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SPECIAL ISSUE: SUPPORTING THE SAFE INTERIM STORAGE OF HIGH-LEVEL NUCLEAR WASTE THROUGH SCIENCE AND ENGINEERING

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JNMM Journal of Nuclear Materials Management

Topical Papers

SPECIAL ISSUE: SUPPORTING THE SAFE INTERIM STORAGE OF HIGH-LEVEL NUCLEAR WASTE THROUGH SCIENCE AND ENGINEERING

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Joint Letter to OMB

By Ken Sorenson
INMM President

Greetings! As I write this, we are fast approaching the INMM 54th Annual Meeting, July 14-18, 2013 at the JW Marriott Desert Springs in Palm Desert, California, USA. In previous articles, I have written about the serious issue we are facing in the United States regarding government-sponsored travel to conferences. The INMM is directly affected by this new policy and attendees to the annual meeting will see a reduction in U.S. government-sponsored registrants. This is an issue that affects all technical societies in the United States and is one that will need to be managed over the next several years. We are working with other technical societies to get our message to government leaders that this policy is having serious negative impacts on our ability to engage in effective collaborations with fellow professionals. In this regard, a letter that Larry Satkowiak and I wrote jointly with the American Nuclear Society (ANS) president is reprinted here. This letter went to high-level government officials, members of Congress as well as their staffers who may have influence in moderating this policy. Here is the letter.

> The Honorable Sylvia Burwell
> *Director*
> *Office of Management and Budget*
> *Washington, DC 20503*
>
> Dear Ms. Burwell,
>
> As leaders of the two primary professional societies involved in the utilization of nuclear technology, we are writing to express our deep concern about the unintended impacts of OMB's recent travel restrictions. The current policy severely limits the federal government's participation in technical meetings and conferences related to nuclear reactor and fuel cycle technology, as well as nuclear nonproliferation and security. Simply put, these restrictions will not only sap the vitality of our respective organizations through reduced technical meeting attendance; they will ultimately harm U.S. nuclear energy and nonproliferation efforts by stifling scientific and technical exchange.

The American Nuclear Society (ANS) and the Institute of Nuclear Materials Management (INMM) are dedicated to establishing best practices and advancements in safety through technology development in all areas associated with the production of commercial nuclear power, as well as areas associated with physical security, safeguards, arms control, and nonproliferation aspects of materials and technologies directed toward nuclear material production, security, transportation and disposition.

The principal way that nonprofit technical societies such as ANS and INMM conduct their missions is through conferences, workshops, and seminars that bring together the technical and policy communities to discuss a wide range of inter-connected issues that impact the nation's policies in the nuclear field. Since the U.S. government traditionally has been the central stakeholder in nuclear technology development, the nuclear scientific and technical community – including those in, national laboratories, academia, industry and NGOs – requires rich and sustained interaction with their government counterparts in order to effectively sustain relevant and effective research and development efforts.

The OMB guidance has had a particularly harsh impact in the nuclear arena, because a significant percentage of people in the nuclear technical community have a federal affiliation, either as an agency employee, national laboratory personnel, or a university faculty member funded through government contracts. This guidance has resulted in deep cuts in overall attendance at our organizations' meetings.

Worse, other organizations have begun to recognize the decline in U.S. government participation and have limited the attendance of their employees. More importantly, these compounding impacts have begun to tangibly chill the scientific exchange so important to sustaining strong and adaptive nuclear programs and policies in nuclear reactor safety, nonproliferation, safeguards and security, stockpile stewardship, and waste disposal.

ANS meetings provide attendees with in-depth coverage of technical topics which incorporate the latest research findings across the spectrum of nuclear science and technology. In addition, ANS meeting attendees are from a variety of settings, including educational institutions, utility corporations, research laboratories, and domestic and international companies involved in all aspects of nuclear technology.

From the INMM perspective, one specific example on the importance of workshops to administration policy comes from the 2012 Seoul Nuclear Security Summit. An outcome of the summit was a listing of country commitments. The U.S. committed to; "…, intending to host a workshop on nuclear security as the chair of the Global Partnership;…"1 The deliverable for this commitment will be an INMM sponsored workshop entitled, "Risk Informed Security Workshop" that will held October 15-16, 2013 in Stone

Mountain, Georgia. Additionally at the summit, the U.S. committed to; "…intending to support WINS activities."[1] INMM was instrumental in helping to set up WINS when it was first launched in September

2008. Two senior members of INMM currently sit on the board of WINS.

We recognize that in these fiscally constrained times, the federal government is under unprecedented pressure to minimize all non-essential spending. However, OMB should reassess their current policies, and look to create some form of exception for serious scientific and technical meetings directly related to key federal programmatic mission areas. To do otherwise will cause significant harm to our human nuclear infrastructure, and put our nuclear safety and security missions at risk.

On behalf of ANS and the INMM, we thank you for your attention to this matter.

Sincerely,

Michael Corradini
President of the American
Nuclear Society

Ken B. Sorenson
President of the Institute of Nuclear Materials Management

2012 Seoul Nuclear Security Summit, "The Seoul Nuclear Security Summit Preparatory Secretariat, Highlights of Achievements and Commitments by Participating States as stated in National Progress Reports and National Statements"; http://www.thenuclearsecuritysummit.org/userfiles/Highlights%20of%20the%20Seoul%20Nuclear%20Security%20Summit(120403).pdf

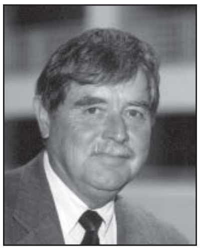
In addition, Mark Schanfein (a member of the Executive Committee) has also taken the lead to send out a letter to numerous similar technical societies to encourage them to actively engage in trying to modify this government policy. Finally, we are making plans with the ANS to visit congressional staffers this summer to continue our efforts to moderate this policy. We will continue to work and manage this issue to the best of our ability and will plan to keep the membership informed as we go down this path.

Despite this policy, we fully expect to have a vibrant and successful 54th Annual Meeting. I look forward to seeing you in Palm Desert!

ESARDA Symposium 2013: 35th Annual Meeting

I had the pleasure of attending and presenting a plenary talk at the ESARDA 35th Annual Meeting in Bruges, Belgium, in May. Several INMM officers and members were in attendance at the meeting. The INMM/ESARDA relationship continues to improve and strengthen to the benefit of both organizations. We signed a Letter of Intent with ESARDA in December 2011 as a way to deliberately leverage our respective missions in collaboratively. We have had a strong collaboration with the International Safeguards Division as well as having two ESARDA members as *JNMM* associate technical editors. This spring, the INMM Executive Committee approved the appointment of Willem Janssens as chair of the Chapter Relations Committee. INMM is seeing strong international growth and interest. Willem, an ESARDA member, will provide a different perspective for this position. At the ESARDA meeting, we met with Klaas van de Meer, Jim Tushingham, and Filippo Sevini (the president, vice president, and secretary–respectively–of ESARDA) to discuss actions to take for further collaborations. Specifically, we look to collaborate on an Export Control Working Group. In addition, we will work together on treaty verification/monitoring, spent nuclear fuel verification, open source/geo-spatial technologies, the state-level approach, and training and education.

Interim Safe Storage Through Science and Technology



By Dennis Mangan
INMM Technical Letter

The president's message by Ken Sorenson is very interesting. He addresses the ongoing issue we have regarding U.S. government-sponsored travel to conferences, and shares a joint INMM-American Nuclear Society letter that has been sent to the Director of the Office of Management with copies to pertinent U.S. Department of Energy personnel. He also shares with us the growing relationship between INMM and the European Safeguards Research and Development Association (ESARDA). I believe you will find Ken's message enjoyable and informative.

As noted on this issue's cover, this issue is a special issue focusing on Supporting the Safe Interim Storage of High-level Nuclear Wastes Through Science and Engineering**.** As you read the various articles you will glean the fact that the effort in the United States to safely store high-level waste on an interim basis is a large, joint effort between engineers and scientists at several U.S. national laboratories as well as industrial and academic organizations. As you read, you will be taken on some historical missions (many of you who will remember with fondness and some of you who will be exposed for the first time) to all of the work that has gone on over the years addressing this problem. You will be exposed to the storage safety concerns, the technology measurements, and various approaches that have been or are being pursued. You will also be exposed to concerns of not only using of storage tanks made of austenitic stainless steel and other alloys, but also about the polymers that are used in the likes of seals, pump/valves components, hoses, piping/tubing, electrical or thermal insulation, etc. Lastly, in the special issue articles, there is an interesting one that addresses the value of using independent technical experts to enhance the management of high-level nuclear waste.

Bruce Wiersma from Savanna River National Laboratory was responsible for assembling these interesting articles and we offer to him our gratitude. I trust you will enjoy reading these special issue articles as much as I did.

In addition to the special issue papers, we offer two outstanding articles. First, Jack Jekowski, Industry News editor and chair of the INMM Strategic Planning Committee, gives us food for thought about where we (the United States and other countries) are going in nuclear material management. Although Jekowski has urged the INMM to become more engaged in additional discussions about what we should be doing, I can't help but suggest that the Institute would benefit from having a dedicated session an INMM Annual Meetings where Jekowski could present his thoughts and recommendations. My thoughts on how we can establish such dialogue, which I believe would be invaluable to the entire Institute, would be for Jekowski to be a plenary speaker in a special session with open discussion on his thoughts.

Secondly, in every issue of *JNMM* I thoroughly enjoy the Book Reviews by Mark Maiello, assistant book editor. In this issue he addresses *Over the Horizon Proliferation Threats* by J. W. Wirtz and Peter R. Lavoy (Stanford University Press, Stanford, CA, USA). Maiello's obviously exciting review has inspired me to get a copy of the book.

Should you have questions or comments, feel free to contact me.

JNMM *Technical Editor Dennis L. Mangan may be reached at dennismangan@comcast.net.*

Topical Papers Special Issue: Supporting the Safe Interim Storage of High-level Nuclear Waste Through Science and Engineering

Foreword

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High-level nuclear waste byproducts incident to nuclear weapon materials production are managed within the U.S. Department of Energy (DOE) Complex. A significant portion of this high-level waste (HLW) is stored as liquid-sludge mixtures in large, underground carbon steel tanks located at the Savannah River Site in South Carolina and at the Hanford site in Washington. Lesser quantities of waste are managed at the Idaho National Laboratory and at the West Valley Demonstration Project in New York. The DOE has used the West Valley Demonstration Project to process high-level wastes resulting from spent commercial and defense fuel reprocessing into glass. Similar conversion of the liquid wastes to glass has occurred at Savannah River and will occur at Hanford in the near future. The liquid wastes produced at Idaho have been calcined to create a granular solid product. The glass and calcined wastes are now stored in stainless steel containers and disposition of these waste products is the final step in the closure of the nuclear fuel cycle. This special issue of the *Journal of Nuclear Materials Management* summarizes some of the engineering and science activities related to the management of high-level nuclear wastes within the DOE Complex.

The waste tanks at Savannah River and Hanford are expected to be in service well beyond their intended design life, thus it is critical that tank structural integrity be ensured during waste storage and processing operations. The DOE requirements for a structural integrity program are given in BNL-UC-406, *Guidelines for Development of Structural Integrity Programs for DOE High-level Waste Storage Tanks*, and include:

1. Identification of potential age-related degradation mechanisms
2. Quantification of the nature, location, and extent of degradation
3. Evaluation of the impact of degradation on tank integrity
4. Verification of leak tightness
5. Verification of structural adequacy

The science and engineering technologies supporting the management of high-level nuclear wastes are devoted to ensuring that the DOE requirements are met and that the waste is processed in a safe, effective, and environmentally friendly manner. Additionally, decades of waste management activities have developed a knowledge base and data set that are applicable to other science/engineering endeavors.

The *Journal of Nuclear Materials Management* in 2010 and 2011 published two special issues that focused on the storage of plutonium bearing materials. This special issue is a logical extension of those two issues because the high-level wastes that are discussed in this issue primarily resulted from the production of plutonium and other nuclear weapons grade materials.

The peer-reviewed manuscripts contained in this special issue of *JNMM* illustrate the broad scope of science and engineering required to support the interim storage of high-level nuclear wastes. The control of waste chemistry is required throughout the waste processing operations to assure that:

1. The waste being processed provides a product that is suitable for glass production
2. Corrosion-induced degradation of waste tanks and waste processing equipment does not occur

Carbon steels, stainless steels, polymers, and other materials are used to handle and contain the wastes. Corrosion testing/release technologies have been developed to enhance materials selection/qualification processes. Expert panels have added value to the engineering and science programs through review and approval of planned activities. Engineers and scientists at Savannah River, Hanford, Idaho, and West Valley, as well as other industrial, academic, and national laboratories, have developed cooperative programs and as a routine matter, shared ideas and data across the DOE Complex.

We are pleased to have played a role in the many of the activities summarized in this special issue and appreciate the willingness of *JNMM* to review and publish this collection of papers. The manuscripts included in this special issue represent only a small fraction of the ongoing work required to mitigate or minimize risks and ensure efficient and environmentally friendly management of high-level nuclear waste. We are hopeful that, opportunities to present additional manuscripts will present themselves in the ever-evolving nuclear waste management arena.

Closing the Fuel Cycle Through Vitrification — The West Valley Demonstration Project

Dan Meess
CH2M HILL B&W West Valley, LLC (CHBWV)

Abstract

The West Valley Demonstration Project (WVDP) demonstrated closure of the commercial nuclear fuel cycle in the United States. However, these closure processes are not being used in the United States even though they are currently taking place in France, United Kingdom, Russia, Japan, and India. Instead of reprocessing spent nuclear fuel, spent fuel assemblies in the U.S. are being stored underwater in pools and in highly shielded dry storage casks, awaiting shipment to a federal repository.

The WVDP is located on the Western New York Nuclear Service Center approximately thirty miles south of Buffalo, New York, and was the only functional U.S. commercial spent fuel reprocessing facility. Approximately 640 metric tons of commercial and defense fuels were reprocessed using the PUREX and THOREX processes. More than 97 percent of the uranium and plutonium in the spent fuel was recovered and returned to government and commercial facilities to recycle these materials into new fuel. The reprocessing facilities operated from 1966 to 1972. High-level wastes (HLW) resulting from the reprocessing operations were left in storage at the site following discontinuing plant operations.

In 1980, the West Valley Demonstration Project Act was signed, directing the U.S. Department of Energy (DOE) to clean up the site and remove most of the hazardous wastes left behind. Under the WVDP Act, the remaining spent fuel assemblies were shipped offsite, certain plant cells were cleared of highly radioactive equipment to reuse these areas for HLW processing, and the HLW liquids and sludge were pretreated to remove the bulk of the chemicals that were not compatible with the conversion of HLW to borosilicate glass. The pretreated HLW was vitrified into a stable borosilicate glass form that was packaged in stainless steel canisters. Additionally, the majority of the former reprocessing plant's equipment was decommissioned, dismantled, packaged, and shipped for disposal. The vitrification facility where the HLW was converted into a stable glass was then dismantled with its equipment decommissioned, packaged, and shipped for disposal except for certain major equipment that will be shipped over the next few years. Demolition of a number of site facilities has already taken place with more to follow in the next six years, including taking the main plant processing building and the vitrification facility down to ground level. To accomplish this, the HLW canisters need to be relocated from storage in the former reprocessing facility to a modular above-ground storage facility. The canisters will be stored in a shipment-ready configuration awaiting access to the federal repository for HLW and spent nuclear fuel. Phase I decommissioning of the former reprocessing facility and support facilities constructed under the WVDP is planned to be complete by 2018, with the remaining facilities to be decommissioned, demolished, and dispositioned in the follow-on Phase II effort. Completion of these Phase I and II activities will mark the complete closure of the fuel cycle at the West Valley site.

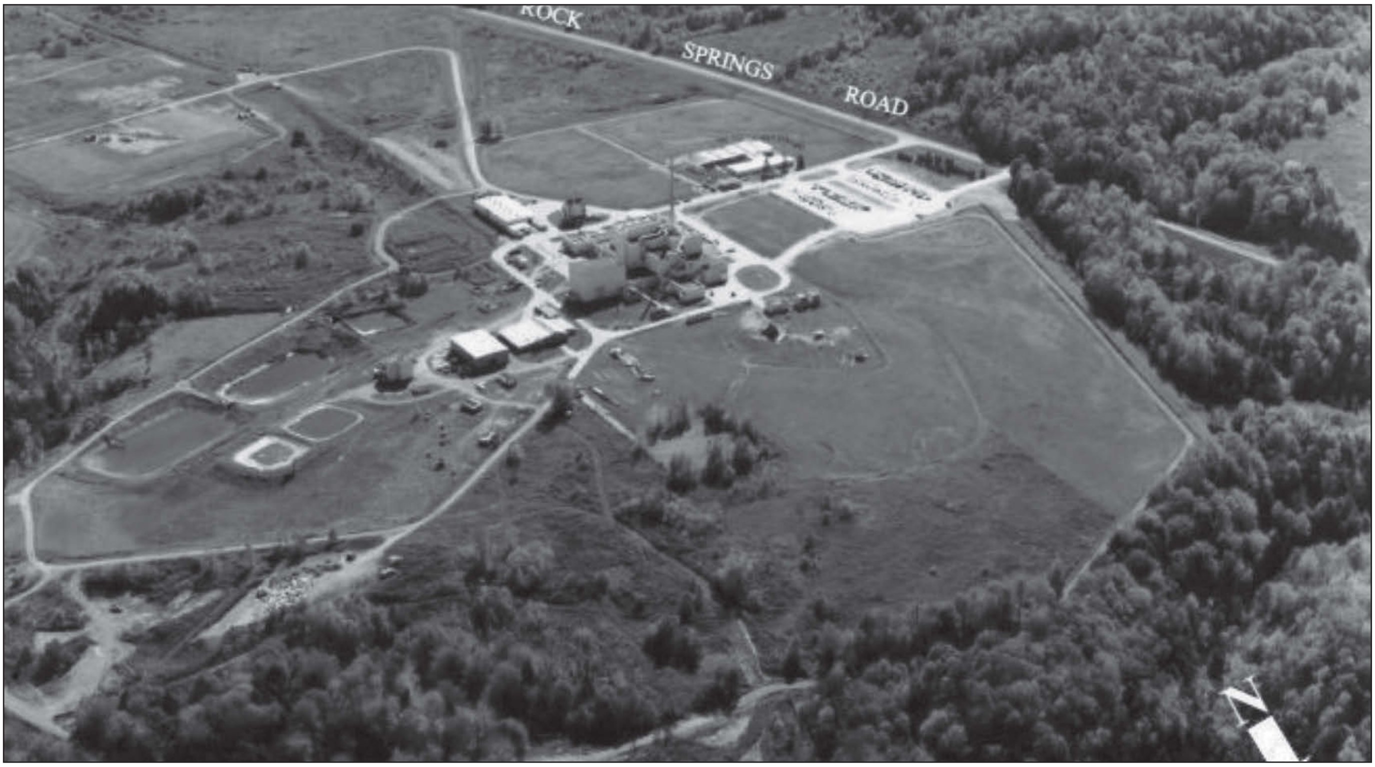
Introduction and Background

The West Valley Demonstration Project (WVDP) is located on the Western New York Nuclear Service Center approximately thirty miles south of Buffalo, New York, and was the site of the only functional U.S. commercial spent fuel reprocessing facility. Nuclear Fuel Services (NFS) operated the reprocessing facility from 1966 to 1972. Approximately 640 metric tons[1] of commercial and defense fuels were reprocessed at the site using the PUREX and THOREX processes. Highly concentrated uranium and plutonium solutions were extracted from the spent fuel using complex chemical reactions. Approximately 98.8 percent of the uranium and 97.5 percent of the plutonium in the spent fuel were recovered in the process.[1] These materials were shipped to government and commercial facilities for commercial and research fuel fabrication. Reprocessing was discontinued due to Atomic Energy Commission (AEC) enactment of more stringent design requirements for reprocessing facilities. These new requirements took place while the West Valley plant was shut down for unrelated upgrades. Due to the large cost to implement new design requirements and construction of a much larger reprocessing facility in Barnwell, South Carolina, NFS decided to terminate reprocessing operations at the West Valley plant and the facility was turned over to New York State (NYS), the owner of the Western New York Nuclear Service Center.

NYS lobbied extensively for the federal government to clean up the site since slightly more than half of the processed fuel originated from federal nuclear facilities and limited NYS funding was available for a cleanup. In 1980, the West Valley Demonstration Project Act[2] (Public Law 96386) was signed by President Carter, directing the U.S. Department of Energy (DOE) to:

a) solidify the high-level wastes (HLW) remaining from reprocessing operations,

Figure 1. WVDP at the start of the project



b) develop containers for the permanent disposal of the solidified HLW,
c) transport the HLW to a federal repository,
d) dispose of lowlevel and transuranic (TRU) wastes resulting from HLW solidification, and
e) decontaminate and decommission the HLW storage tanks, solidification facilities, and any materials/hardware used during the project.

After receiving its mandate to conduct the WVDP, the DOE prepared an Environmental Impact Statement (DOE/EIS0081)[3] to assess the impacts of the proposed high-level waste solidification as required by the National Environmental Policy Act of 1974 (NEPA). Subsequently, a Record of Decision (ROD) was published in 1982 that made it possible for the DOE to process the HLW into a final waste form by vitrification.

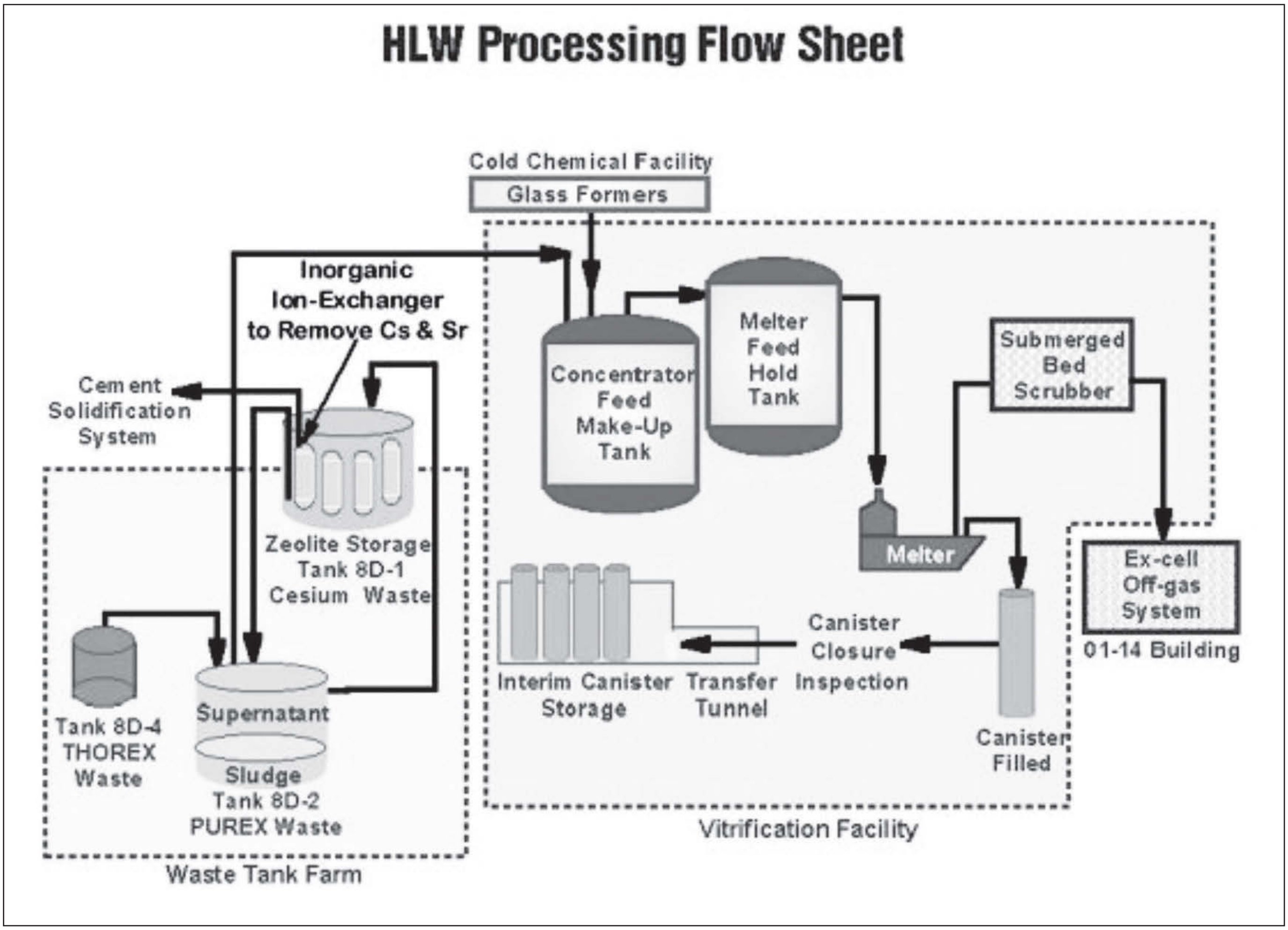
A private company, West Valley Nuclear Services Company (WVNSCO), was awarded the operations contract and started work in February 1982. Although the DOE is responsible for this cleanup project on approximately 167 acres of the 3,338 acre site, New York State owns the property, funds a percentage of project costs and manages the remainder of the Western New York Nuclear Service Center, including a fifteen-acre near-surface low-level waste disposal area (State-licensed Disposal Area), licensed by New York State and operated by NFS, that accepted wastes from commercial generators around the country[4] from 1963 to 1975.

At the start of the demonstration project, facilities included the large, heavily shielded Main Plant Processing Building (MPPB); the 0114 Building that was constructed for off-gas abatement of I129; a 5.5-acre[4] near-surface low-level waste disposal area (U.S. Nuclear Regulatory Commission-licensed disposal area) used to bury plant wastes; an underground tank farm where the high-level waste liquid and precipitated solids remaining from fuel reprocessing were stored; liquid waste treatment and discharge system; maintenance shop; storage buildings; and various utilities to produce various grades of water, treat and discharge sanitary waste, generate steam, produce compressed air and cooling water, and provide emergency power generation for critical site systems. Figure 1 illustrates site facilities at the start of the project.

West Valley Demonstration Project Activities

The critical initial project activity focused on developing an economical and acceptable process to vitrify the approximately 600,000 gallons of neutralized PUREX waste and 8,200 gallons of acidic THOREX waste, commingled with the recovered thorium.[5] The PUREX HLW remained in a 760,000 gallon, underground, carbon steel tank designated Tank 8D-2. This waste consisted of insoluble hydroxides and other salts that precipitated out of the highly concentrated waste solution to form a bottom sludge layer, and a liquid (supernatant) upper layer rich in sodium nitrate and sodium nitrite. The THOREX waste was contained in a 14,300-gallon, under-

Figure 2. HLW processing overview



ground, stainless steel storage tank designated Tank 8D4. Together these tanks contained approximately 30 million curies (1986 basis) of fission products[5] left over from uranium and plutonium recovery operations. Other key activities included the decontamination and decommissioning of highly contaminated areas and cells, notably the Equipment Decontamination Room (EDR), Chemical Process Cell (CPC), Extraction Cell 3 (XC3), and the Plutonium Purification Cell (PPC), within the MPPB to house the various processes that would be required to support HLW vitrification, characterization of the HLW stored in the two underground tanks and operation of the plant's infrastructure.

Vitrification Process Development

Scientists, engineers, operators, maintenance workers, and administrative staff were assembled to develop the vitrification process. Initial process development began with sampling and analysis of the HLW to determine the radiochemical and chemical composition, as well as the physical properties of the waste to be processed. Based on analyses of the first HLW samples taken, a decision was made to separate the 8 million curies of Cs-137[5] fission products from the HLW liquid to avoid vitrifying all the salts contained in the liquid. The Cs-137 activity would then be combined with the PUREX sludge, which contained essentially all the remaining fission products and the long-lived alpha-transuranic isotopes. The resulting HLW mixture would then be vitrified into a glass waste form. The proposed approach to chemically separate (pretreat) the HLW also involved developing processes to stabilize the RCRA constituents and solidify the resulting decontaminated liquid into an approved low-level waste (LLW) form suitable for land disposal under the U.S. Nuclear Regulatory Commission's (NRC) 10CFR61. By taking this approach, it was possible to significantly reduce the amount of HLW glass that needed to be produced while also ensuring the integrity of the final glass product. Once this processing decision was made, efforts began to select the best methods to achieve Cs-137 decontamination of the HLW liquid, process the LLW form, and produce a final HLW glass form. The WVDP staff collaborated with experts at the Savannah River Site as well as the staffs of other national laboratories.

As methods for accomplishing liquid decontamination were being developed, parallel efforts were made to select a final HLW glass form and advance vitrification process development. Melter design began shortly after borosilicate glass was selected as the final HLW glass form. In early 1983, a design for a slurry-fed ceramic-lined melter had been approved and was ready for fabrication. By the end of 1984 a unit was built to approved design specifications and was ready for use in the Functional and Checkout Testing of Systems (FACTS) program. A full-scale testing program was developed to check out vitrification system processing operations and to demonstrate the WVDP waste glass qualification approach.[6] The final HLW pretreatment method separated the majority of the radioactive species (Cs-137 and much lower amounts of Sr-90) from the waste liquid, combined these fission products with the PUREX sludge, and processed the HLW mixture into the approved glass waste form. After removing Cs-137 and Sr-90 from the waste liquid, the resulting mixed RCRA-hazardous and low-level waste (LLW) liquid was treated and processed into a solid waste form, meeting RCRA treatment standards and NRC stability criteria for Class C LLW. The basic overall method and systems used to process liquid HLW into approved HLW and LLW forms are illustrated in Figure 2.

Functional and Checkout Testing of Systems Vitrification Program[6]

Full-scale testing of the vitrification system was accomplished through the Functional and Checkout Testing of Systems (FACTS) Program. Conducted from 1984 until 1989, this program provided the opportunity to evaluate process system, subsystem, and component performance, confirm the HLW glass qualification approach, and use the Vitrification System to produce high-quality glass on a production schedule. Systems and subsystems tested as part of the FACTS program included the melter, canister turntable, off-gas system, (excluding components used for oxides of nitrogen [NOx] abatement) and the slurry feed preparation system. Thirty-seven different system tests were performed and approximately 150,000 kilograms of glass were produced during the FACTS program using non-radioactive isotopes in lieu of radioactive species. These operations produced a waste glass that was as close as practical to the projected HLW glass form. Following the final FACTS run, the vitrification system, including the melter, was disassembled for examination of test components and potential conversion for radioactive service. A number of components that performed well during FACTS were reassembled for reuse, including the tanks used to prepare and feed slurry: concentrator feed makeup tank (CFMT) and melter feed hold tank (MFHT), as well as portions of the facility used to prepare the glass former recipe to be blended with the HLW slurry. After the FACTS program and the remote facility construction were completed, a phased program of remote-handling demonstrations, integrated testing, and operations was carried out. Remote-handling demonstrations involved performing each activity to be carried out during vitrification system operations using remote techniques as far as was practicable to further develop operating proficiency. Jumpers and high-maintenance items in particular were tested to verify successful remote replacement. Performance testing progressed from component and subsystem demonstration using water to the testing of non-radioactive slurry to fully integrated system test runs known as integrated operations (IO). The IO runs culminated with an operational readiness review and approval to begin radioactive operation in June 1996.

HLW Pretreatment[7,8]

During HLW pretreatment, the liquid portions of the alkaline PUREX waste and neutralized THOREX waste were processed to separate the highly radioactive constituents from the soluble salts. This separation allowed the RCRA-hazardous salt solution to be processed into a cement-stabilized waste form meeting the NRC's stability requirements for low-level radioactive waste as specified in 10 CFR 61 and the EPA's treatment standard for land disposal. The pretreatment system consisted of four subsystems, collectively known as the Integrated Radwaste Treatment System (IRTS). These subsystems were the supernatant treatment system, liquid waste treatment system, cement solidification system and the drum cell. In the supernatant treatment system (STS), the highly radioactive Cs-137 in the HLW was adsorbed onto UOP IE-96 zeolite contained in up to four separate columns. The STS had nearly all of its process vessels inside a spare HLW tank. Spent zeolite from these columns was discharged in batches or campaigns after the zeolite could no longer remove Cs-137 from the liquid. Mobilization pumps in tank risers distributed the discharged zeolite within the tank and kept the zeolite under the tank liquid. The liquid was treated with sodium hydroxide and sodium nitrite to suppress corrosion of the carbon steel tank.

The Cs-137 decontaminated effluent solution was concentrated in the liquid waste treatment system (LWTS) using a steam fired evaporator. The decontaminated concentrate was then processed with the cement solidification system (CSS) into a cement waste form that met NRC stabilization criteria for LLW disposal and U.S. Environmental Protection Agency (EPA) treatment standards for RCRA-hazardous waste. Approximately 20,000 square 71-gallon drums of cement-stabilized low-level waste were produced in this process. Four different cement recipes that underwent NRC review were employed. The filled drums were remotely transported from the CSS and placed in the drum cell for storage and potential future in-place disposal. As discussed later in this paper, all of these drums were subsequently shipped and disposed of at the Nevada National Security Site (NNSS). Table 1 provides summary data for HLW pretreatment processing.

Pretreatment of 618,000 gallons of supernatant took place in twenty-one campaigns (campaign defined as fully loading of the lead zeolite column with Cs-137). These campaigns produced 10,393 drums (71-gal) of solidified liquid LLW and 99,400 lbs of zeolite containing 5.30 megacuries of Cs-137.

Table 1. WVDP HLW pretreatment statistics

Pretreatment Process	Waste Volume Processed (Gallons)	Cs-137 Radioactivity* (MCi)	Zeolite Used (pounds)	LLW Cement Waste Drums
Supernatant	618,000	5.30	99,400	10,393
PUREX Sludge Wash #1	410,000	0.909	25,800	7,219
PUREX Sludge Wash #2	356,000	0.125	3,600	814
PUREX/THOREX Sludge Wash #3	316,000	0.304	10,800	1,451
TOTAL	1,700,000	6.638	139,600	19,877

*Radioactivity measured at time of processing

Two PUREX sludge washes and eight-and-a-half additional campaigns of STS operation were performed to further extract soluble salts from the HLW and reduce the volume of HLW glass that would be produced. The sludge washing was accomplished by adding alkaline-adjusted demineralized water to the PUREX waste and agitation of the sludge using five mobilization pumps installed in new tank risers. The alkalinity was increased to further precipitate the soluble uranium, plutonium, and strontium from the sludge wash solution. Following washing operations and subsequent sludge settlement, each of the two sludge wash solutions was processed through STS and the other downstream IRTS subsystems as was done with the PUREX supernatant. A newly developed zeolite (UOP TIE-96) was used for decontamination of the sludge washing liquids to remove plutonium, as well as Cs-137 and Sr-90, and limit the amount of plutonium in downstream IRTS systems and in the 71-gallon cement waste drums. This sludge wash pretreatment of 766,000 gallons of solution resulted in 8,033 drums of solid LLW and 29,400 lbs of IE96 and TIE96 zeolite containing 1.03M curies of Cs-137.

In January 1995, the THOREX waste was then added to and neutralized within the primary HLW tank, together with water flushes of the THOREX storage tank. Mobilization pumps were again used to agitate the PUREX sludge and the precipitate formed from the THOREX addition. This final sludge wash was processed through the pretreatment system in one-and-a-half campaigns to remove soluble salts deleterious to the vitrification product and minimize the volume of the vitrified waste. A total of 316,000 gallons of this third sludge wash were processed into 1,451 drums of solid LLW and 10,800 lbs. of IE-96 and TIE-96 zeolite containing 304,000 curies of Cs-137.

Pretreatment of the HLW was successful in removing soluble sodium and sulfate salt constituents reducing the amount of vitrified waste by approximately 90 percent.[9] The zeolite removed more than 99 percent of the major radioactive species in the waste liquid (Cs-137 and Sr-90) and over 99.99 percent of the Cs-137 from the liquids processed. This removal resulted in an average contact dose on the LLW drums of 23 mR/hr, well below the 1,000 mR/hr design limit. In total, more than 1.7 million gallons of liquids were processed through the STS to decontaminate the process liquids. References 7 and 8 provide additional detail on the pretreatment of the WVDP HLW in the Integrated Radwaste Treatment System.

