effects of 93wt% H_2SO_4 at the application temperatures were unknown.

- 93% H_2SO_4 at 55+/-2°C is specified as a test reagent in ASTM D1784 [4], presumably due to its widespread use in industry and known aggressiveness. Sulfuric acid is also specified in other ISO standards for PVC classification, but concentrations are typically based on that found in domestic waste water treatment or sewer service which are much lower. The definitive technical basis for its use was not determined. According to ASTM, these tests have recently been eliminated from D1784 because chemical resistance testing is covered separately under ASTM D5260 [18] and ASTM D543 [19].

- The current chairman of the ASTM D20 committee on plastics informed SRTC/Materials Technology that variation in chemical resistance and performance of PVC/CPVC fittings and piping not surprising, but could not comment on specific variation in hot, concentrated sulfuric acid [20]. Such variation could not only be due to compound differences but to processing variation between batches within the same production facility, making the determination of such variation more difficult to evaluate. This subject is of current interest and will be discussed at the upcoming ASTM D20 committee meeting in Toronto, CAN.

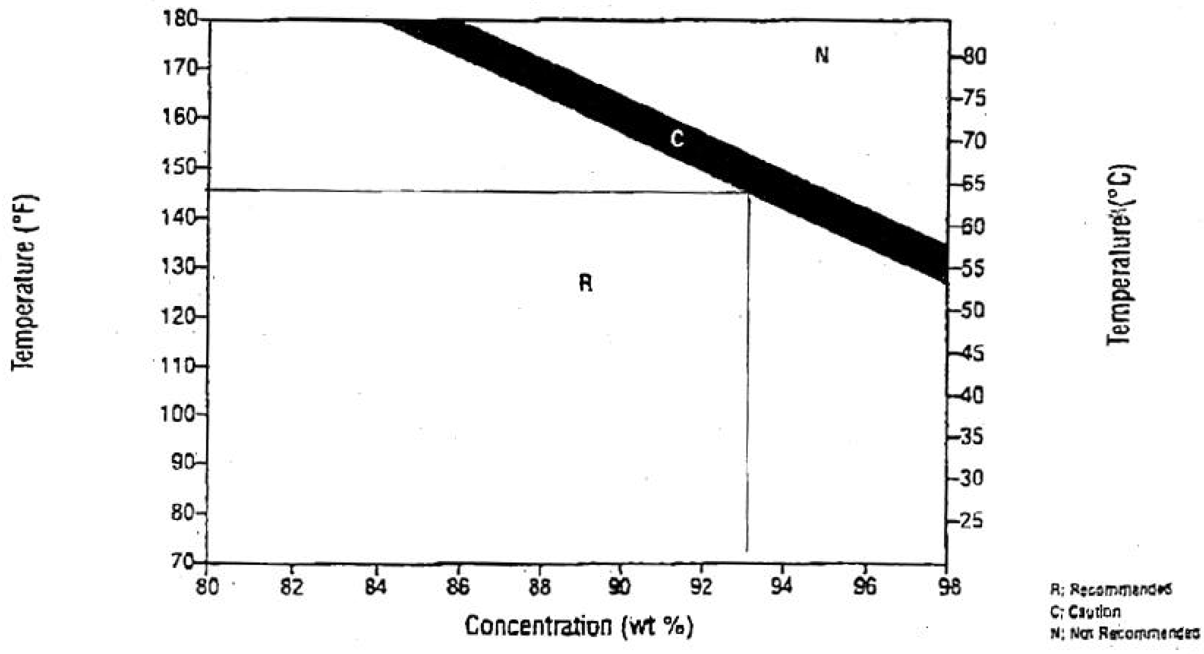


Figure 10. Resistance of generic Corzan® CPVC in sulfuric acid [14].

4.0 FAILURE ANALYSIS

4.1 Technical Approach

As is typical for most failure analyses, the first step was to document the overall as-received condition of the component(s), showing various angles and orientations of the components to reveal certain features, particularly manufacturer markings, indications of flow direction, orientation during failure, etc. Second, a failure analysis diagram or map was developed so that each piece or section to be removed for specific characterization or testing was identified. The components were then sectioned or cut apart as needed to facilitate further characterization and/or testing as appropriate.

4.2 As-Received Condition/Visual Examination

Photographs of the failed CPVC drain line assembly (up to the CPVC ball valve) are shown in Figures 11-18. The overall assembly is shown in Figure 11, with the flow direction and top of the assembly labeled for orientation. Note the color variation between the piping (manufacturer unknown) and the fittings (Spears), as well as the presence of CPVC solvent cement at the fitting joints. Figure 12 shows the pipe marking “CPVC 4120”, with a closer view of the failed fitting revealing the manufacturer and part # identification, Figure 13.

The arrow and markings in Figure 13 indicate the region of post-failure removal (bottom of pipe) from the pump casing. The remaining threaded portion was removed separately, Figure 14. Note that the threads from within the pump casing were more severely discolored on both interior and exterior surfaces, indicating greater degradation due to more severe chemical attack and/or higher temperature. Acid residue also possible on the pump casing threads prior to piping installation.

The opposite end of the drain line assembly (valve fitting/adapter) is shown in Figure 15, revealing similar discoloration and build-up of residue, particularly along the bottom interior surface. A closer view of the fracture surface (fitting side) reveals regions of plastic deformation, final fracture, post-failure fracture, and degree of discoloration and residue build-up particularly at the bottom of the piping assembly, Figure 16. The darker area at the top of the fracture surface is attributed to post-failure acid exposure. The opposing fracture surface (pump side) is shown in Figure 17. Note the severe degree of blackening and cracking observed on the end of the threads installed in the pump casing, Figure 18. The large slot in the wall of the threads is from the tool used for fitting removal from the pump post-failure.

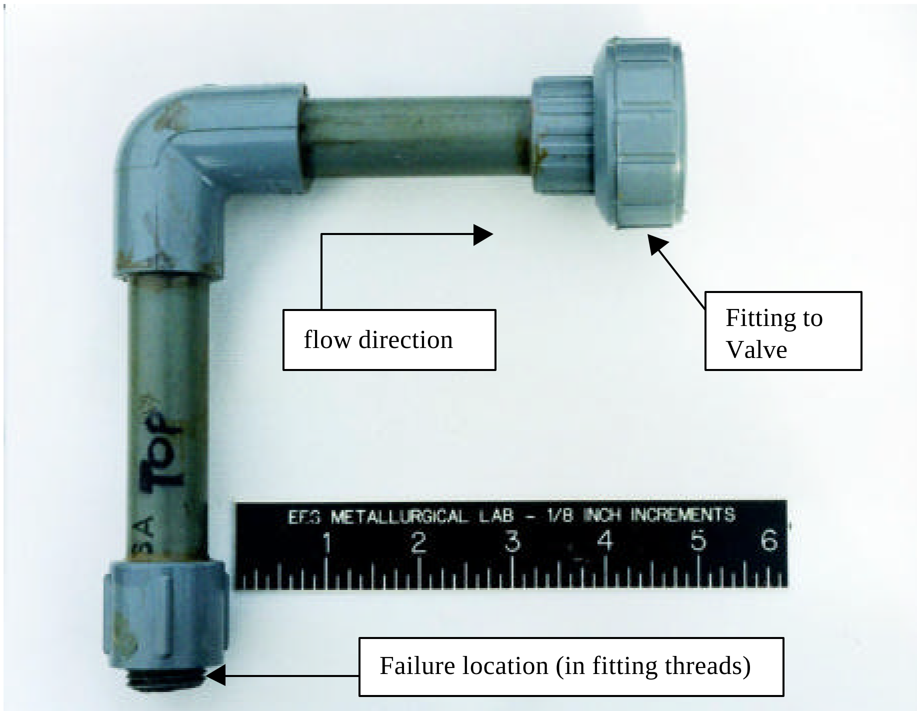


Figure 11. CPVC drain line assembly, as received condition, top side (Neg.#54967, ~1X)

Figure 12. Marking of CPVC piping, supplier/manufacturer unknown (Neg#55014, ~0.75X)