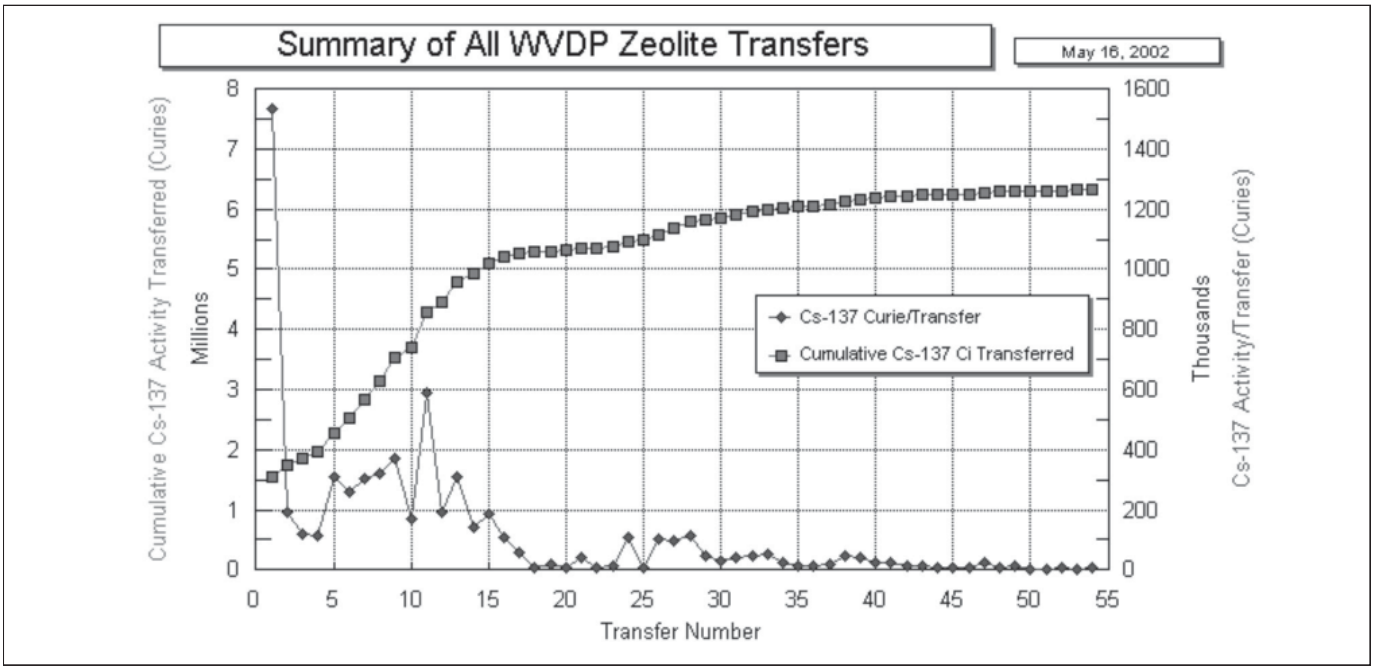
Zeolite Mobilization and Retrieval

Following HLW pretreatment, the Cs-137 laden zeolite stored in the spare HLW tank was transferred back into the primary HLW tank and mixed with the washed sludge to provide the feed material for vitrification. Zeolite was mobilized in the spare HLW tank using five 150-horse-power mobilization pumps, identical to those used for sludge washing. These pumps and a transfer pump were all installed in new tank risers. The zeolite was size-reduced to less than 50 microns utilizing an in-line grinder so that the zeolite particles would form a more homogenous mix with similar-sized sludge particles. The size reduction also made the zeolite easier to retrieve from the HLW tank and simplified operations during vitrification processing. Retrieval of the zeolite proved to be more difficult than previous 1/6-scale model testing had indicated.

As shown in the zeolite retrieval graph (Figure 3), more than 1.5 million curies of Cs-137 representing approximately 22 percent of the stored zeolite were removed from the storage tank during the first transfer. After the zeolite solids settled to the bottom of the primary HLW tank with the washed sludge, the clarified liquid was decanted back to the zeolite storage tank to aid in further zeolite removal. As indicated in Figure 3, subsequent mobilization and retrieval of the zeolite slurry became much more difficult. This was attributed primarily to the retrieval of the smaller, more easily mobilized zeolite particles during the initial transfer, leaving the larger zeolite particles behind. Other factors that limited more effective retrieval included zeolite storage tank dilution with 545,000 gallons of demineralized water due to leaky zeolite mobilization pump seals, the complex internal tank bottom structure that limited solids mobilization, and solids plugging both mobilization and zeolite removal pump suctions. Due to the difficulty in zeolite retrieval, vitrification of the sludge/zeolite was initiated after approximately 85 percent of the stored zeolite was combined with the HLW sludge.

Additional zeolite was retrieved and mixed with the HLW sludge and zeolite vitrification feed in parallel with ongoing HLW retrieval and glass production. The continued use of the pretreat-

Figure 3. Zeolite retrieval results



ment system to process excess liquid resulting from both zeolite and sludge mobilization pump seal leakage produced more Cs-137 laden zeolite that needed to be retrieved from the spare HLW storage tank. As Figure 3 illustrates, retrieval of spent zeolite from the storage tank had reached very diminishing returns toward the end of vitrification operations. Since it was determined to be no longer economically practical to continue zeolite retrieval as vitrification feed, zeolite transfers were concluded after the fifty-fourth transfer. In all, 8.7 million gallons of increasingly dilute zeolite slurry were removed from the zeolite storage tank to support retrieval of 97 percent of Cs-137 laden zeolite. During these operations, more than 530,000 gallons of clean mobilization pump seal water were added to the HLW volume. Reference 10 provides additional detail on zeolite retrieval activities.

HLW Mobilization, Retrieval and Vitrification[11]

Following HLW pretreatment and bulk zeolite transfer, the HLW liquid and solids in the tank farm were mobilized, retrieved, and transferred to the vitrification facility in batches. The first HLW transfer to the vitrification facility of 1,900 gallons was performed with approximately 250,000 gallons of liquid and solids in the HLW Tank. Four 150-horse-power mobilization pumps were used to mix the slurry in the HLW tank for this transfer. The HLW consisted of washed PUREX and THOREX sludge commingled with the size-reduced zeolite. Vitrified waste from the first HLW melter feed batch was produced on July 2, 1996. Subsequent HLW transfers were performed with four to six mobilization pumps operating and transfer volumes as high as 5,200 gallons to produce a single vitrification batch, typically producing four canisters or 18,000 pounds of HLW glass. As solids were depleted from the HLW tank, excess tank liquid from mobilization pump seal water in-leakage was decanted in stages and stored in the spare HLW tank to maintain a concentrated HLW feed to the vitrification facility. Following the forty-fourth transfer of HLW feed to the vitrification facility, 71,000 gallons of waste remained in the HLW tank and multiple transfers of the increasingly dilute HLW were necessary to produce a full vitrification feed batch. Figure 4 illustrates the cumulative retrieval of Sr-90 (one of the sludge components) and Cs-137 (zeolite component), together with the number of HLW transfers performed and illustrates that as many as thirty-six transfers of the increasingly dilute HLW were necessary to make up a single vitrification batch during the last three years of vitrification operations. Figure 5 depicts the cumulative retrieval of the long-lived alpha-transuranic isotopes and shows that very diminishing returns were reached after three years of processing. Various methods were employed to aggressively expedite retrieval of the remaining HLW. These methods included lowering all mobilization pumps closer to the tank bottom, indexing pump jets at deposits observed with in-tank video cameras, providing variable speed/programmable controls on mobilization pump rotary positioners, synchronizing pump rotary positioners with each other, operating the mobilization pumps above their rated speed, washing tank bottom structures with in-tank sluicers and creating specific wave action from special mobilization pump operations.

In parallel with the final retrieval of WVDP HLW, efforts were initiated to determine the amount of key radionuclides remaining in the three tanks that contained HLW. This data was necessary to help establish when waste retrieval activities could

Figure 4. Cumulative retrieval of Sr-90 and Cs-137

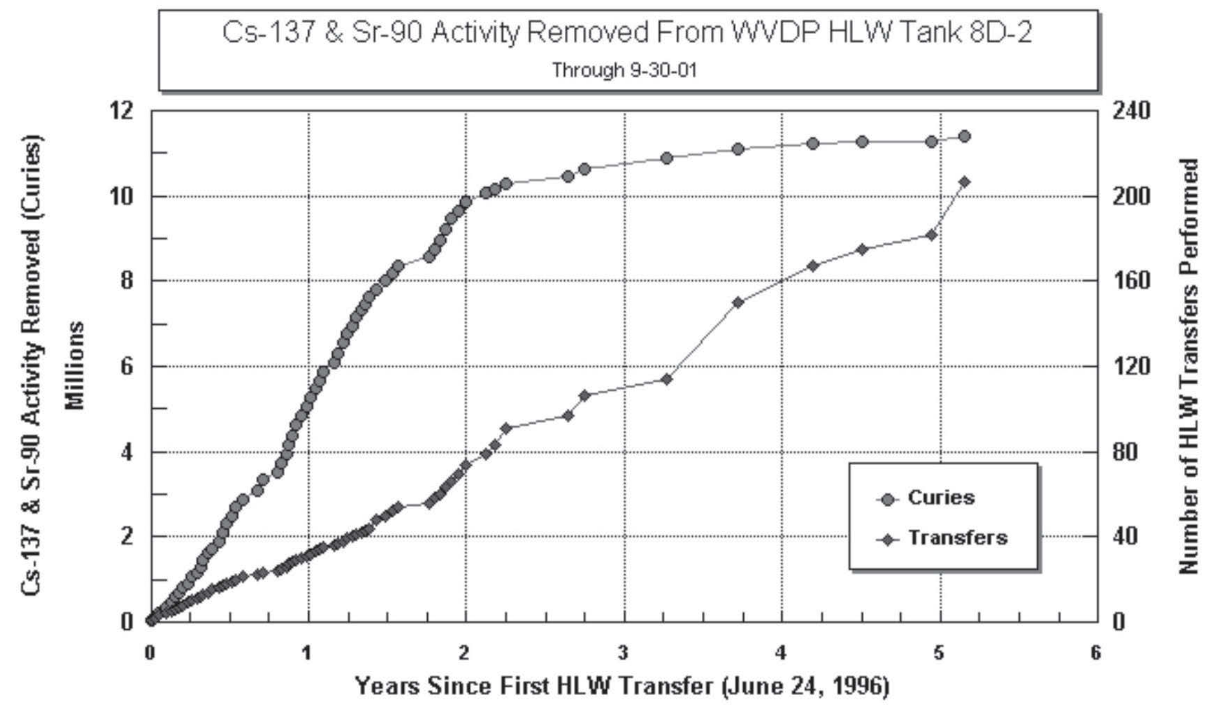
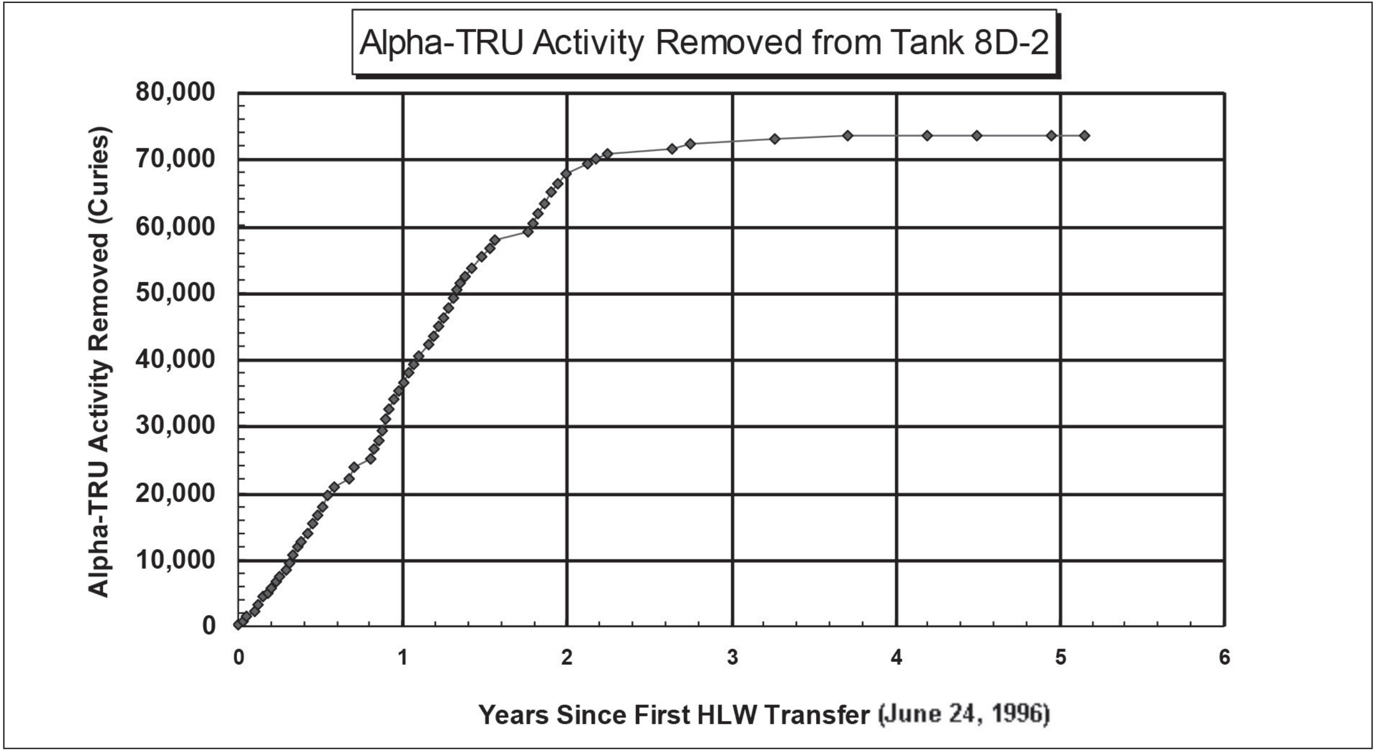


Figure 5. Cumulative retrieval of alpha-transuranic activity



cease and vitrification processing finish. Characterization techniques employed included visual inspection via radiation-resistant black-and-white and color video cameras in the two larger tanks, beta-gamma general field radiation probes and modeling, shielded beta-gamma measurements obtained from internal surfaces of the PUREX HLW tank, gamma camera imaging system modified to WVDP requirements, physical sampling of the residual waste remaining, and sampling surface deposits from inside the primary HLW tank. Additional detail on the characterization of WVDP HLW tank residuals is provided in Reference 12.

Early characterization efforts inside the primary HLW tank performed in July 2000 revealed significantly more Sr-90 and alpha-TRU nuclides on the upper wall surfaces than projected. This discovery led to the actual sampling of internal surface deposits and the installation of two sluicers to wash these surfaces using the diluted waste liquid in the tank. One of the six mobilization pumps had to be removed to provide the second sluicer access to the tank. The internal upper surfaces and bottom gridwork of the tank were washed using the two remotely operated sluicers to remove as much of the deposits as practical and allow the radionuclides removed to be transferred to the melter in the final HLW transfers to vitrification. Following the extensive washing of the tank's surfaces with the installed sluicers, additional characterization activities were conducted to establish the radioisotope inventory remaining. The characterization efforts produced conservative inventories for each of the tanks and major systems in the Tank Farm. Other radioisotope inventory estimates were prepared for each of the MPPB cells, with these and the tank farm inventories used in the preparation of the performance assessment for the WVDP Phase I Environmental Impact Statement.

HLW vitrification was carried out in two phases. Each phase involved transferring the HLW slurry mixture from the HLW tank to the Concentrator Feed Make-up Tank (CFMT) in the vitrification cell where it was blended with batches of cold chemicals (including glass formers), concentrated, transferred to MFHT, continuously fed to the melter, with the glass poured into stainless steel canisters to produce the final HLW form. During Phase I, which was conducted from July 1996 until June 1998, 211 canisters were made, for a production total of 436,546 kilograms of HLW glass. Phase I processing comprised fifty-five batches of HLW glass produced from seventy-three HLW transfers. Phase II processing differed from Phase I in that the waste being supplied to the vitrification facility had become much more dilute due to less solids available in the HLW tank and the need to maintain sufficient liquid level in this tank to operate the HLW mobilization pumps and facilitate solids retrieval. During Phase II processing, 134 transfers of waste were required to produce eleven batches of HLW glass. Waste retrieval had reached very diminishing returns. Phase II was conducted from July 1998 until August 2002, resulting in the production of 64 canisters, for a production total of an additional 132,756 kilograms of HLW glass.

HLW mobilization and retrieval from Tank 8D2 in the Tank Farm was stopped on September 26, 2001, with completion of the 207th transfer, which finished the sixty-sixth HLW melter feed batch. The termination of waste retrieval was based on analysis that indicated that it was no longer technically and economically practical to retrieve additional waste from the tank. This determination was supported by economic analysis, the melter reaching its design life and the increasingly smaller amounts of radioactive materials retrieved from the tank waste heel (Figures 4 and 5). Solids retrieval had reached a very inefficient level due to mobilization pump seal water in-leakage that in some cases equaled the volume of waste removed from the tank during the transfer to the vitrification facility, essentially flushing the bottom of Tank 8D-2, and reaching the limits of mobilization pump and sluicer effectiveness in suspending the tank bottom solids.

Flushing of the HLW storage and processing systems was initiated in conjunction with final HLW retrieval. Although the continued use of these HLW facilities with increasing dilute waste provided significant flushing, additional water and nitric acid flushes were necessary for the various systems. The effectiveness of the flushing and the determination of when the flushing could cease were indicated by either radiation probes adjacent to the systems, by remote video inspection or by sampling. The Supernatant Treatment System, used since 1988 to adsorb primarily Cs-137, and to a lesser degree Sr-90 and plutonium, from the HLW onto zeolite, was selectively flushed with water and nitric acid, depending on the specific flush path. The stainless steel tank, which originally stored the acidic THOREX waste and then held various vitrification facility byproduct waste, was flushed twice with nitric acid and then water. The HLW transfer system connecting the Tank Farm to the vitrification facility was flushed multiple times with the acid solutions and water.

In the vitrification facility, the submerged bed scrubber on the off-gas ventilation system was flushed with nitric acid and water, as were other smaller vessels. The radioactivity remaining in the batch make-up and melter feed tanks, and the melter itself, was minimized by processing only these flush solutions in the last two vitrification batches with additional glass-former materials added. These actions produced glass having a decreasing radionuclide content. During this flushing process, the main glass discharge port of the melter plugged necessitating reconfiguration to the backup discharge port. This event highlighted the need to complete vitrification processing and shut the melter down in a controlled fashion before it failed unexpectedly due to age-related issues.

After vitrification processing ended, two more special canisters were filled using the Evacuated Canister Process to essentially empty the melter of its molten glass at shutdown. All HLW canisters were placed into storage within racks erected remotely in the HLW Interim Storage Facility, the former Chemical Processing Cell of the reprocessing plant. The processing sequence used to accomplish HLW glass production during both Phase I and Phase II is described briefly as follows.

Vitrification Operations[9,13]

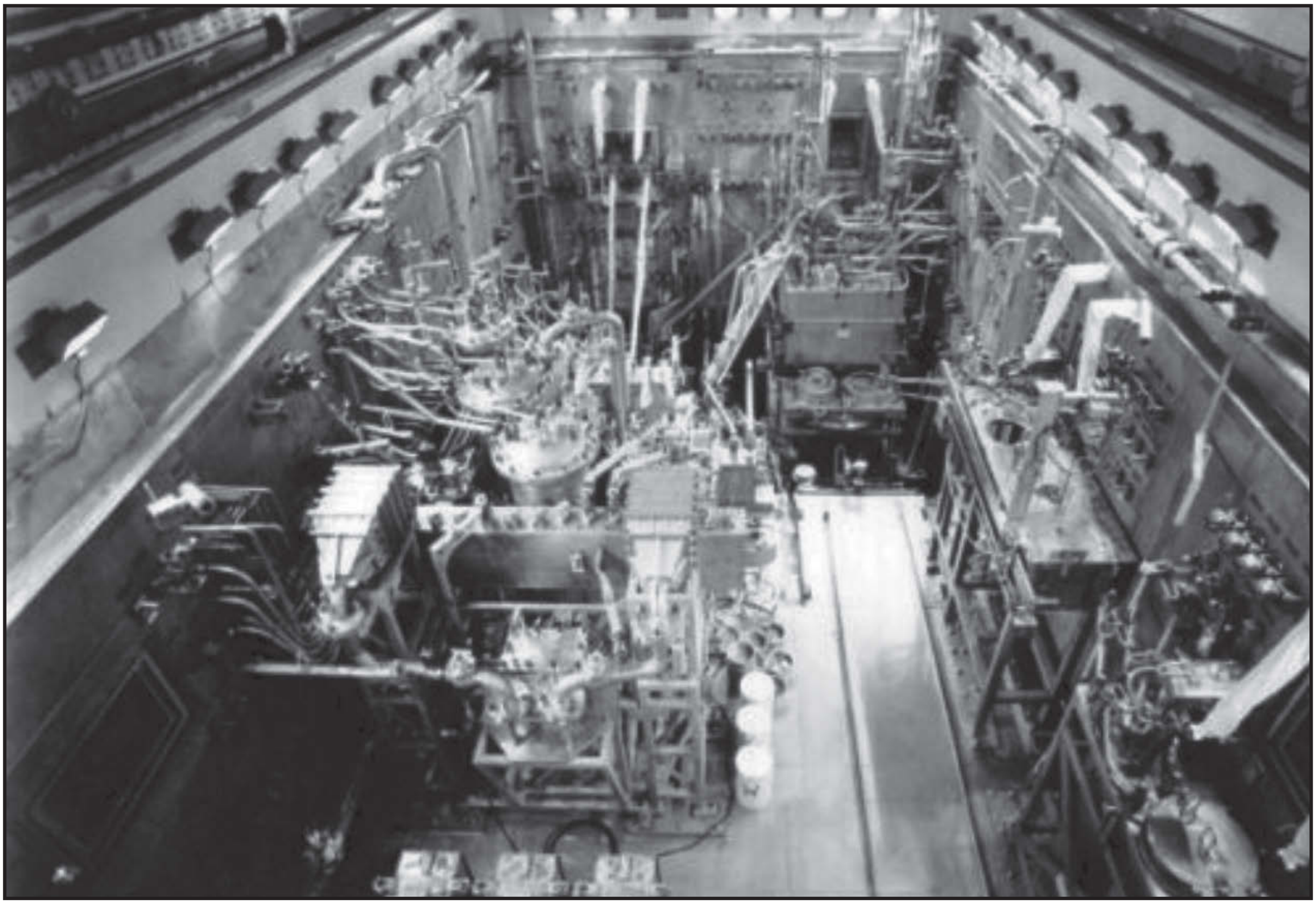
The interior of the highly shielded and remotely operated vitrification cell is shown in Figure 6 with an illustration of the melter and canister turntable in Figure 7. The basic process used to produce canisters of HLW glass began by combining the radioactive species captured in the zeolite media during HLW pre-treatment with the HLW sludge, blending in recycled waste liquids resulting from off-gas treatment, and transferring the HLW slurry to the CFMT, where the first step of HLW processing was initiated. This processing step involved taking slurry samples and sending them to the on-site Analytical and Process Chemistry (A&PC) Lab for chemical and radiochemical analysis to determine the exact glass-making recipe needed to process the slurry into HLW glass. While slurry samples were analyzed, the batch of slurry in the CFMT was concentrated to remove excess water. After the batch recipe was determined and a pre-mix of glass-forming chemicals prepared, the pre-mix was transferred into the CFMT, mixed with the concentrated slurry and sampled again to ensure target glass composition. This feed preparation cycle was the most critical stage in HLW glass production because the time to prepare a feed batch had to be less than the time to transfer a full tank of feed from the MFHT to the melter, about 180 hours. The greatest portion of feed preparation time involved slurry analysis. Modifications made to improve batch preparation cycle time during both testing and early radioactive operations proved to be critical to the success of Phase I vitrification operations. The next step in HLW processing involved transferring feed to the melter, allowing water to evaporate, salts to decompose, and remaining solids to calcine. Inside the melter, calcined wastes and glass-formers melted and fused into a glass pool where they homogenized. During melter operation, molten glass was periodically airlifted into a stainless steel canister held in position under the melter by the canister turntable. The turntable is a four-position, four-canister device that provides one position for filling, one position for canister removal and replacement, and two positions for filled canisters to cool. After being allowed to cool, the filled canister was moved from the canister turntable to the weld station where canister fill height was measured, glass shard samples were obtained, and a stainless steel lid was welded onto the canister. From the weld station, the canister was moved to the decontamination station, where the surface of the canister was decontaminated by chemical etching. The decontamination solution used was recirculated back into the melter feed. The final step in canister production involved moving decontaminated canisters from the vitrification cell to the storage racks in the High-Level Waste Interim Storage Facility (HLWISF) which is the former Chemical Process Cell in the MPPB (Figure 8).

Canisters used in HLW glass production were brought into the vitrification cell through a pathway that began in the canister load-in facility. From this location, canisters were inserted horizontally through a cylindrical shield door into the equipment decontamination room (EDR). In the EDR, the canisters were uprighted, placed onto the remotely operated and radio controlled transfer cart, moved into the vitrification cell, and placed into a canister storage rack for eventual loading into the canister turntable. During the glass-melting process, steam, volatile elements evaporating from the glass pool, and feed particles entrained in the process off-gas were vented to the off-gas treatment system. The first component of this system, the submerged bed scrubber (SBS), was used to quench the off-gas and remove particulate by scrubbing through a submerged bed of ceramic spheres. Quenched off-gases were then drawn through a mist eliminator and a high-efficiency mist eliminator (HEME) to remove mist and fine particulate. Scrubbed and treated off-gas was then heated and passed through a high-efficiency particulate air (HEPA) filter to remove particulate. Essentially free of radiological pollution at this point, the treated off-gas stream was piped through an underground trench to another building where final stages of HEPA filtering and NOx abatement were completed before venting the treated off-gas through the main plant stack. The vessel ventilation system was used to maintain all primary process vessels under slight vacuums during radioactive operations. This system operated by passing vessel vent gas from a header through a condenser to the off-gas stream directed toward the HEME. The vessel vent system also served as a means to bypass the SBS if the melter off-gas line became plugged. In-cell pressure and contamination control was provided by the heating, ventilation, and air conditioning (HVAC) system. This system was designed such that any air leakage associated with the cell shield walls flows back into the vitrification cell where it is exhausted through the cell ventilation HEPA filters.

HLW mobilization and retrieval operations were successful in removal and vitrification of 99.5 percent of the sludge, with its long-lived radioactivity and approximately 97 percent of the shorter-lived Cs-137.[12] Reference 11 provides a more in-depth description of WVDP HLW retrieval. During HLW processing operations, nearly 24 million curies (1996 basis) of radioactive material (daughter products of Cs-137 and Sr-90 included) were vitrified into 275 canisters of HLW glass. Each canister of HLW holds approximately 2,000 kilograms of glass with an average contact dose rate of more than 2,600 rem per hour during production. After vitrification processing ended, the final molten radioactive glass remaining in the melter was removed by vacuum into two specially outfitted evacuated canisters (Figure 9). This effort removed 88 percent or 2,200 kg of the molten glass from the pool, allowing the melter to be ultimately packaged as LLW and marking the end of the successful WVDP HLW retrieval and vitrification program.

Systems and system hardware used in HLW processing and glass-filled canister production at the WVDP functioned beyond design expectations. The system had 86 percent availability in its first year of operation and 71 percent availability over the two-year Phase I operational period. A total of 570,000 kg of HLW glass was produced over seventy-four months of operation. As a

Figure 6. Vitrification cell layout



result of reprocessing and vitrification, the volume of the HLW produced was greatly reduced from the original volume of the spent fuel.

Tank Farm Layup

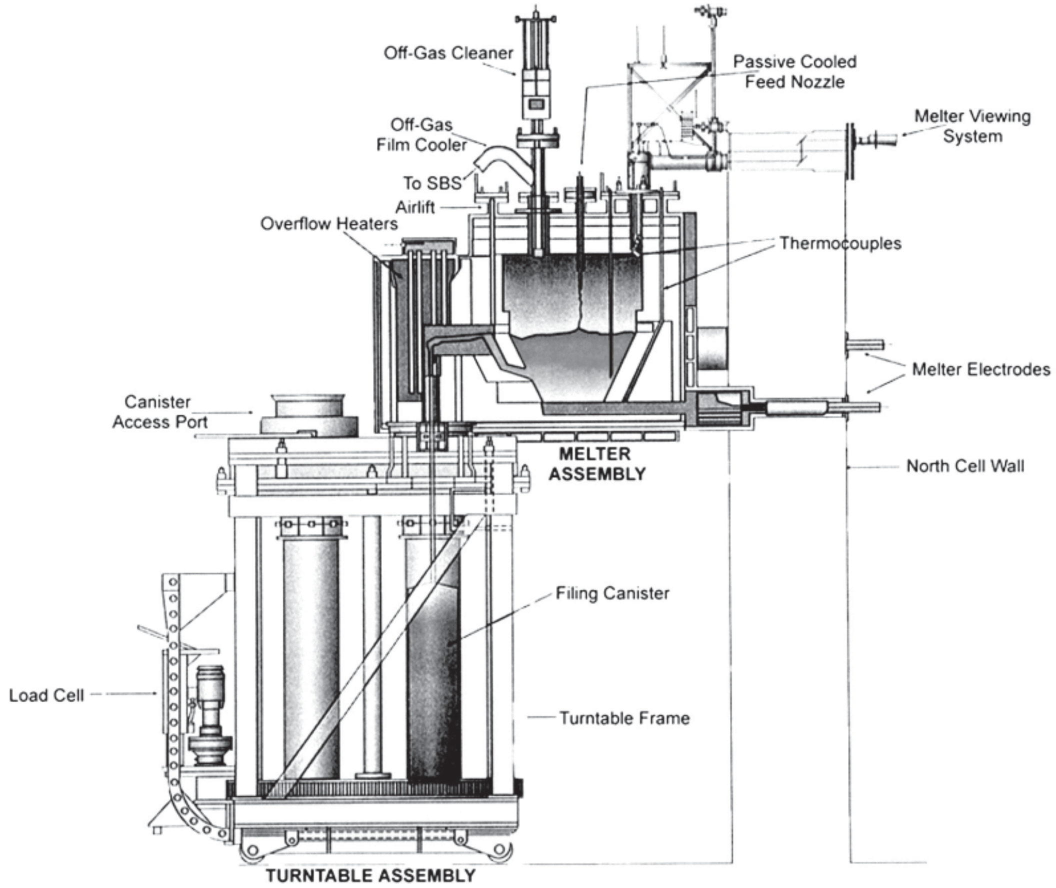
Following completion of HLW retrieval, system flushing, and vitrification of the wastes, approximately 275,000 gallons of very dilute waste liquid remained in the two large HLW tanks. The low concentration of radionuclides: 20 µCi/ml Cs-137, 0.3 µCi/ml Sr-90, and 0.003 µCi/ml gross alpha, as well as the high sodium content of the liquid from addition of corrosion inhibitors, made processing of this liquid into glass uneconomical. Based on the sodium limit in the vitrification feed, an additional sixty canisters of glass would have been produced. Instead, this liquid was volume reduced to 130,000 gallons by decontaminating the liquid in the STS and concentrating the effluent with the LWTS evaporator, with the concentrate returned to the tanks. This remaining liquid was then processed through the STS again to strip out the Cs-137 onto existing partially spent zeolite remaining in two columns, allowing the decontaminated liquid to be subsequently concentrated in the liquid waste treatment system (LWTS) evaporator to 11,500 gallons of concentrate and held in the two concentrate tanks as was done during pretreatment processing. This RCRA-hazardous low-level waste liquid was characterized, treated to Universal Treatment Standards and solidified into seventeen 170 cubic foot waste packages resulting in LLW that could be land disposed. This waste was then shipped for disposal. Following liquid removal from the tank farm, due to pump suction limitations and the tilt of the tanks, 13,000 gallons of liquid remained in the two former HLW tanks.

The STS was deactivated after decontamination of the last tank liquid as described above. Over its lifetime, this system decontaminated 3,560,000 gallons of tank liquids, exclusive of the additional 600,000 gallons of demineralized dilution water added during the process to achieve better Cs-137 adsorption onto the zeolite.

Vitrification Facility Dismantlement

Following vitrification operations and melter shutdown, dismantlement of the highly contaminated process equipment in the cell began. One of the first steps in the process was to flush

Figure 7. HLW melter and canister turntable



and empty the dilute waste heels from various process vessels in the cell. These wastes were collected in the CFMT, where they were sampled and then transferred to the tank farm for future disposition. This paved the way to begin to dismantle the various systems, components and piping. Although the equipment had been repeatedly flushed, radiation and contamination levels within the vitrification cell prohibited personnel entries. Therefore, all dismantlement activities had to be performed remotely. The existing two overhead cranes and manipulators were used to remove bolted piping sections and package the waste into highly shielded waste containers for disposal or future waste processing. To aid in dismantlement and size reduction, a commercial BROKK remote tooling platform with a variety of end-effectors was modified for use in the high radiation and contamination environment and deployed in the cell. This equipment proved to be a valuable contributor in the dismantlement effort because of its ability to remotely saw and shear components and package waste into containers (Figure 10). Other remote tooling was developed and deployed to facilitate the entirely remote dismantlement of the equipment in the vitrification cell.

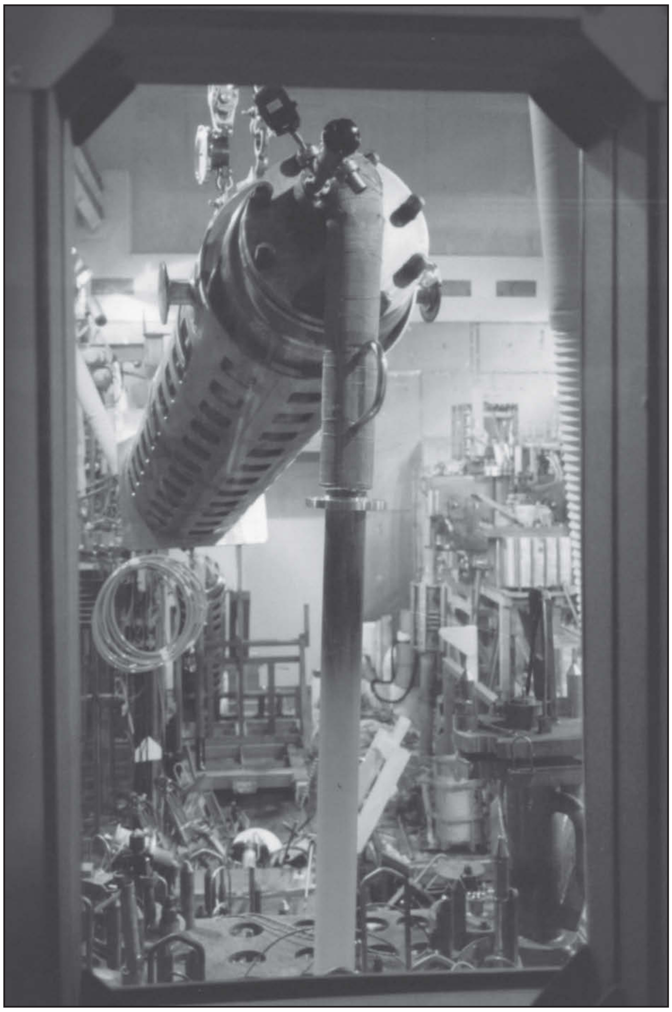
Extensive characterization of the melter and the two large waste slurry feed vessels (CFMT and MFHT) was conducted and led to special, highly shielded IP2 containers being designed and fabricated for these three components without the need for component size reduction. Each of the components was semi-remotely loaded into its waste container and low-density grout was added within the CFMT and MFHT packages to stabilize the remaining residue on the surfaces for storage and transportation to off-site disposal. Grouting of the melter within its container is planned in the next few years. Waste incident to reprocessing (WIR) documentation for these components has been prepared to show that they can be disposed of as LLW. Dismantlement began in late 2003 and was completed in 2006 with more than 160 waste containers generated. Figure 11 illustrates the vitrification cell after its processing systems were removed.

WVDP Interim End State Activities

A contract for completion of WVDP Interim End State Activities was placed by DOE with West Valley Environmental Services, LLC (WVES) as prime contractor on September 1, 2007, taking

Figure 8. Canisters stored in HLW interim storage facility

Figure 9. Evacuated canister with molten glass



over from predecessor WVNSCO. The scope of work included critical work that could be performed under existing National Environment Policy Act (NEPA) coverage while the WVDP Environmental Impact Statement for Decommissioning and Long-Term Stewardship was finalized. During this four-year contract, an engineered cap and groundwater barrier was installed on the NDA to minimize water intrusion into the buried wastes, a tank and vault drying system was installed in the tank farm to evaporate residual liquids in the tanks and vaults and maintain dry tanks at a low relative humidity to essentially halt tank corrosion. A permeable treatment wall was installed on the north plateau of the premises to limit the migration of Sr-90 in the groundwater plume and legacy waste processing and shipments were expedited. Additionally, major main plant process building decommissioning and cell dismantlement continued.

Remote disassembly of highly radioactive original reprocessing systems in Extraction Cell 1 was performed with the cell approximately 90 percent cleared. Hands-on disassembly of off-gas cell systems was 75 percent completed. Hot acid cell tanks and equipment were removed and a high-capacity ventilation blower and High-efficiency particulate air (HEPA) filter system was installed as a back-up to the primary main plant ventilation HEPA filtration train. The walls and floors in the process mechanical cell and general purpose cell were decontaminated remotely using ultra-high-pressure liquid nitrogen to strip off existing fixative and underlying contamination. The stripped materials were packaged for future disposition. The MPPB was moved much closer to its demolition state by the decontamination of 155,000 cubic feet of space, removal of fifty-seven additional vessels (40 percent of the total) and the removal of more than 34,000 linear feet of process piping. Extensive asbestos abatement activities were also conducted to remove this hazardous material from the main plant process building and other project facilities.