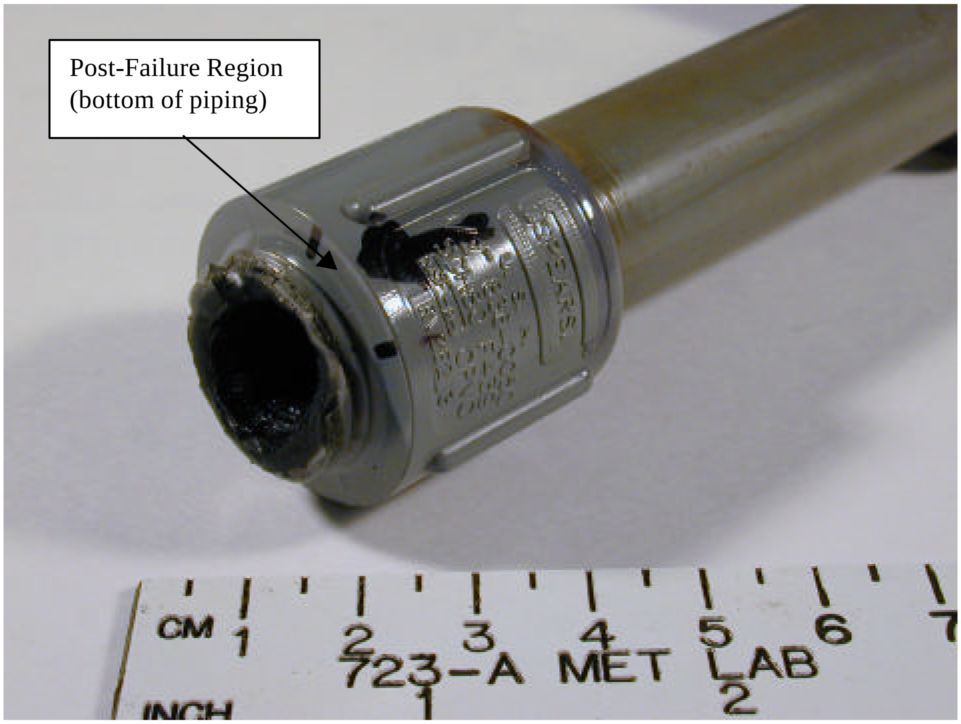


Figure 13. Failed ½" diameter Sch. 80 CPVC fitting, Spears Mfg. Part#836-005C

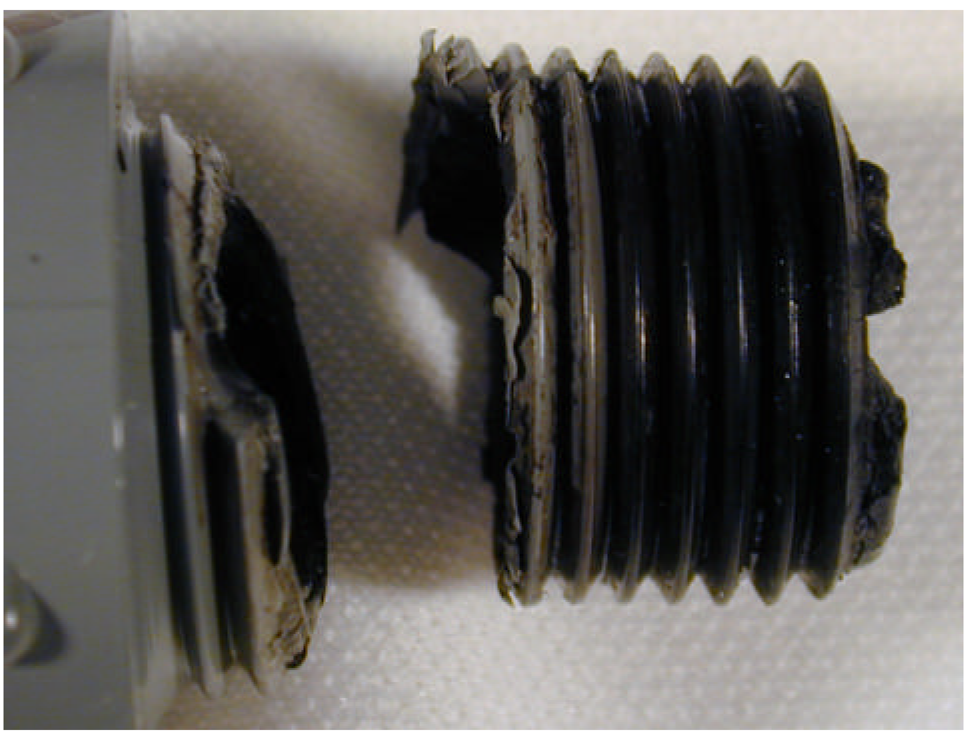


Figure 14. Remaining threaded portion from within pump casing

Figure 15. Photograph of the opposite end of the assembly (valve fitting)
(Note blackened interior and residue build-up along bottom of pipe)
(Neg#54967, ~5X)

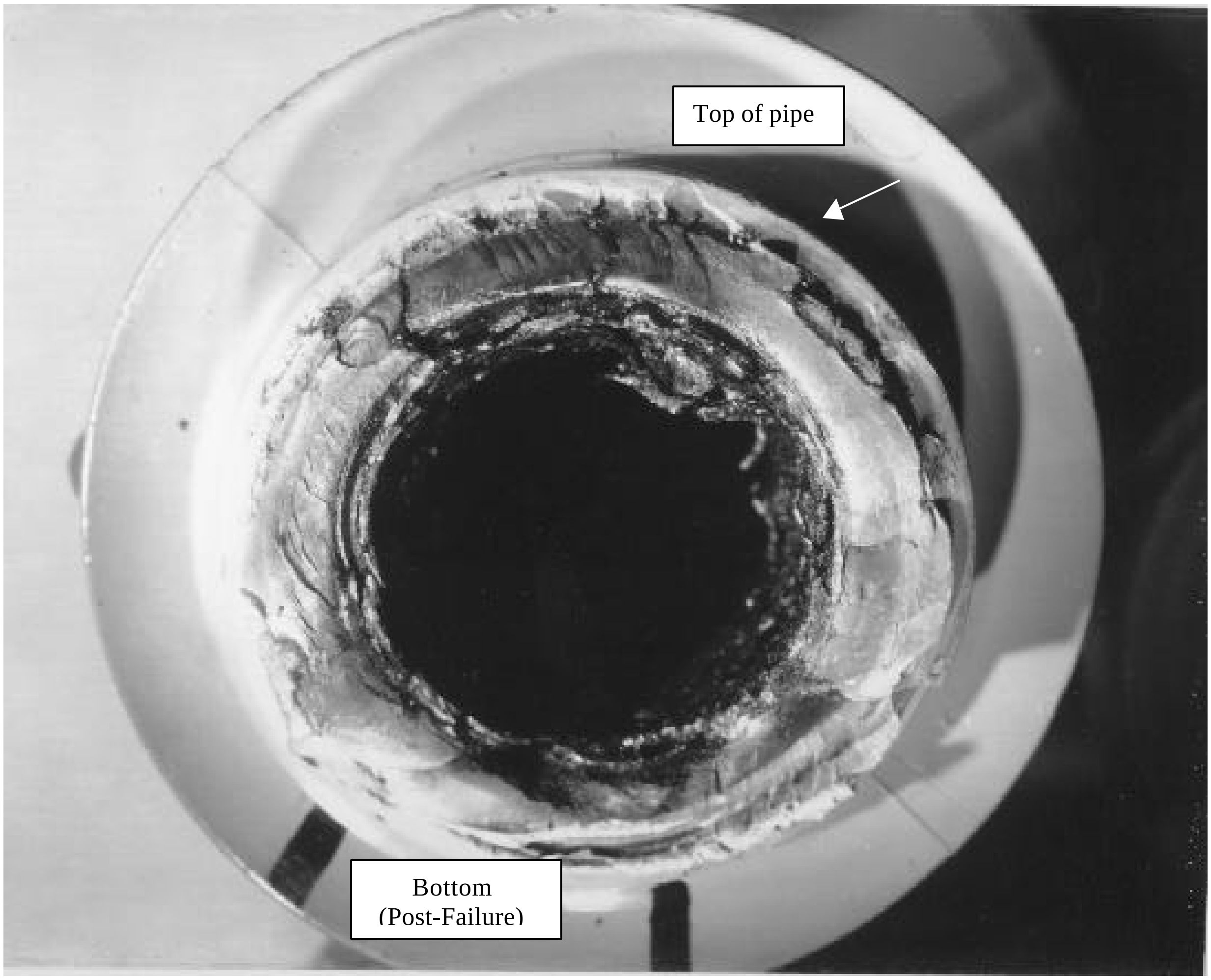


Figure 16. Close-up view of the fitting fracture surface (Neg#54965, ~3X)
(Markings indicate region still attached toward bottom of piping post-failure)

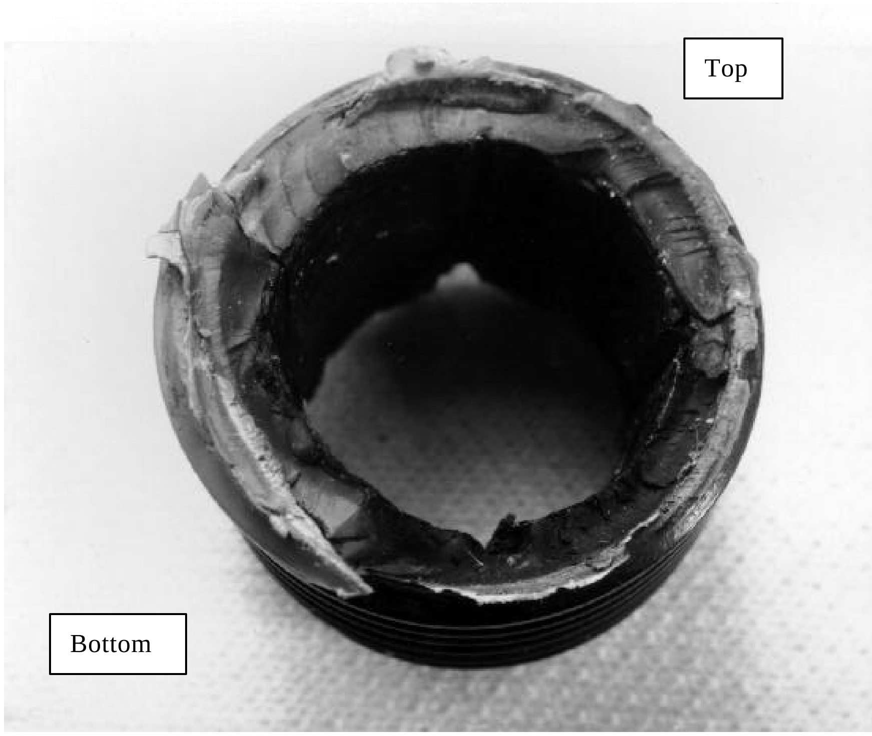


Figure 17. Opposing fracture surface of the fitting threads (Neg#54965, ~4X)

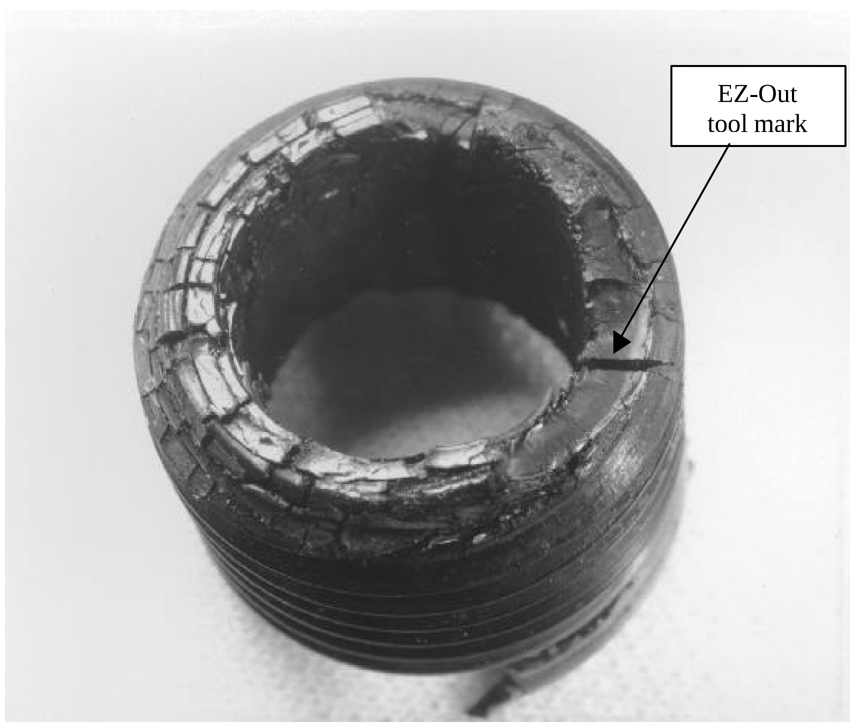


Figure 18. Opposite end of fitting threads (pump side) (Neg#54965, ~4X)

The threads of the failed fitting were sectioned to examine the extent of degradation, Figure 19. Note both the significant degree of darkening and the cracking pattern. A severe lack of structural integrity is also evident at the end from within the pump casing. The depth of discoloration is over 50% through-wall in the threaded region. However, it should be noted that cracks were not observed to initiate from the roots of the threads, which are considered to be the most highly stressed regions.

The degradation pattern appears to follow what may be flow lines in the injection-molded fitting, protruding like fingers into the threads (Figure 20). This may be due to a number of factors including variation in resin/chlorine content, degree of fusion, molecular weight, selective attack of one or more additives, and/or molding stresses. It is also possible that solvent cement from the fitting/piping joining process may have run along the interior of the fitting and penetrated the surface, reducing the chemical resistance and providing a path for degradation.

Severe cracking was present near the interior surface of the fitting, Figure 21. Degradation tended to be more severe along solvent-cement paths (Figures 22 and 23), which can be resin-poor and are common failure locations in these systems [27, 28].

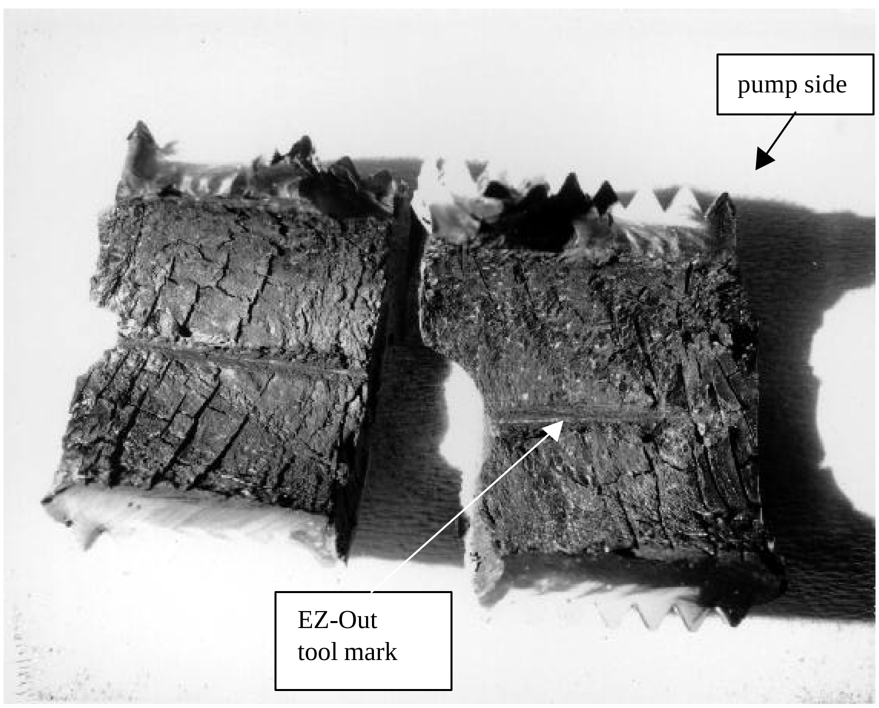


Figure 19. Interior view of fitting threads (Neg# 54970, ~5.5X)
(severe oxidation and cracking)

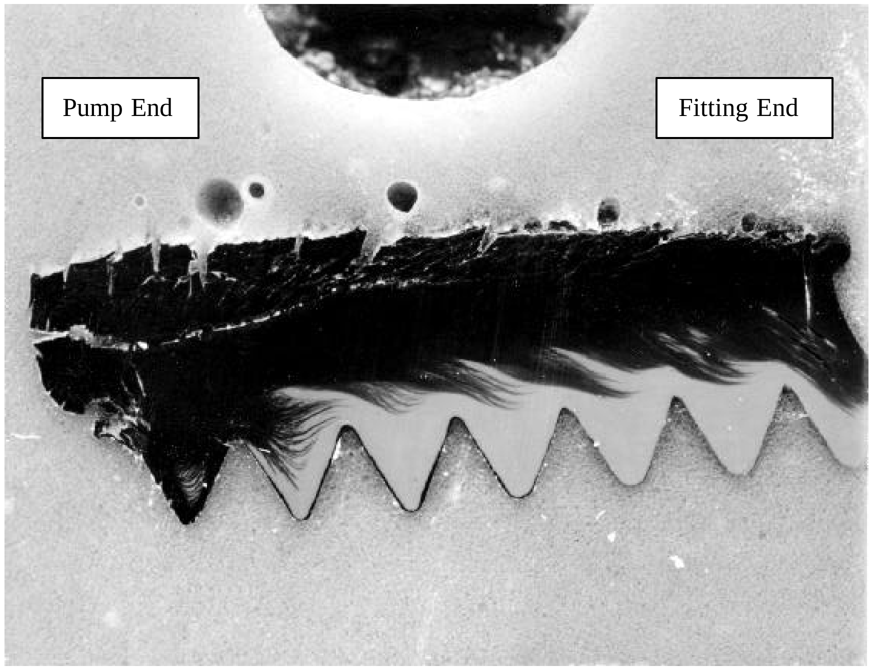


Figure 20. As-polished cross-section of fitting threads (Neg#55000, ~3X)
(Note degradation following what may be flow lines into threads)

Figure 21. Severe cracking along interior surface of threaded fitting (Neg#54970, 100X)

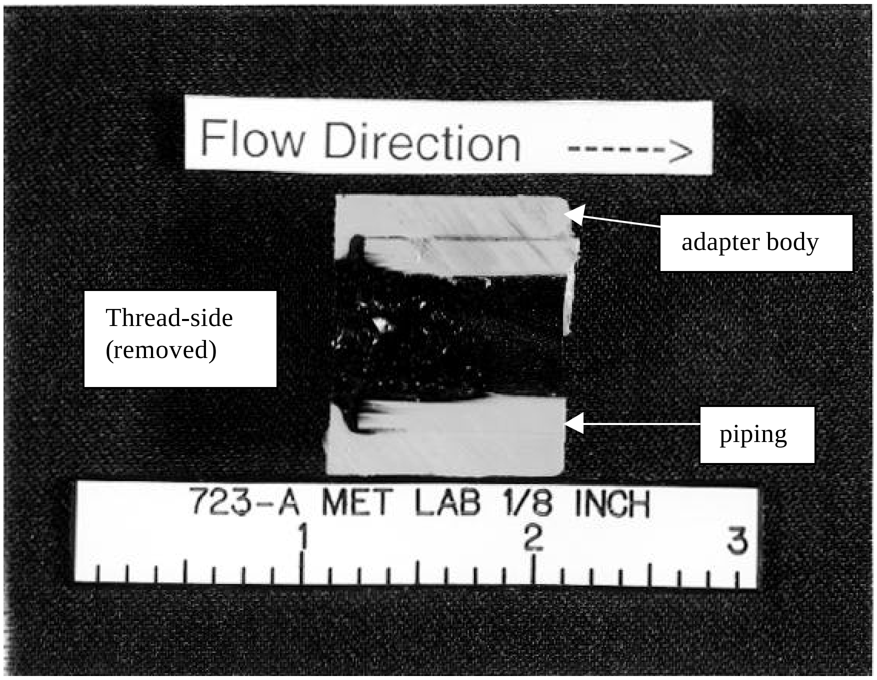


Figure 22. Cross-section of failed fitting adapter and joined piping (Neg#54980, 1X)