Remote waste processing and size-reduction was expedited by reusing the vitrification cell and its infrastructure to assist in this effort, in addition to fully utilizing the remote handled waste facility. More than 100,000 cubic feet of waste was prepared for shipment, including legacy wastes that had been stored for twenty-five years, and 170,000 cubic feet of legacy and newly generated wastes were shipped for off-site disposal. Size reduction and reprocessing of legacy waste was successful in reducing the volume of TRU waste on site by nearly 80 percent. The drum Cell was emptied of the last few thousand remaining 71-gallon cement waste drums from HLW pretreatment and these drums were shipped to the Nevada Nuclear Security Site (NNSS) for disposal.

WVDP Phase I Decommissioning

DOE awarded the WVDP Phase I Decommissioning contract to CH2M HILL B&W West Valley, LLC on July 29, 2011, with this work expected to extend for at least six years. Under this contract, the HLW canisters will be overpacked, five canisters per overpack, with the overpacks placed in highly shielded concrete and steel casks in a modular outdoor array. In this storage configuration, the overpacks are in a transportation-ready configuration. The

Figure 10. Vitrification equipment dismantlement

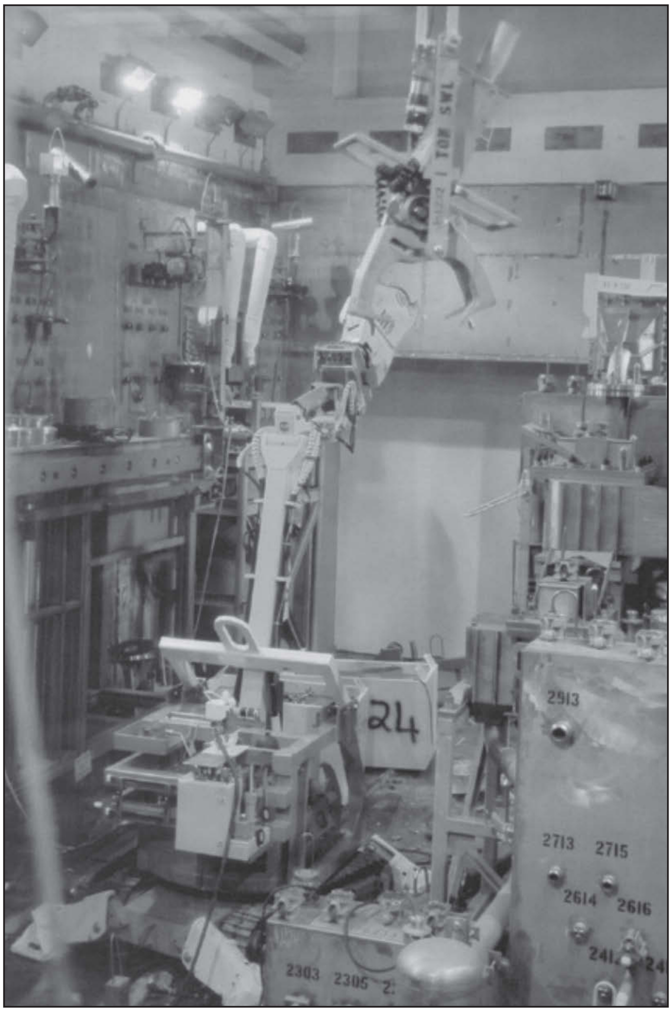
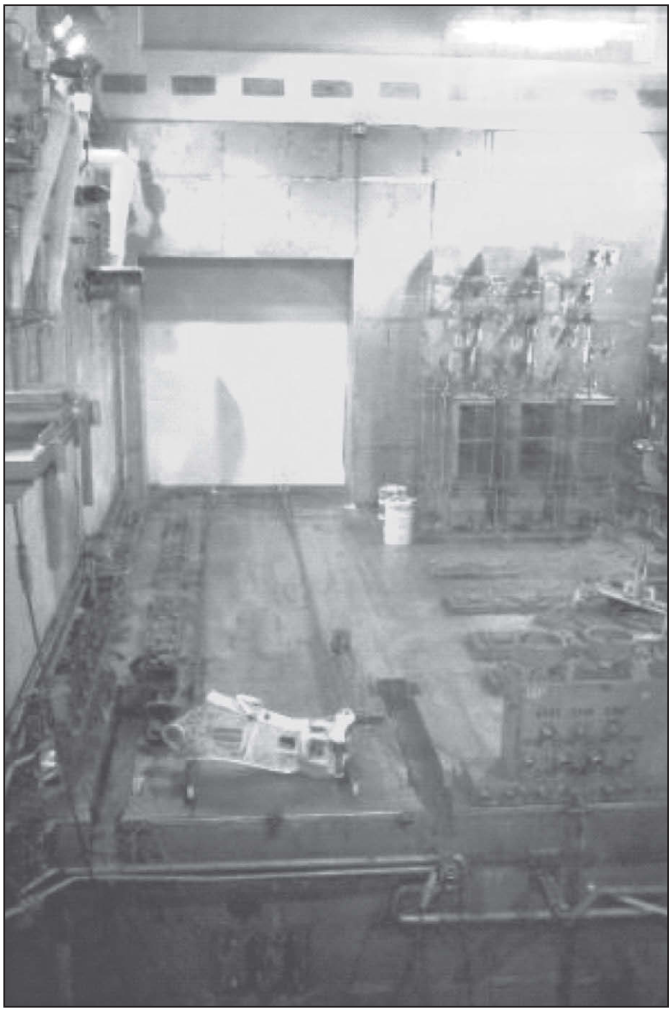


Figure 11. Vitrification cell after equipment removal



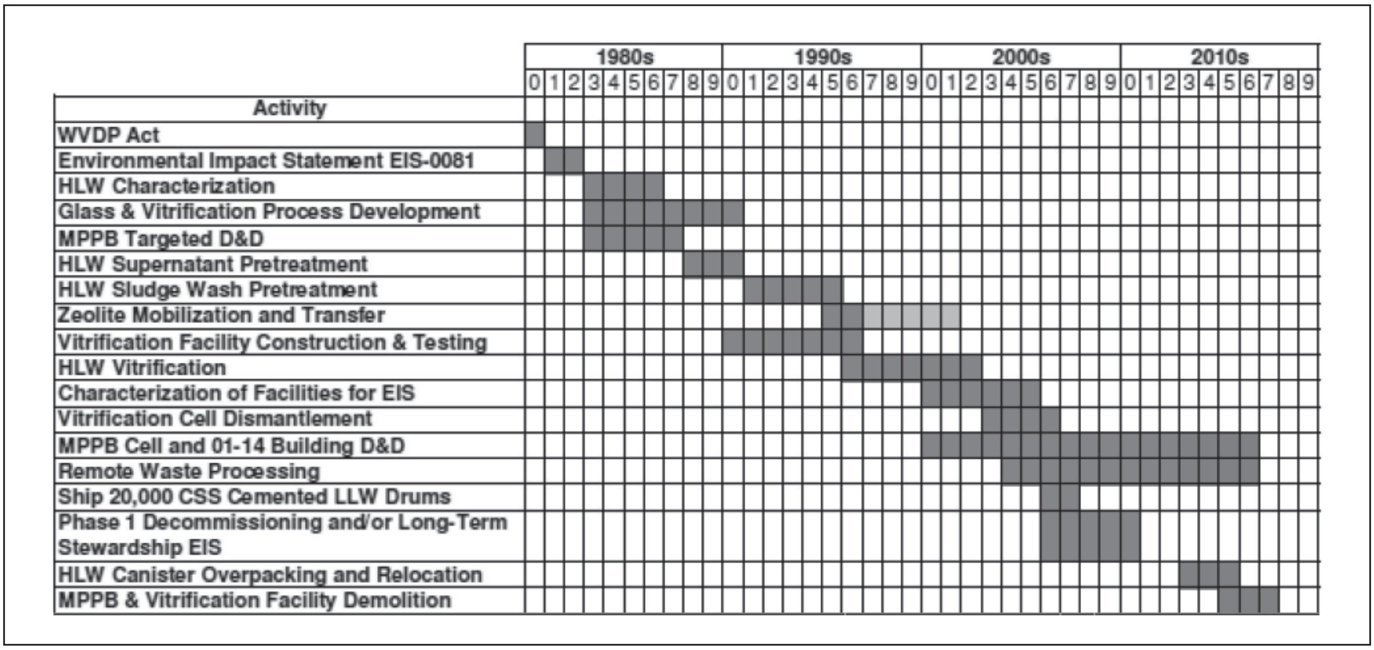
storage/disposition volume of the resulting HLW canister overpacks will be approximately the same as the original reprocessed commercial spent fuel assemblies, if these fuel assemblies were overpacked in a similar manner as is being done at commercial nuclear power plants instead of undergoing fuel reprocessing.

Under the current contract with CH2M HILL B&W West Valley, LLC, most of the facilities on the site, including the challenging main plant process building and vitrification facility, will be decommissioned and demolished down to grade with the wastes shipped off site for disposal. All legacy waste and newly generated wastes that have a viable disposal option will be characterized and shipped for disposal. Those wastes without a disposal pathway, primarily TRU waste, will be safely stored while a disposal option is pursued. The former HLW tanks, north plateau strontium groundwater plume and the NDA will be closely monitored and maintained awaiting dispositions anticipated in a Phase II WVDP Environmental Impact Statement[4] and Record of Decision.[14]

Two Interim End State Projects implemented earlier, continued operations under this phase of the project. By the end of December 2011, the tank and vault drying system had evaporated all residual liquid in the bottoms of the two former carbon steel HLW Tanks and significantly lowered the tanks' internal relative humidities. In addition, all standing liquid in the vault containing the two smaller stainless steel tanks was dried out and the relative humidity in the vault limited to 30 percent. By summer 2012, liquids in the containment pans of Tanks 8D1 and 8D2 had evaporated and resulted in low relative humidity inside the vaults on the tank exterior surfaces. These conditions combine to prevent a tank leak and prolong the lifetimes of the tanks until a final disposition is determined. The permeable treatment wall also demonstrated success in halting the increase of Sr-90 in the groundwater downgradient of this subsurface barrier.

Other Phase I Decommissioning activities not yet contracted include the removal of the remote handled waste facility, the foundations and sub-grade structures of the major facilities, the

Figure 12. WVDP timeline



source of the north plateau strontium plume and the low-level waste-water treatment system, including its lagoons, used to treat contaminated water before being released from the site. DOE will also obtain additional characterization data and perform specific scientific studies to support decision making for Phase II Decommissioning.

WVDP Phase II Decommissioning[4,14]

Future Phase II decommissioning plans are being developed by the DOE and New York State Energy Research and Development Authority with input from regulators and public. Site activities expected to be included in this work include closure of the Tank Farm, disposition of contaminated site soils, shipment of the accumulated transuranic waste that currently is not able to be accepted at the Waste Isolation Pilot Plant, disposition of the HLW canisters, closure or continued monitoring of the NDA and SDA and long-term monitoring and maintenance activities covering the 167-acre WVDP site as well as the remainder of the Western New York Nuclear Service Center.

Summary

The WVDP is the first HLW immobilization project brought to completion in the United States. The nuclear materials management processes required for this completion involved extensive integration of activities and resulted in multiple waste forms that met the appropriate standards for disposition and disposal. HLW pretreatment took place over eight years to reduce the quantity of HLW glass that would be produced by a factor of ten. Vitrification operations, conducted in two phases over six years, resulted in the immobilization of about 24 million curies of radioactive material into 275 canisters of HLW glass having an average 90 percent fill volume. Phase I vitrification operations included continuous melter operation and 71 percent plant availability (86 percent in the first year)[6] resulted in the production of 211 canisters made from fifty-four feed batches that were filled to 90 percent. The second phase of radioactive operations resulted in the production of sixty-four canisters from fifteen batches of HLW feed material prepared from increasing dilute HLW and cleaning and flushing of the HLW tanks, cell walls, sumps, and slurry transfer lines. After the last canister of HLW was produced using the Vitrification System, the melter was powered down. Two evacuated canisters were partially filled to empty approximately 88 percent of the molten glass remaining in the melter. These operations were completed in September 2002, marking the end of six years of successful vitrification facility operation and solidification of HLW at the WVDP. The vitrification cell was dismantled from 2003 to 2006. The HLW canisters will be overpacked, five canisters to an overpack in the next few years and placed into modular shielded casks to allow demolition of the Main Plant Processing Building. The HLW canisters will stored in this way until a federal repository is available for their ultimate disposition. Figure 12 depicts the timeline of significant WVDP activities.

Conclusions

True to the Congressional Act, the West Valley Demonstration Project has been a demonstration showcase for innovative technologies and regulatory strategies to help address the needs of all stakeholders. Remote decontamination and decommissioning, HLW pretreatment and vitrification, remote size-reduction of processing equipment, RCRA stabilization and solidification of high-activity wastes, and waste shipping methods are all areas where the WVDP team has demonstrated time and again its ingenuity and innovation to safely solve difficult challenges in its quest to close the nuclear fuel cycle. Nuclear Fuel Services had recovered and recycled all but approximately 2 percent of the uranium and plutonium in the fuel reprocessed. During the WVDP, approximately 99.5 percent of the long-lived alpha-transuranic isotopes and more than 98 percent of the shorter half-life Cs-137 and Sr-90 remaining in the HLW resulting from fuel reprocessing were immobilized into a robust glass waste form, with this waste maintained in safe storage awaiting transportation to a federal repository. In the next few years, the HLW canisters will be overpacked, five canisters per stainless steel overpack, moved out of the main plant process building and placed in a safe outdoor modular shielded storage array, as is being done with commercial spent nuclear fuel assemblies at many power plants around the United States. Following this, main plant process building and vitrification facility demolition will begin. The HLW overpacks will be designed and licensed to interface with an existing licensed transportation cask capable of transporting the HLW to the future repository. The specified design life of the storage system is fifty years, with the expectation that this waste will be safely transported and emplaced within the federal repository well before reaching the storage system design life.

Dan Mess has worked in engineering for the prime contractor at the West Valley Demonstration Project since 1989 with direct responsibilities for process engineering involving Integrated Radwaste Treatment System pretreatment of the HLW; mobilization, retrieval, and transfer of the HLW to the vitrification process; Tank Farm characterization; HLW tank lay-up and STS deactivation; RCRA stabilization and solidification of residual tank liquids and implementation of the Tank and Vault Drying System.

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Corrosion Control Measures for Liquid Radioactive Waste Storage Tanks at the Savannah River Site

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Abstract

The Savannah River Site has stored radioactive wastes in large, underground, carbon steel tanks for approximately sixty years. An assessment of potential degradation mechanisms determined that the tanks may be vulnerable to nitrate-induced pitting corrosion and stress-corrosion cracking. Controls on the solution chemistry and temperature of the wastes are in place to mitigate these mechanisms. These controls are based upon a series of experiments performed using simulated waste solutions on materials of construction used for the tanks. The technical bases and evolution of these controls is presented in this paper.

Introduction

Liquid radioactive wastes from the Savannah River Site (SRS) separation process[1] are stored in large underground carbon steel tanks. The high-level wastes are processed in several of the tanks and then transferred by piping to other site facilities for further processing before they are stabilized in a vitrified or grout waste form. Based on current waste removal and processing schedules, many of the tanks will be required to be in service for times exceeding the initial intended life (i.e., greater than sixty years). Until the waste is removed from storage, transferred, and processed, the materials and structures of the tanks must maintain a confinement function by providing a barrier to the environment and maintain acceptable structural stability for normal service as well as design basis events such as accidents and earthquakes (i.e., abnormal conditions). A program is in place to mitigate potential corrosion mechanisms and thereby maintain the structural and leak integrity functions of these waste tanks throughout their intended service life. This paper provides a brief introduction to the waste tank design and fabrication, the waste composition, possible corrosion degradation mechanisms, and the technical basis for the control scheme that is used to manage the integrity of the tanks and provide secure containment.

Waste Tank Fabrication and Design

SRS has three types of Double Shell Tanks (DSTs) that are currently in service, identified as Types I, II, and III. The Types I and II tanks were made of ASTM A285 steel during the 1950s and 1960s. The Type III tanks were made of ASTM A516 or A537 steel during the 1960s and 1970s.

Types I and II Tanks

Type I and Type II waste tanks were made of ASTM Type A285-50T, Grade B steel, with the nominal composition shown in Table 1. The tanks were fabricated from semi-killed, hot-rolled plate material.

Type I tanks (shown in Figure 1) have a nominal capacity of 750,000 gallons, are 22.86 m (75 feet) in diameter, and 7.47-meters (24.5-feet) high. The primary tanks are a closed cylindrical tank with flat top and bottom constructed from 1.27-cm-thick (0.5 inch) steel plate. The top and bottom are joined to the cylindrical sidewall by curved knuckle plates. Type II tanks (shown in Figure 2) have a capacity of 1,030,000 gallons, are 25.91 m (85 feet) in diameter, and 8.23 m (27 feet) high. The primary container for Type II tanks consists of two concentric steel cylinders assembled with a flat bottom and flat top forming a doughnut. The top and bottom are joined to the outer cylinder by rings of curved knuckle plates. Single-butt girth welds join each of the plates in both Type I and Type II waste tanks. These tanks are constructed with a top weld to the top of the tank, middle welds between plates, and bottom welds to the bottom of the plate. The thickness of the steel plate used for the primary wall varies depending on location. Plates for the roof and bottom were 1.27 cm (0.5 in) thick. The knuckle connecting the roof to the outer cylinder is 1.43 cm (0.56 in) thick, while the knuckle connecting the bottom to the outer cylinder is 2.22 cm (0.875 in) thick. The primary tank wall thickness is 1.59 cm (0.625 in) thick. A 1.52 m (5-feet) high steel pan provides partial secondary containment for the tanks and a concrete vault encompassing the primary tank and the steel pan provides another barrier before waste can reach the ground. Neither Type I nor Type II waste tanks were stress relieved after fabrication.

Table 1. ASTM requirements for chemical composition for A285-50T, Grade B firebox quality

	Composition, percent			
	C_{max}	Mn_{max}	P_{max}	S_{max}
For plates ≤ 1.91-cm (0.75-in.) thickness	0.2*	0.8	0.035	0.04
* C = 0.22 wt. percent for plate of 1.91-cm (0.75-in.) < thickness ≤ 5.08 cm (2-in.).				

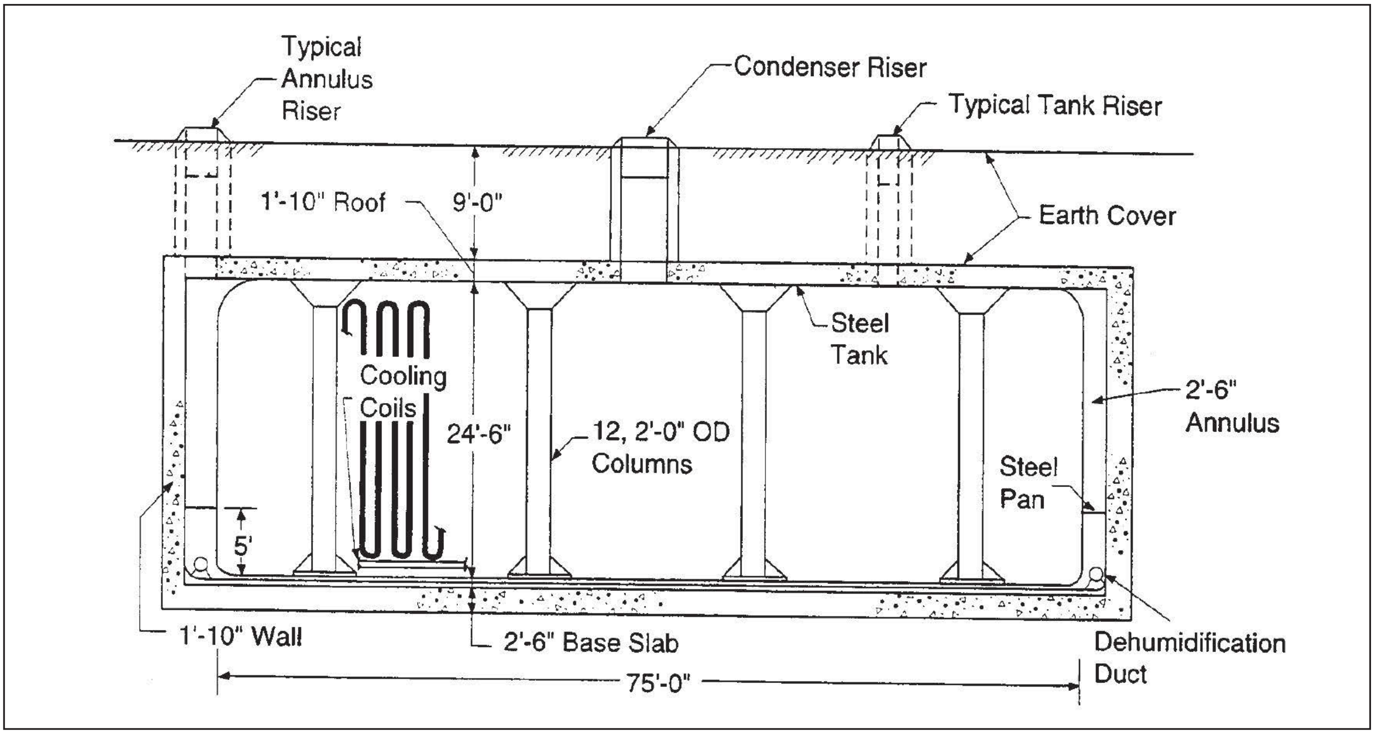


Figure 1. Type I high-level waste tank schematic

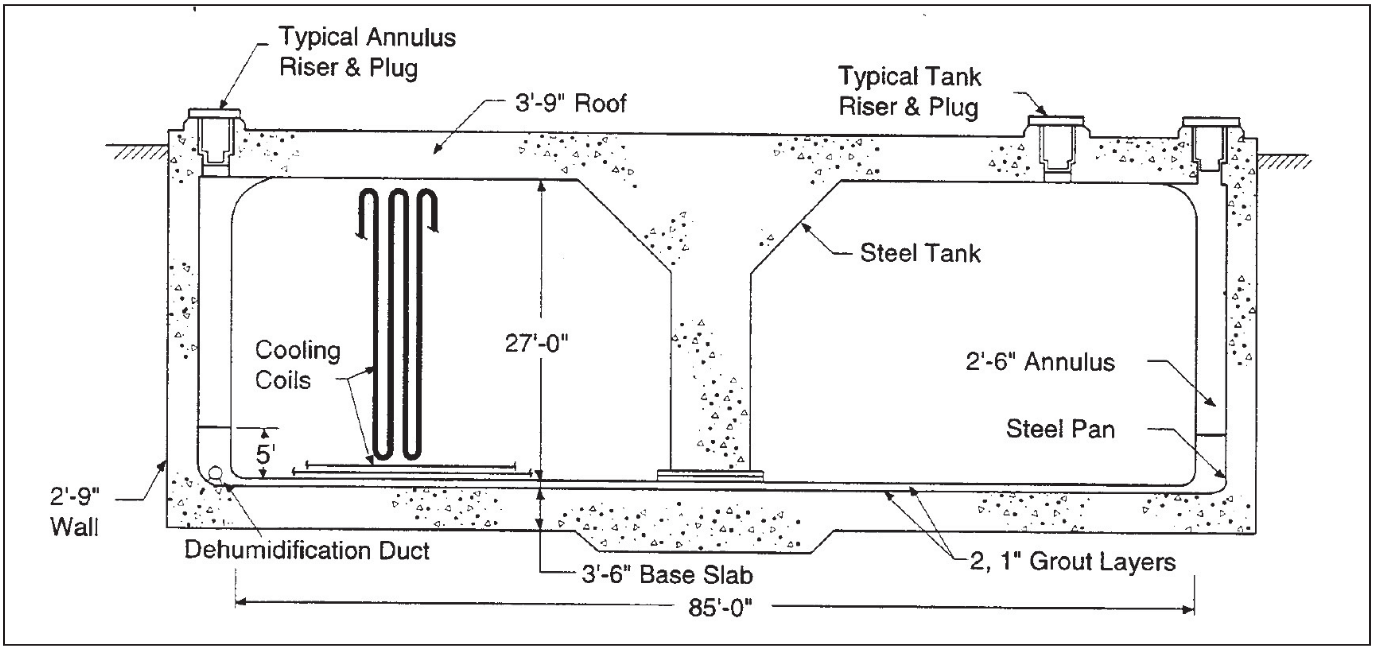


Figure 2. Type II high-level waste tank schematic

Type III Tanks

The most recently constructed tanks, designated Type III, were built from hot-rolled ASTM A516Grade 70 or hot-rolled ASTM537-CL.1 normalized steel. The normalizing heat treatment (analogous to annealing) optimizes notch toughness and hence increases resistance to brittle fracture. The nominal compositions for the steels according to ASTM Standards are shown in Table 2.

Each tank (as shown in Figure 3) is 25.91 m (85 feet) in diameter and 10.06-m (33-feet) high with a capacity of 1,300,000 gallons. Type III tanks have a toroidal shape similar to the Type II design. Each primary vessel is made of two concentric cylinders joined to washer-shaped top and bottom plates by curved knuckle plates. The plates used to form the primary wall were of varying thickness depending upon location. Plates for the roof and bottom were 1.27 cm (0.5 in) thick. The knuckle connecting the roof to the outer cylinder is 1.27 cm (0.5 in) thick, while the knuckle connecting the bottom to the outer cylinder is 2.22 or 2.54 cm (0.875 or 1 in) thick. The primary tank wall ranges between 1.27 to 1.9 cm (0.5 to 0.75 in) thick. The secondary vessel is 27.43 m (90 feet) in diameter and 10.06-m (33-ft) high (i.e., the full height of the primary tank) and is made of 0.95 cm (0.375 in.) thick steel.

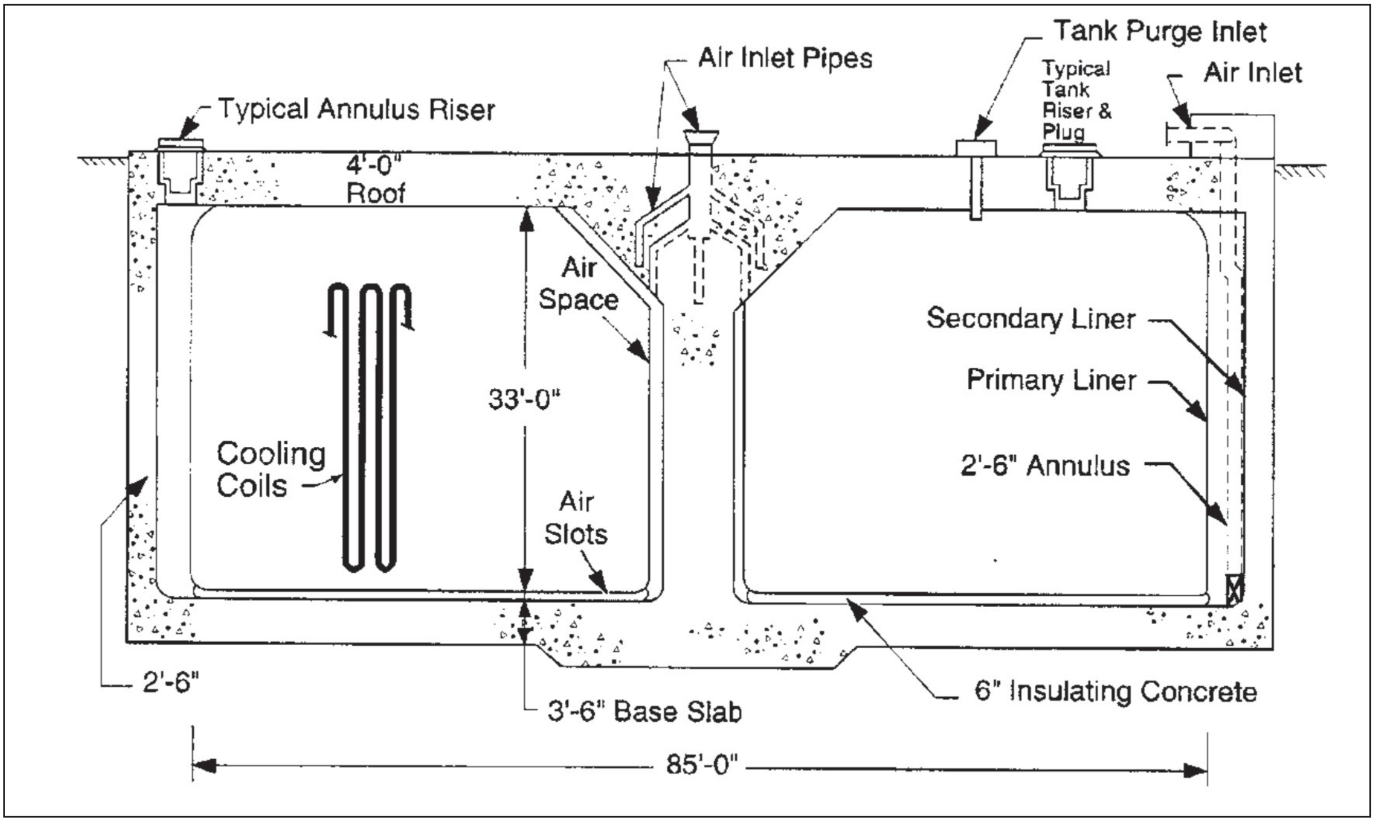
The primary tank sits on a 15.24-cm (6-inch) bed of insulating concrete within the secondary containment vessel. The concrete bed is grooved radially so that ventilating air can flow from the inner annulus to the outer annulus. Any liquid leaking from the tank bottom or center annulus wall would move through the slots and would be detected at the outer annulus.

The secondary vessel is 1.52 m (5 feet) larger in diameter than the primary vessel, making the outer annulus 0.76 m (2.5 feet) wide. The secondary vessel is made of 0.95-cm (0.375-in.) steel throughout. Its sidewalls rise to the full height of the primary tank. The nested two-vessel assembly is surrounded by a cylindri-

Table 2. Nominal compositions of A516-70 and A537-Cl.1

Steel specification	C_{max} (wt percent)	Mn_{max} (wt percent)	P_{max} (wt percent)	S_{max} (wt percent)
A516 – Grade 70	0.28	0.85 – 1.2	0.035	0.04
A537 – Class 1	0.24	0.7 – 1.35	0.035	0.04

Figure 3. Type III high-level waste tank schematic



cal reinforced concrete enclosure with a 76.2-cm (30-inch) wall. The enclosure has a 121.92-cm- (48-inch) flat-reinforced concrete roof, which is supported by the concrete wall, and a central column that fits within the inner cylinder of the secondary vessel.

Each Type III primary tank was stress-relieved in place after all burning, cutting, welding, and other high-temperature work below the liquid fill line had been completed. Full stress relief at 1,100°F (593°C) was accomplished in accordance with the general requirements of the ASME Boiler and Pressure Vessel code.[2]

Waste Chemistry

Most of the high-level wastes are products of the PUREX and enriched uranium (H-area Modified [HM]) processes.[3] In the PUREX process, plutonium and uranium are recovered from irradiated natural and depleted uranium. In the HM process, uranium enriched in ^{235}U and ^{236}U is recovered from irradiated uranium fuel for reuse. Each recovery process produces a characteristic waste. However, generalization of waste compositions in storage tanks based on flowsheet or process analysis is complicated because during processing and storage the wastes are blended and evaporated, salts and insoluble solids precipitate, and radiation induces changes in the composition.

The waste that is stored in the SRS tanks may be classified into two broad general categories defined by their rate of heat generation, high-heat waste (HHW) and low-heat waste (LHW). The majority of the HHW is a byproduct of the PUREX and the HM or enriched uranium processes. A majority of the LHW is also byproduct of these processes. However, other processes and facilities such as resin regeneration, decontamination, and laboratories also contribute significant quantities of LHW. A third category of wastes includes processed wastes (PW), which result from the removal of waste from tanks that are being prepared for closure. The waste is being prepared as feed for either the Defense Waste Processing Facility (DWPF) where it is vitrified or the Saltstone facility where it is blended and immobilized within a grout mixture.

Both HHW and LHW are present in three waste form phases: supernate, sludge, and salt cake. The supernate is a multicomponent aqueous mixture of soluble sodium salts. The primary salts present are sodium nitrate, sodium hydroxide, and sodium nitrite. Sludge is a gel-like substance that consists of approximately 20 vol. percent insoluble solids and 80 vol. percent entrapped supernate.[4] The insoluble solids consist of oxides and hydroxides of iron, aluminum, and manganese that precipitated from the caustic solution and have settled to the tank bottom. The insoluble solids also contain small amounts of uranium, plutonium and longer lived fission products, which supply a significant quantity of decay heat. Therefore temperatures are greater in the sludge than the other two waste forms. Salt cake contains approximately 78 vol. percent salt crystals, which form after the evaporated supernate is cooled, and 22 vol. percent interstitial concentrated supernate (i.e., high hydroxide concentration).[5] The PW is present primarily in two forms: supernate and sludge. Whether these wastes are stored or processed, the supernate, which contains dissolved aggressive anions, is the most corrosive of these waste forms. However, during waste removal operations, salt dissolution[6] and sludge slurrying[7] dissolution of solids will form an aqueous phase which may result in a potentially corrosive condition.

The waste compositions exhibit variability from tank-to-tank, depending on the detailed history of transfers in and out of the tank. In addition to transfers, the waste ages over time and this results in changes in the chemical and radionuclide composition. The major changes are:

1. Radiolytic conversion of NO_3^- to NO_2^-
2. Absorption of CO_2 from air, converting $NaOH$ to Na_2CO_3
3. Evaporation of supernates
4. Separation of radionuclides into soluble and insoluble fractions
5. Decay of radionuclides

The first three changes occur in the supernate and are significant from a corrosion perspective. Nitrate is an aggressive species and promotes both stress-corrosion cracking and pitting corrosion in carbon steel. Nitrite on the other hand is a corrosion inhibitor. Thus, as the waste ages, the more aggressive component has been depleting, while the inhibitor species increases. Absorption of CO_2 from air, on the other hand results in depletion of hydroxide which acts as a corrosion inhibitor.[8] However, this inhibitor depletion mechanism can be managed by transfers from other tanks that contain higher hydroxide concentrations. Water is removed from the supernate as it is transferred through a continuous evaporator. The concentrate from the evaporator is transferred to a tank with cooling coils. In the tank, the salts crystallize and settle as the liquid cools. The remaining supernate is returned to the evaporator for further concentration. The process continues until the liquid has been converted to a damp salt cake that consists primarily of sodium nitrate crystals and a concentrated supernate. The supernate composition during evaporation changes because the ratio of hydroxide to nitrate increases due to the high solubility of sodium hydroxide. Thus, the supernate chemistry in tanks that receive evaporator concentrate becomes more benign towards the carbon steel as evaporation continues.

Concentration ranges of the major components in the current supernates are shown in Table 3. Studies have shown the measured chemistry within a given tank may show differences of 50 to 60 percent in the concentration of a chemical species.[9] These differences are attributed to the non-homogeneity of the waste and analytical error. Given this variability, the tanks are operated such that the inhibitor concentrations in the supernate are maintained 50 percent above the minimum levels required to inhibit corrosion.

Table 3. Molar (M) concentration ranges of major constituents in the waste supernate

Constituent	Concentration Range
Na+	< 0.5-15
NO3-	0.11-4.2
NO2-	0.09-3.2
Al(OH)4-	< 0.3-1.6
OH-	0.12-12.2
CO3=	< 0.1-0.45

Table 4. Environmental conditions during aluminum dissolution

Temperature	60-100°C
NaOH	3.0-8.0 M
$NaNO_3$	0.02-2.0 M
$NaNO_2$	0.005-0.5 M
$NaAlO_2$	0.0-1.0 M

The objective of waste processing is to prepare feed for the vitrification and grout facilities. During waste processing, the carbon steel tanks will be utilized to dissolve aluminum, wash sludge, or dissolve salt cake. The goal of the aluminum dissolution stage is to add sodium hydroxide until approximately 75 percent of the aluminum in the sludge is dissolved. The expected conditions during aluminum dissolution are shown in Table 4. If these solutions were pure NaOH at these molar concentrations, carbon steel may be susceptible to hydroxide stress-corrosion cracking.[10] However, laboratory testing has shown that at these conditions this mechanism is unlikely[11-13] because of the presence of other chemical species.

The objective of the sludge washing was to remove the soluble salts and Cs-137 from the sludge. The goal was to reduce the soluble salts to less than 2 percent of the sludge on a dry weight basis. This washing process is carried out in thirteen stages. The expected sludge supernate concentration at selected wash stages is shown in Table 5.[14] The steady state pH is the assumed pH in the wetted film region above the liquid/vapor interface, which can be an area where pitting initiates. At low pH values, carbon steel tanks become susceptible to pitting as the inhibitors are diluted or depleted. The ranges shown for the hydroxide and nitrite concentrations reflect decisions that are made by operations personnel on what would be the optimal inhibitor scheme based on downstream processes. The sodium nitrite concentration shown in the table is the minimum value at a temperature of 50°C. The solution is evaluated by mass balance or sampled at the end of each washing stage to determine if sufficient inhibitor is present to prevent pit initiation. If not, sodium nitrite is added to the solution to prevent pit initiation.

Temperature is also an important parameter affecting corrosion response. Due to fission products in the sludge layer, the temperature in the sludge is generally higher than in any other waste form. The maximum temperatures in the sludge for fresh waste, i.e., within the first two years, was typically between 100°C and 150°C. Temperature in the sludge region is maintained by auxiliary cooling coils, and in the case of the Type III tanks air-cooled slots beneath the tanks. Although, the auxiliary cooling does not preclude a local hot spot, a majority of the decay heat is removed. Temperatures in the sludge have decreased over the decades due to the decay-induced decrease of the radionuclides. Sludge temperatures are currently less than 60°C.