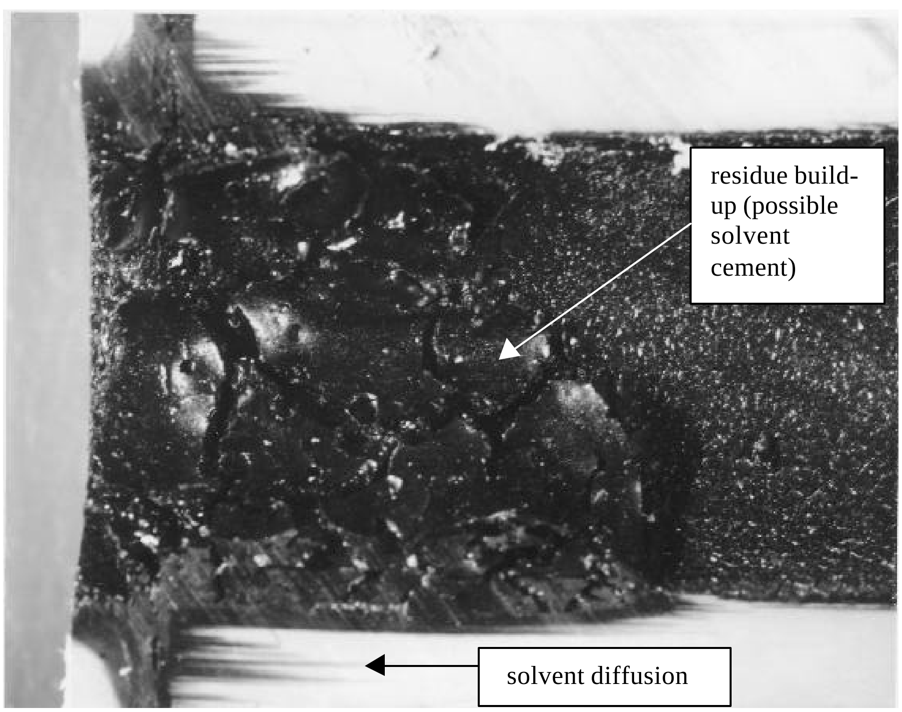


Figure 23. Closer view of adapter fitting/piping cross-section (Neg#54980, 5X)

To further evaluate the possibility of chemical resistance variation between piping and fittings, the 90° elbow was also sectioned (Figures 24-25). Cracking and blackening of the elbow is greater than in the adjoined piping, but not nearly to the extent observed for the failed threaded fitting. Attack of the solvent-cement joints is also evident.

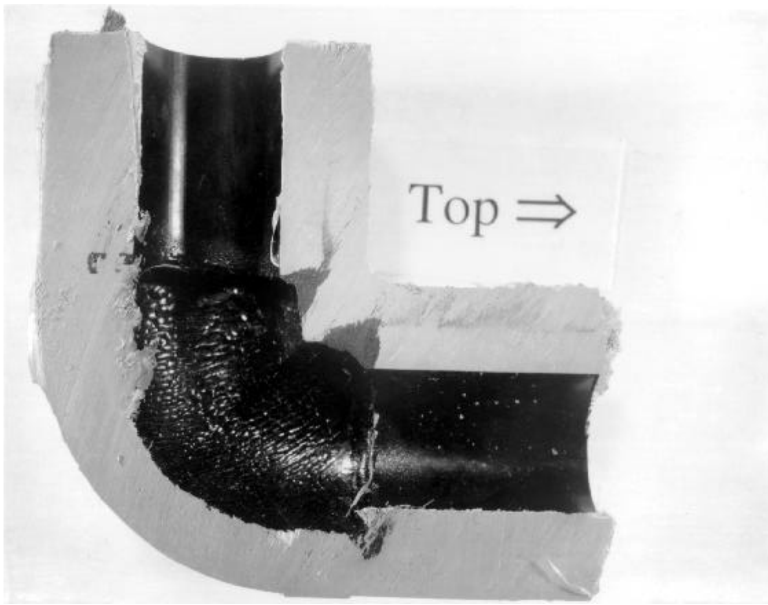


Figure 24. Interior surface of elbow, top half (Neg#55014, ~1.5X)

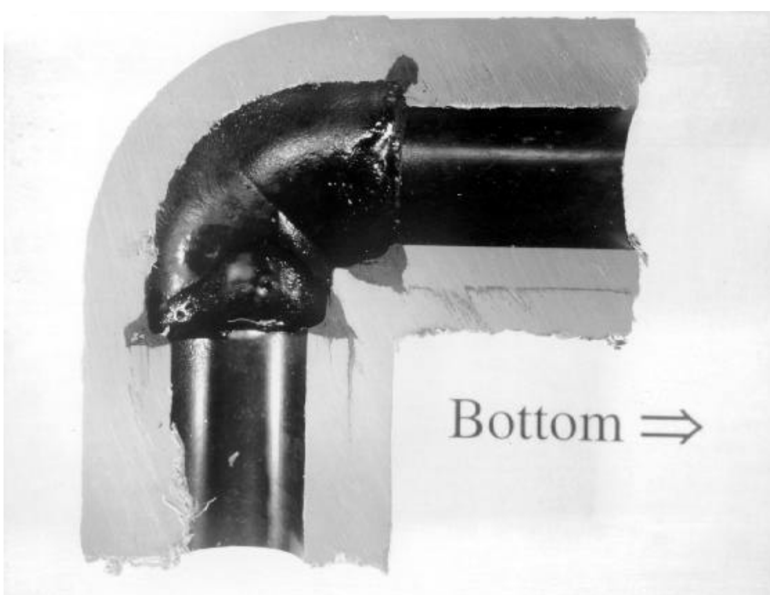


Figure 25. Interior surface of elbow, bottom half (Neg#55014, ~1.5X)

4.3 Scanning Electron Microscopy (SEM)

The fracture surface from the fitting was sectioned, gold-coated for conductivity, and examined under the Hitachi S2500 Scanning Electron Microscope (SEM). Several areas of the fracture surface were studied to locate the failure initiation site and to examine specific features. Figure 26 reveals what is believed to be the failure initiation site, located towards the top right of the as-installed piping orientation. It appears that fracture initiated in the thread root under a tensile stress, and rapidly propagated outward and upward towards the edge of the threads.

Note the significant amount of degradation and loss of integrity in the inner diameter surface. Other regions exhibit the characteristics of brittle band formation in amorphous polymers such as PVC/CPVC, which are similar in appearance to fatigue striations [27]. These regions may have been enhanced by cyclic stresses imposed by thermal expansion differences between the fitting and the pump casing.

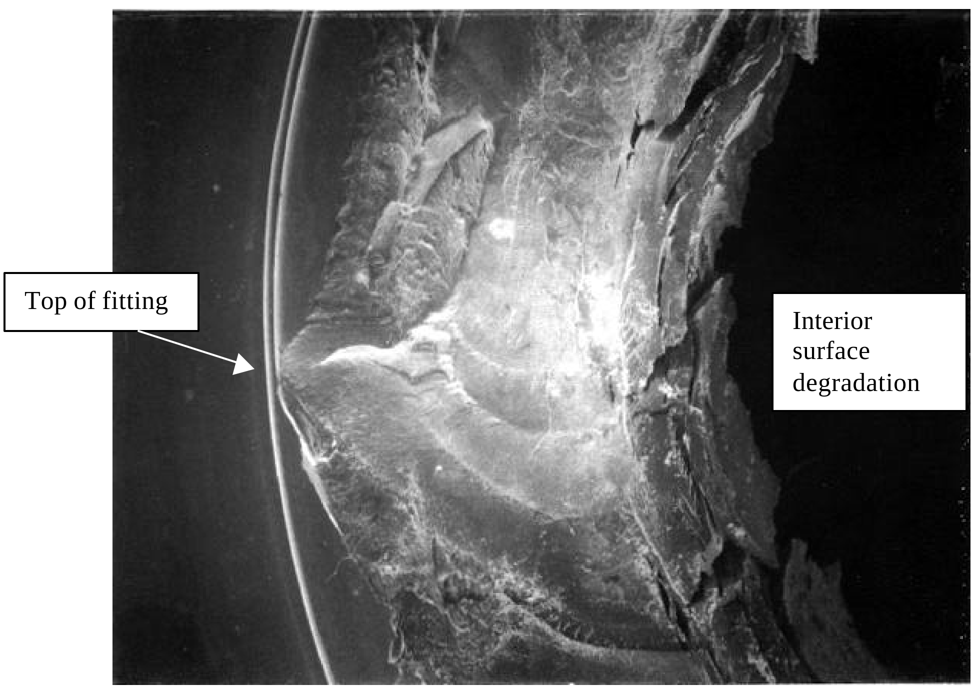


Figure 26. Probable fracture initiation site and brittle band formation (Neg#54985, 15X)

4.4 Energy Dispersive X-Ray Analysis

In order to further determine the cause of possible variation in chemical resistance between the fitting and piping, a section of the failed fitting/piping joint was carbon-coated and analyzed under the SEM using energy dispersive X-ray analysis (EDX). Whereas gold is typically used for superior imaging, carbon provides superior X-ray transparency. Measurements were taken in both point and raster mode for the bulk piping and fitting components to determine composition variation and evidence of selective attack.