Corrosion Degradation Mechanisms

Corrosion of carbon steel in the waste environments occurs by three primary mechanisms: general, pitting, or stress-corrosion cracking (SCC). Details of the corrosion mechanism, the corrosion rate, and mitigating strategies are presented next.

General Corrosion

General corrosion or uniform corrosion refers to corrosion by an electrochemical reaction that proceeds uniformly over the entire exposed surface or over a large area. Although this is an active mechanism, it rarely leads to failure of industrial components. The literature indicates that at normal temperatures (72-104°F [22-40°C]) in the pH range 4.5 to 9.5 in nitrate-free solutions the tank steel will initially experience a uniform corrosion rate of 10 to 15 mils per year (mpy) near the surface of steel.[15-16] The surface of steel, in aqueous solutions such as these, is always in contact with an alkaline saturated solution of hydrous ferrous ox-

Table 5. Expected molar concentrations of sludge constituents at selected wash steps

Component	Unwashed Sludge	4th Wash Step	9th Wash Step	13th Wash Step
NaNO3	1.44	0.388	0.076	0.02
Na_2SO_4	0.095	0.026	0.005	0.0014
NaCl	0.022	0.0059	0.0012	0.00031
NaNO2	0.0-0.432	0-1.65	0.0-0.324	0.0-0.085
NaOH	0.144-0.576	0.0-1.0	0.0-1.0	0.0-1.0
Steady State pH	10.28	10.06	9.79	9.51

ide (pH = ~ 9.5), which significantly reduces the corrosion rate. Although the ferrous oxide (FeO) is porous in this pH range, further corrosion is limited by the rate at which oxygen can diffuse through the oxide layer.

Further increase in alkalinity to levels normally expected in the DSTs (pH = 11-13) makes the steel passive by decreasing the permeability of the corrosion product layer and also decreasing the surface reaction rate. These, in turn, will decrease the steel corrosion rate to very low levels (<<1 mpy). In nitrate containing solutions, such as those present in the DSTs, the main products formed by corrosion are magnetite (Fe_3O_4) and nitrite ions. The following reactions are expected for general corrosion:

The net anodic reaction at the metal/film interface is:

$$3/4\ Fe = 1/4\ Fe_{film}^{2+} + 1/2\ Fe_{film}^{3+} + 2\ e^- \qquad (1)$$

and the net cathodic reaction at the film/solution interface is:

$$NO_{3sol} + 2\ e = NO_2 + O_{film}^{2} \qquad (2)$$

The measurement methods routinely used for general corrosion are traditional weight loss technique using coupons immersed in simulated wastes in the laboratory or in-tank measurement with *in situ* coupons. The general corrosion rates can also be calculated from ultrasound thickness (UT) measurements. Although corrosion rates were calculated for the tanks on which the first set of UT thickness measurements were made, i.e., the Type I and II tanks, the calculated rates were not very accurate because there is no record of the starting thicknesses of the tank wall plates. However, the measurements showed that the wall thickness of the primary wall was typically at or greater than the nominal thickness after more than twenty years of service. Wall thickness measurements for the Type III tanks indicate that the general corrosion rate is less than 1 mpy after approximately thirty years of service.[17]

Pitting

Pitting is a localized form of corrosion that occurs on passivated metallic materials exposed to aggressive environments.[18] Pitting requires the breakdown of the passive film on the alloy and subsequent anodic dissolution of the metal. Once the pits are initiated, an aggressive environment quite different from the bulk solution may develop within the pit and rapid autocatalytic growth may occur.

Pitting is a broad identification typically described by the morphology of the pit. Fontana and Green[18] have described pitting as part of a continuum of corrosion appearances from broad and shallow to narrow and deep. Aspect ratios (width to depth) as high as six have been arbitrarily set for dividing pitting from localized general corrosion. Pits in iron and carbon steel tend to be of higher aspect ratios since they are not as strongly passivated as aluminum and stainless steels and ferrous ions do not hydrolyze as strongly as aluminum or chromium ions.

The net anodic reaction and the net cathodic reaction that occur during pitting of carbon steel in nitrate solutions have generally been accepted to be the following.

The net anodic reaction is:

$$3/4\ Fe + H_2O = 1/4\ Fe_3O_4 + 2\ H^+ + 2\ e^- \qquad (3)$$

and the net cathodic reaction is:

$$NO_3^- + H_2O + 2\ e^- = NO_2^- + 2\ OH^- \qquad (4)$$

On the basis of these reactions, if the anodic and cathodic areas of the surfaces are separated, for example, if the anode is the bottom of a pit and the cathode is the wall of the pit, the anode becomes more acidic and the cathode more basic. Once a pit begins to propagate, the conditions that develop are such that further pit growth is promoted, i.e., autocatalytic. The conditions within the pit become significantly different than those in the bulk solution.

Because of the uncertainties in predicting the growth rate of the deepest pits, pitting-control measures often depend upon the establishment of conditions under which pits do not initiate. Mitigating actions include inhibiting the bulk solution or selecting more resistant materials. Research efforts at SRS have focused on determining inhibitor levels that will prevent pit initiation since replacing million-gallon waste tanks is cost prohibitive.

Pitting is a viable corrosion mechanism in the regions of the tanks exposed to liquid and sludge if the wastes are deficient in inhibitors. Furthermore, if there is the possibility of condensation under conditions of inadequate ventilation flow and high humidity above the waste surface in the tank, pitting corrosion of the carbon steel primary wall in the dome space is a viable mechanism. The pit growth rates in the vapor space will be comparable to those recorded in the literature for atmospheric aqueous corrosion. [19]

Pitting corrosion is not expected in the liquid and sludge regions of the tank if the waste is compliant with the waste chemistry and temperature controls. Crevice/pitting attack of waste tank cooling coils from extremely diluted sludge washing solutions was observed at the SRS.[7] However, the SRS in-service inspection program indicates that no significant pitting attack of the tank walls has occurred. [19]

Stress-corrosion Cracking

Stress-corrosion cracking is an environmentally assisted cracking of engineering materials through crack initiation and propagation as a result of the combined and synergistic interaction of tensile stress and a corrosive environment.[20] The tensile stresses required to cause SCC are usually below the macroscopic yield stress. The stresses can be applied, but residual tensile stresses often provide the necessary stress component for SCC failures.

Corrosion reactions that occur during SCC of carbon steel in nitrate solutions are the same as those that occur during pitting. In the case of SCC, however, the anode is the tip of a crack and the cathode is the wall of the crack. Since the cathodic reaction takes place on the walls of the crack on the metal surface, and the anodic reaction takes place at the crack tip, the H^+ and the OH^- do not react. However, the crack tip may become acidic due to the hydrolysis of the ferrous ion by the following reaction:

$$Fe^{2+} + H_2O = Fe(OH)^+ + H^+ \qquad (5)$$

The acidic crack tip leads to a more anodic open circuit potential and stimulation of the cathodic reactions. This leads to more aggressive crack growth.

Cracks are initiated at carbon present in solid solution or as iron carbides (Fe_3C) at the grain boundaries. The carbon acts as an efficient cathode with the adjacent metal surface acting as the anode. Cracks propagate along the grain boundaries of a material as the tensile stress leads to opening the area that exposes the fresh metal surface to the aggressive solution. The corrosion rate is influenced by the nitrate reduction kinetics and diffusion of reactants to cathodic sites.[21] Nitrate is more easily reduced as the solution becomes more acidic. Work at the Naval Research Laboratory has shown that during cracking the solution at the crack tip has approximately a pH of 3 even when the bulk solution is highly basic.[22]

The propagation of nitrate stress-corrosion cracking in mild steel can be controlled by the anodic dissolution rate at the crack tip or the time necessary for the oxide film to rupture. The controlling mechanism was determined by measuring the activation energies for continuous crack growth (typical of anodic dissolution) and discontinuous crack growth (typical of oxide film rupture or crack growth by fracture). The activation energy for nitrate SCC is reported to be 27 kJ/mol for continuous crack growth as measured in wedge opening loaded (WOL) specimens, and 56 kJ/mol for discontinuous crack growth as measured with compact tension specimens (CT).[23] Typically, the initiation time for continuous crack growth can be controlled by the time it takes for formation of oxides along the grain boundaries, or for the crack tip chemistry to become aggressive. The activation energy for discontinuous crack growth is typical of oxygen diffusion in grain boundaries or the oxide-metal interface. Ultimately, the activation energies indicate that nitrate SCC is controlled by anodic dissolution in specimens with decreasing stress intensity, and by fracture of grain boundary oxide in specimens with increasing stress intensity.

The waste solutions contain anions which can both cause or inhibit SCC. Nitrate or hydroxide may initiate SCC, however, the presence of either will inhibit cracking by the other. Nitrite which is present in the waste will also inhibit SCC. [24] Electrochemical polarization studies were performed to determine if nitrate or hydroxide caused the stress-corrosion cracking observed in the tanks. The studies showed that carbon steels are susceptible to nitrate SCC in potential ranges between -0.3 to 1.1 V vs. SCE, while hydroxide SCC occurs at potentials between -0.8 V to -1.0 V vs. SCE. [25] Open circuit potential measurements were performed in several waste tanks and the potentials varied between -0.44 to -0.064 V. Thus, it is most likely that the nitrate ion was responsible for inducing the SCC in the SRS waste tanks.

Eleven tanks that were not stress-relieved developed through-wall cracks at the SRS. Small surface cracks were observed perpendicular to butt welds and extended through the heat-affected zone before stopping after short penetrations into the base metal.[26] No loss of containment has been observed in the newer stress-relieved tanks (i.e., Type III design). In addition, no cracks were observed in the Type III tanks examined recently by the in-service inspection program.[19]

Waste Chemistry and Temperature Controls

Waste chemistry control is one of the means by which corrosion degradation of the waste tanks is minimized at SRS. Chemistry controls are based on *in-situ* coupon tests, waste tank experience, and laboratory testing. Laboratory testing has had a significant role in determining corrosion mechanisms, identifying the aggressive species, and determining the inhibitor concentration and temperature requirements necessary to prevent corrosion. These requirements comprise the technical standards for corrosion control.[27] The standards are utilized then as guidelines for operational procedures.

Since the beginning of operations at SRS, chemistry controls have existed to minimize corrosion of the tanks. Initially, the controls consisted primarily of neutralizing the waste in the separations area by addition of sodium hydroxide prior to storage in the tanks and maintaining the temperature of the waste below the boiling point with the use of internal cooling coils.[28] In 1962, after cracks had been discovered in four of the tanks, corrosion standards for the waste stored in the tanks were developed.[28] The temperature limits were 55°C in the supernate and 150°C in the sludge. The minimum pH of the supernate was to be 8 while the maximum sodium hydroxide concentration in the waste stream sent to the tanks was to be 6 wt percent. The former restriction ensured that the waste was alkaline and the latter prevented excess sodium hydroxide which may lead to caustic stress-corrosion cracking. Finally the organic material content in the waste streams sent to the tanks was limited to 0.5 wt percent. Radiolytic decomposition of the organic material in the waste produces carbon dioxide which depletes the hydroxide and may result in localized regions where the tanks are uninhibited.

In the 1970s extensive experimental work was performed to develop inhibitor and temperature requirements which would prevent the initiation of nitrate-induced stress-corrosion cracking.[29] The main indicator used to determine the susceptibility of carbon steel to SCC was based on ductility (total elongation)

Table 6. Inhibitor requirements for corrosion control

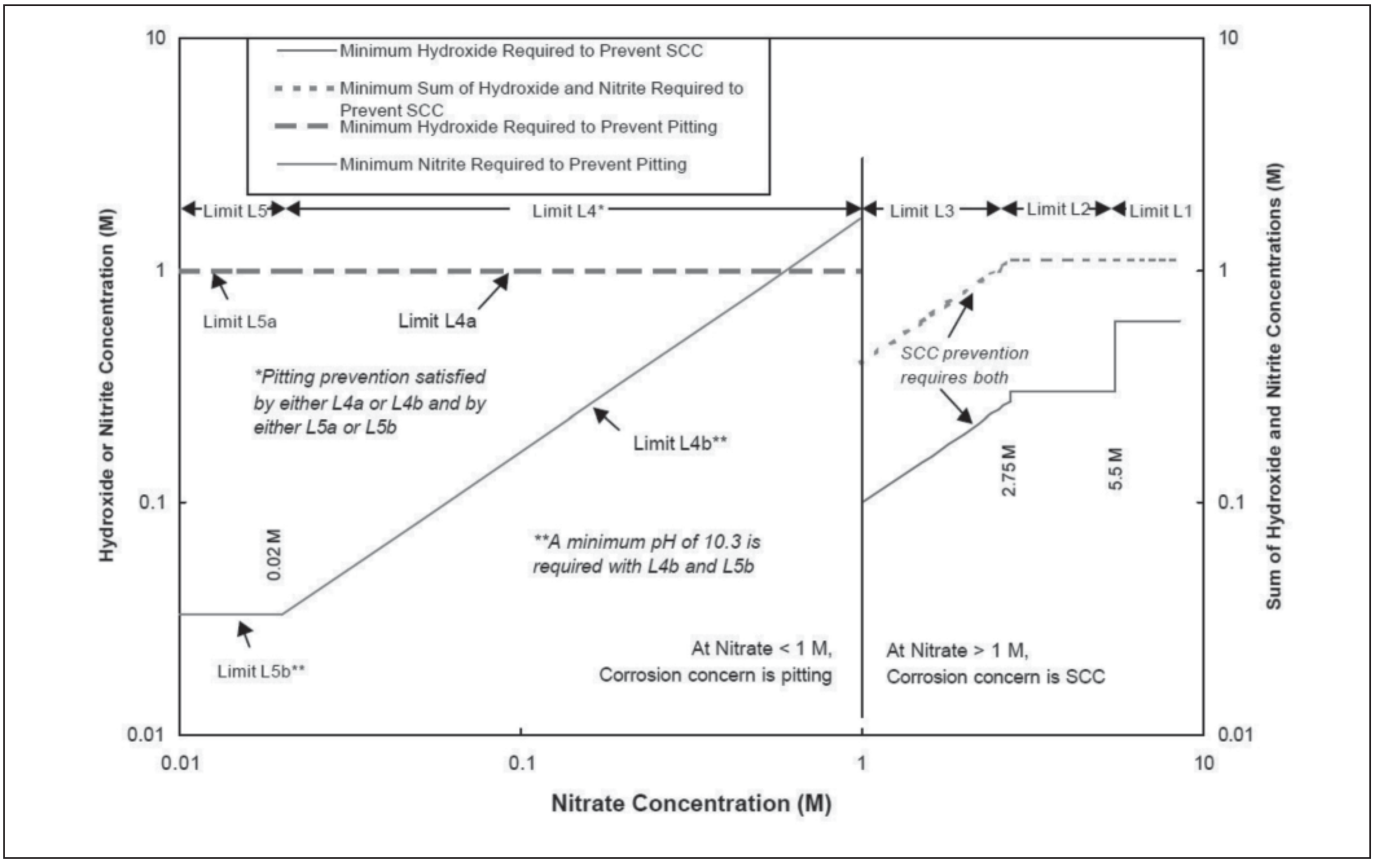
Applicability	Limit		Parameter	Minimum Needed	Units
5.5M < $[NO_3^-]$ ≤ 8.5M	1 $[OH^-]$ + $[NO_2^-]$		$[OH^-]$	0.6	Molar
			1.1	Molar	
2.75M < $[NO_3^-]$ ≤ 5.5M	2 $[OH^-]$ + $[NO_2^-]$		$[OH^-]$	0.3	Molar
			1.1	Molar	
1.0M ≤ $[NO_3^-]$ ≤ 2.75M	3 $[OH^-]$ + $[NO_2^-]$		$[OH^-]$	$0.1[NO_3^-]$	Molar
			$0.4[NO_3^-]$	Molar	
0.02M < $[NO_3^-]$ < 1.0M AND $[OH^-]$ < 1.0M	4	4a	$[OH^-]$	1.0	Molar
			OR		
		4b	$[NO_2^-]$	$0.038_*[NO_3^-]_*10^{1.64}$	Molar
		4c	AND $[NO_2^-]$	$6.11_*10^{[1.64+1.34*\log[Cl-]]}$	Molar
		4d	AND $[NO_2^-]$	$0.04_*10^{[1.64+0.84*\log[SO4-2]]}$	Molar
		4e	AND pH	10.3	pH
$[NO_3^-]$ ≤ 0.02 M AND $[OH^-]$ < 1.0 M	5	5a	$[OH^-]$	1.0	Molar
		5b	$[NO_2^-]$ (if $[Cl^-]$ & $[SO_4^{-2}]$ is not known)	0.033	Molar
		5c	$[NO_2^-]$	$0.038_*[NO_3^-]_*10^{1.64}$	Molar
		5d	AND $[NO_2^-]$	$6.11_*10^{[1.64+1.34*\log[Cl-]]}$	Molar
		5e	AND $[NO_2^-]$	$0.04_*10^{[1.64+0.84*\log[SO4-2]]}$	Molar
		5f	AND pH	10.3	pH
Influents to waste tanks from other areas on site			pH	9.5	pH

contour maps determined from slow strain rate tensile testing (SSRT). The 13 percent total elongation was chosen as a minimum for SCC occurrence because test samples always showed evidence of secondary cracking along the gage length if the ductility was at or below 13 percent total elongation. At greater elongations, such cracking was unusual and always minor. The contour maps were developed from the results of two statistically designed SSRT test series on ASTM 285-B carbon steel specimens exposed to various temperatures (122-212°F [50-100°C]) and molar concentrations of nitrate (1.5 to 5.5 M), nitrite (0 to 3.5 M), and hydroxide (0 to 5.0 M). The application of the ASTM A285-B elongation contour maps to the behavior of the ASTM A516 and A537 carbon steels of the four DSTs of interest is considered conservative because ASTM A285 steel appears to be more susceptible to SCC. The inhibitor levels for stored wastes were a function of the nitrate concentration in the supernate. The maximum allowable temperatures were the boiling point for concentrated and aged wastes and 70°C for fresh wastes received recently from the separations facility. These requirements went into effect in 1977.

In the early 1980s during salt removal operations, new operating conditions were experienced. Higher nitrate concentrations occurred in the re-dissolved salt solution than had been experienced during waste storage. Experimental work determined the maximum temperature (70°C) and the inhibitor requirements for these higher nitrate concentrations.[30] Revisions to the technical standards were made in 1984 to accommodate these results.

In the middle to late 1980s, with the prospect of future waste processing operations, nitrate induced pitting in dilute wastes became a concern. Experimental work was performed to determine the required inhibitor levels for waste processing.[31] In summary, if the hydroxide concentration is greater than 1 M, pits will not initiate. However, if the hydroxide concentration is less than 1 M, sodium nitrite is utilized to prevent pit initiation. The amount of sodium nitrite necessary depends on the nitrate concentration and the temperature of the waste. The wastes from the two processes also require different nitrite inhibitor levels due to differ-

Figure 4. Corrosion control limits as a function of nitrate concentration



ences in the waste. The corrosion controls were revised in 1992 to reflect these results.

The inhibitor concentration limits are organized and listed in Table 6 by nitrate concentration range. The hydroxide and nitrite concentration limits address nitrate-induced corrosion in the concentration range 0.02 M to 8.5 M nitrate in five steps, labeled L1 to L5, as shown in Figure 4. Limits L1, L2, and L3 cover the range 1 M to 8.5 M and specify the minimum hydroxide concentration and the minimum sum of the hydroxide and nitrite concentrations that are required to prevent SCC. Limits L4 and L5 cover nitrate concentrations below 1 M and specifically address pitting corrosion.

Limit L1: 5.5 M < [NO3-] ≤ 8.5 M

Limit L1 defines inhibitor requirements to prevent SCC and is based upon experimental results of crack propagation tests with wedge-opening-loaded (WOL) specimens of A285 Grade B carbon steel in the temperature range of 35°C to 75°C and the nitrate concentration range 5.5 to 8.5 M.[30] The dependent variable in these tests was the presence or absence of growth of a pre-formed crack after the immersion of the specimen in the test environment. The results were statistically analyzed to produce a plot of the probability of crack growth as a function of the hydroxide and nitrite concentrations. The probability of crack growth was found to be independent of the temperature and the nitrate concentration over the range studied. Figure 5 shows the graph of the probability of crack growth, from 0 to 1, at the given nitrite

Figure 5. Probability of crack growth as a function of nitrite and hydroxide concentration[30]

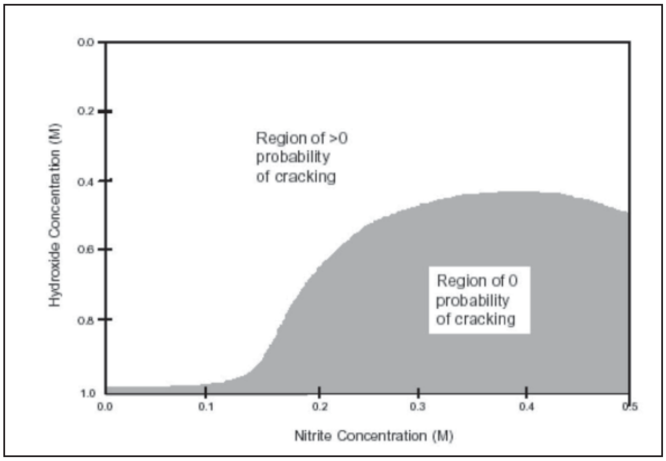
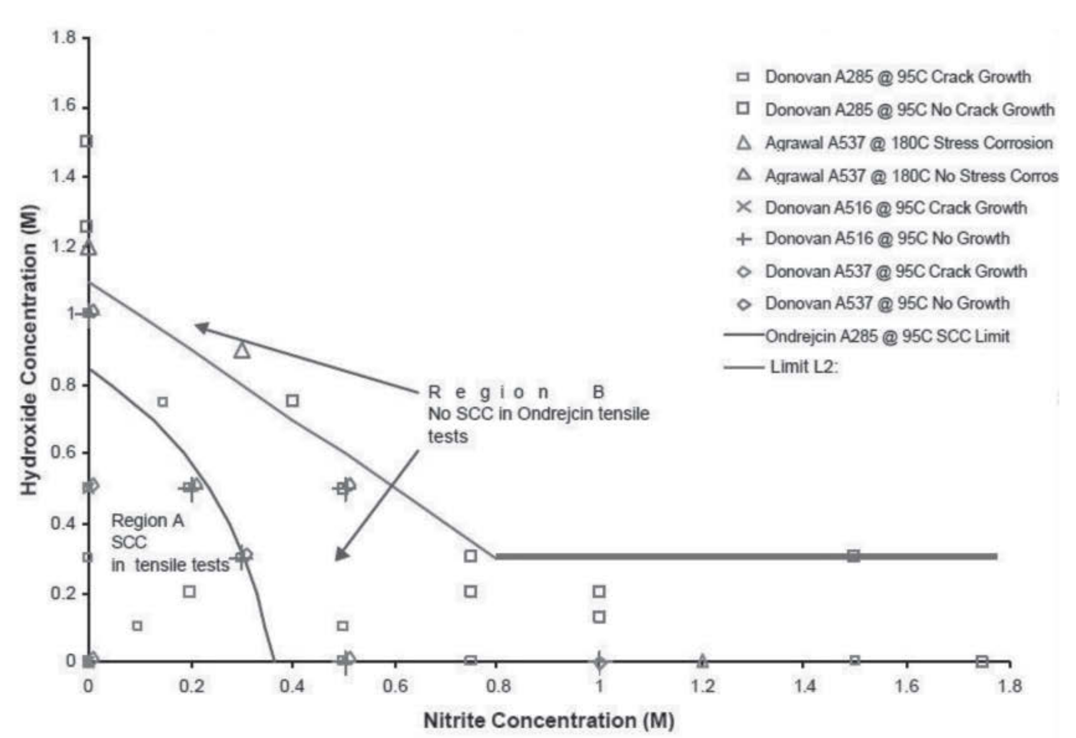


Figure 6: Corrosion control limit L2 with supporting SCC data for ASTM A285, A516, A537 steels in 5M sodium nitrate[32-34]



and hydroxide concentrations. The region of zero-probability of crack growth in the lower right portion of the graph is the desired operating region, and it is conservatively bounded by a minimum of 0.6 M hydroxide and a minimum of 0.2 M nitrite. Increasing the hydroxide concentration above 0.6 M allows the decreasing of the nitrite concentration while maintaining zero-probability, such that a minimum hydroxide and nitrite concentration sum of 1.1 M is specified, as shown in Table 6 and Figure 4. A maximum temperature of 70°C is applied to Limit L1.

Limit L2: 2.75 M < [NO3-] ≤ 5.5M

Limit L2 also specifies the nitrate concentration ranges encountered in on-going waste receipt, storage, and evaporation operations. Wastes subject to L2 are typically those that are aged or partially evaporated. The primary corrosion mechanism identified in this chemistry range is nitrate-induced SCC. Pitting has not been observed in wastes containing > 1 M nitrate, because these wastes contain high hydroxide concentrations, which prevent this form of localized corrosion.

Limit L2 identifies the inhibitor requirements to prevent SCC and specifies a minimum hydroxide concentration of 0.3 M along with a minimum sum of the hydroxide and nitrite concentrations of 1.1 M for nitrate in the range 2.75 to 5.5 M. Limit L2 is based on the results of SSRT test in the range 1.5 to 5.5 M nitrate and on WOL tests at 5 M nitrate, both on A285 Grade B carbon steel.[29] Figure 6 shows WOL data points, representing the presence or absence of crack growth from A285 tests, along with supporting data from newer waste tank steels A516 and A537 used in the SRS Type III and IIIA tanks and data from a Battelle Columbus Laboratories study.[32-34] Figure 6 also shows a curve representing the hydroxide and nitrite concentrations that satisfy the criterion for the onset of SCC, as determined by SSRT tests. The SSRT tests were concluded to reveal the presence of stress-corrosion cracking when the specimen's total elongation to failure fell below 13 percent. The elongation to failure was modeled as a second-order polynomial in the nitrate, nitrite, and hydroxide concentrations and the temperature. Figure 6 also shows the combinations of hydroxide and nitrite concentrations that solve this polynomial at 95°C at 13 percent elongation (i.e., region A). Limit L2 carries a maximum temperature of 105°C, or 112°C if the sum of hydroxide and nitrite concentrations exceeds twice the nitrate concentration.

Limit L3: 1 M < [NO3-] ≤ 2.75 M

Limit L3 addresses the nitrate range that is typical of fresh waste, historically received from nuclear reprocessing operations at SRS. The limit is specified to prevent nitrate-induced SCC. The Limit L3 is based on an engineering judgment, historical experience of waste tank corrosion prevention, and the previously mentioned SSRT test data. A minimum hydroxide concentration of 0.1 M was conservatively selected to maintain inhibiting conditions in 1 M nitrate waste solutions. The minimum hydroxide concentra-

Figure 8: Corrosion control limits L4b and L5b with supporting data at 40°C[31]

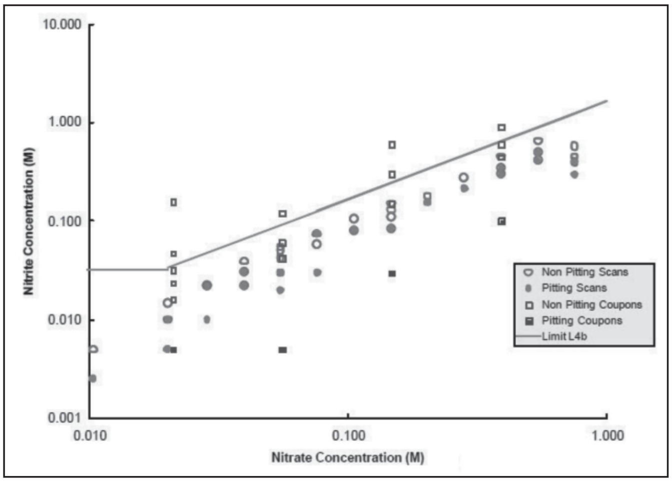
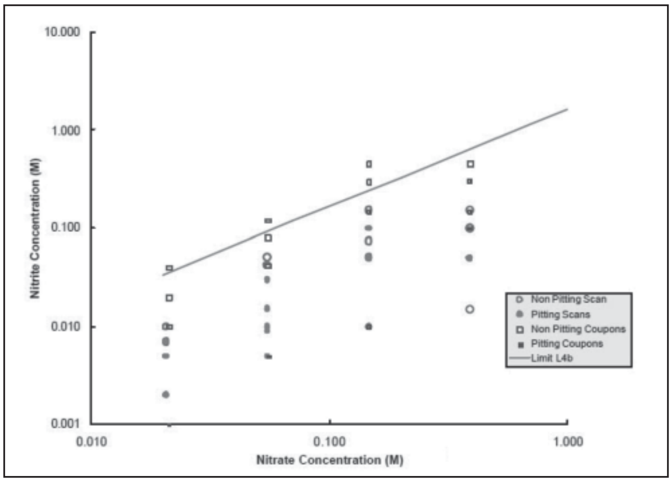


Figure 9: Corrosion control limits L4b and L5b with supporting data at 30°C[31]



tion and the minimum sum of hydroxide and nitrite in L3 over the range 1 M nitrate to 2.75 M nitrate were selected to transition smoothly to the L2 limit at 2.75 M nitrate (see Figure 4). Limit L3 carries a maximum temperature of 70ºC, or 105ºC if the sum of hydroxide and nitrite concentrations exceeds twice the nitrate concentration.

Limit L4: 0.02 M < [NO3-] < 1.0 M and Limit L5: [NO3-] < 0.02 M

Limits L4 and L5 apply to dilute waste solutions, i.e. solutions with a nitrate concentration < 1 M, where nitrate-induced pitting, chloride-induced pitting, and sulfate-induced pitting are the corrosion mechanisms of concern. Pitting has not been observed in wastes containing > 1 M nitrate because these wastes contain high hydroxide concentrations, which prevent this form of localized corrosion. SCC is not a concern in waste solutions with < 1 M nitrate, based on the historical experience of SRS waste tanks. Tanks subject to the L4 and L5 limits are those that prepare waste for transfer to the waste vitrification facility and those that store dilute low-heat wastes. Pitting may be prevented by either a minimum hydroxide concentration or by a minimum nitrite concentration along with a minimum pH. Limit L4a specifies the minimum hydroxide concentration of 1 M and is based on the historical experience of the absence of pitting for hydroxide concentrations greater than 1 M. Limit L4b specifies the minimum nitrite concentration required to prevent pitting over the 0.02 to 1 M nitrate concentration range at 40°C. Limit L4 is based on the results of electrochemical polarization scans and coupon immersion test.[31] A least squares fit of the relevant nitrate concentration and test temperature to the minimum nitrite concentration established by the polarization scans at temperatures of 23, 30, 40, 50, and 60°C forms the basis. Figure 8 and Figure 9 show the data at 40ºC and 30ºC with the L4b limit. Limit L4b incorporates a safety factor of 1.5 on the required nitrite concentration that was selected based on engineering judgment. Nitrite inhibition is allowed by Limit L4b (and L5b) only up to 40°C; higher temperatures require the application of L4a (and L5a), to which a maximum temperature of 100°C applies. The addition of the L5 limits sets a lower bound on the required nitrite concentration independent of the nitrate concentration. Limits L4 and L5 also contain experimentally determined minimum nitrite limits for chloride and sulfate containing solutions, which are also known to be able to induce pitting in carbon steel.[35] In the event that the nitrate anion is in low concentration and is not the principal corrosive anion, minimum nitrite levels can be calculated based upon the chloride or sulfate concentrations. The greatest nitrite concentration based on nitrate, chloride, or sulfate becomes the controlling limit.

Waste Chemistry Monitoring

Samples of the waste supernate are removed on a periodic basis to ensure that the waste chemistry control limits are not being exceeded. The frequency of sampling depends on the function of the tank and the activity level in the tank. Active tanks receive inter-tank transfers on an annual frequency at a minimum, while inactive tanks have not received a transfer in more than a year. The sample frequencies in Table 7 are set based on a statistical analysis of the historical corrosion chemistry sample data of the tanks in each category[36] and on an understanding of mechanisms that may change the concentrations of either aggressive or inhibitor species, e.g., hydroxide depletion.[8]

Active Tanks

Evaporator Feed and Drop Tanks

The sample frequency for active evaporator feed and drop tanks does not exceed 180 days. The relatively frequent transfers into these tanks from several different sources (canyons, DWPF, etc.)

Table 7. Sampling frequency for waste tank chemistry monitoring

Status	Category	Inhibitor Levels (S = $[OH^-] + [NO_2^-]$)	Frequency
ACTIVE WASTE TANKS	Evaporator Feed and Drop Tanks	$[NO_3^-] < 1M$ or $[OH^-] < 2.35M$ or $[S] < 3M$	90 days
		$[NO_3^-] \geq 1M$ or $[OH^-] \geq 2.35M$ or $[S] \geq 3M$	180 days
	Fresh Canyon Waste Receiver with Nitrate Concentration Greater Than or Equal to 1M	$[OH^-] < 3M$ or $[S] < 4M$	180 days
		$[OH^-] \geq 3M$ or $[S] \geq 4M$	365 days
	Receiver with Nitrate Concentration Less Than 1M	$[NO2^-]/[NO3^-] < 3.4$ or $[OH^-] < 0.02M$	90 days
		$3.4 \leq [NO2^-]/[NO3^-] < 4.8$ and $0.02M \leq [OH^-] < 2.35M$	180 days
		$[NO2^-]/[NO3^-] \geq 4.8$ or $[OH^-] \geq 2.35M$	365 days
	Receiver with Nitrate Concentration Greater Than or Equal to 1M	$[OH^-] < 2.35M$ or $[S] < 3M$	180 days
		$2.35M \leq [OH^-] < 3M$ and $3M \leq [S] < 4M$	365 days
		$[OH^-] \geq 3M$ or $[S] \geq 4M$	730 days
INACTIVE WASTE TANKS	Nitrate Concentration Less Than 1M	$[NO_2^-]/[NO_3^-] < 3.4$ or $[OH^-] < 0.02M$	180 days
		$3.4 \leq [NO_2^-]/[NO_3^-] < 4.8$ and $0.02M \leq [OH^-] < 2.35M$	365 days
		$[NO_2^-]/[NO_3^-] \geq 4.8$ or $[OH^-] \geq 2.35M$	730 days
	Nitrate Concentration Greater Than or Equal to 1M	$[OH^-] < 2.35M$ or $[S] < 3M$	365 days
		$2.35M \leq [OH^-] < 3M$ and $3M \leq [S] < 4M$	730 days
		$[OH^-] \geq 3M$ or $[S] \geq 4M$	1460 days

may result in significant changes in the solution chemistry that need to be trended to assure corrosion control is maintained. Models for hydroxide depletion indicate that for dilute solutions (i.e., nitrate concentration is less than 1 molar) the hydroxide concentration can deplete to the steady state pH level of 9.5-10.3 within 3 to 180 days.[8] Therefore tanks with these composition ranges shall be sampled every 90 days. Models for hydroxide depletion in tanks with concentrated wastes at high hydroxide concentrations (nitrate greater than 1 molar and hydroxide greater than or equal to 2.35 molar) indicate that changes to the hydroxide concentration will take more than five years to attain the steady state pH level.[8] Therefore a 180-day sample frequency that will monitor changes in the chemistry due to waste transfers will be sufficient for the more concentrated wastes.

Fresh Canyon Waste Receiver with Nitrate Concentration Greater Than or Equal to 1 Molar

Fresh canyon waste receivers are considered to be special case waste receivers. Previous service history show that these tanks, in addition to having relatively lower inhibitor concentrations compared to other waste receivers, also historically have higher temperatures. The higher temperatures result in a greater susceptibility to corrosion degradation mechanisms. Therefore, the sample frequency shall not exceed 365 days. If the hydroxide concentration is less than 3 M, or the total inhibitor concentration is less than 4 M, the tanks will be sampled on a 180-day frequency.

Receivers with Nitrate Concentration Less Than 1 Molar

The ratio of the concentration of nitrate to nitrite typically determines whether dilute wastes are within corrosion chemistry limits. The hydroxide depletion models were reviewed to confirm that these frequencies were adequate. If the hydroxide concentration is less than 2.35 M, depletion models indicate that the steady state pH may be attained within a year.[8] Therefore the 90- and 180-day frequencies are justified. On the other hand, if the hydroxide concentration was greater than 2.35 M, it will take more than five years to attain the steady state pH. Therefore, the 365-day frequency is justified.

Dilute wastes may also be inhibited with 1 molar sodium hydroxide as shown in Table 6. An exception to these frequencies may occur at very dilute solutions (i.e., nitrate concentrations on the order of 0.01 M). If the chloride or sulfate becomes the aggressive species rather than nitrate, the sample frequency will be 90 days because the lower pH of the dilute wastes (~pH 10). The equations for the minimum nitrite calculations are shown in Table 6. The nitrate will be the most aggressive species except in some rare cases of dilute waste where chloride or sulfate may become the most aggressive species.[35]

Receivers with Nitrate Concentration Greater Than or Equal to 1 Molar

Inhibition of concentrated wastes (nitrate greater than or equal to 1 M) is achieved with a minimum hydroxide concentration and the combination of hydroxide and nitrite concentrations (see Table 6). Statistical analysis of the sample data was utilized to determine the frequencies based on the risk of being outside the corrosion chemistry controls.[36] The hydroxide depletion models were reviewed to confirm that these frequencies were adequate. If the hydroxide concentration is less than 2.35 M, depletion models suggest that the steady state pH may be attained within a year. Therefore 180 days is an adequate sample frequency. For hydroxide concentrations greater than or equal to 2.35 M, the steady state pH level will not be attained for more than five years.[8] Therefore these tanks may be sampled on a 365-day or 730-day basis as determined by Table 7.

Inactive Tanks

Receivers with Nitrate Concentration Less Than 1 Molar

Inactive tanks have not received any transfers for more than 365 days. Thus any change in the supernate chemistry would be due to hydroxide depletion. The ratio of the concentration of nitrate to nitrite typically determines whether dilute wastes are within corrosion chemistry limits. The statistical analysis of the historical sample data was utilized to establish the frequencies shown in Table 7. The hydroxide depletion models were reviewed to confirm that these frequencies were adequate. If the hydroxide concentration is less than 2.35 M, depletion models indicate that the steady state pH may be attained within a year.[8] Given that there are no transfers into the tank within a year, the 180- and 365-day frequencies are justified. On the other hand, if the hydroxide concentration was greater than 2.35 M, it will take more than five years to attain the steady state pH. Therefore, the 730-day frequency is justified. Dilute wastes may also be inhibited with 1 molar sodium hydroxide per Table 6. An exception to these frequencies may occur at very dilute solutions (i.e., nitrate concentrations on the order of 0.01 M) where chloride or sulfate may become the primary aggressive species. If the chloride or sulfate species becomes the aggressive species rather than the nitrate, the sample frequency will be 90 days.

Receivers with Nitrate Concentration Greater Than or Equal to 1 Molar

Inactive tanks have not received any transfers for more than 365 days. Thus any change in the supernate chemistry would be due to hydroxide depletion. Inhibition of concentrated wastes (nitrate greater than or equal to 1 molar) is achieved with a minimum hydroxide concentration and the combination of hydroxide and nitrite concentrations (see Table 6).

Statistical analysis of the sample data was utilized to determine the frequencies based on the risk of being outside the corrosion chemistry controls.[36] The hydroxide depletion models were reviewed to confirm that these frequencies were adequate. If the hydroxide concentration is less than 2.35 M, depletion models suggest that the steady state pH may be attained within a year. Given that there have not been any transfers into this tank for over a year, 365 Days is an adequate sample frequency. For hydroxide concentrations greater than or equal to 2.35 M the steady state pH level will not be attained for more than five years.[8] Therefore these tanks are sampled on a 730- or 1,460-day basis.

Summary

Liquid radioactive waste has been stored in large, underground, carbon steel tanks for approximately sixty years at the Savannah River Site. Effective utilization of chemistry and temperature controls has been used to mitigate localized corrosion due to the presence of the aggressive nitrate, chloride, or sulfate species. These chemistry and temperature controls are based on decades of research at the Savannah River National Laboratory and have been verified by no loss of containment from tanks that have been managed by these controls for their entire service life. The facility continues to verify the effectiveness of these controls via waste sampling, temperature monitoring and ultrasonic inspections.

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Radioactive High-level Waste Tank Pitting Predictions: An Investigation into Critical Solution Concentrations

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Abstract

A series of cyclic potentiodynamic polarization tests was performed on samples of ASTM A537 carbon steel in support of a probability-based approach to evaluate the effect of chloride and sulfate on the steel's susceptibility to pitting corrosion. Testing solutions were chosen to systemically evaluate the influence of the secondary aggressive species, chloride, and sulfate, in the nitrate based, high-level wastes. The results suggest that evaluating the combined effect of all aggressive species, nitrate, chloride, and sulfate, provides a consistent response for determining corrosion susceptibility. The results of this work emphasize the importance for not only nitrate concentration limits, but also chloride and sulfate concentration limits.

Introduction

Underground carbon steel tanks are located at the Savannah River Site (SRS) to store radioactive liquid waste. A waste tank chemistry control program, with the goal of reducing the susceptibility of the tank wall to pitting corrosion, has thus far been implemented, in part, by applying engineering judgment safety factors to experimental data.[1] It is proposed that a probability-based approach can be used to quantify the risk associated with the chemistry control program.[2-5] This approach can lead to the application of tank-specific chemistry control programs reducing overall costs associated with the overly conservative use of inhibitor. Furthermore, when using nitrite as an inhibitor, the amount of inhibitor required by the current chemistry control program is based on a linear model of a log scale relationship between aggressive and protective species. Primarily supported by experimental data obtained from dilute solutions with nitrate concentrations less than 0.4 M, this linear model was used to produce the current chemistry control program at 1.0 M nitrate or less. Based on the current chemistry control program, the minimum molar concentrations of nitrite species required to prevent pitting in the 0.02 to 1.00 M nitrate concentration range at T ≤ 40°C depends on the concentration of chloride and sulfate and are:

$$[NO_2^-] = 1.66 \text{ x } [NO_3^-]$$
$$[NO_2^-] = 6.11 \text{ x } 10^{[1.64+1.34 \text{ x } \log[Cl^-]]}$$
$$[NO_2^-] = 0.04 \text{ x } 10^{[1.64+0.84 \text{ x } \log[SO_4 2^-]]}$$

The control program limits are based on the results of electrochemical polarization scans and coupon immersion tests.

Studies were conducted to evaluate the corrosion controls at the SRS tank farm and to assess the minimum nitrite concentrations to inhibit pitting in ASTM A537 carbon steel when the nitrate concentration is below 1.0 M.

A summary of the combined results that illustrate the potential importance of chloride and sulfate ions as well as the nitrite content in the high-level waste is shown in Figure 1. While areas of corrosion (solid symbols) and no corrosion (open symbols) are evident, significant areas of the graph are ambiguous, having both corrosion and no corrosion results.

Logistical regression was utilized to design a statistically based experimental matrix to develop a tool for predicting corrosion vulnerability and realistically determining the required inhibitor concentrations as a function of aggressive ion content. This paper presents the experimental program, provides the test results, and develops the data/analyses to show how chloride and sulfate concentrations should be included in the waste tank chemistry control program to minimize both the susceptibility to corrosion and the addition of nitrite to inhibit the waste solution. The data package is included in the paper to provide the reader the opportunity to further evaluate the assessments.

Figure 1. Optical results of electrochemical testing

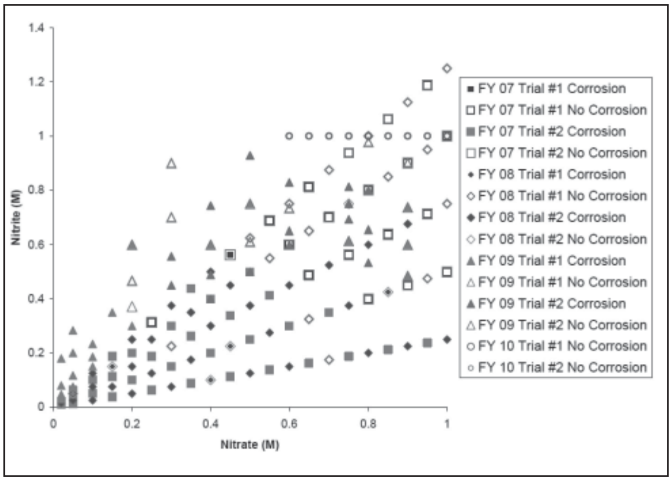


Table 1. Test matrix #1. Each testing solution was run in duplicate totaling twenty tests

Test #	Nitrate (M)	Nitrite (M)	Chloride (M)	Sulfate (M)	Tank 51 Washing Cycle Basis
1	0.2	0.5	0.002	0.025	After Decant G
2	0.2	0.6	0.002	0.025	After Decant G
3	0.4	0.5	0.005	0.055	After Decant D
4	0.4	0.6	0.005	0.055	After Decant D
5	0.4	0.75	0.005	0.055	After Decant D
6	0.6	0.6	0.025	0.09	After Decant C
7	0.6	0.75	0.025	0.09	After Decant C
8	0.8	0.5	0.032	0.121	After Decant B
9	0.8	0.6	0.032	0.121	After Decant B
10	0.8	0.75	0.032	0.121	After Decant B

Experimental Method

Cyclic potentiodynamic polarization (CPP) scans have been performed routinely to experimentally determine the pitting propensity of various alloys exposed to aqueous environments. The CPP technique qualitatively evaluates the pitting propensity based on a slow linear sweep of the electrochemical potential of a metal. Potential scans are applied beginning slightly below the corrosion potential, E_{corr}, and continuing in the positive direction at a constant rate. The current is recorded during the voltage scan to measure the corrosion rate at each potential. After the scan reaches a set potential value, the applied potential is scanned back to the corrosion potential. The scan is analyzed to determine pitting and crevice corrosion susceptibility of the alloy. Significant hysteresis in the potential vs current plots with higher currents generated on the reverse scan (positive hysteresis) provide an indication of pit formation. The scan results are also used to characterize the stability of the surface oxide and to determine the effectiveness of inhibitors.

Materials

Material

Semi-killed, hot-rolled ASTM A537 Class I carbon steel was used for experimentation. The nominal chemical composition for the alloy is 0.24 wt percent C, 0.7-1.60 wt percent Mn, 0.040 wt percent S. 0.035 wt percent P, and 0.15-0.5 wt percent Si with small amounts of Cu, Cr, and Ni, and the balance being Fe. The electrochemical tests were conducted on disc samples of A537 that were nominally 5/8 inches diameter (Metal Samples, Munford, Al). Samples were ground using 600 grit SiC grinding sheets to remove the native oxide layer and provide a flat surface.

Simulated Tank Solutions

The aqueous phase of the liquid radioactive waste stored in the SRS Waste Tanks is a complex solution containing numerous ionic species. Corrosive nitrate anions are in relatively high concentration. Other corrosive ions, chloride and sulfate, are present in relatively low concentrations. Protective, corrosion inhibiting anions in the solution are predominantly nitrite and hydroxide. Protective anions such as phosphate, chromate, and molybdate are also present, but have relatively low concentrations compared to nitrite. Corrosion testing experience in Savannah River National Laboratory (SRNL) has shown that non-radioactive laboratory simulants of waste yield similar results to those of actual waste solutions.[1] Non-radioactive laboratory test solutions were used as cost-effective simulant high-level waste solutions.

A simplified non-radioactive simulant of waste was chosen for the testing reported here. The major constituents were nitrate, nitrite, bicarbonate, carbonate, chloride and sulfate. Sodium nitrate and sodium nitrite were varied based on statistical modeling values with sodium nitrite at deliberately high molar concentrations, as shown in Table 1. The chloride and sulfate limits were chosen based on SRS Waste Tank 51 washing cycles, which contains waste that consistently crosses the 1.0 M nitrate, rather than using the maximum chemistry control limits.

A second matrix, Table 2, was designed to test a series of molar concentration ratios, or mixtures, of NO_2^- and NO_3^- as well as a series of total concentrations, or amounts, of NO_2^- and NO_3^-. The testing is a systematic evaluation of Cl^- and SO_4^{2-} on the minimum NO_2^- required to inhibit pitting. The test matrix focuses on the solution concentration space below the maximum critical ratios of 0.3 and 0.03 for SO_4^{2-}/NO_3^- and Cl^-/NO_3^-, respectively. The concentrations of NO_3^-, NO_2^-, Cl^- and SO_4^{2-} tested are listed in Table 2, as well as the corresponding sums and ratios used to arrive at the prescribed concentrations. Ratios of Cl^-/NO_3^- and SO_4^{2-}/NO_3^- were chosen based off of recommended concentration limits for chloride and sulfates. The ratios of NO_2^-/NO_3^- were chosen to explore the transition region between pitting to no pitting that was determined based off of previous testing. The molar concentrations of Cl^- and SO_4^{2-} (as well as the ratio to the NO_3^- at NO_3^- concentrations of 0.0125 and 0.150 M, respectively) were chosen based on Tank 51 Decants D-I from

Table 2. Test matrix #2. Each testing solution was run in duplicate totaling 208 tests

Test	NO2/NO3 (M)	NO2+NO3 (M)	Cl/NO3 (M)	SO4/NO3 (M)	NO3 (M)	NO2 (M)	Cl (M)	SO4 (M)
1	0.50	0.15	0.0050	0.15	0.10	0.05	0.00050	0.01500
2	0.50	0.38	0.0050	0.15	0.25	0.13	0.00125	0.03750
3	0.50	0.60	0.0050	0.15	0.40	0.20	0.00200	0.06000
4	0.50	0.83	0.0050	0.15	0.55	0.28	0.00275	0.08250
5	0.50	1.05	0.0050	0.15	0.70	0.35	0.00350	0.10500
6	0.50	1.28	0.0050	0.15	0.85	0.43	0.00425	0.12750
7	0.50	1.50	0.0050	0.15	1.00	0.50	0.00500	0.15000
8	0.50	1.80	0.0050	0.15	1.20	0.60	0.00600	0.18000
9	1.00	0.20	0.0050	0.15	0.10	0.10	0.00050	0.01500
10	1.00	0.50	0.0050	0.15	0.25	0.25	0.00125	0.03750
11	1.00	0.80	0.0050	0.15	0.40	0.40	0.00200	0.06000
12	1.00	1.10	0.0050	0.15	0.55	0.55	0.00275	0.08250
13	1.00	1.40	0.0050	0.15	0.70	0.70	0.00350	0.10500
14	1.00	1.70	0.0050	0.15	0.85	0.85	0.00425	0.12750
15	1.00	2.00	0.0050	0.15	1.00	1.00	0.00500	0.15000
16	1.00	2.40	0.0050	0.15	1.20	1.20	0.00600	0.18000
17	1.50	0.25	0.0050	0.15	0.10	0.15	0.00050	0.01500
18	1.50	0.63	0.0050	0.15	0.25	0.38	0.00125	0.03750
19	1.50	1.00	0.0050	0.15	0.40	0.60	0.00200	0.06000
20	1.50	1.38	0.0050	0.15	0.55	0.83	0.00275	0.08250
21	1.50	1.75	0.0050	0.15	0.70	1.05	0.00350	0.10500
22	1.50	2.13	0.0050	0.15	0.85	1.28	0.00425	0.12750
23	1.50	2.50	0.0050	0.15	1.00	1.50	0.00500	0.1500
24	1.50	3.00	0.0050	0.15	1.20	1.80	0.00600	0.1800
25	0.50	0.15	0.0700	0.15	0.10	0.05	0.00700	0.0150
26	0.50	0.38	0.0700	0.15	0.25	0.13	0.01750	0.0375
27	0.50	0.60	0.0700	0.15	0.40	0.20	0.02800	0.0600
28	0.50	0.83	0.0700	0.15	0.55	0.28	0.03850	0.0825
29	0.50	1.05	0.0700	0.15	0.70	0.35	0.04900	0.1050
30	0.50	1.28	0.0700	0.15	0.85	0.43	0.05950	0.1275
31	0.50	1.50	0.0700	0.15	1.00	0.50	0.07000	0.1500
32	0.50	1.80	0.0700	0.15	1.20	0.60	0.08400	0.1800
33	1.00	0.20	0.0700	0.15	0.10	0.10	0.00700	0.0150
34	1.00	0.50	0.0700	0.15	0.25	0.25	0.01750	0.0375
35	1.00	0.80	0.0700	0.15	0.40	0.40	0.02800	0.0600
36	1.00	1.10	0.0700	0.15	0.55	0.55	0.03850	0.0825
37	1.00	1.40	0.0700	0.15	0.70	0.70	0.04900	0.1050
38	1.00	1.70	0.0700	0.15	0.85	0.85	0.05950	0.1275
39	1.00	2.00	0.0700	0.15	1.00	1.00	0.07000	0.1500
40	1.00	2.40	0.0700	0.15	1.20	1.20	0.08400	0.1800
41	1.50	0.25	0.0700	0.15	0.10	0.15	0.00700	0.0150
42	1.50	0.63	0.0700	0.15	0.25	0.38	0.01750	0.0375
43	1.50	1.00	0.0700	0.15	0.40	0.60	0.02800	0.0600
44	1.50	1.38	0.0700	0.15	0.55	0.83	0.03850	0.0825

Table 2. (cont.) Test matrix #2. Each testing solution was run in duplicate totaling 208 tests

Test	NO2/NO3 (M)	NO2+NO3 (M)	Cl/NO3 (M)	SO4/NO3 (M)	NO3 (M)	NO2 (M)	Cl (M)	SO4 (M)
45	1.50	1.75	0.0700	0.15	0.70	1.05	0.04900	0.1050
46	1.50	2.13	0.0700	0.15	0.85	1.28	0.05950	0.1275
47	1.50	2.50	0.0700	0.15	1.00	1.50	0.07000	0.1500
48	1.50	3.00	0.0700	0.15	1.20	1.80	0.08400	0.1800
49	0.50	0.15	0.0125	0.05	0.10	0.05	0.00125	0.0050
50	0.50	0.38	0.0125	0.05	0.25	0.13	0.00313	0.0125
51	0.50	0.60	0.0125	0.05	0.40	0.20	0.0050	0.0200
52	0.50	0.83	0.0125	0.05	0.55	0.28	0.00688	0.0275
53	0.50	1.05	0.0125	0.05	0.70	0.35	0.00875	0.0350
54	0.50	1.28	0.0125	0.05	0.85	0.43	0.01063	0.0425
55	0.50	1.50	0.0125	0.05	1.00	0.50	0.01250	0.0500
56	0.50	1.80	0.0125	0.05	1.20	0.60	0.01500	0.0600
57	1.00	0.20	0.0125	0.05	0.10	0.10	0.00125	0.0050
58	1.00	0.50	0.0125	0.05	0.25	0.25	0.00313	0.0125
59	1.00	0.80	0.0125	0.05	0.40	0.40	0.0050	0.0200
60	1.00	1.10	0.0125	0.05	0.55	0.55	0.00688	0.0275
61	1.00	1.40	0.0125	0.05	0.70	0.70	0.00875	0.0350
62	1.00	1.70	0.0125	0.05	0.85	0.85	0.01063	0.0425
63	1.00	2.00	0.0125	0.05	1.00	1.00	0.01250	0.0500
64	1.00	2.40	0.0125	0.05	1.20	1.20	0.01500	0.0600
65	1.50	0.25	0.0125	0.05	0.10	0.15	0.00125	0.0050
66	1.50	0.63	0.0125	0.05	0.25	0.38	0.00313	0.0125
67	1.50	1.00	0.0125	0.05	0.40	0.60	0.0050	0.0200
68	1.50	1.38	0.0125	0.05	0.55	0.83	0.00688	0.0275
69	1.50	1.75	0.0125	0.05	0.70	1.05	0.00875	0.0350
70	1.50	2.13	0.0125	0.05	0.85	1.28	0.01063	0.0425
71	1.50	2.50	0.0125	0.05	1.00	1.50	0.01250	0.0500
72	1.50	3.00	0.0125	0.05	1.20	1.80	0.01500	0.0600
73	0.50	0.15	0.0125	0.50	0.10	0.05	0.00125	0.0500
74	0.50	0.38	0.0125	0.50	0.25	0.13	0.00313	0.1250
75	0.50	0.60	0.0125	0.50	0.40	0.20	0.00500	0.2000
76	0.50	0.83	0.0125	0.50	0.55	0.28	0.00688	0.2750
77	0.50	1.05	0.0125	0.50	0.70	0.35	0.00875	0.3500
78	0.50	1.28	0.0125	0.50	0.85	0.43	0.01063	0.4250
79	0.50	1.50	0.0125	0.50	1.00	0.50	0.01250	0.5000
80	0.50	1.80	0.0125	0.50	1.20	0.60	0.01500	0.6000
81	1.00	0.20	0.0125	0.50	0.10	0.10	0.00125	0.0500
82	1.00	0.50	0.0125	0.50	0.25	0.25	0.00313	0.1250
83	1.00	0.80	0.0125	0.50	0.40	0.40	0.00500	0.2000
84	1.00	1.10	0.0125	0.50	0.55	0.55	0.00688	0.2750
85	1.00	1.40	0.0125	0.50	0.70	0.70	0.00875	0.3500
86	1.00	1.70	0.0125	0.50	0.85	0.85	0.01063	0.4250
87	1.00	2.00	0.0125	0.50	1.00	1.00	0.01250	0.5000
88	1.00	2.40	0.0125	0.50	1.20	1.20	0.01500	0.6000

Table 2. (cont.) Test matrix #2. Each testing solution was run in duplicate totaling 208 tests

Test	NO2/NO3 (M)	NO2+NO3 (M)	Cl/NO3 (M)	SO4/NO3 (M)	NO3 (M)	NO2 (M)	Cl (M)	SO4 (M)
89	1.50	0.25	0.0125	0.50	0.10	0.15	0.00125	0.0500
90	1.50	0.63	0.0125	0.50	0.25	0.38	0.00313	0.1250
91	1.50	1.00	0.0125	0.50	0.40	0.60	0.00500	0.2000
92	1.50	1.38	0.0125	0.50	0.55	0.83	0.00688	0.2750
93	1.50	1.75	0.0125	0.50	0.70	1.05	0.00875	0.3500
94	1.50	2.13	0.0125	0.50	0.85	1.28	0.01063	0.4250
95	1.50	2.50	0.0125	0.50	1.00	1.50	0.01250	0.5000
96	1.50	3.00	0.0125	0.50	1.20	1.80	0.01500	0.6000
97	1.50	1.90	0.0700	0.15	0.10	1.80	0.00700	0.0150
98	1.50	2.05	0.0700	0.15	0.25	1.80	0.01750	0.0375
99	4.50	2.20	0.0700	0.15	0.40	1.80	0.02800	0.0600
100	3.27	2.35	0.0700	0.15	0.55	1.80	0.03850	0.0825
101	2.57	2.50	0.0700	0.15	0.70	1.80	0.04900	0.1050
102	2.12	2.65	0.0700	0.15	0.85	1.80	0.05950	0.1275
103	1.80	2.80	0.0700	0.15	1.00	1.80	0.07000	0.1500
104	1.50	3.00	0.0700	0.15	1.20	1.80	0.08400	0.1800

FY10 washing process.[6] Additional ratios of Cl^-/NO_3^- and SO_4^{2-}/NO_3^- were based on values cited in the Congdon[7] and Zapp[8] memos. Critical ratios for Cl^-/NO_3^- and SO_4^{2-}/NO_3^- were 0.03 and 0.3, respectively, when the primary aggressive species in the test solution was NO_3^-.

Simulated waste tank solutions were prepared using distilled water and reagent-grade chemicals: sodium chloride, sodium sulfate anhydrous, sodium carbonate, sodium bicarbonate, sodium nitrite, and sodium nitrate. The pH was maintained at 10.0 using a constant carbonate/bicarbonate molar ratio of 7 to 13. The gram amount of carbonate and bicarbonate added was based on the nitrite concentration in the solution. A total of 104 solutions were used for electrochemical testing. Solutions were prepared based on a statistically determined experimental design.[6]

Electrochemical Testing

The electrochemical cell used had the A537 test samples attached to a conductive wire and mounted in metallographic mount material that was used as the working electrode and two graphite rods were used as counter electrodes. The reference electrode was saturated calomel. The cyclic potentiodynamic polarization (CPP) testing was performed at 40°C. Prior to each CPP test, the samples were allowed to equilibrate for 2.5 hours at 40°C to determine the corrosion potential. The CPP curve started at an initial potential of -0.1 V versus the open circuit potential. The potential was increased at a rate of 0.5 mV/sec until either a vertex potential of 1.2 V with respect to the saturated calomel reference electrode or a maximum current of 0.001 Amps was reached. The reverse scan rate of 0.5 mV/sec was used until a final potential of 0 V with respect to the open circuit potential was reached. Steel samples in each solution were tested in duplicate for a total of 208 electrochemical tests. Digital optical images were taken of the sample surface upon completion of electrochemical testing for visual analysis of pit formation. The visual presence or absence of pits on the sample surface was the basis for the pit/no pit criteria and analysis because the optical/visual results lent towards a simple binary observation compared to the much more complex electrochemical response which yielded several CPP curve shapes spanning a range of current densities and electrical potentials.

Post-Electrochemical Evaluation

The surface of samples post-electrochemical testing was visually evaluated using a microscope, see Figure 2. Ranking for optical results were categorized as follows:

Category 1: No corrosion
Category 2: Moderate corrosion
Category 3: Significant corrosion

Figure 2. Degrees of corrosion: (left) significant, (center) moderate, (right) no corrosion. Note: Crevice corrosion was not taken into account.

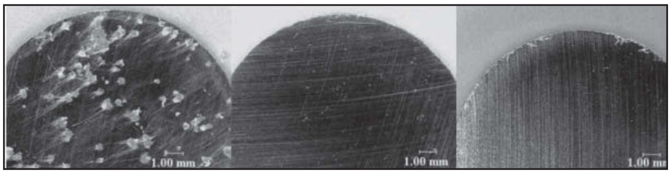
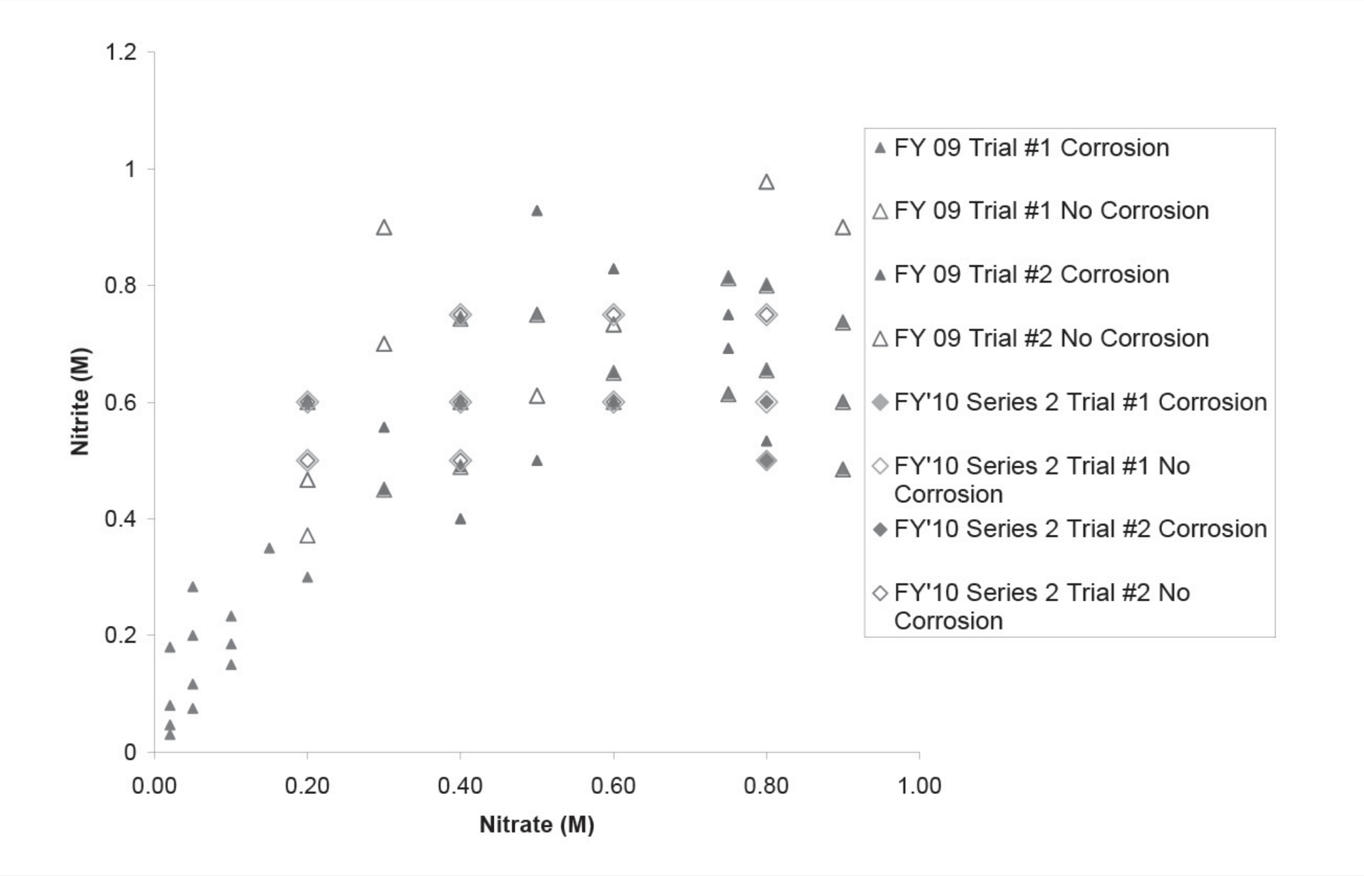


Figure 3. Test matrix #1 with constant chloride and sulfate concentrations compared to testing in similar nitrate and nitrite concentrations with chloride and sulfate concentrations that scaled with the nitrite concentration. Chloride and sulfate concentrations were dependent on the nitrite concentration and were based on chemistry control limits for FY09 data. Chloride and sulfate concentrations were constant and based on recent washing cycles in Tank 51 in FY10 data.



Results

Risk-based Corrosion Testing

Test matrix #1 was performed to evaluate the effect of chloride and sulfate on corrosion, thereby allowing the concentration of the species to vary independently compared to the nitrite concentration. The results of the experimentation are shown in Figure 3.

The results test matrix #1 provided a semi-clean break between regions of corrosion and no corrosion in the nitrite/nitrate space, especially when the chloride and sulfate concentrations were constant. This result strongly suggested the need for further evaluation of the effect of chloride and sulfate.

The optical results of the test matrix #2 solutions tested are provided in Table 3.

Duplicate runs for each solution showed relatively repeatable results. The concentration of nitrite is compared to nitrate (Figure 4), to chloride (Figure 5), and to sulfate (Figure 6). A distinct area of high corrosion susceptibility at low nitrite concentrations is apparent in all of the figures. Figure 4 shows a clear distinction between regions of pitting and no pitting in the nitrite versus nitrate space. The single data point at 1.2 M NO_2^- and 1.2 M NO_3^- in Figure 4 is considered a *borderline* result because a moderate amount of pitting was found in one sample and no pitting was found in the duplicate sample.

To further evaluate the influence of chloride and sulfate ions, the optical results at various nitrite concentrations were plotted against the aggressive species, see Figures 5 and 6.

Based on Figures 4-6, increasing the amount of sulfate (Figure 6) does not have as significant effect on the probability for pitting corrosion as increasing the amount of chloride (Figure 5) or nitrate (Figure 4).

Additionally, nitrate concentrations greater than 1.0 M were evaluated to address the abrupt change in concentration limits that currently exists in the chemistry control program at 1.0 M nitrate. The experimental results do not show an abrupt change in response occurring at 1.0 M nitrate. Therefore, the rapid change in the corrosion control program at this nitrate concentration cannot be justified.

The results can also be viewed in a three-dimensional plot of NO_2^-, Cl^-, and SO_4^-, as seen in Figure 7. The results show that NO_2^- levels can be raised to overcome the influence of Cl^- and

Table 3. Test matrix #2 optical results

Test	NO3 (M)	NO2 (M)	Cl (M)	SO4 (M)	Optic. 1	Optic. 2
1	0.1	0.05	0.0005	0.015	2	2
2	0.25	0.13	0.0013	0.0375	1	1
3	0.4	0.2	0.002	0.06	2	1
4	0.55	0.28	0.0028	0.0825	1	1
5	0.7	0.35	0.0035	0.105	1	1
6	0.85	0.43	0.0043	0.1275	1	1
7	1	0.5	0.005	0.15	1	1
8	1.2	0.6	0.006	0.18	1	1
9	0.1	0.1	0.0005	0.015	1	1
10	0.25	0.25	0.0013	0.0375	1	1
11	0.4	0.4	0.002	0.06	1	1
12	0.55	0.55	0.0028	0.0825	1	1
13	0.7	0.7	0.0035	0.105	1	1
14	0.85	0.85	0.0043	0.1275	1	1
15	1	1	0.005	0.15	1	1
16	1.2	1.2	0.006	0.18	1	1
17	0.1	0.15	0.0005	0.015	1	1
18	0.25	0.38	0.0013	0.0375	1	1
19	0.4	0.6	0.002	0.06	1	1
20	0.55	0.83	0.0028	0.0825	1	1
21	0.7	1.05	0.0035	0.105	1	1
22	0.85	1.28	0.0043	0.1275	1	1
23	1	1.5	0.005	0.15	1	1
24	1.2	1.8	0.006	0.18	1	1
25	0.1	0.05	0.007	0.015	3	2
26	0.25	0.13	0.0175	0.0375	3	3
27	0.4	0.2	0.028	0.06	3	3
28	0.55	0.28	0.0385	0.0825	3	3
29	0.7	0.35	0.049	0.105	3	3
30	0.85	0.43	0.0595	0.1275	3	3
31	1	0.5	0.07	0.15	2	2
32	1.2	0.6	0.084	0.18	2	2
33	0.1	0.1	0.007	0.015	2	2
34	0.25	0.25	0.0175	0.0375	2	2
35	0.4	0.4	0.028	0.06	2	2
36	0.55	0.55	0.0385	0.0825	1	1
37	0.7	0.7	0.049	0.105	1	1
38	0.85	0.85	0.0595	0.1275	1	1
39	1	1	0.07	0.15	1	1
40	1.2	1.2	0.084	0.18	1	1
41	0.1	0.15	0.007	0.015	1	1
42	0.25	0.38	0.0175	0.0375	1	1
43	0.4	0.6	0.028	0.06	1	1
44	0.55	0.83	0.0385	0.0825	1	1

Table 3. (cont.) Test matrix #2 optical results

Test	NO3 (M)	NO2 (M)	Cl (M)	SO4 (M)	Optic. 1	Optic. 2
45	0.7	1.05	0.049	0.105	1	1
46	0.85	1.28	0.0595	0.1275	1	1
47	1	1.5	0.07	0.15	1	1
48	1.2	1.8	0.084	0.18	1	1
49	0.1	0.05	0.0013	0.005	2	2
50	0.25	0.13	0.0031	0.0125	2	NA
51	0.4	0.2	0.005	0.02	2	2
52	0.55	0.28	0.0069	0.0275	2	2
53	0.7	0.35	0.0088	0.035	2	2
54	0.85	0.43	0.0106	0.0425	2	2
55	1	0.5	0.0125	0.05	1	1
56	1.2	0.6	0.015	0.06	1	2
57	0.1	0.1	0.0013	0.005	2	2
58	0.25	0.25	0.0031	0.0125	2	1
59	0.4	0.4	0.005	0.02	2	2
60	0.55	0.55	0.0069	0.0275	1	1
61	0.7	0.7	0.0088	0.035	1	1
62	0.85	0.85	0.0106	0.0425	1	1
63	1	1	0.0125	0.05	1	1
64	1.2	1.2	0.015	0.06	1	1
65	0.1	0.15	0.0013	0.005	1	1
66	0.25	0.38	0.0031	0.0125	2	2
67	0.4	0.6	0.005	0.02	1	1
68	0.55	0.83	0.0069	0.0275	1	1
69	0.7	1.05	0.0088	0.035	1	1
70	0.85	1.28	0.0106	0.0425	1	1
71	1	1.5	0.0125	0.05	1	1
72	1.2	1.8	0.015	0.06	1	1
73	0.1	0.05	0.0013	0.05	2	2
74	0.25	0.13	0.0031	0.125	3	3
75	0.4	0.2	0.005	0.2	2	2
76	0.55	0.28	0.0069	0.275	2	2
77	0.7	0.35	0.0088	0.35	1	1
78	0.85	0.43	0.0106	0.425	1	1
79	1	0.5	0.0125	0.5	2	1
80	1.2	0.6	0.015	0.6	1	1
81	0.1	0.1	0.0013	0.05	2	1
82	0.25	0.25	0.0031	0.125	1	1
83	0.4	0.4	0.005	0.2	1	1
84	0.55	0.55	0.0069	0.275	1	1
85	0.7	0.7	0.0088	0.35	1	1
86	0.85	0.85	0.0106	0.425	1	1
87	1	1	0.0125	0.5	1	1
88	1.2	1.2	0.015	0.6	2	1

Table 3. (cont.) Test matrix #2 optical results

Test	NO3 (M)	NO2 (M)	Cl (M)	SO4 (M)	Optic. 1	Optic. 2
89	0.1	0.15	0.0013	0.05	1	1
90	0.25	0.38	0.0031	0.125	1	1
91	0.4	0.6	0.005	0.2	1	1
92	0.55	0.83	0.0069	0.275	1	1
93	0.7	1.05	0.0088	0.35	1	1
94	0.85	1.28	0.0106	0.425	1	1
95	1	1.5	0.0125	0.5	1	1
96	1.2	1.8	0.015	0.6	1	1
97	0.1	1.8	0.007	0.015	1	1
98	0.25	1.8	0.0175	0.0375	1	1
99	0.4	1.8	0.028	0.06	1	1
100	0.55	1.8	0.0385	0.0825	1	1
101	0.7	1.8	0.049	0.105	1	1
102	0.85	1.8	0.0595	0.1275	1	1
103	1	1.8	0.07	0.15	1	1
104	1.2	1.8	0.084	0.18	1	1

Figure 4. Nitrite versus nitrate concentrations. Note: The data point from optical 1 corrosion set at 1.2 M nitrate and 1.2 M nitrite resulted in two visible pits; however, the electrochemical scan resulted in a negative hysteresis. Due to the conflicting optical and electrochemical results, significant emphasis should not be placed on this outlying data point.