Spectra obtained from the bulk fitting and piping indicate the presence of calcium, tin, titanium, sulfur and silicon in trace amounts for both components. No significant differences in composition were observed, though the fitting spectrum indicates slightly higher amounts of titanium and calcium. Titanium is highly susceptible to attack by sulfuric acid [11], and is most likely present as titanium dioxide (TiO_2).

Calcium and tin are most likely from additives such as calcium stearate and organotin complexes used for heat stabilization and/or lubrication. Sulfur-tin complexes are considered to be the most effective non-lead based heat stabilizers for PVC [4, 27]. The presence of sulfur is attributed to both the presence of sulfuric acid and the probable use of sulfur-tin complexes.

Silicon was observed in both components, but to a slightly greater extent in the piping. This could be present as a lubricant/heat stabilizer constituent or simply as a trace impurity. Silicon is known to enhance the resistance of cast irons to concentrated sulfuric acid through the formation of abrasion-resistant silicon-rich films, but must typically be added in substantially higher amounts than expected in CPVC compounds (14.5wt%) [11].

Since most plastics additives are used in the lowest amount possible in order to optimize final properties, such additives often constitute less than 1 wt% which is less than the detection limit on conventional X-ray analysis equipment. Therefore, accurate quantatative values could not be determined. Without knowing the exact compound formulation, additional testing would have to be performed to confirm if compound variation is the cause of the observed difference in chemical resistance.

Assuming that internal lubrication is generally more important for injection molding as compared to extrusion and that CPVC can be more difficult to injection-mold than unplasticized PVC, internal lubricants are expected to be present in the injection-molded fittings to a somewhat greater extent. These lubricants may or may not be more susceptible to sulfuric acid attack, but could be a contributing factor. If such differences exist, they would normally be expected to have little to no effect upon chemical resistance. However, it may be possible that such a small variation is selectively attacked at the upper limits of the recommended service conditions. As this analysis is inconclusive, additional investigation is recommended to evaluate the effects of other factors such as chlorine content, residual stresses, molecular weight, morphology, density, degree of fusion, etc. which could affect chemical resistance.

4.5 Fourier-Transform Infrared (FT-IR) Spectroscopy

For organic composition analysis, samples of both the fitting and piping were analyzed by the Analytical Development Section (ADS) of SRTC using Fourier-Transform Infrared (FT-IR) spectrophotometry. FT-IR spectra represent the IR absorption profile of all organic and many inorganic compounds materials in the 4000 to 400 cm^{-1} (2.5 to 25 um) range [29]. Although FT-IR analysis is one of the most definitive methods for characterization of polymeric materials, very complex FT-IR spectra are often produced. Unknown polymer samples are often best identified by comparing spectra to those of known materials. Samples of Corzan® CPVC compound# 3114 were obtained from B.F. Goodrich and used for baseline comparison.

The samples were prepared by grinding the surface with 400 grit silicon carbide sandpaper. The powder was subsequently analyzed directly by diffuse reflectance FT-IR. Spectra were obtained using a Nicolet 210 FT-IR instrument, employing a Michelson interferometer with a KBr beamsplitter to accomplish frequency discrimination. The spectral resolution of the instrument is nominally 2 cm^{-1}. Background scans were obtained prior to sample scanning. Improvement in the signal to noise ratio was obtained by averaging multiple interferograms for background and sample spectra.

Although relatively dark in color (due to carbon black additives), the gray CPVC materials produced very clean and distinguishable spectra. Spectra obtained for all samples were matched with reference CPVC spectrum in the instrument software library. Spectra obtained for the Corzan® resin, Spears Mfg. fittings and piping (unknown supplier) are shown in Figures 27-30. No significant variation in spectra was observed. Because most additives for processing are used at very low levels (less than 1 wt%) and can be transparent to IR radiation, detection by this technique may not be possible. As with most resin manufacturers, B.F. Goodrich likely adds certain proprietary additives to their CPVC compounds for identification, but specific information on these could not be obtained.

The main aspect of these spectra to note is the location (wavenumber) of the relative peaks. The percentage of transmittance and relative intensity of the peaks are more dependent upon sample preparation and form and are not indicative of composition variation.

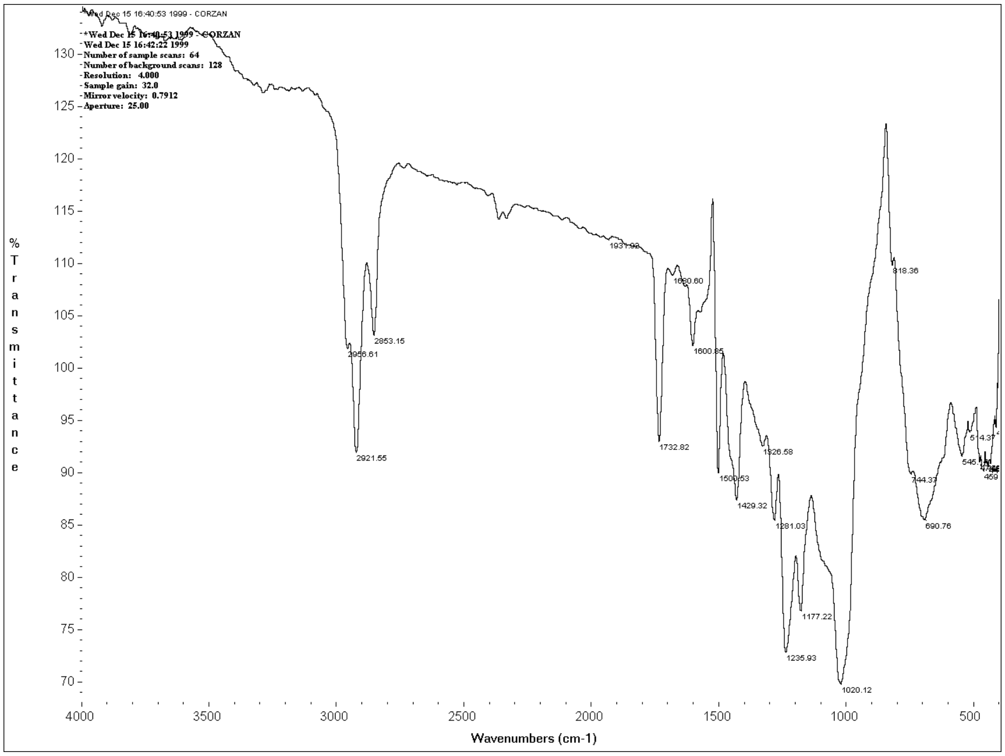


Figure 27. FT-IR spectrum for base Corzan® resin, compound 3114, B.F. Goodrich

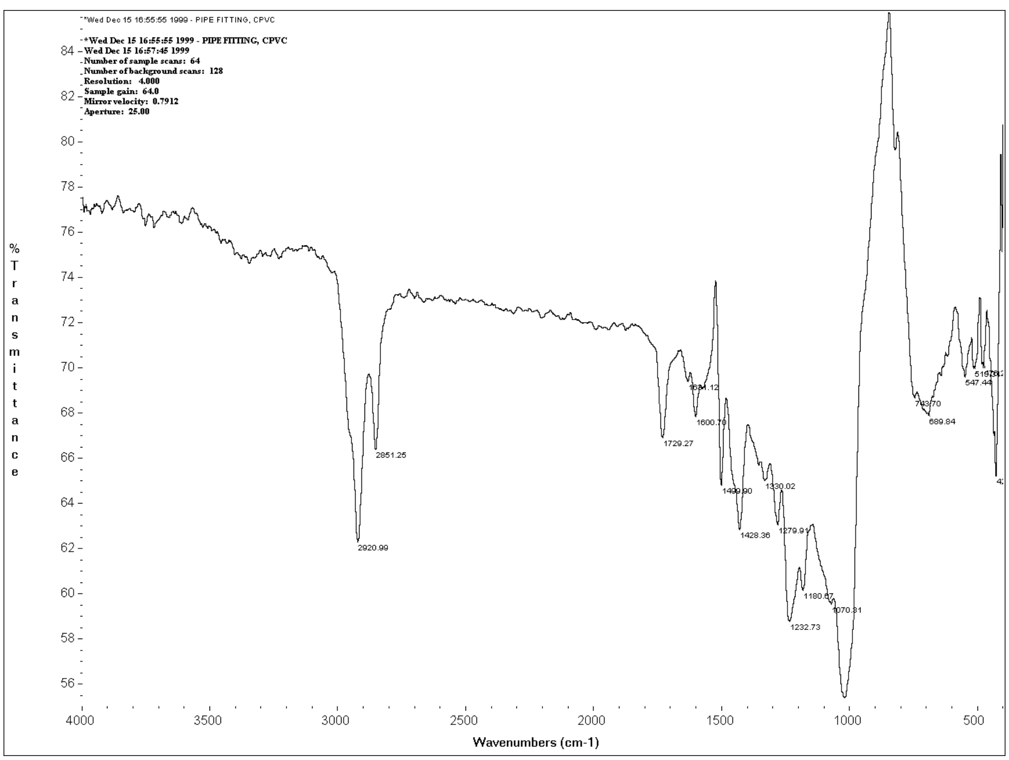


Figure 28. FT-IR spectrum for Spears fitting, part#836-005C (non-degraded)

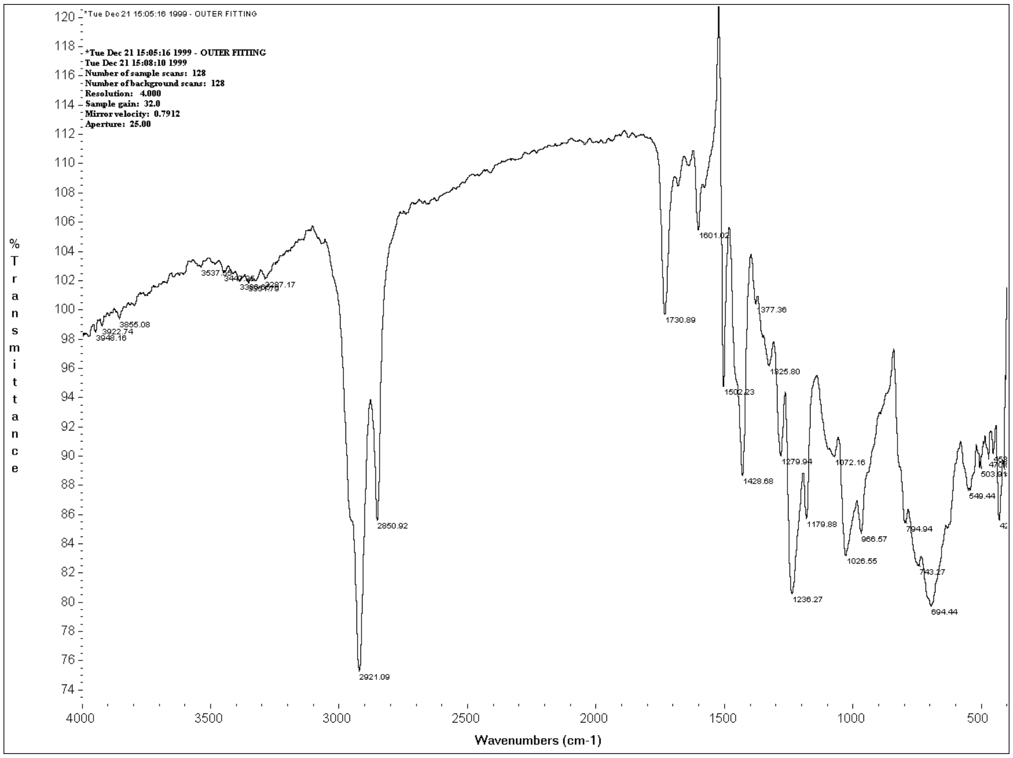


Figure 29. FT-IR spectrum for failed Hanford fitting

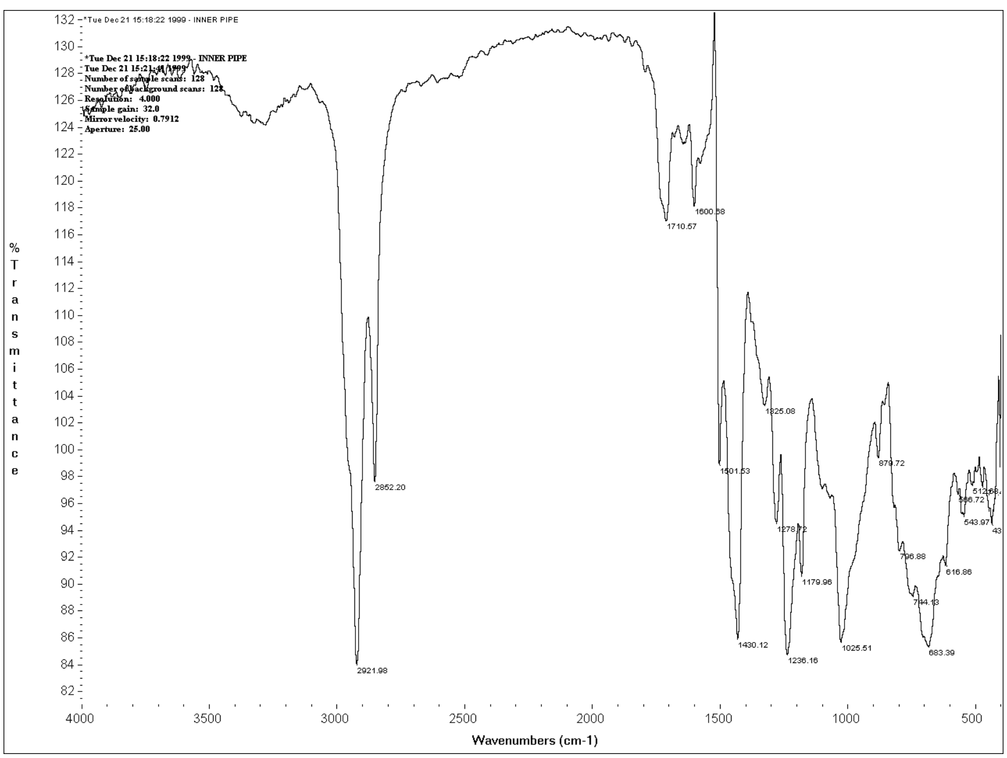


Figure 30. FT-IR spectrum for bulk piping (manufacturer/resin unknown)

4.6 Mechanical Testing

To determine the effects of degradation upon mechanical properties of the failed fitting, the remaining section of the fitting threads was subjected to compression/bend testing. Standard test specimens could not be obtained from the failed fitting due to its small size, condition, and configuration. As no ASTM test method exists for this particular technique, duplicate samples were cut from several unexposed fittings of the same schedule, model, and manufacturer for comparison purposes. Although not a standard test method, this approach is considered to be most similar to that of bend testing of rectangular specimens per ASTM D790 [30], only in reverse and with the exception of the thread pattern.

A test sample was made from one half of the threaded Hanford fitting (Figure 30) and ten test samples were made from five new (CPVC) fittings. The sample preparation consisted of cutting off the threaded portion of new fittings and half-sectioning, to make two samples from each fitting. A cut was made longitudinally in three of the new samples to simulate the cut in the Hanford sample (#6) that was made with an EZ-Out tool during post-failure extraction from the sulfuric acid pump (Figure 32). The test sample shape and the nominal dimensions are shown in Figure 33.

The samples were tested using a screw-driven mechanical testing frame, Sintech 1125, serial no. 6272, and a load cell with a capacity of 1000 lbs., serial no. 690, MTE 3-1876. The load cell was calibrated in accordance with the recommended practices of ASTM E4-98 [31] by an off-site vendor. The samples were compressed to failure at a crosshead speed of 0.04 in./minute and to a maximum compression value of 0.200”. Most samples achieved approximately 0.198” of displacement.

Failure was defined as the load at which the sample fractured and or compressed at maximum displacement of test method (0.200”) or when the load drops 75 percent below the maximum load produced during each test. The samples that did not reach this cut-off value were the ones that broke or fractured during the test, which triggered the break sensitivity feature on the machine and shut down the test. Peak loads and displacement values were recorded from the load cell and crosshead movement on a computer.

A summary of the test results with individual sample data are summarized in Table 1. The load-elongation plots are attached for selected distribution. The samples made from non-degraded fittings without slots that compressed only (without fracture), had an average load value of 281 lbs. and were compressed to an average displacement value of 0.197”. The new samples (without slots) that fractured had a lower average peak load value of 107 lbs. and lower elongation of 0.099”. Samples CPVC-2 and CPVC-7 fractured and the break sensitivity shut down the tests and therefore did not reach the full 0.200” displacement and therefore the peak loads were lower. Sample-to-fitting traceability was not maintained during the machining of the samples, therefore no conclusions can be drawn as to the relative strength of the individual, non-degraded fittings. Photographs of samples during testing are shown in Figures 34-35.