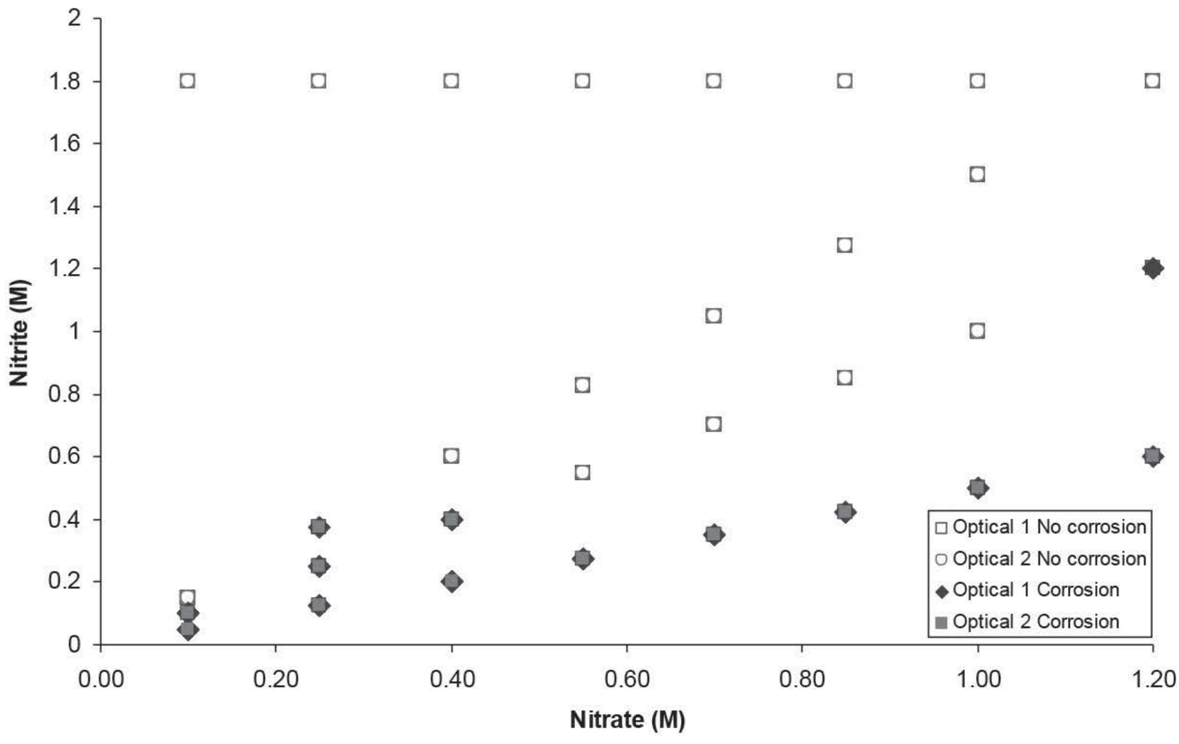


Figure 5. Nitrite versus chloride concentrations

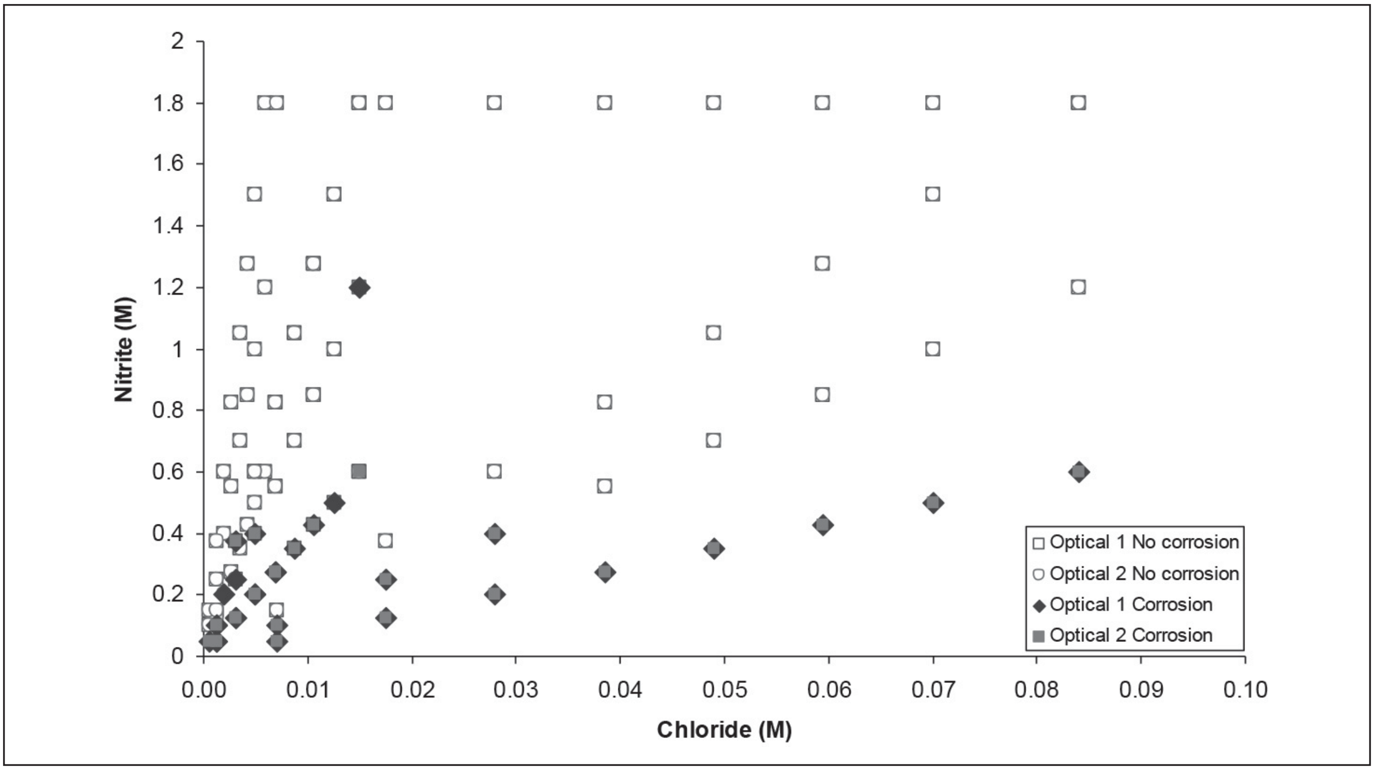


Figure 6. Nitrite versus sulfate concentrations

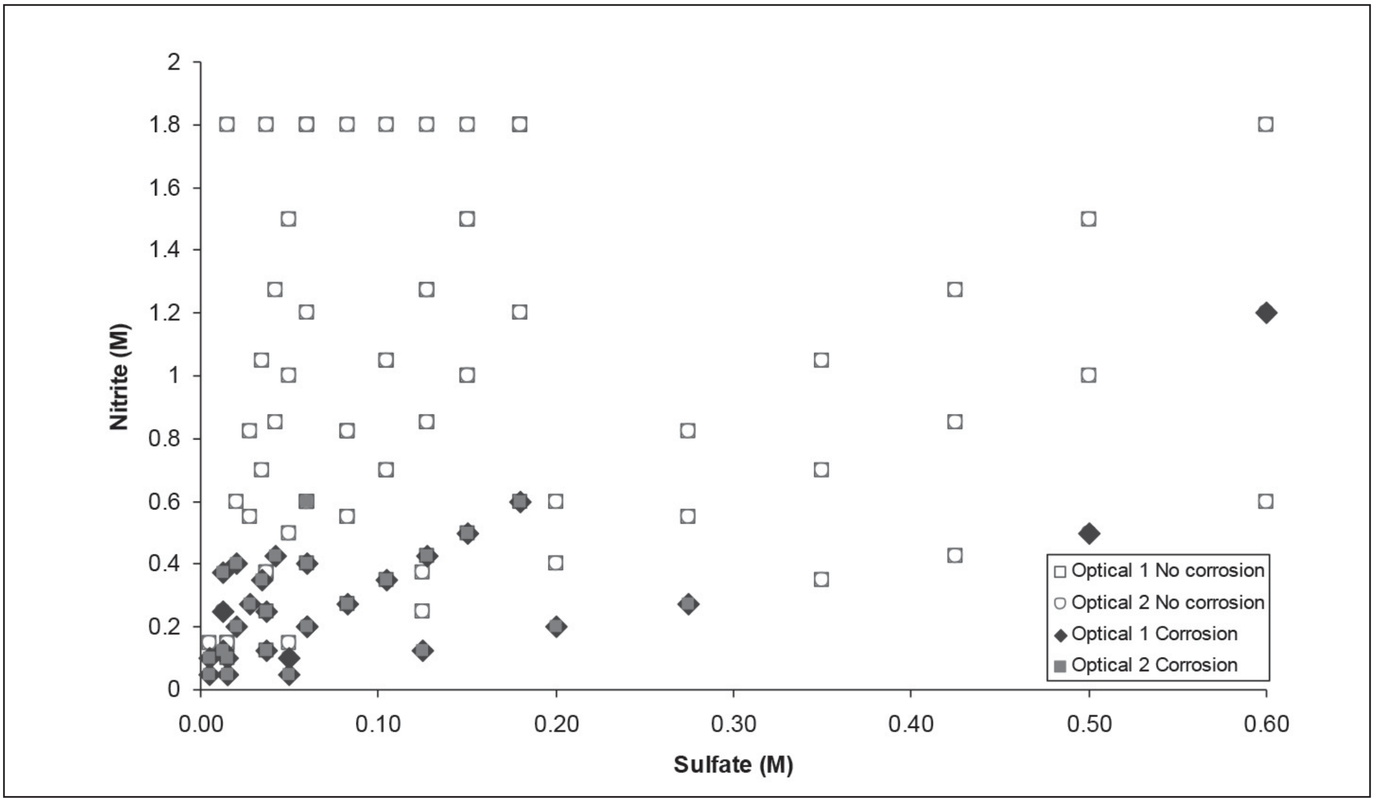


Figure 7. Three-dimensional plot of optical pitting results. Corrosion is denoted by an "X". No corrosion is denoted by a "+".

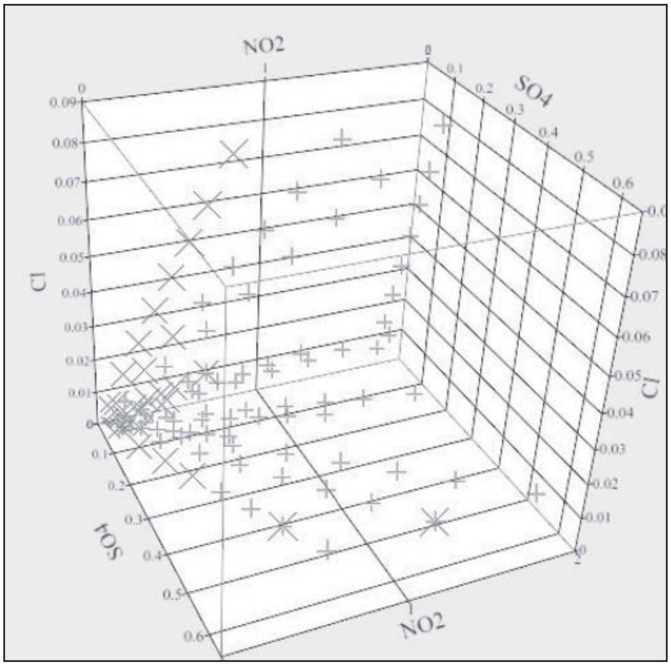
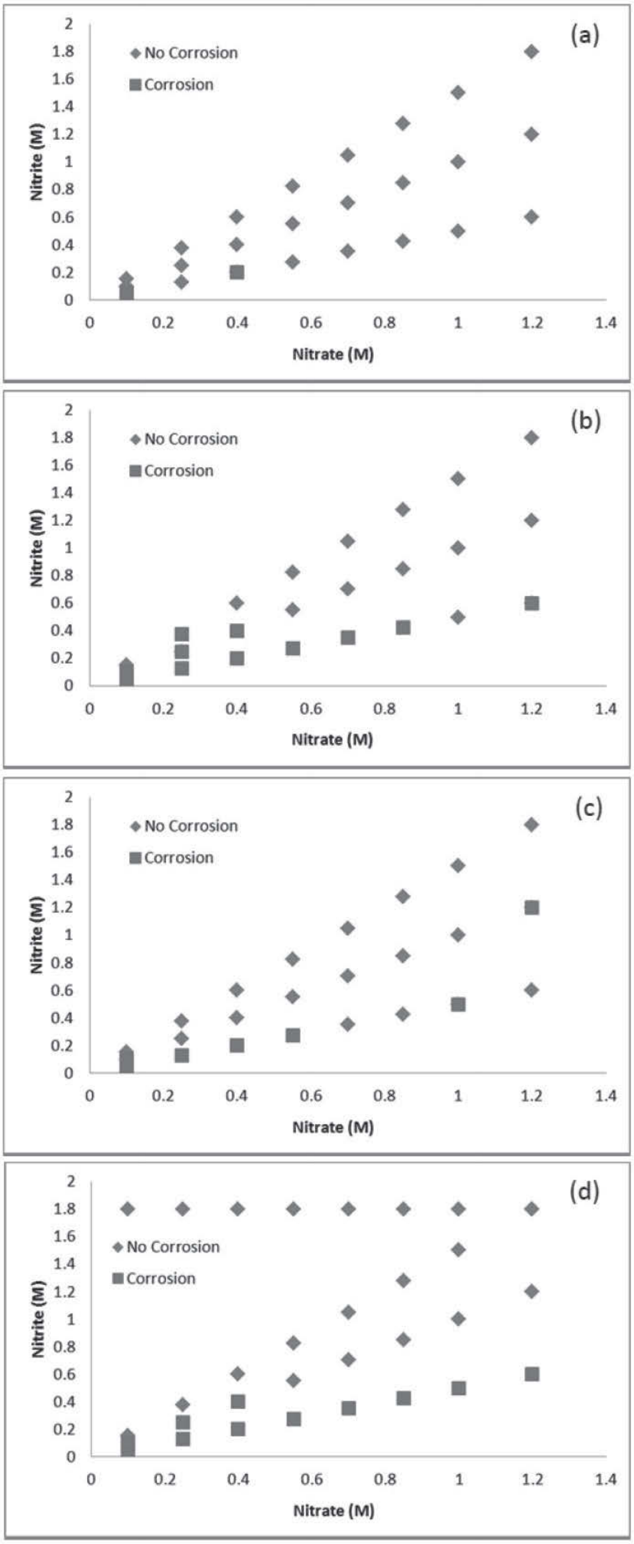


Figure 8. Partitioning of test matrix #2 optical results based on NO3- concentration and ratios of SO_4^2/NO_3- and Cl-/NO_3- as: (a) 0.15 and 0.005, (b) 0.05 and 0.0125, (c) 0.5 and 0.0125, and (d) 0.15 and 0.07



SO_4^- concentrations; however, at low levels of NO_2^-, even low levels of Cl^- would result in pitting. For SO_4^-, however, even at high concentrations of SO_4^-, and relatively low levels of NO_2^-, pitting was deterred. This result suggests that Cl^- has a greater contribution to pitting compared to SO_4^-.

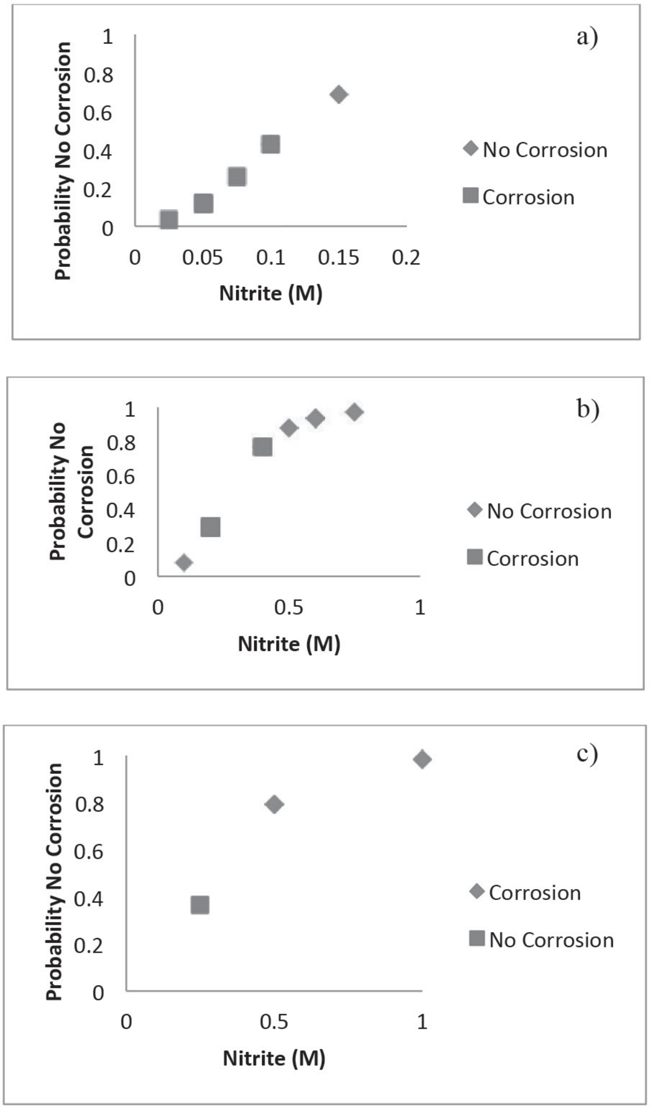
When the results are partitioned based on NO_3^- concentration and the ratios of Cl^- and SO_4^{2-} to the partitioned concentration, it is clear that the pitting probability increases with increasing Cl^-/NO_3^- ratio for a given concentration of inhibitor species, NO_2^-, see Figure 8.

Furthermore, when extreme ratios of SO_4^{2-}/NO_3^-, greater than 0.3, and Cl^-/NO_3^-, greater than 0.03, are removed the optical results show further defined clustering in the NO_2 versus NO_3 space, see Figure 9.

The results demonstrate that the relative concentration of Cl^- and SO_4^{2-} to NO_3^- should not be overlooked when evaluating the risk of corrosion in solutions containing species NO_2 and NO_3^-.

While the region of nitrite > 1.5 M and high nitrate > 0.8 M appears to be consistently safe with no pitting outcomes, the majority of the nitrate/nitrite space is littered with both pitting and no pitting responses. By removing the ratios of Cl^-/NO_3^- and SO_4^{2-}/NO_3^-, the region consistently free of pitting becomes significantly larger, see Figures 10 and 11. (See page 46.)

Figure 9. Partitioning of test matrix #2 optical results based on NO3- and NO2- concentrations. Ratios of SO42/NO3- > 0.3 and Cl-/NO3- > 0.03 were removed: a) 0.1 M NO3, b) 0.4 M NO3, and c) 1.0 M NO3.



Conclusions

The influence of chloride and sulfate concentration in dilute nitrate solutions was evaluated. The results suggest that, of the aggressive species evaluated, nitrate concentrations have the largest effects on corrosion but the effects of chloride and sulfate ions should not be overlooked when evaluating a chemistry control program. In particular, solutions containing $SO_4^{2}/NO_3^{-} > 0.3$ or $Cl^{-}/NO_3^{-} > 0.03$ have a marked increase in corrosion potential. The net result will be a reduction in inhibitors resulting in fewer inhibitor additions to the tanks to control corrosion.

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Figure 10. Nitrite versus nitrate concentrations with inclusion of minor ratios. The solid line denotes the current chemistry control limit, "×" denotes pitting response, "◊" denotes non-pitting response.

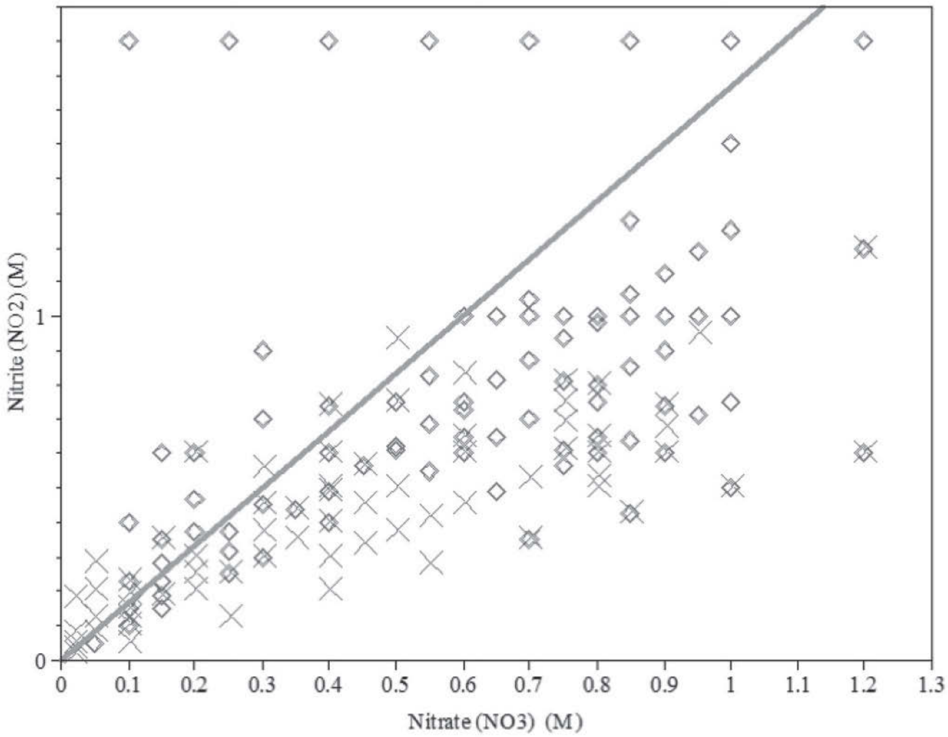
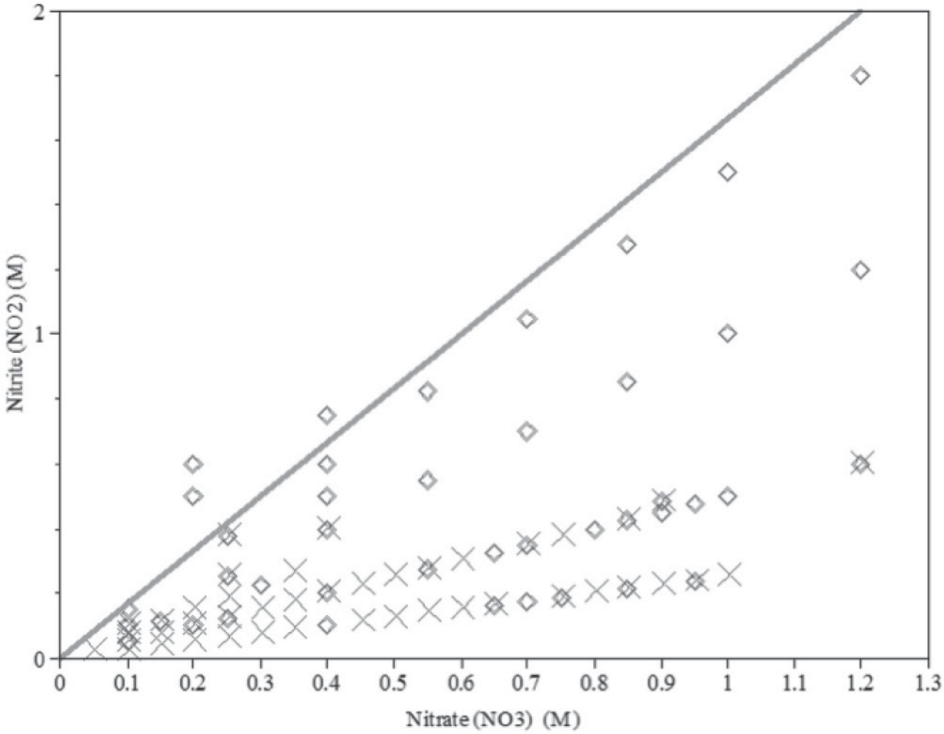


Figure 11. Nitrite versus nitrate concentrations with the exclusion of minor ratios. The solid line denotes the current chemistry control limit, "×" denotes pitting response, "◊" denotes non-pitting response.



The Evolution of Corrosion Monitoring in Hanford High-level Waste Tanks

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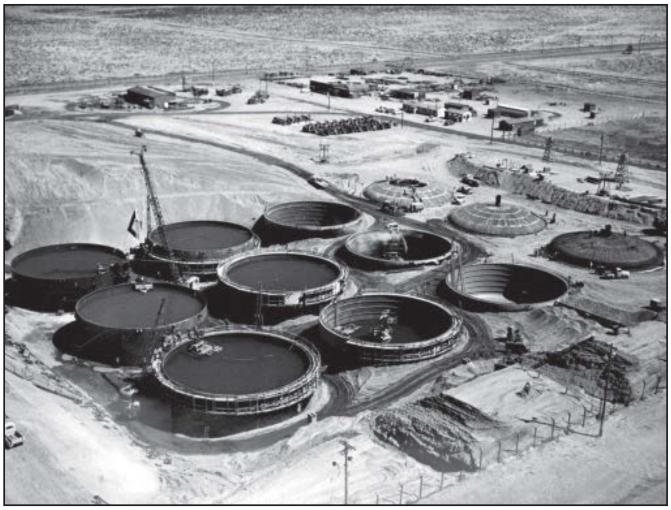
Abstract

Plutonium production and environmental cleanup activities at the Hanford Site have produced a broad range of contaminated materials and facilities, including 57 million gallons of high-level (i.e., highly-radioactive) nuclear waste stored in 177 underground carbon-steel tanks of either a single-shell or double-shell design. Due to age and leakage, all single-shell tanks had been removed from service by 1980 and all pumpable liquids had been transferred from single-shell tanks to sound double-shell tanks by 2004. The double-shell tanks have either exceeded or are expected to exceed their design life prior to the conclusion of site cleanup and waste processing activities. Because of the age and importance of the double-shell tanks to the site's environmental cleanup mission, double-shell tank corrosion control and maintenance activities are guided by a comprehensive Double Shell Tank Integrity Project. This project implements a variety of controls and inspections, including corrosion monitoring, to help ensure double-shell tank integrity. Though all provisions of the Double Shell Tank Integrity Project program plan are important to the management of the double-shell tanks, this paper focuses on the development of double-shell tank corrosion monitoring systems.

Introduction

The Hanford Site is a 560-square-mile complex located along the Columbia River in southeastern Washington state. The site was established in 1943 by the U.S. government as part of the Manhattan Project to produce the plutonium necessary for the development of nuclear weapons used to bring an end to World War II. Following the end of the war, the Hanford Site continued to play a critical role in the nation's defense. Between the Cold War years of 1944 and 1987, the site constructed and operated nine graphite-moderated, light-water, production reactors to irradiate fuel and produce plutonium, six large chemical separations plants to extract the plutonium from the fuel, and a variety of laboratories, support facilities, and related infrastructure to support production.[1] Ultimately, these facilities produced approximately 60 percent of the weapons-grade plutonium produced in the United States.[2] In 1988, plutonium extraction operations were halted and the site has been engaged in a comprehensive environmental cleanup effort since that time.

Figure 1. 241-BY Tank Farm showing various stages of SST construction



Plutonium production and cleanup activities at the site resulted in a broad range of contaminated materials and facilities that must be managed and remediated. Major waste types include approximately 25 million cubic feet of solid waste, 40 billion cubic feet of contaminated soil and ground water, 175 million cubic feet of contaminated facilities, 25,000 cubic feet of nuclear materials, and 57 million gallons of high-level (i.e., highly radioactive) nuclear waste, stored in 177 underground steel tanks, awaiting final processing and long-term repository storage.[2]

Background

Of all the steps involved in the production of plutonium at Hanford, the chemical separations plants used to extract plutonium from irradiated fuel produced some of the most complex and contaminated waste streams. The enormous volume and extreme health and environmental hazards posed by high-level wastes made waste management a high priority immediately after the start of plutonium production. Between 1943 and 1964, 149

Figure 2. 241-AP Tank farm showing various stages of DST construction

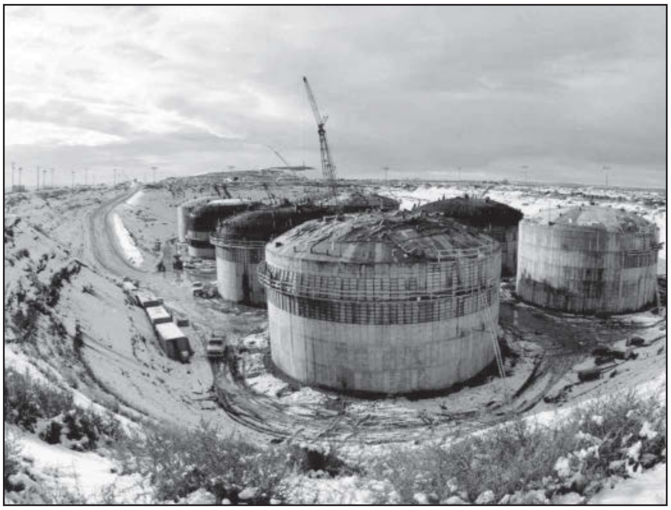


Figure 3. DST 241-AZ-102 tank wall, instruments, and waste surface

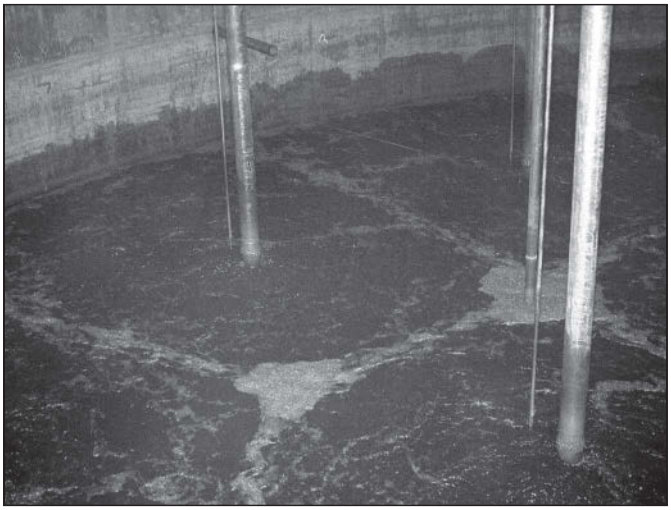
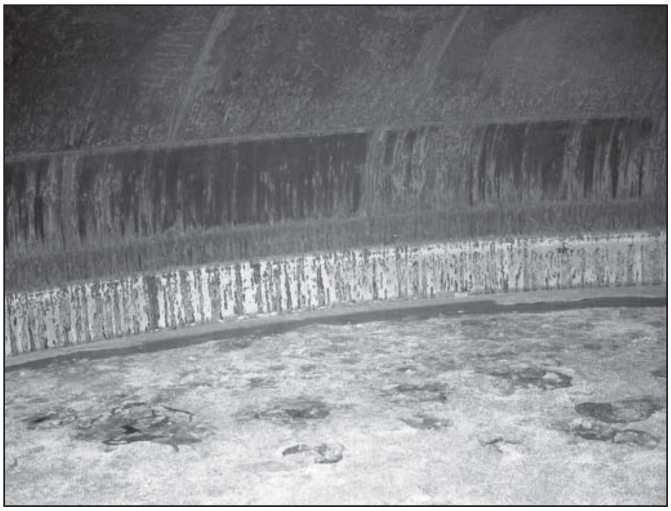


Figure 4. DST 241-AN-104 tank wall and dome above waste surface



single-shell tanks (SSTs) were constructed at the site, providing approximately 94 million gallons of high-level waste storage capacity (Figure 1).[3] To meet increased demands for storage capacity, twenty-eight additional tanks, of a double-shell design [i.e., double-shell tanks (DSTs)], were constructed between 1968 and 1986, providing an additional 32 million gallons of storage capacity (Figure 2).[4]

Both the SSTs and DSTs were fabricated on site from welded plates of mild steel. Leaks began to appear in the SSTs shortly after the introduction of nitrate-based wastes in the 1950s. Sixty-seven of the 149 SSTs are now known or assumed to have leaked waste to the surrounding soil.[5] The SSTs were not stress-relief annealed following fabrication. Laboratory studies and failure analyses indicate that the SST failures are most likely the result of nitrate-induced stress corrosion cracking (SCC), though pitting corrosion, crevice corrosion, and uniform corrosion may also have contributed to their degradation.[6-8] Under normal operating procedures, leaking SSTs were removed from service (i.e., not allowed to receive additional waste) upon discovery of leakage. Due to their age and the risk of leakage, all remaining SSTs were removed from service by November 1980.[4] By March 2004, all pumpable liquids had been transferred from SSTs into sound DSTs.[4,5] Work is currently underway to transfer all remaining waste out of the SSTs and into sound DSTs.[6]

To reduce the risk of SCC, the DSTs were stress-relief annealed following fabrication. Each DST consists of a primary steel tank (bottom, walls, and dome) that sits inside a secondary steel liner surrounded by a reinforced-concrete shell. Approximately 27 million gallons of high-level waste are currently stored in DSTs.[5] Waste is in both supernatant (liquid) and solid (sludge/salt cake) forms (Figure 3). There is also a vapor space above the waste surface (Figure 4). Over the years, waste stratification, mixing, bulk reduction operations, radioactive decay, isotope recovery operations, chemical treatments, and thermal mixing have complicated the makeup of DST waste. To date, only one DST has suffered leakage. (On August 22, 2012, the U.S. Department of Energy's Office of River Protection (ORP), working with its Hanford tank operations contractor, Washington River Protection Solutions, announced the discovery of a slow leak of chemical and radioactive waste into the annulus space of DST 241-AY-102. The annulus space is the approximately 30-inch area between the inner primary tank and the outer tank that serves as the secondary containment in these types of tanks. This is the first time a DST leak from the primary tank into the annulus has been identified. There is no indication of waste in the leak detection pit outside the DST, indicating that no waste has leaked out of the annulus and into the environment. Tank 241-AY-102 was the first double-shell tank constructed at Hanford and has been in operation for more than forty years. It contains about 850,000 gallons of sludge and liquid waste. Details of the leak are available in *RPP-ASMT-53793, Tank 241-AY-102 Leak Assessment Report.[7])*

Corrosion is controlled in the DSTs by sampling, analyzing, and controlling certain key components of tank waste chemistry. Laboratory work performed at the Pacific Northwest National Laboratory on simulated DST wastes stored in Hanford Site tanks and work performed at the Savannah River National Laboratory on Savannah River Site waste led to the establishment of waste chemistry controls to minimize DST corrosion and the risk of tank failure from general corrosion, pitting, and SCC.[8,9] The current revision of the DST waste chemistry specification contains the original waste chemistry limits and reflects updates and changes to a variety of other DST operational and management requirements.[10,11]

Because of the age and importance of the DSTs to the site's environmental cleanup mission, DST integrity management activities now go far beyond waste chemistry controls. Today, DST integrity is managed under a comprehensive Double Shell Tank Integrity Project (DSTIP) via the Double Shell Tank Integrity Program Plan.[12] The DSTIP implements controls and inspections to help ensure DST system integrity is maintained throughout the Hanford cleanup mission. Key features of the DSTIP include waste chemistry sampling, analysis, and adjustment; waste chemistry optimization studies; DST ultrasonic testing and video examinations; structural analysis and operational studies; and in-tank corrosion monitoring. Though all the provisions of the DSTIP are important to maintaining DST integrity, this paper focuses on the relatively recent development and application of DST corrosion monitoring systems.

Program Development

At Hanford, internal corrosion of the DSTs has always been controlled by controlling waste chemistry. As of the mid-1990s, this approach had been successful in preventing leakage from the DSTs, but concerns were mounting over corrosion of the DSTs. A number of studies had suggested that localized forms of corrosion (i.e., SCC, pitting, crevice corrosion, etc.) could threaten the integrity of the DSTs.[13-15] In addition, six DSTs were discovered between 1995 and 1996 with out-of-specification waste chemistries, raising new questions about the adequacy of the waste chemistry control program.[16] Based in part on these events, an effort was initiated in 1995 to improve the site's approach to DST corrosion monitoring and control.

Early in the effort, personnel involved in the program recognized that new corrosion monitoring technologies were available, or would soon be available, that could possibly be developed to facilitate real-time or near real-time monitoring for localized forms of corrosion in the DSTs. Somewhat surprisingly, as of 1995, almost no *in-situ* corrosion monitoring work had previously been performed at any of the nuclear waste storage sites across the DOE complex, if the use of corrosion coupons was excluded from the list. Prior *in-situ* waste tank corrosion monitoring work at the two largest DOE sites, Hanford and SRS, had included only coupon exposure programs and small-scale projects designed to directly measure waste tank corrosion potentials and/or corrosion rates.[17-21] At the West Valley Demonstration Project, a small in-tank corrosion monitoring system, including linear polarization resistance (LPR) and electrical resistance (ER) sensors, had been designed for Tank 8-D2, but the system was badly damaged during installation and full functionality was never recovered.[22] Although LPR and ER sensors can be effective tools for monitoring the rate of general (i.e., uniform) corrosion, they are not well-suited for the detection of localized forms of corrosion.