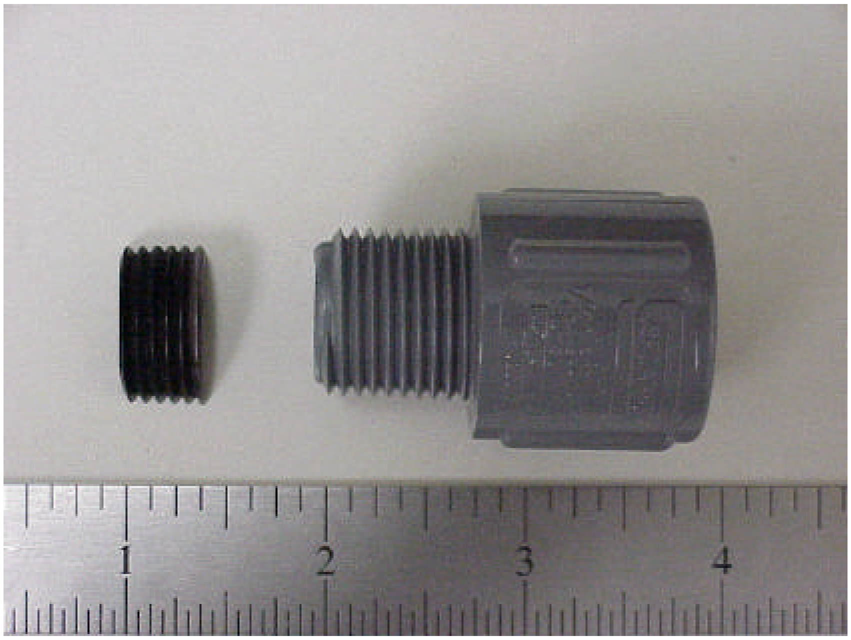


Figure 31. Failed fitting specimen and new, non-degraded fitting

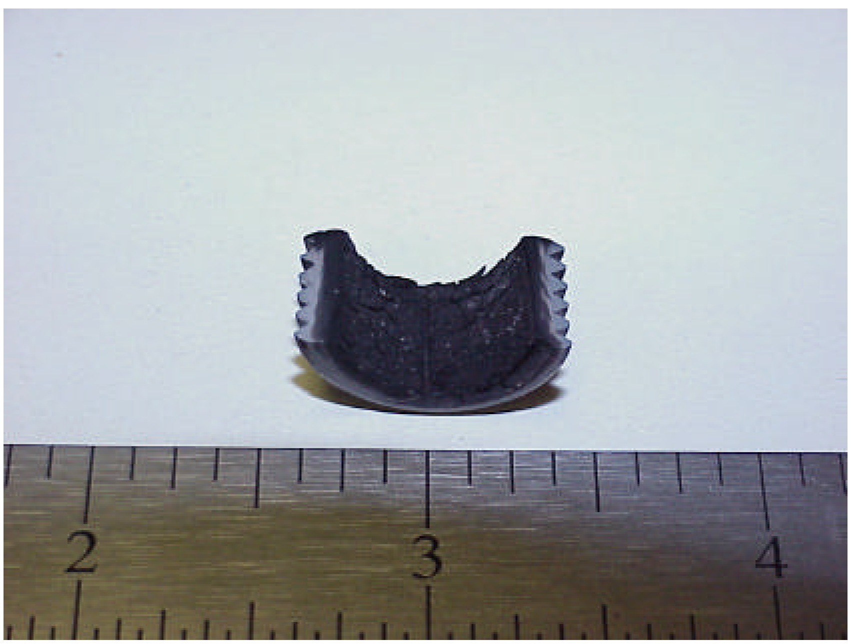
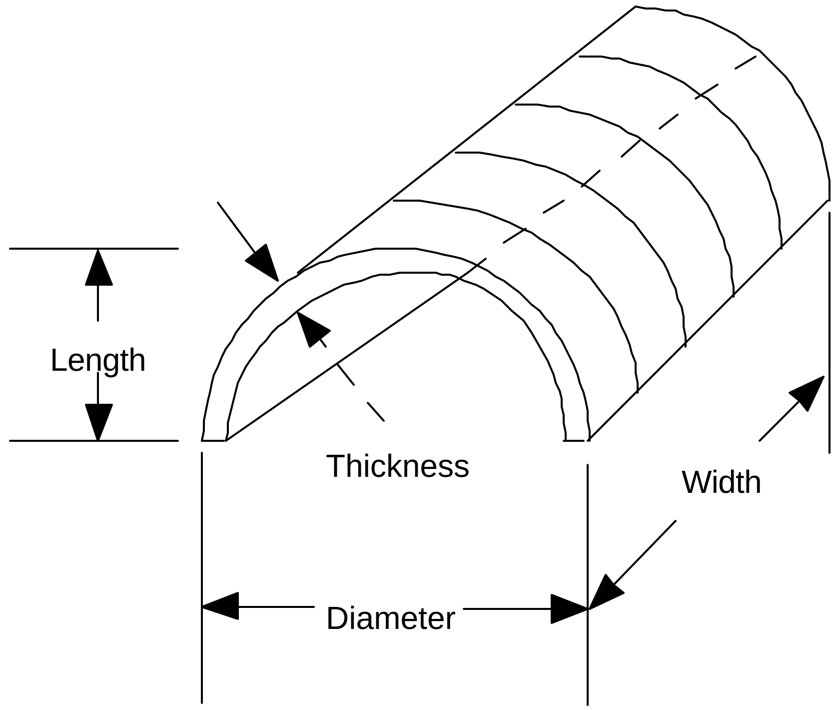


Figure 32. Failed fitting specimen (C-shape), with EZ-Out mark



Sample ID	Diameter (in.)	Length (in.)	Thickness (in.)	Width (in.)
CPVC-1	0.814	0.374	0.155	0.416
CPVC-2	0.814	0.375	0.157	0.416
CPVC-3	0.812	0.373	0.154	0.416
CPVC-4	0.812	0.375	0.151	0.418
CPVC-5	0.812	0.375	0.156	0.417
Hanford-6	0.804	0.375	0.154	0.414
CPVC-7	0.812	0.375	0.155	0.416
CPVC-8	0.812	0.372	0.152	0.416
CPVC-9	0.805	0.374	0.152	0.415
CPVC-10	0.809	0.373	0.152	0.416
CPVC-11	0.810	0.373	0.151	0.417

Figure 33. General shape and nominal dimensions of test samples.

Figure 34. Model 1125 Sintech/MTS Tensile Testing Machine w/test sample

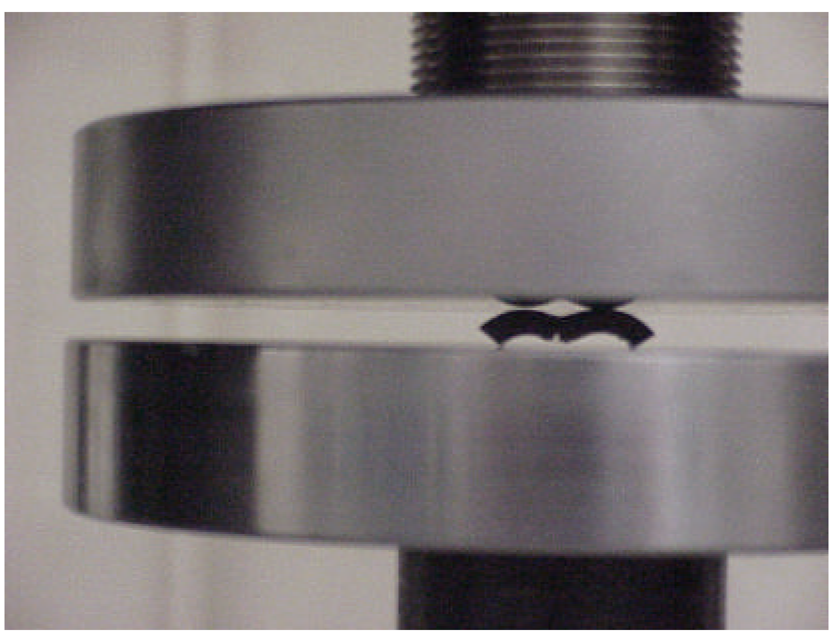


Figure 35. Test sample under compression

Table 1. Mechanical Test Results

Sample ID	Crosshead Speed (in./min.)	Peak Load (lbs.)	Displacement (in.)	Mold-Line Location	Failure Type and Location
CPVC-1	0.04	250.92	0.193	Off Center	Compressed
CPVC-2	0.04	130.25	0.146	Off Center	Fracture off Center
CPVC-3	0.04	280.05	0.197	Off Center	Compressed
CPVC-4	0.04	275.86	0.198	On Center	Compressed
CPVC-5	0.04	280.90	0.198	On Center	Compressed
CPVC-7	0.04	84.40	0.052	Off Center	Fracture in Center
CPVC-8	0.04	318.85	0.198	Off Center	Compressed
Averages		**231.60**	**0.169**		
Hanford-6	0.04	50.17	0.015	Unknown	Fracture in Center
CPVC-9	0.04	109.25	0.105	On Center	Fracture in Center
CPVC-10	0.04	387.97	0.198	On Center	Fracture in Center
CPVC-11	0.04	455.19	0.199	Off Center	Fracture in Center
Averages		**317.47**	**0.167**		

As shown in Table 1, the maximum load sustained by the Hanford fitting sample was approximately 50 lbs., as compared to the average load sustained by all non-degraded samples of 232 lbs. (without slot) and 318 lbs. (with slots). For samples that actually fractured, the average load sustained was approximately 108 lbs. Therefore, the sample from the Hanford fitting exhibits a reduction in flexural strength of approximately 54% using this sample design and method. Higher values for the samples with slots represent those that compressed but did not fracture. Lower values are for samples that fractured. Also, the failed fitting sample broke much earlier in the test as compared to the non-degraded samples, which exhibited much more deformation prior to fracture.

Additional tests would be required to establish a greater statistical basis, or if a different specimen design is required. Tensile strength and/or compression strength may also have been obtained by compression in the longitudinal direction, and can still be performed if desired on remaining material. Compression modulus could have also been obtained via dynamic mechanical analysis (DMA), but variation between complex modulus values and those directly obtained from tensile testing are known to exist.

Bend testing of actual 6” Sch.80 CPVC pipe nipples was also performed to determine the amount of force required to bend a 6” section and break in the threaded region, similar to the failed drain line. A large tensile specimen was used to apply a bending moment to a 6” pipe nipple, with approximately 5-6 threads engaged and 2-3 threads remaining outside the fitting, similar to the drain line fitting (Figure 36).

It is acknowledged that a specimen of pipe solvent-cemented to a fitting would be more representative of the failed drain line assembly, but the dimensions and pitch of the threaded region of the pipe nipple are identical to that of a ½" fitting. As the material is notch-sensitive, the threaded region is the most susceptible to failure. Therefore the need to fabricate a solvent-cemented pipe/fitting specimen was considered unnecessary for test purposes.

Using the maximum displacement rate possible on the 723-A Instron Tensile Machine (15 in./min.) and a 2000 lb. load cell, a maximum force of approximately 90 lbs. (89.5 lbs) was determined to be necessary to break the pipe in the threads. Additional tests at varying rates and under impact conditions would have to be performed to fully evaluate such behavior, but this value gives an indication of the high notch-sensitivity of PVC/CPVC compounds, even in the non-degraded condition.