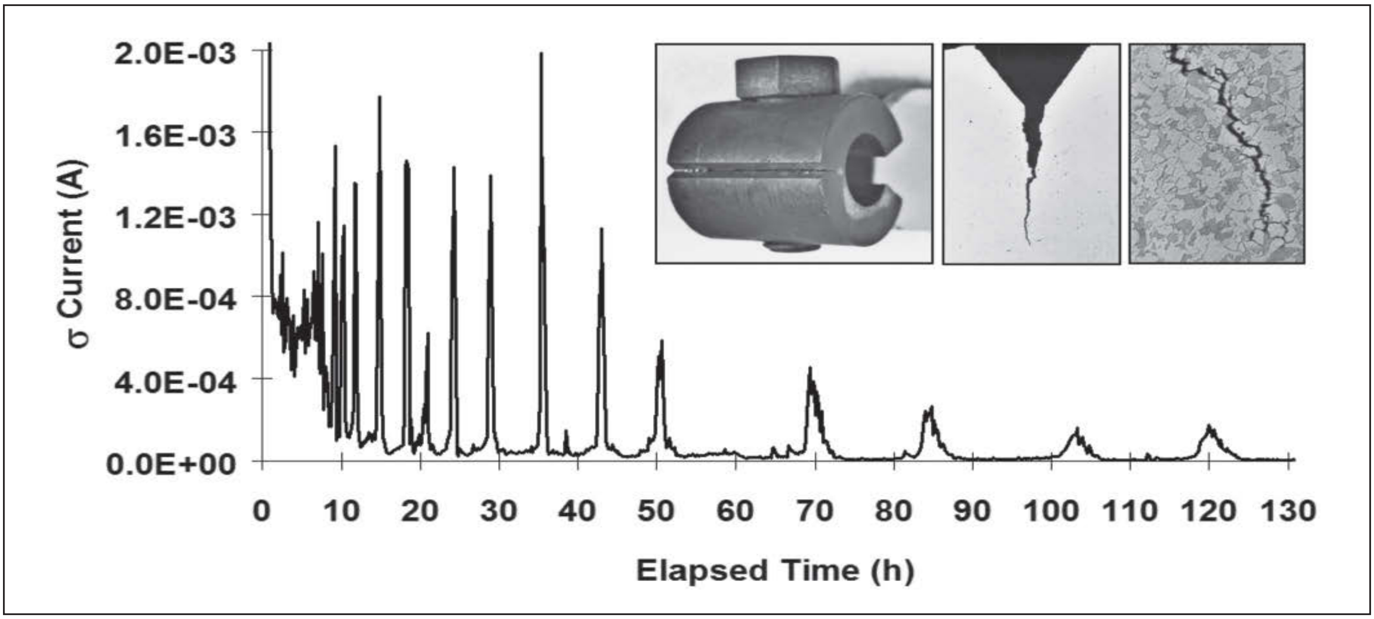
Due to the lack of precedent for localized corrosion monitoring in nuclear waste environments, a formal alternatives analysis was conducted to identify methods and technologies that could be used to improve the approach to DST corrosion monitoring and control.[16] The alternatives analysis concluded that a multi-phase approach should be developed, utilizing ultrasonic and visual examinations for direct evaluation of tank liner condition, in-tank corrosion probes for rapid detection of changes in waste corrosivity, and waste sampling and analysis for determination of corrective action. For in-tank corrosion monitoring, the alternatives analysis recommended the development of an electrochemical noise (EN)-based system, based on preliminary studies of the technique at SRS, the unique capability of the technique to detect the onset of localized corrosion, the commercial availability of EN-based corrosion monitoring equipment, and the relative simplicity of the overall system. The analysis also recommended that the new system include LPR equipment for measuring uniform corrosion rate in the tanks.

Technology Development

A full explanation of the principles and operation of EN-based corrosion monitoring systems is beyond the scope of this work, but a brief explanation is provided here for clarity. Typical EN-based corrosion monitoring systems measure and record low frequency (< 1 Hz) and low amplitude (0.1μV - 10mV and 10nA/cm^2 - 10μA/cm^2) fluctuations in current and voltage spontaneously generated by electrochemical reactions on the corroding surfaces of a set of nominally identical electrodes.[23-26] More simply, EN-based systems record fluctuations in current and potential *caused* by corrosion. It is this ability to make passive measurements that sets EN-based systems apart from LPR and other corrosion monitoring and electrochemical test techniques that induce a change in the corrosion potential or flow of current between electrodes.

For monitoring purposes, EN-based systems typically utilize three electrodes (a working, a counter, and a pseudo-reference electrode) made of the material of interest (i.e., tank steel) immersed in the environment of interest (i.e., tank waste). Time-dependent fluctuations in corrosion current between the working and counter electrodes are referred to as "electrochemical current

Figure 5. EN data from proof-of-principle testing, standard deviation of current during CC of A537 CL1 C-ring in 4 M NH4NO3 at 97°C



noise." Time-dependent fluctuations of the difference in the corrosion potential between the working/counter electrode assembly and the pseudo-reference electrode are referred to as electrochemical potential noise [note that since the working and counter electrodes are electrically shorted through a zero resistance ammeter (ZRA) in the measurement hardware, potential differences are measured between the working/counter electrode assembly and the pseudo-reference electrode]. The EN instrumentation does not directly measure corrosion occurring on the internal surfaces of the tank. Tank wall corrosion must be inferred from the measurements made on the EN electrodes.

Data analyses techniques vary in complexity, but are based on the principle that different forms of corrosion produce different fluctuations in current and voltage over time. The most straightforward methods of data analyses involve simple visual evaluation or statistical examination of the temporal data record with more detailed investigations of identified regions of interest.[27] Other methods of analysis involve transformation of temporal data to the frequency domain for analysis.[28,29] At the time of its initial consideration at Hanford as a method monitoring corrosion in DSTS, the application of EN to plant and field corrosion monitoring was a relatively new idea. Since that time, operational guidelines have emerged for designing and operating EN-based systems and systems have been successfully applied in a variety of corrosion monitoring applications.[30,31]

Proof-of-Principle Testing

In 1995 and 1996, EN proof-of-principle tests were conducted on ASTM A516 and A537-CL1 mild steel specimens immersed in a variety of simulated normal and off-normal DST waste solutions at Oak Ridge National Lab (ORNL) and PNNL.[32] The purpose of these tests was to verify the capability of EN-based corrosion monitoring systems to detect and discriminate between general and localized forms of corrosion. Testing confirmed that, with proper electrode design, EN-based corrosion monitoring systems are capable of detecting and discriminating between uniform and localized forms of corrosion in steels exposed to nitrate-based DST waste simulants.[1] General corrosion, pitting, and SCC events were identified in the test data and confirmed with post-test metallographic examination (Figure 5). Crack advance rates during SCC, as calculated from the duration of SCC EN signal generation and post-test crack depth measurements, compared favorably with previously published results.[33] By mid-1996, site engineering personnel deemed laboratory testing to have provided sufficient evidence that EN-based corrosion monitoring systems were capable of detecting the localized forms of corrosion that could occur in DSTs.

Prototype EN System

Based on the results of the proof-of-principle testing, a three-channel prototype EN-based corrosion monitoring system was designed for DST 241-AZ-101.[34] The prototype system was composed of an in-tank probe that held the monitoring electrodes in the waste and corrosion monitoring instrumentation housed in a nearby instrument building in the tank farm. The system was primarily designed to collect EN data, but could also be used to make potentiodynamic polarization scans and/or LPR scans for determining corrosion rate.

The in-tank probe was constructed from a 33-foot length

Figure 6. Prototype EN-based corrosion monitoring probe for 241-AZ-101

of 1.5-in. diameter AISI 304L stainless steel pipe (Figure 6). Three sets of electrodes were positioned at various elevations along the in-tank probe. Each electrode set was composed of three, nominally identical C-rings constructed of archived ASTM A537-Class 1 tank steel (to closely match the age and metallurgy of the actual tank wall material). To facilitate SCC detection, the working electrode in each array was pre-cracked by cyclic fatigue and strained beyond the proportional limit just prior to attachment to the probe body and immersion in the waste. Once installed in the tank, the upper two sets of electrodes were positioned in the vapor space above the waste, and the lowermost set of electrodes was positioned approximately five feet below the surface of the waste.

A ten-conductor shielded data cable running through the interior of the sealed pipe was used to make the electrical connections between the corrosion monitoring instrumentation and the electrodes. Commercially available glass-to-metal seals and radiation-resistant ethylene propylene (EPDM) gaskets were used to electrically isolate the electrodes from the probe body. Data were collected with a laboratory-grade CMS-100 system from Gamry Instruments, Inc. Data were processed manually in custom-made Microsoft Excel spreadsheets developed specifically for the project.

The prototype system was installed in August 1996 and monitored through 1998. During its operation, EN data indicated that uniform corrosion was the dominant active mode of corrosion in the tank, not an unexpected result given that tank waste chemistry was within the bounds of the waste chemistry specification. More interestingly, however, were the effects of large water additions to the tank. When large additions of condensate were returned to the tank, EN data indicative of pit initiation and growth were generated on the immersed set of electrodes. (Note: Due to waste composition and associated radioactive decay heat, the waste in DST 241-AZ-101 is hotter (thermally) than most other tank waste. To prevent the waste from drying out and solidifying, evaporative water losses are collected, condensed, and periodically returned to the tank.) Data indicative of pitting were typically recorded for two to three weeks following a large water addition, with data indicative of uniform corrosion slowly returning as tank chemistry re-equilibrated and steady-state uniform corrosion returned as the dominant mode of corrosion on the electrodes. After several water additions of varying volumes, it was noted that the relationship between volume of water added to the tank and the generation of pitting data was consistent with previously published predictions of pitting behavior following water additions to SRS waste tanks.[35]

Despite some operational difficulties (primarily due to the use of a laboratory-grade system in a field environment), the performance of the prototype system suggested that EN-based systems could be effectively used to detect changes in DST waste corrosivity. Based on the first year of operation of the 241-AZ-101 prototype system, plans were made to expand the size and scope of the corrosion monitoring program.

Full-Scale EN-based Corrosion Monitoring Systems

In 1997, a larger, more complex EN-based corrosion monitoring system was designed and installed in DST 241-AN-107.[36] This first-generation full-scale system reached from top to bottom in the tank, positioning multiple sets of stressed and unstressed electrodes across all regions of the tank (i.e., vapor space, supernatant, and sludge/saltcake regions). This basic design was used as a starting point for the design of four additional full-scale systems, including a second-generation system installed in 241-AN-102 in August 1998, a third-generation system installed in 241-AN-105 in January 2000, a fourth-generation system installed in 241-AN-104 in January 2001, and a fifth-generation system (replacing the first-generation system) installed in 241-AN-107 in August 2001.[37-41] Minor system design changes were made with each new generation, correcting problems identified in previous systems, and improving the use of tank riser space by incorporating additional sensors and equipment into the probe body.

All of the full-scale EN-based corrosion monitoring systems were composed of two main assemblies, an in-tank probe (Figure 7) and an ex-tank set of data collection hardware, software, and other equipment to support field operation (Figure 8). The in-tank probes were fabricated from 1-in. Schedule XXS ASTM A312 Type 304/304L stainless steel tubing. The in-tank probes were approximately 55 ft. in length, required two cranes for installation (Figure 9), and reached from the riser at tank top to the bottom of the tank.

Eight sets of EN electrodes (three nominally identical electrodes per set) were distributed along the probe body (Figure 10). Electrodes were fabricated from ASTM A537 CL1 steel, heat-treated to match the tank wall heat treatment. Four channels on each probe were formed from sets of bullet-shaped electrodes (~25 cm^2/per electrode); the remaining four channels were formed from

Figure 7. In-tank probe from typical full-scale EN-based corrosion monitoring system

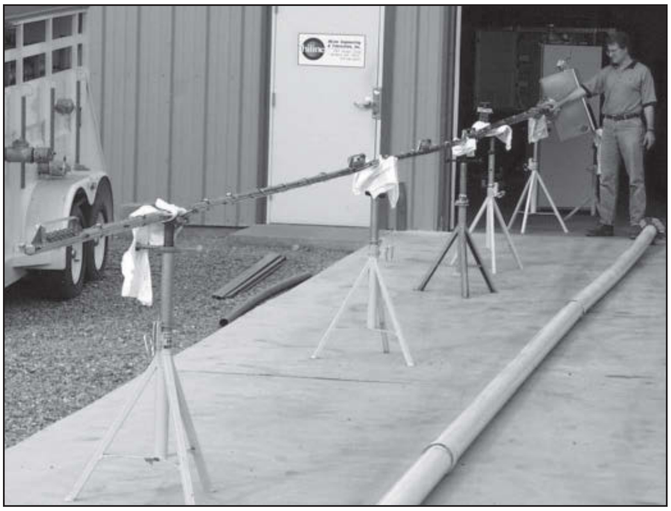
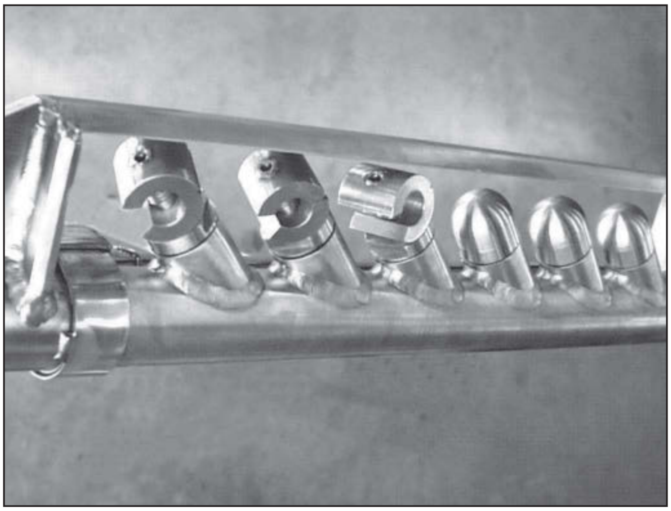


Figure 8. Instrumentation for full-scale EN-based corrosion monitoring system

Figure 9. Two crane pick, installation of 241-AN-107 EN-based corrosion monitoring system

Figure 10. Detail of electrodes on 241-AN-105 EN-based corrosion monitoring system



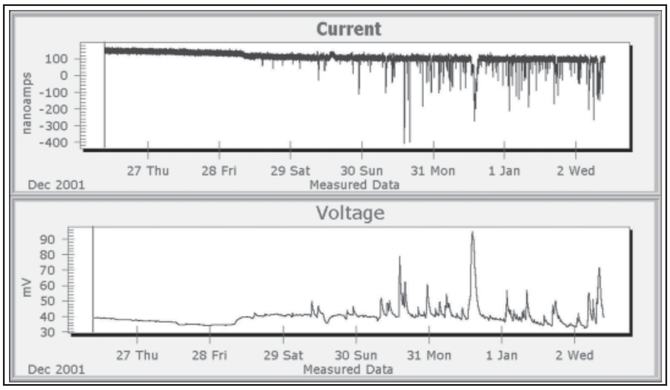
sets of custom-made, thick-walled C-rings (~44 cm^2/electrode). The bullet-shaped electrodes were used to monitor for pitting and uniform corrosion. The C-ring electrodes were used to monitor for the onset of SCC (working electrode in each C-ring set was notched, pre-cracked, and stressed to facilitate crack growth should tank chemistry conditions change to allow the onset of cracking). Typically, bullet and C-ring electrode sets alternated up the length of the probe. None of the electrodes contained welds.

Commercially available data cables running through the interior of the sealed pipe were used to make the electrical connections between the corrosion monitoring instrumentation at the probe top and the electrodes in the waste. Custom fabricated glass-to-metal seals and radiation-resistant ethylene propylene (EPDM) gaskets or O-rings were used to electrically isolate the electrodes from the probe body. Data were collected from the electrodes using commercially-available, field-hardy EN hardware from Capcis March Ltd.[II] and Petroleum Research and Production, Inc.[III] for early systems, then Capcis Systems, Ltd.[IV] for later systems. Data were processed using the Amulet software package from Corrosion & Condition Control, Ltd.

In addition to the corrosion monitoring electrodes, the in-tank probes were fitted with LPR electrodes, gas sampling ports, strain gauges, water lances (to facilitate installation through tank solids/sludge layers), thermocouple arrays, high-level detectors, and pressure/gas sampling ports. These features provided for a better understanding of the relationship between recorded data and other in-tank operations and condition changes.

Data procesing in most any EN-based corrosion monitoring

Figure 11. EN data from 241-AN-107 showing transition from uniform corrosion to pitting



system is a major concern and the Hanford DST systems were no different. When operating, each DST corrosion monitoring system was capable of continuously collecting two points of raw data per channel per second (i.e., sixteen points of data per second, or more than 41 million points per month). Fortunately, automated statistical analyses algorythms could be used to identify time periods of interest in the data, making data analyses a reasonable proposition.

The vast majority of EN data from the DST systems were indicative only of low rates of uniform corrosion, a result that was not surprising for tanks with waste chemistry within the bounds of the waste chemistry corrosion specification, but a bit more surprising for tanks like 241-AN-107 with waste that had been outside the bounds of the waste chemistry specification for some time. LPR data from these systems confirmed the results of EN data analyses, indicating corrosion rates of well under 1 mils per year (mpy).

In addition to corrosion data, EN-based corrosion monitoring systems periodically recorded data transients that did not match laboratory test data indicative of corrosion. Much attention was paid to these data transients at the time, particularly early on in the operation of the systems. However, it is quite common for EN systems (in both laboratory and field applications) to capture events outside the realm of corrosion since the systems record *any* fluctuation in electrode surface potential, including non-corrosion-related events such as hydrogen bubble evolution, changes in flow, temperature variations, vibration, electrical interference, photosensitive reactions, etc.

Data indicative of pitting were recorded on the fifth generation system installed in 241-AN-107 for a short period of time in December 2001. On the morning of December 28, 2001, EN data from Channel 4 began to gradually change from being dominated by uniform corrosion to being dominated by pitting corrosion (Figure 11).[41] Data indicative of pitting were recorded for the next several weeks before slowly returning back to uniform corrosion. Despite a careful review of tank farm operation records from that period of time, and interviews with engineering and operations personnel, the reason for the change in data was never determined. Pitting is a notoriously stochastic phenomena, initiating and subsiding somewhat randomly on surfaces, even when those surfaces are maintained at corrosion potentials conducive to pitting. Pitting data were not recorded at any other time in the system.

The fifth-generation 241-AN-107 system was the focus of attention again in February 2002 when 37,000 gallons of 19M sodium hydroxide solution were added to the tank to bring it back within the bounds of the site's waste tank chemistry specification.[41] Corrosion rates were measured by running LPR scans on the EN electrodes before, during and after the sodium hydroxide addition. A large mixer pump was operated during the hydroxide addition and for about a month afterward to help blend the concentrated sodium hydroxide solution into the tank waste, minimizing the precipitation of solids. Corrosion rates measured before, during, and well after the termination of mixer pump operation on the four sets of electrodes immersed in supernatant were unsurprising (approximately 0.1 mpy prior to mixer pump operation, 0.4 mpy during hydroxide addition and mixer pump operation, and back to 0.1 mpy well after the termination of mixer pump operation). However, corrosion rates measured over the same period of time on the two sets of electrodes embedded in sludge at the bottom of the tank did not follow this trend. Corrosion rates measured on the sludge electrodes did not change over the course of events, indicating that the sludge layer, or at least part of it, was undisturbed by the sodium hydroxide addition or mixer pump operation.

Although corrosion probe data were not used to impact the decision to make this hydroxide addition (corrosion monitoring systems were not yet officially recognized at that time), data collected during these operations showed that the corrosion monitoring systems could be used to confirm the need for hydroxide additions, or to monitor the impact of future hydroxide additions or other tank waste-disturbing operations. Additionally, these data supported the growing realization that corrosion was not a severe problem in 241-AN-107, despite the fact that the waste in the tank had been outside the bounds of the waste chemistry specification for more than ten years (i.e., corrosion monitoring data confirmed that there was a good deal of conservatism built into the waste chemistry specification).

Integrated Multifunction Corrosion Probe

In 2005, the functions and requirements for a new "Integrated Multifunction Corrosion Probe" (IMCP) were developed at Hanford.[42] A complete redesign was performed during the development of this system to add additional measurement capabilities and to address design, fabrication, and operational issues identified with previous DST corrosion monitoring systems.[43] To support field operation and data interpretation, laboratory testing was performed to characterize the types of data expected from

Figure 12. FRP body of IMCP during electrode installation

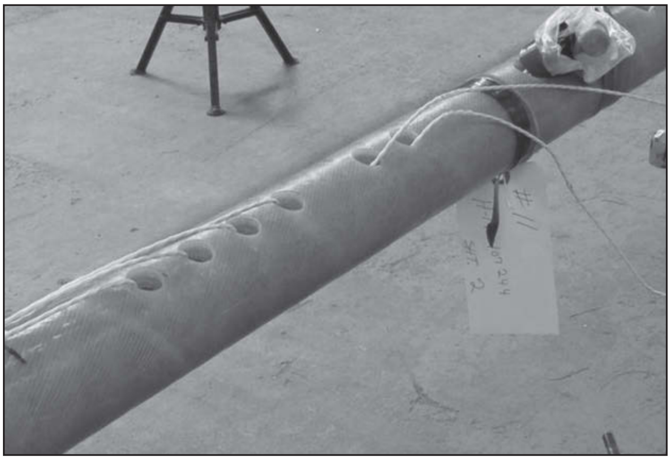
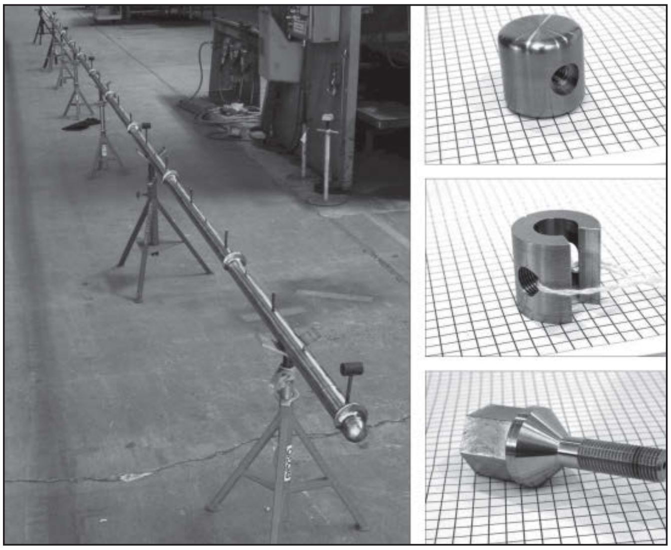


Figure 14. IMCP passive probe and coupon details



the new system.[44] The resulting design was significantly different than the previous DST corrosion monitoring systems, capable of collecting a more comprehensive set of tank corrosion and other environmental data.

One of the most significant departures from previous designs was the IMCP's use of two in-tank probes instead of one: an *active* probe containing actively-monitored electrodes, and a *passive* probe (installed in a separate riser) containing only mild steel corrosion coupons. This two-probe design was selected to facilitate the early detection of the onset of localized forms of corrosion (via the active system) plus validation of active probe data through the inspection of passive probe coupons.

Figure 13. IMCP instrument cabinet showing EN, LPR, and ER instrumentation

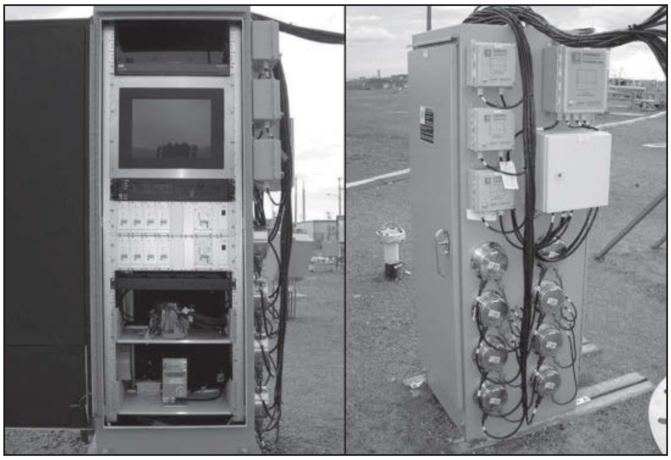
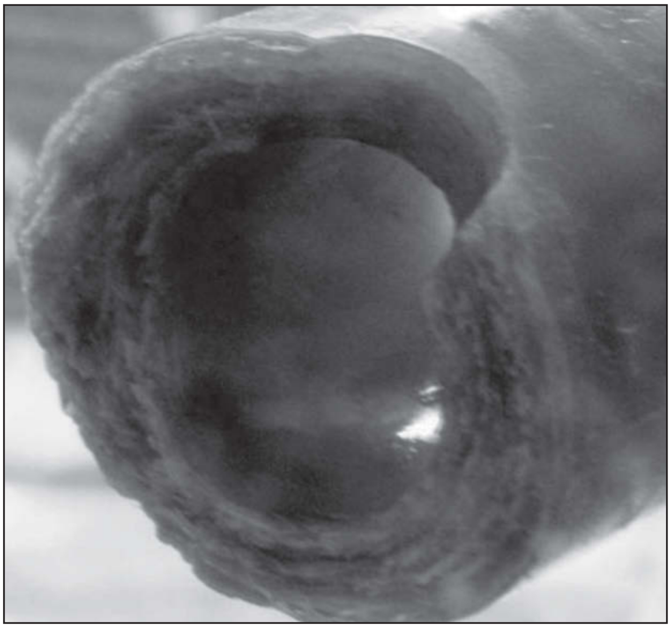


Figure 15. Failed end of IMCP active probe body



Active Probe Design

Although all previous DST corrosion probe bodies had been fabricated from stainless steel tubing, the IMCP active probe was custom made from E type fiberglass impregnated with a vinyl ester resin covered with a 0.01-in. C glass veil and an ultraviolet inhibited top coat (Figure 12). The outside diameter of the probe body was 2.5 in. and it had a wall thickness of 0.5-in. Following fabrication, testing per ASTM D790-03 showed that the fiberglass reinforced plastic (FRP) materials exceeded the design requirements for bending stress (10,000 psi) and flexural modulus of elasticity (1,000 ksi). Additional design details are available in References 42 and 43.

FRP was selected as the material of construction for the IMCP active probe body primarily because it simplified the electrical isolation of the probe electrodes from the probe body, eliminating the need for the electrical feed-throughs and EPDM gaskets that had been troublesome necessities on all previous stainless steel probe designs. Although FRP is not an immediately-obvious choice for use in nuclear waste tanks, it is exceedingly strong and met all requirements for chemical and radiation resistance. In addition, similar FRP composites had been used to construct numerous liquid observation wells (LOWs) used successfully for years in Hanford SSTs.[45,46]

Six sets of EN electrodes (three electrodes per set) were installed at various elevations on the IMCP active probe. Three EN electrode geometries were used: two sets of C-rings and bullet-shaped electrodes in the supernatant and sludge layers (respectively), and a set of C-rings and a new concentric ring electrode in the vapor space.[V] Electrodes were fabricated from either ASTM A537 CL1 steel or ASTM A1018 carbon steel. To facilitate SCC monitoring, the working electrode in each set of C-ring electrodes was pre-cracked and loaded to yield prior to installation on the probe. Other electrodes were not stressed. In addition to the EN electrodes, the active probe also contained three sets of LPR electrodes ER sensors (to measure the rate of uniform corrosion in the vapor space, supernatant, and sludge regions), plus two silver/silver-chloride reference electrodes used in measuring the corrosion potential of the tank and tank material electrodes on the probe.

A climate-controlled instrument cabinet containing the corrosion monitoring instrumentation, computers, uninterruptable power supplies, intrinsic safety barriers, and wireless data transmission hardware was mounted next to the riser housing the IMCP active probe (Figure 13). Corrosion potential and EN data were collected with a commercially-available system from Capcis Systems, Ltd. Uniform corrosion rate data were collected with commercially-available systems from Rohrback Cosasco Systems, Inc.[VI] Individual radiation-resistant, shielded data cables, running through the interior of the active probe body, connected the corrosion monitoring instrumentation with the in-tank electrodes. All data were processed with commercially available software from Capcis Systems, Ltd., customized to match the IMCP electrode set. Once installed, the system was capable of making full-time, automated EN, LPR, ER, and corrosion potential measurements and could be wirelessly controlled from any computer connected to the Hanford local area network.

Passive Probe Design

The IMCP passive probe primarily functioned as a rack for holding corrosion coupons. The passive probe was fabricated from a 2-inch diameter ASTM A106 carbon steel pipe coated in epoxy. Threaded carbon steel studs and inserts were welded to the passive probe body to hold twenty C-rings (identical to the active probe design) and twenty cylindrical coupons, all fabricated from ASTM A537 CL1 steel (Figure 14). Coupons were equally spaced and alternated along the lower 42 feet of the probe. C-rings were pre-cracked and loaded to yield (net section) prior to attachment on the passive probe. Coupon weights were recorded just prior to installation to facilitate corrosion rate calculations after removal.

Operation

The IMCP was installed in DST 241-AN-107 in September 2006. The system started up and operated as expected for approximately two months. However, at approximately the two-month mark, data from the system suddenly became erratic and inconsistent.[47] Troubleshooting efforts indicated malfunctions in much of the wiring leading to the electrodes installed on the probe body. After several months of investigation, tank waste in-leakage condensate water collection became the most suspected modes of failure, but this could not be confirmed without removing the probe from the tank. Based on the inability to remove and/or repair the in-tank probe, and the continued generation of data that could not be interpreted, automated data collection from the system was terminated in May 2007 and the IMCP active probe was abandoned in place (i.e., not removed from the tank).[48]

In June 2010, an operation to remove the IMCP active probe was conducted. During the operation, it was discovered that the probe body had suffered brittle failure at some previous point in time, allowing the bottom portion of the probe body to separate and fall to the bottom of the tank (Figure 15). As a result, only the top portion of the in-tank probe was recovered, including three vapor space C-ring electrodes and six supernatant bullet-shaped electrodes.[49] Macrophotography of the recovered electrodes indicated that corrosion was slight in the vapor space and extremely slight in the supernatant (Figure 16). Actual corrosion rates could not be determined from weight loss measurements because of difficulty in cleaning epoxy resin (used to seal the electrodes in the probe body) from threaded surfaces on the electrodes. No crack advance was observed in the single pre-cracked C-ring recovered from the vapor space.

The time of probe body failure has never been proven, but it is assumed to coincide with the sharp shift in data a few months after installation of the system. During investigations following probe removal and discovery of the in-tank failure, interviews with field installation personnel indicated that the active FRP probe had come to a stop during installation a few feet above the planned installation depth, presumably due to contact between the lowermost tip of the probe and sludge/solids at the bottom of the tank. This prohibited connection of the flange at the top of the probe body with the mating flange on the tank riser. To complete installation, operations personnel forced the probe the rest of the way down into the tank. Based on the damage to the probe discovered upon removal, it is assumed that these actions may have caused the probe body to arch, crack at a stress riser in the probe body, and ultimately to fail a few months after installation.

Figure 16. Hot cell photography of as-received segment of active probe body showing electrodes from supernatant and remains of ER probe

Multi-Probe Corrosion Monitoring System

Prior to the failure of the IMCP in 2007, periodic difficulties in interpreting EN data plus a number of field operation and fabrication problems had begun to call into question the validity of some EN data and the ability to consistently operate complex real-time corrosion monitoring systems in the tank farm environment. The failure of the IMCP brought these issues to the forefront, resulting in a revision not only to the design of the corrosion monitoring systems, but also to the overall approach to DST corrosion monitoring. Fortunately, a path conducive to both of these needs was already underway at the site.

In 2004, a group of corrosion and nuclear waste chemistry experts from industry, academia, and other DOE sites, that ultimately became known as the Expert Panel Oversight Committee (EPOC), was assembled to review and evaluate proposed initiatives to modify (i.e., optimize) the site's waste chemistry specification requirements for a small set of DSTs with waste chemistries that were particularly difficult to adjust. By optimizing waste chemistry specifications, it could be possible to avoid certain difficult and/or costly waste chemistry adjustment operations. By the end of 2004, EPOC members indicated that optimized waste chemistry control limits could likely be established by conducting laboratory tests to determine the range of corrosion potentials conducive to SCC for a given DST waste type, then monitoring the corrosion potential of the associated DST(s) with relatively simple in-tank corrosion monitoring systems.[50] In 2005 and 2006, researchers performing laboratory corrosion testing, under the guidance of the EPOC, successfully identified the relationship between corrosion potential and the initiation of pitting and SCC in the DST 241-AN-102 and DST 241-AN-107 waste types.[51]

Figure 17. Installation of 241-AN-102 MPCMS, May 2008

Once the range of potentials for pitting and SCC were defined in the laboratory testing for the DST 241-AN-102 and 241-AN-107 waste types, focus shifted to measuring the corrosion potential of those tanks. In 2007, the functions and requirements were completed for the first new corrosion monitoring system associated with this program, known as the Multi-Probe Corrosion Monitoring System (MPCMS).[52] The first MPCMS was installed in 241-AN-102 in May 2008 (Figure 17).

Additional laboratory test programs have been completed, or are currently underway, for other DST waste types and modes of corrosion. To date, four additional MPCMSs have been installed in DSTs at the site: 241-AY-102 in March 2009, 241-AY-101 in April 2009, 241-AN-107 in June 2010, and 241-AW-104 in July 2010.[53-56] All five DSTs are currently in operation.

In general, the five MPCMSs share a similar design and are composed of two main assemblies: a fixed probe (designed to remain in the tank for the life of the system), and a set of removable probes (designed to be removed and inspected as required). Minor modifications and improvements have been made with each successive system to address lessons learned during system fabrication, operation, and installation, but the basic MPCMS design has not been significantly changed since its conception.

Figure 18. Top of MPCMS fixed probe body showing guide plates for removable probes

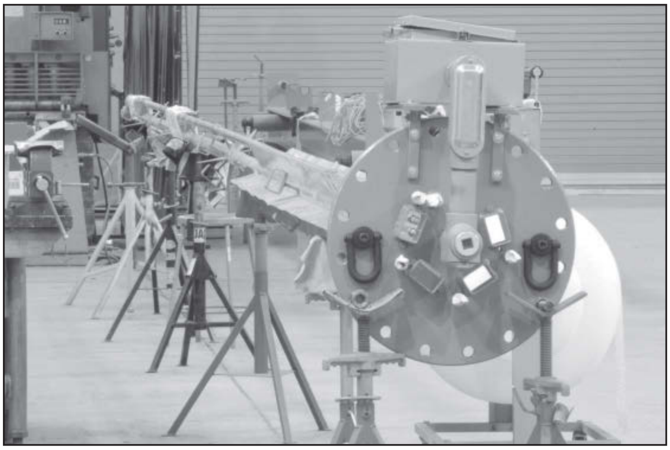
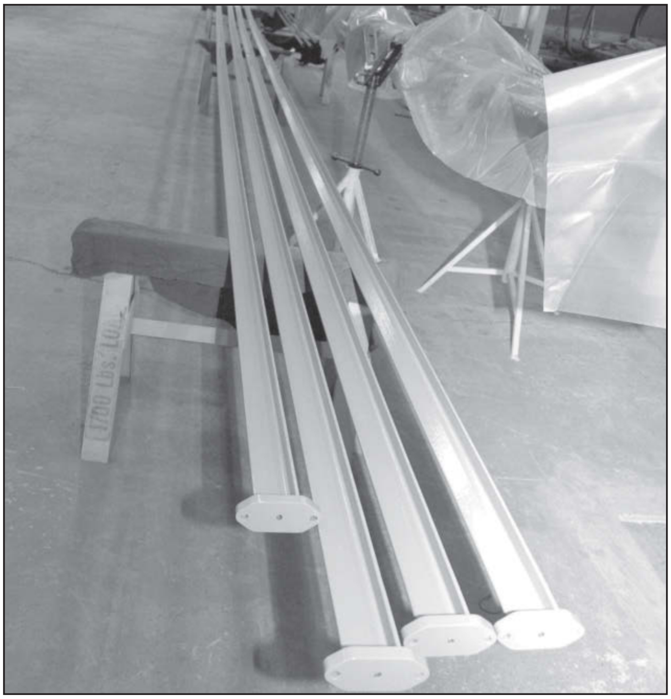


Figure 19. Partially complete MPCMS removable probes prior to installation in fixed probe



Additional laboratory test programs (not tied to the previously-described EPOC-directed programs) have been performed to optimize materials of construction, electrode design, expected data types, and other design and operational issues.[57-59]

Fixed Probe Design

The fixed probe of each MPCMS is fabricated from 2-inch diameter Schedule 80 ASTM A106 Grade B carbon steel pipe with mounting brackets guide plate assemblies to house four removable probes (Figure 18-19). The primary function of the fixed probe is to house electrodes and sensors dedicated to monitoring tank corrosion potential and general corrosion rates in the vapor space, supernatant, and sludge/solids layer. To accomplish these functions, the fixed probe is fitted with sets of custom-made radiation-resistant primary reference electrodes (of either silver/silver-chloride, Calomel, and/or copper/copper-sulfate type, depending on system), surrogate tank steel electrodes (for corrosion potential measurements), metallic secondary reference electrodes (for making corrosion potential measurements upon the failure of the primary reference electrodes), ER sensors, and a variety of stressed C-ring and unstressed corrosion coupons (made of steel similar to that used in tank construction) (Figure 20).[VII] In addition, the fixed probe also contains mounting brackets guide plate assemblies designed to house four removable probes, holding them in place during system installation and operation.