Figure 36. Bend testing of 6" Sch.80 CPVC pipe nipple (non-degraded)

5.0 DISCUSSION

Review of the literature and discussion with several resin and product suppliers indicates that chlorinated polyvinyl chloride (CPVC) is commonly used for low to moderate concentrations of sulfuric acid at low to moderate temperatures. Low concentrations may generally be handled within the maximum allowable temperature and pressure ratings of the material. CPVC is consistently rated as satisfactory or recommended for 93 wt% sulfuric acid to at least 100°F and often to the rated service temperature of the drain line application (120°F), with the exceptions as previously noted. Therefore, the initial selection of CPVC for this application is considered reasonable.

However, as temperature increases, the resistance of CPVC becomes less satisfactory and ratings become less consistent. Above 140-150°F (depending upon the reference) and certainly at 180°F, CPVC is consistently rated "unsatisfactory" or "not recommended". It appears from the literature that data and recommendations for use at temperatures between 120 and 150°F are the most lacking and inconsistent. Resin manufacturers such as B.F. Goodrich understandably make no claims on the performance of as-fabricated components due to possible variations in processing and lack of direct control over component suppliers and manufacturers. Testing by the end-user is therefore recommended, if only for product liability reasons.

Published data by B.F. Goodrich indicates that 145°F is the maximum "recommended" service temperature for Corzan® CPVC in 93 wt% sulfuric acid. Verbal and written comments by B.F. Goodrich technical representatives to both SRTC/Materials Technology and previous Hanford personnel indicate that the service life would be reduced to 12-24 months if continuously exposed above such temperatures. However, the extent of previous discussion about certain relevant factors to the customer is not known. Such factors include the frequency and degree of pump thermal excursions, the pressurized nature of the application, the degradation observed in the previous drain line, and accessibility of personnel.

From both previous observations and the current failed component, there appears to be a definite difference in chemical resistance between CPVC fitting and piping materials, at least for this service environment. Although additional investigation would be required to conclusively determine the cause(s), several factors are considered to affect such behavior. These factors include, but are not limited to: variation in chemical composition, possible presence of solvent cement (resin-poor), effects of processing parameters, molecular weight, density/porosity, degree of fusion, etc. Since the primary modes of degradation is considered to be general oxidation and possible dehydrochlorination, the effect of internal molding stresses is not considered as significant as in solvent stress-cracking (SSC) or environmental stress-cracking (ESC) degradation modes, but may also be a factor.

The specific cracking pattern and degradation observed in the threaded fitting is attributed in part to thermal expansion of the inner surface relative to the threads during thermal cycles. Although less than some thermoplastics, the thermal expansion coefficient of Corzan® is approximately 5 times that of steel, which could induce localized stresses and strains. These probably initiated microvoid development, surface crazes, and subsequent cracks along the interior surface. As cracks initiated and propagated over time, oxidation of deeper layers penetrated into the threads, eventually reaching the thread root. Crack development and propagation was most likely greatest during the periodic thermal excursions beyond 140°F. Spears technical representatives have stated that threaded fittings can exhibit permanent deformation of the threads when subjected to sufficient thermal expansion and restriction.

Although it is also possible that temperatures at the fitting location (pump casing) were slightly higher than those of the adjacent piping, any difference at all may be negligible due to the low thermal conductivity of CPVC and high heat capacity of sulfuric acid. Variation of the interior surface appearance of the elbow, fitting, and piping may also be attributed in some degree to flow characteristics and/or differences in surface properties such as hardness and porosity.

Fracture of the fitting is believed to have occurred in the thread root as indicated in Section 4.3, towards the top orientation of the piping, which would correspond with the region under the highest tensile stress if force was applied in a downward direction. There is also matching evidence of nearly through-wall oxidation and cracking at the same location. Whether failure occurred primarily as a result of internal pressure, vibration, pressure surges, etc. in absence of external forces cannot be conclusively determined. However, the extent of degradation in the fitting was significant. Crack development due to thermal expansion/contraction cycles could have also contributed to final fracture.

Based on the appearance of the fracture surface, the orientation of the piping assembly post-failure, the general piping configuration, and the presence of the operator in the immediate vicinity of the pump during failure, the probability of an externally applied force is considered relatively high. Also, based on the extent of degradation observed and the mechanical test results, the force required to initiate failure is considered relatively low. Therefore, the fitting is considered degraded to the point where any inadvertent contact could have initiated fracture, particularly if applied at locations with mechanical advantage. Once initiated, the material would have very little resistance in the degraded region to crack propagation.

As with nearly all plastics, CPVC is notch-sensitive, which makes threaded joints much more susceptible to failure. Generic impact resistance data of unplasticized PVC materials in both the notched and unnotched conditions indicates that approximately 90% of the applied force is required to initiate failure, but only 10% is required to propagate the crack [27]. Therefore, if enough force were applied, particularly at a high rate, failure at the fitting location could have also occurred in the absence of any environmental degradation. The mechanical test results also illustrate that the force required to initiate failure in non-degraded material is not significant.

Although not a direct cause, failure of the fitting is also attributed in part to the lack of physical protection and/or continuous support of the drain line. It is common industry practice to take such measures for thermoplastic piping where possible contact with equipment and/or personnel may occur, particularly in confined spaces or high traffic areas. This would be especially recommended for pressurized applications.

6.0 CONCLUSIONS AND RECOMMENDATIONS

The following conclusions and recommendations are based on physical examination and characterization of the failed CPVC drain line assembly, as well as independent review of CPVC chemical resistance and discussions with CPVC resin and product suppliers:

- Published generic B.F. Goodrich data indicates that Corzan® CPVC was suitable for the drain line application up to 145°F. Published disclaimers indicate that the full hydrostatic pressure rating of the pipe may not apply to the "Recommended" range and that determining compatibility is the end-user's responsibility. Previous and recent discussions with B.F. Goodrich technical representatives indicated that service life would be reduced to 12-24 months upon continuous exposure at 150°F, but this is not indicated in the published data. Infrequent, short-term excursions approaching 150°F were not adequately addressed, and possible variation in resistance of injection-molding and extrusion compounds to this service environment was not specifically indicated.

- With a few exceptions, CPVC materials are typically rated as satisfactory or recommended for 93% sulfuric acid at room temperature to 100°F, with some references indicating acceptability at 120°F. Temperatures of 140-150°F are typically considered to be the maximum continuous use temperature range for 93 wt% sulfuric acid, with service life sometimes acknowledged to be limited, particularly for stressed or pressurized applications. Although the Hanford CPVC drain line was infrequently operating at the upper bound of the recommended range, such periods were of limited duration and normal service temperatures never exceeded 150°F.

- Failure of the CPVC fitting is attributed to a combination of environmental degradation and probable impact or bending stresses. Based on the extent of degradation observed, any inadvertent contact with the piping would have likely resulted in failure. Inherent failure in the absence of external forces would have also been expected at some point in service, particularly in metal-to-plastic joints (threads) and/or solvent-cement joints.

- Variation in appearance between the failed fitting and adjoined piping is attributed to several possible causes, including but not limited to: thermal expansion, variation in chemical composition, processing parameters, residual stresses, morphology, degree of fusion, and possible presence of solvent cement on fitting interior. Such variation may be lot or batch-specific or could be inherent between molded and extruded components. Although the effects of such variation are expected to be insignificant in most service environments, they may have been specifically targeted or enhanced by this particular application. Additional investigation would be necessary to determine the individual contribution of such effects and is strongly recommended.

- Structural integrity of the failed fitting was significantly reduced as indicated by mechanical test results. It is acknowledged that such testing was performed using non-standard techniques due to limited material and part geometry. Additional tests and material characterization can be performed if necessary.

- As with many thermoplastics, CPVC is notch-sensitive and exhibits low fracture toughness. Threaded fittings are therefore the most susceptible to failure, in the absence of major defects or poor joining techniques. For this reason and the generally lower strength of thermoplastics compared to metals, additional support and/or shielding is commonly recommended for thermoplastic piping particularly in areas where contact is possible or for pressurized applications.

- Observations from previous CPVC components in the same application seemed to indicate some degree of degradation occurring, particularly in the threaded fitting. Although this component did not fail after approximately 2 years of service, such observed degradation is considered insightful. The cracking pattern and degraded appearance was similar to that observed in the failed fitting, but was less extensive and the exact service conditions to which the previous assembly was exposed are not known.

- Generic chemical resistance ratings are typically based on short-term immersion tests and nominal mechanical properties of laboratory-prepared samples. Although useful for general comparison, such ratings are not adequate to evaluate the long-term performance of as-fabricated components under actual service conditions. Testing by the end-user is recommended if only for product liability reasons, but should be performed particularly if degradation has been previously observed or if material performance is questionable under the expected service conditions.

- Excess solvent-cement on thermoplastic surfaces should be avoided and/or removed during application, particularly if components will subjected to potentially aggressive chemical exposures. Solvent-joints may be resin poor and more susceptible to chemical attack.

7.0 QUALITY ASSURANCE

Activities performed under this contract were performed under the guidance of Westinghouse Savannah River Company Quality Assurance Manual and implementing quality assurance documents. Although configuration-controlled (specified on design drawings), this application is considered to be non-baseline per the customer. In accordance with the Westinghouse Savannah River Company QA Manual and subsequent adaptations at the operating division level, this task was therefore considered to be non-baseline. Tests were performed in accordance with the applicable ASTM standards as identified, or as modified to accommodate sample/material-specific variations when required. M&TE (materials and test equipment) calibration records, qualification records, etc. are maintained in accordance with site/company policies.

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