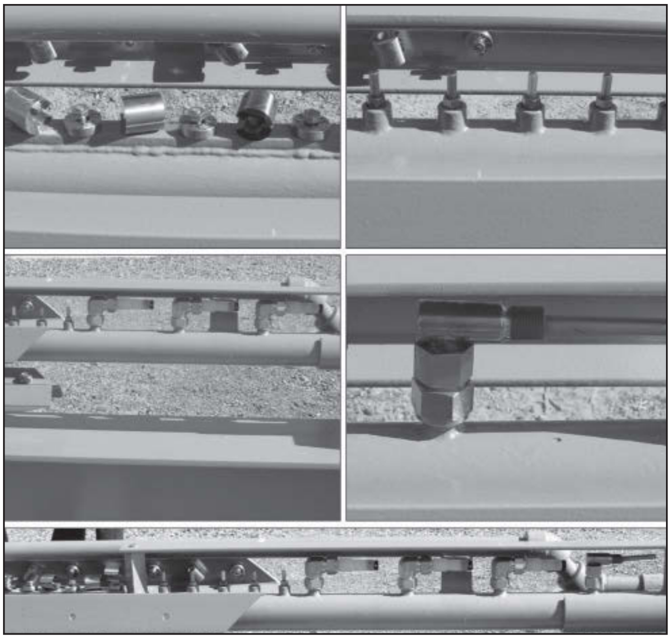
Electrodes, sensors, and coupons are installed along the fixed probe at various elevations to facilitate corrosion monitoring in regions of interest (e.g., vapor space, supernatant, sludge/solids region), or in regions that are expected to be of interest in the future. Electrode and sensor elevations vary from system to system depending on tank volume and waste type. Electrodes and sensors are isolated from the probe body with commercially-available glass-lined feed throughs. Individual radiation-resistant shielded data cables, running through the interior of the fixed probe body, connect the in-tank electrodes and sensors to measurement test points located in a weather-tight terminal box at probe top.

Unlike previous DST corrosion monitoring systems, no electrically-powered corrosion monitoring hardware is installed in the MPCMS field cabinets. Likewise for simplicity, the systems do not provide for automated data collection. Instead, measurement and test equipment is periodically carried out to the cabinets by tank farm operations personnel and used to gather data from the in-tank electrodes. The frequency at which data are collected and the type and amount of data collected vary by system and length of operation. In general, more data are collected on a more frequent basis at the start of system operation than later in the life of the system. See References 52-56 for system-specific design details.

Removable Probe Design

The MPCMS fixed probe houses four removable probes that essentially serve as simple, albeit lengthy, coupon racks. Removable probes are similar in each of the MPCMS designs. Removable probes are fabricated from ASTM A36 carbon steel angle iron or 1.5-inch diameter schedule 40 ASTM A106 Grade B carbon steel pipe (depending on system). Each removable probe holds numerous stressed and unstressed coupons at a variety of elevations in the DST. Coupon elevations vary from system to system depending on tank volume and waste type. Because of the metallurgical similarity in the composition of the carbon steel removable probes and the carbon steel electrodes that they house, the coupons are not electrically isolated from the removable probe

Figure 20. MPCMS fixed probe components: coupons (upper left), secondary reference electrodes and surrogate tank steel electrodes (upper right), primary reference electrodes (lower left), ER sensor (lower right), overview (bottom)



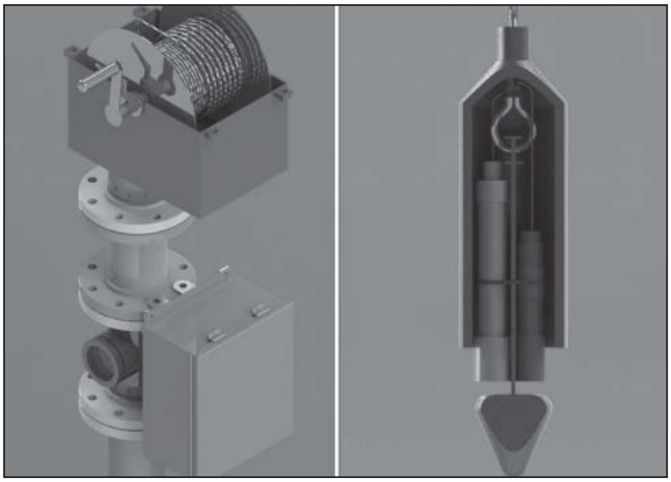
bodies. The MPCMS design facilitates the complete removal of a removable probe while minimizing the associated disturbance to the fixed probe electrodes and coupons on any remaining removable probes. Once removed, removable probes cannot be re-installed. See References 52-56 for system-specific details of removable probe design.

Operation

As with previous DST corrosion monitoring systems, the harsh DST operating environment has taken its toll on the MPCMSs. All systems have suffered at least one electrode failure and four of the five have suffered multiple electrode failures. However, because redundant electrodes are installed on each system, all systems are still in operation and performing their primary functions (i.e., to measure waste tank corrosion potential and corrosion rates in the various regions in the tanks). Aside from periodic electrode failures, not other significant failures or malfunctions have been recorded.

Corrosion potential data from the MPCMSs are periodically collected and compared with the ranges of corrosion potential shown to induce SCC in the EPOC-guided laboratory test programs. Prior to January 1, 2012, data and system performance were periodically summarized for each MPCMS in standalone reports. In January 2012, this format was changed to combine data from all five MPCMSs into a single quarterly operational summary report.[60] A detailed review of all MPCMS corrosion potential data, tank operational information, electrode failures, and other system performance information is beyond the scope of this work, but in general, the systems have shown the DST corrosion potentials to be outside the range of potentials shown to induce SCC in the EPOC-guided laboratory test programs. In addition, ER sensors mounted on the fixed probe have consistently shown uniform corrosion rates to be well under 1 mpy in all monitored regions.

Figure 21. Conceptual RCMP Design: Reel Assembly (Left), Probe Head (Right)



Retractable Corrosion Monitoring Probe

A significant problem with the MPCMS (and all previous DST corrosion monitoring systems) is that, once installed in a DST, it is nearly impossible to troubleshoot, inspect, repair, or replace any of the in-tank electrodes or other waste-contacting components. Historically, malfunctioning systems have had to be either abandoned in place or removed and replaced—oftentimes at great expense. In 2011, MPCMS designers and equipment engineers began discussing ways to address this fundamental design problem with in-tank equipment, and in May 2012, a set of design requirements for a new Retractable Corrosion Monitoring Probe (RCMP) were issued.[61]

Formal design of the RCMP is currently underway at ARES Corporation in conjunction with DST tank farm engineering and operations personnel. As with the MPCMS, the primary purpose of the RCMP is to facilitate the measurement of DST corrosion potential. Given this relatively simple purpose, designers were able to greatly simplify the design of the RCMP. Though the design is not yet complete, this new system promises to address historical troubleshooting and repair issues in a somewhat surprising fashion: by reducing the complexity and cost of the system to the point it will not be cost prohibitive to remove and replace the in-tank components upon malfunction, damage, failure, or change in monitoring needs. Preliminary estimates indicate that RCMP fabrication and installation costs could be reduced by 75 percent or more over that of the MPCMS.

To achieve such radical changes in system cost, the form and function of historical DST corrosion monitoring systems were completely revisited. Instead of using a large, fixed, in-tank probe to hold electrodes at various elevations in the DST (and requiring two cranes for installation), the RCMP assembly consists of a small replaceable cable reel assembly and associated housing. The entire assembly is approximately 3 feet x 3 feet x 2 feet and can be carried and installed by hand. The cable reel assembly consists of a simple reel wound with cable leading to a probe head containing the required electrodes. The probe head can be raised and lowered in the tank via the cable reel assembly (Figure 21). At the end of system life, the probe head is retracted completely out of the waste and into the cable reel housing at the top of the riser where it can be glove bagged, removed, and replaced. Note that a permanently installed spray ring (not part of the RCMP design) mounted below the cable reel housing assembly is used in this process to aid in cable decontamination.

The ability to monitor DST corrosion potential from a single reference electrode suspended at a central location in the tank is supported by MPCMS operational data and a formal boundary element analysis conducted in 2012 in support of this design work.[62] Electrodes, sensors, and other components installed on the probe head are determined on a tank-by-tank basis. Other probe heads could be developed to include additional primary reference electrodes, secondary reference electrodes, electrical resistance (ER) sensors, thermocouples, or other elements and sensors. However, the design must remain relatively simple so as to fit through a small 4-inch diameter riser and facilitate retraction via the cable reel mechanism. The first new RCMP is planned for installation in DST 241-AW-105 in 2013 and will contain two commercially-available primary reference electrodes (both Ag/AgCl type).

Summary and Conclusions

The Hanford Site's DSTs must store the inventory of high-level waste until the waste can be removed and processed into a solid form for storage in a long-term repository. Some DSTs have exceeded their design life and all are expected to exceed their design life by the time waste removal and treatment is completed. Because of the importance of the DSTs to the site's ultimate cleanup mission, they are managed under a comprehensive DSTIP, including the installation and use of in-tank DST corrosion monitoring systems.

The design of DST corrosion monitoring systems has evolved steadily, from the prototype system installed in 1996 to the five MPCMSs installed and operating today. These systems have provided a great deal of information on waste corrosivity and waste tank operations. Together with the EPOC-guided waste chemistry optimization program, these systems have become an integral part of DST integrity management. The RCMP promises to be the next step in the evolution of DST corrosion monitoring, providing for in-tank corrosion potential measurements with an inexpensive, serviceable platform. Together with the balance of DSTIP elements, these programs help ensure the availability of the DSTs for the balance of the site cleanup mission.

End Notes

I. Note that, by design, localized forms of corrosion are inhibited by "in-specification" DST waste simulants. Thus, more aggressive, uninhibited nitrate-based waste simulants were required to generate pitting and SCC data in the laboratory test program.
II. Capcis March Ltd., Manchester, UK.
III. Petroleum Research and Production, Witney, Oxfordshire, England.
IV. Capcis Systems, a UMITEK Company, Sycamore Court, Witney, Oxfordshire, England.
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Corrosion Issues Associated with Austenitic Stainless Steel Components Used in Nuclear Materials Extraction and Separation Processes

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Abstract

This paper illustrates the magnitude of the systems, structures, and components used at the Savannah River Site for nuclear materials extraction and separation processes. Corrosion issues, including stress-corrosion cracking, pitting, crevice corrosion, and other corrosion-induced degradation processes are discussed and corrosion mitigation strategies as well as a chloride exclusion program or corrosion acceptance testing.

Introduction

The initial mission of Savannah River Plant (now called the Savannah River Site [SRS]) was the production of nuclear weapons materials. The mission began in 1950 when President Harry S Truman formally asked DuPont to design, construct, and operate a nuclear facility. Construction began in 1951 and by 1956 construction of the basic plant was completed. In 1953 nuclear criticality was obtained in a nuclear materials production reactor. Radioactive operations in the chemical separation facility began in 1954 and the first high-level wastes were transferred to waste storage tanks in the same time frame. SRS produced approximately 36 metric tons of ^{239}Pu between 1953 and 1988 when production operations ceased. The magnitude of this achievement is apparent in the 310-square mile footprint of the plant, in the number of major facilities constructed, including five reactors, two chemical separation plants, a nuclear fuel and target fabrication facility, a tritium extraction facility, as well as nuclear waste management facilities, and in the infrastructure necessary to move people and materials throughout the plant.

Nuclear materials production processes included the manufacture of fuel and target elements, irradiation of these elements in production reactors, storage of the irradiated elements in water pools to obtain sufficient radioactive decay, transfer and dissolution of fuel and target elements, separation of the radioisotopes into production (^{239}Pu for example) and waste products, and storage and disposition of the nuclear wastes. The handling, storage, and disposition of the legacy nuclear materials and wastes by-products that resulted from the nuclear materials production operations continue to be major missions at SRS. Figure 1 illustrates some of the facilities and process flows associated with the disposition of the nuclear materials and the waste handling missions, including the waste storage tanks, the waste vitrification facility (DWPF), and salt processing.

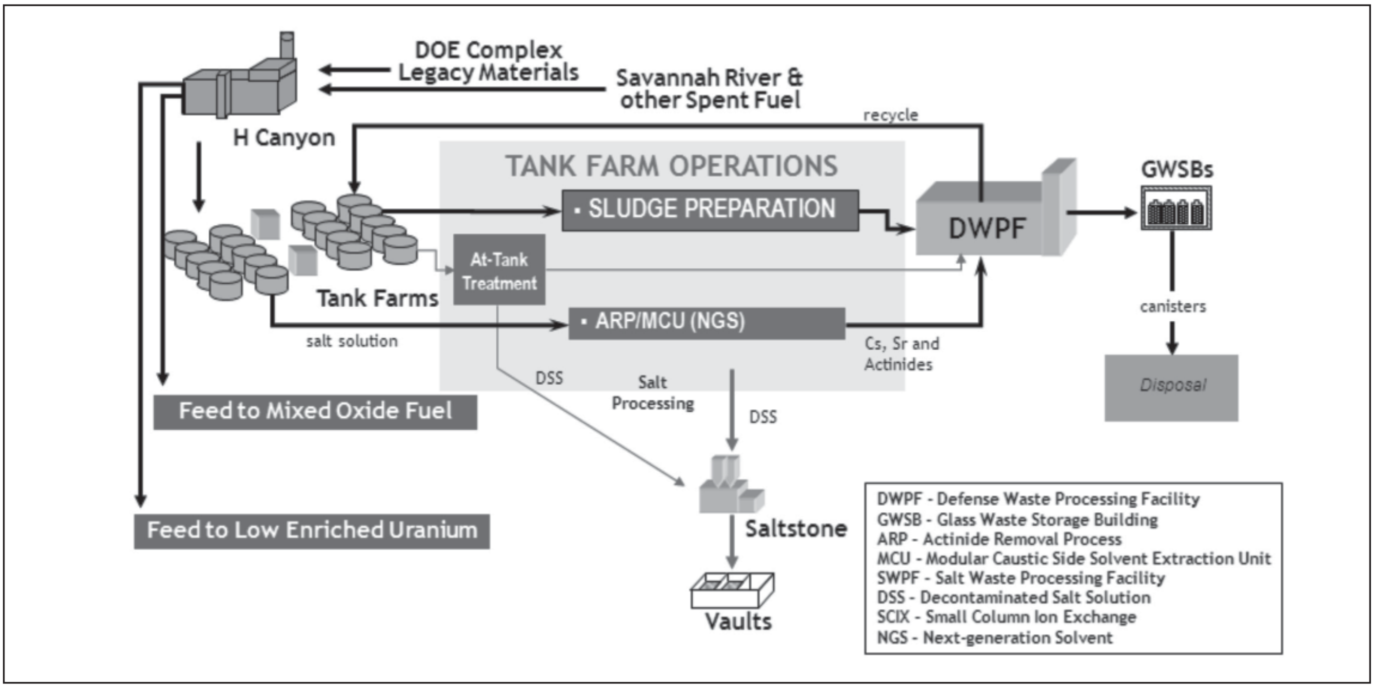
The facilities and infrastructure that support the past, present, and emergent SRS missions are both large and complex. As a rule, material issues generally accompany the construction, start-up, operation, and closure of any new and complex facility. SRS has been proactive in developing safe and efficient operations in large and complex nuclear systems through the resolution of the material issues. The material issues at SRS, as well as nationally, frequently involve corrosion-induced degradation processes as shown by the general observation that "the annual direct cost of metallic corrosion to the United States is approximately 3.1 percent of the gross domestic product and 25 to 30 percent of that cost could be eliminated if optimum corrosion management practices were employed."[1] SRS has addressed corrosion through engineering practices that successfully mitigated numerous material issues.

This paper provides an illustration of nuclear materials management through facility design and construction and discusses the mechanisms that have caused degradation of austenitic stainless steels used for selected systems, structures, and components (SSCs) of the nuclear materials separations and waste processing facilities at SRS. These separation facilities, referred to as canyons, contain processes for the dissolution of irradiated fuel and target elements, the separation of nuclear materials, the processing and storage of nuclear wastes, and associated systems for the handling and transfer of nuclear materials and wastes. A wide variety of materials have been used throughout these material/waste processing areas. Some of these materials have corrosion or degradation issues which have been mitigated through corrosion engineering practices as illustrated in several other manuscripts in this issue of the *Journal of Nuclear Materials Management.* [2-5]

Scope

Degradation mechanisms were evaluated for their potential impact on austenitic stainless steels used in the construction of the SSCs for facilities involved with the separation of nuclear materials. The issues discussed are primarily those affecting the SSCs

Figure 1. Schematic of SRS nuclear and waste material cycle from processing of nuclear materials



that are safety class and safety significant systems that maintain both a confinement function and a safe, reliable processing capability. Confinement of the SSCs is demonstrated through evaluations, inspections (where accessible) and monitoring. The degradation evaluation consisted of compiling the service history of failures, reviewing inspection reports and literature data, and analyzing the material response of the fluid/gas retaining boundary to known environmental conditions. The evaluation also included an assessment of confinement and process functions which the materials of construction must provide to support safe operations. The SSCs include the canyons or chemical separation buildings, process cells and tanks, dissolvers, evaporators, cooling coils, and the ventilation system. An evaluation of electrical and control systems is not included.

Confinement Function of Materials and Structures

Confinement is achieved through leak-tightness, structural stability, and administrative controls that are established to mitigate identified leakage. This function of the SSCs maintains a boundary against radioactive process fluids and vapors releases to the environment and provides the building confinement function, e.g., HVAC, filters, fans, etc.

Degradation of the materials can lead to a loss in the confinement function and limit the useful service life of an SSC. Failures in confinement of process vessels and connecting piping would not necessarily eliminate the overall confinement of process solutions and waste streams provided by the canyon facilities. For example leakage from processing equipment can be collected in sumps (through the sloped grade construction of floors). Understanding the degradation mechanisms along with monitoring of vessel conditions or operational parameters provide a means to manage the leaks effectively and plan for vessel replacement.

The remaining operational SRS chemical separation building is the only such facility in the United States and contains processing systems to perform chemical separations of spent fuels and targets elements that had been irradiated in the SRS production reactors as well as legacy materials around the nuclear complex. The canyon buildings were constructed as Class 1 structures and required approximately 1,350 reinforced concrete slabs (individually weighing an average 18 tons). The buildings rest on a 66 inch (167.6 cm) thick concrete mat, 139 feet (42.4 m) wide by 835 feet (254.5 m) in length. Total quantity of materials of construction for the canyon buildings included 202,410 yard^3 (154, 761 m^3) of concrete and 13,585 tons of reinforcing steel.[6] The second canyon building design incorporated construction cost reductions and "lessons learned" from the construction of the first building. The building structures serve to isolate the processing equipment from the public, environment, and operating personnel.

Process Function of Materials and Structures

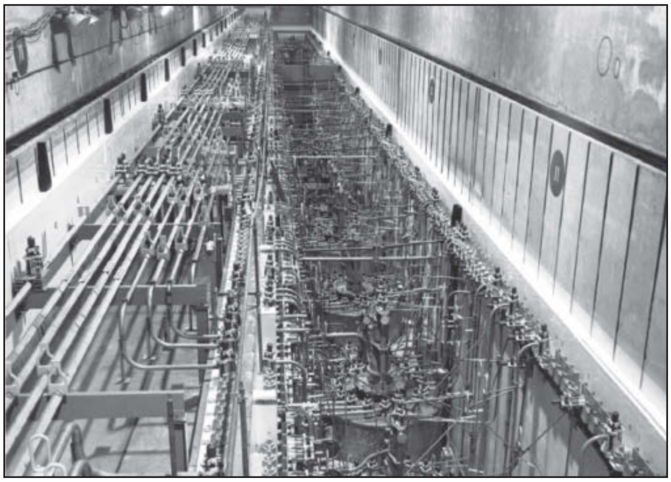
The SRS separation buildings contain two parallel canyons separated from each other by a central operating and service section. One canyon is for highly radioactive (presence of fissile materials) processes and the other is for the less radioactive or warm processes. Each canyon is divided into eighteen sections, generally 43 feet (13.1 m) long, and is designed for a single row of process vessels. Each section is subdivided into four process cells. The locations of tank trunnions and wall nozzles are the same in each of these sections as shown in Figure 2. The floors in each section are sloped so that spills, leaks, and overflows drain to a sump.

The hot canyon contains processing systems for highly radioactive materials and chemical solutions, such as nuclear material dissolution, high activity waste processing, and the first cycle solvent extraction. The warm canyon contains lower activity chemical solutions including second cycle solvent extraction and low activity waste processing. Remote operation of bridge cranes in both the hot and warm canyons provides servicing of the equipment including assembly and disassembly of process systems and equipment replacement. Due to the high radiation field and contamination potential, the reinforced concrete structures comprising the canyon cells are not readily repairable or replaceable. All other process equipment is replaceable when failure occurs. The magnitude of the resources required to provide a facility similar to the SRS separation capabilities of dissolving, separating and processing nuclear materials is huge. Therefore, sustaining these capabilities is important to the country's nuclear future.

Materials of Construction and Service Environments

A listing of the materials of construction and the service environment are shown in Table 1 for the SSCs that provide the containment and process function for the SRS separation facilities. The SSCs that were not fabricated from austenitic stainless steels are included since they demonstrate the complete containment function.

Figure 2. Interior of canyon building showing vessels and jumper piping



Summary of Service-Induced Degradation

After numerous years of service the SSCs continue to maintain confinement through the repair and replacement of degraded materials. AISI Type 304L stainless steel (304L) is the material of construction for many of the SSCs. Significant, widespread service-induced degradation of 304L process tanks has not been observed to date, although failures have occurred in heated vessels such as cooling coils for dissolvers and evaporators. The cooling coils' failures act as an indicator for potential tank failure because they are thinner than the vessel wall. Replacement materials were investigated and coils made of Inconel 690 were used subsequently since this alloy was more resistant in these applications.

The concrete structures of the canyon facilities show some signs of aging. During periodic inspections, spalling of the concrete cells was observed. The spalling resulted from exposure to acidic process fluid that spilled, especially in the cells that have contained evaporators. Stainless steel plates have been used under the process vessels on the floor of the cells to maintain the vessels in a level position and allow processing to continue. Erosion of the concrete of the exhaust tunnel for the canyon has also been

Table 1. Materials of construction and service environments for the SSC for SRS separation facilities

SSC	Material of Construction	Service Environment
Canyon building	Reinforced concrete slabs	Ambient air temperature below 70°C, some leaking fluids
Process tanks	304L and 347 stainless steel (select vessels)	Nitric acid based solutions, temperatures generally below 100°C
Cooling coils	304L, 309Cb, 690	Internal – treated well water External – nitric acid solutions
Piping and valves	304L, 316, 416, 690, 309Cb, 347, 304 ELC, Hastelloy C	Generally low temperature except for steam lines and jumpers and dip tubes in heated vessels
Equipment ventilation system	Carbon steel, 304L	Ambient temperature, nitric acid fumes, temperatures generally below 70°C
Building ventilation	Reinforced concrete	Ambient temperature and humidity, nitric acid fumes
Sand filter	Reinforced concrete with multiple grades of filtering material	Ambient temperature and humidity

observed. The exhaust stack brick liners are in good condition but show some minor cracking and or erosion/spalling.

Degradation Mechanisms

The primary degradation mechanisms of the SRS canyon facilities discussed in this paper are those that affect austenitic stainless steels, even though carbon steels, and concrete materials are clearly affected by service conditions. The mechanisms discussed are those likely to be active under the conditions of service and could impact the integrity of the materials and structures within their desired service lives.

Austenitic stainless steels are widely used in the chemical processing industry due to their corrosion resistance and excellent fabrication characteristics. The corrosion resistance of austenitic stainless steel is attributable to the surface chromium-oxide film that forms in the presence of oxygen and is essentially insoluble, self-healing, and non-porous. A minimum of 12 percent chromium is required for film formation and the alloying of 18 percent Cr and 8 percent Ni broadens the film forming range in non-oxidizing environments. The integrity of the oxide film must be maintained for corrosion resistance.

The corrosion of austenitic stainless steel is well documented and its behavior in many environments is readily predictable. The resistance of stainless steel to acids depends on the hydrogen ion (H^+) concentration, the oxidizing capacity of the acid, the steel composition (chromium, nickel, and carbon content), welding, and heat treatment.[7] Type 304L stainless steel is widely used throughout the canyon process equipment and is the material of choice for nitric acid service. Therefore, Type 304L is the focus of much of this paper.

General Corrosion

General corrosion is the uniform attack over the entire exposed surface of a structure or component that results in gradual thinning of the material. General corrosion has not led to any known failures for austenitic stainless steels in the canyon buildings. This type of degradation proceeds without any perceptible localized attack. Laboratory experiments have shown that at 16°C the corrosion rate for Type 304 stainless steel (304) is 0.003 mm/yr (0.118 mils per year (mpy)) for all concentrations of nitric acid.[8] The corrosion rate increases to 0.2 mm/yr (7.9 mpy) in 65 percent boiling nitric acid.[9] Table 2 lists the corrosion rates for 304 and 304L to the different cold feed chemicals for canyon processes.[10, 11] If literature sources differed, the higher or more conservative value was listed. These data are non-specific since actual conditions (i.e., material heat, surface morphology, aeration, flow rate, etc.) are not well characterized and impact the actual corrosion rates.

General corrosion of 304L exposed to nitric acid has not been a significant degradation mechanism at the processing conditions of the SRS separation processes. Ultrasonic thickness measurements of a canyon tank removed from service due to a coil failure revealed that after twenty-five years of service the observed wall thickness was approximately the original nominal thickness.[12] There have been no failures that have been caused by general corrosion at the SRS.

Table 2. Corrosion rates of 304/304L in H-Canyon cold feed Chemicals*

Cold Feed Chemical	Concentration (percent)	Corrosion Rate (mpy)	Temperature Range (°C)
34 percent Aluminum Nitrate	Saturated	<20	<40
Boric Acid	16	<2	22
Ferrous Sulfamate	40	ND	<50
Manganese Nitrate	50	ND	<50
Mercuric Nitrate	10	<20	<100
Nitric Acid	0.75-50	20	<100
Potassium Permanganate	10-20	<20	<100
Sodium Carbonate	30	<20	<100
Sodium Hydroxide	50	<20	<100
Sodium Nitrite	40	<20	<100
TBP w/ Paraffin	7.5	ND	ND

* No data

Stress-corrosion Cracking

Stress-corrosion cracking (SCC) is an environmentally assisted, slow-crack propagation process caused by the simultaneous combination of mechanical stress and corrosive chemical reactions with a susceptible material. For the stainless steel embedded piping, several environments are present in the canyon building that can lead to SCC as described below. The mechanical stress may be either applied or residual and usually is tensile in nature. The residual stresses that are associated with fabrication, welding, and thermal cycling are generally responsible for the SCC catastrophic failure of pressurized equipment.

SCC may develop as intercrystalline or transcrystalline cracks typically with little or no evidence of general corrosion. For 304, cracking generally propagates along the intergranular pathways if the material is sensitized, but in non-sensitized material transgranular cracking is predominant. Intergranular SCC of austenitic stainless steels results from the precipitation of chromium, forming chromium-carbide particles ($Cr_{23}C_6$) along the grain boundary if heated and allowed to cool slowly (e.g., welding) over a temperature range of 500 to 850°C (932 to 1,562°F). This process is termed sensitization and depletes the chromium concentration in the surrounding matrix to below 12 percent, which is needed to preserve the protective nature of the surface oxide. The presence of manganese sulfides in the material, unlike the chromium carbides, has no effect on stress-corrosion cracking in austenitic stainless steels.[17]

Figure 3. Effect of chloride concentration on the SCC susceptibility of 304 stainless steel exposed at 100°C (212°F) under the concentrating condition of the Wick tests[17]

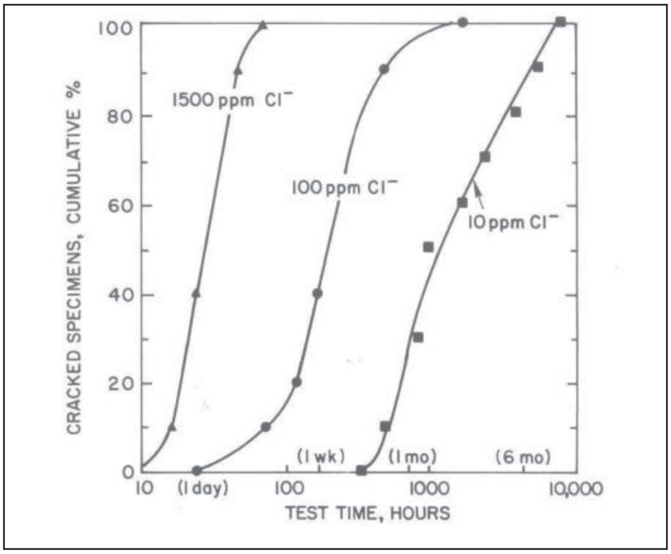
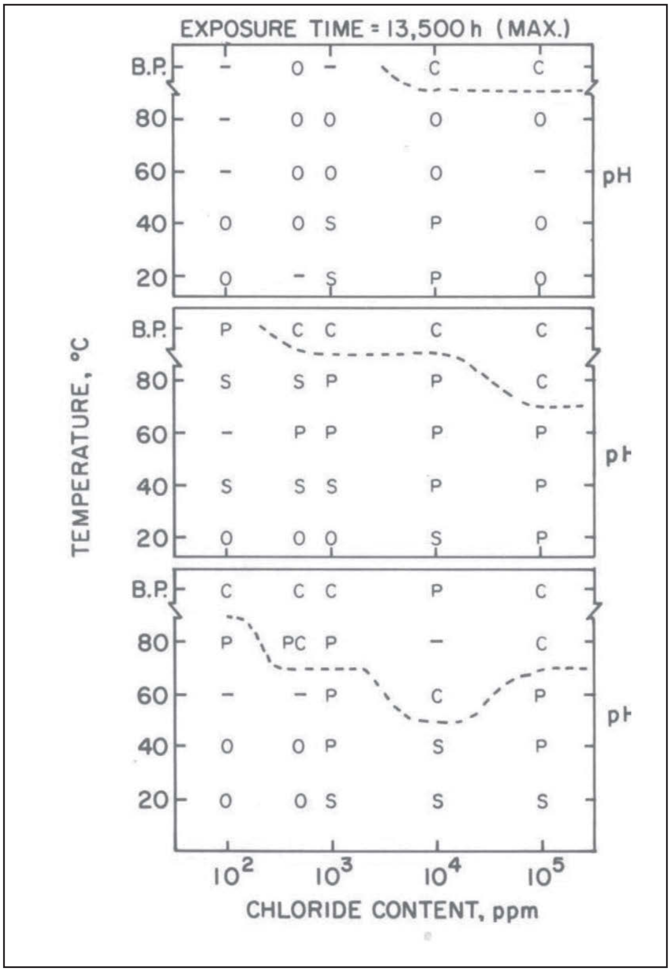


Figure 4. Effect of temperature, pH, and chloride concentration on SCC susceptibility of 304 stainless steel in sodium chloride solutions (C=SCC, P=Pits, S=stains, O=no effect)[17]



Transgranular SCC is affected by numerous metallurgical factors, such as, crystal structure, yield strength, grain size and shape, composition, dislocation density, and stacking fault energy. The key metallurgical factor is the alloying effects on slip planarity. The primary fracture facets for austenitic stainless steel tested in aqueous magnesium chloride at 155°C (311°F) were on (100) planes.[14]

One additional metallurgical factor that affects stress-corrosion cracking in austenitic stainless steels is the amount of cold work. The forming of a metal results in plastic deformation occurring to the metal which results in an increase in tensile and yield strength with a decrease in ductility. The cold work leads to a greater time to failure by SCC for a constant applied stress or a greater stress to obtain cracking in a similar time.

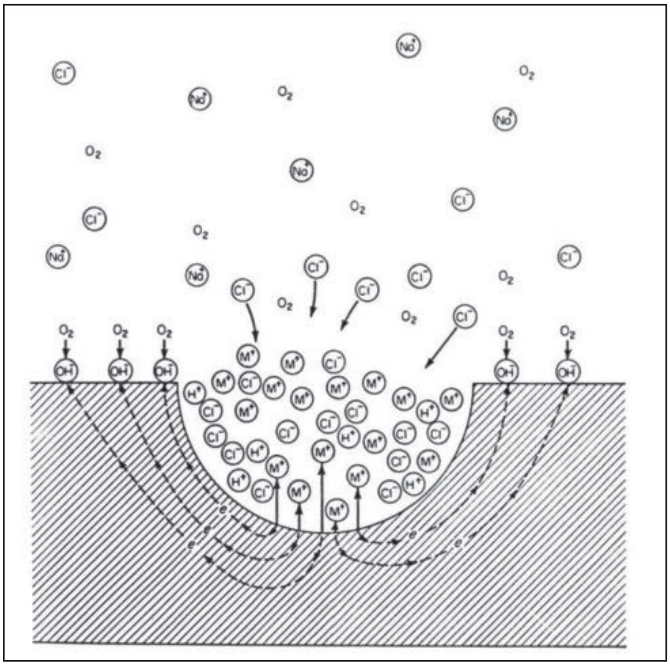
For chloride-bearing environments, defining a minimum chloride concentration below which SCC will not occur is difficult because of the effects of metallic cations, pH, oxygen concentration, and other reducible or adsorbed species. Some general minimum concentrations have been defined by American Petroleum Institute (API) depending on the application. For example, API 650, which covers storage tanks, specifies a maximum chloride concentration of 200 ppm for temperatures less than 40°C (104°F) and 100 ppm for temperatures between 40 and 65°C (104 and149°F), whereas API 651 specifies a maximum of 50 ppm for hydrotesting water. For SRS, an engineering standard specifies a maximum chloride level of 250 ppm at >40°C (<104°F).[15] As noted below, chloride levels as low as 5-10 ppm Cl can result in SCC.

The occurrence of SCC is a function of chloride concentration. As chloride concentration increases, the time to failure decreases. Figure 3 shows this effect for 304 stainless steel samples that were exposed at 100°C (212°F) under the concentration conditions of a Wick test. In this test the chloride solution is brought to the stainless steel surface through a porous medium. For the chloride concentrations shown, all the samples failed eventually.

The hydrogen concentration, i.e., pH, has a significant effect on cracking. As the pH is lowered time to failure via SCC decreases while at higher pH the failure time increases. Cracking occurs in 304 stainless steels at neutral pH (6-8) with temperatures at 185-200°F (85-93°C) and chloride levels as low as 5 ppm Cl. In a study by Rideout at SRS, sensitized 304 samples were found to crack in a 10 ppm Cl at 194°F (90°C) with pH in the range of 2.5 to 7.[17] At lower pH values cracking was not observed since the solution pH was adjusted with nitric acid and the sample passivated.

Temperature also has a significant effect on SCC. A temperature of 60°C (140°F) was once thought to be a lower limit below which chloride stress-corrosion cracking did not occur. However, SCC failures have occurred in swimming pools and near marine

Figure 5. Autocatalytic growth of pit associated with metal dissolution, water hydrolysis and hydrogen or oxygen reduction leading to pit growth[20]



environments at ambient temperature.[16] Increasing temperature does lead to decreases in time to failure but also a transition from pitting to SCC. Figure 4 shows the results of a study with 304 in which the chloride concentration, pH and temperature were varied. These tests were performed in sodium chloride solutions with pH adjustments made with additions of either sodium hydroxide or hydrochloric acid.

Some additional factors that affect SCC are the presence of oxygen and metallic cations. Although not necessary for SCC depending on other conditions, the presence of oxygen can accelerate SCC. Metallic cations that are present can affect SCC occurrence. Mercury aids in cracking and manganese does accelerate the attack intergranularly.

Embedded piping in the SRS canyon building has been subjected to a high chloride environment from the use of a PVC pipe wrap over cork insulation. This environment coupled with elevated temperature in steam piping led to SCC. Between 1956 and 1976 there were seventy-six embedded pipe failures with the chief cause of failure as chloride stress-corrosion cracking. These cracks were tight since SCC was identified by macro-etching in hot 50 percent HCl but not by dye penetrant testing. The majority of these failed pipes/nozzles were used in steam or condensate service. These failures highlight the effect that chloride-bearing non-metallic parts, such as gaskets, can have on stainless steel components since degradation of these parts leads to SCC. Most of the other fluids that are fed through the embedded piping are free of chlorides and not expected to lead to SCC.

Nitric acid seepage past gasket material on HNO_3 absorber columns resulted in the SCC of 36 percent of the 240 (416 stainless steel) nuts and studs on one column. Only six of the nuts and studs were damaged in another column primarily because double gaskets were used as compared to a single gasket in the first column. Chemical analysis of fluids revealed that chlorides were present in undetermined quantities, but less than 200 ppm. These failures highlight that chlorides can concentrate during service and provide corrosion conditions.

The site has significantly reduced the instances of stress-corrosion cracking in austenitic stainless steels through a chloride exclusion program that requires the leachable chloride content of any gasket, coating, tape, paint or ink contacting austenitic stainless steels be below 250 ppm.[15]

Pitting Corrosion

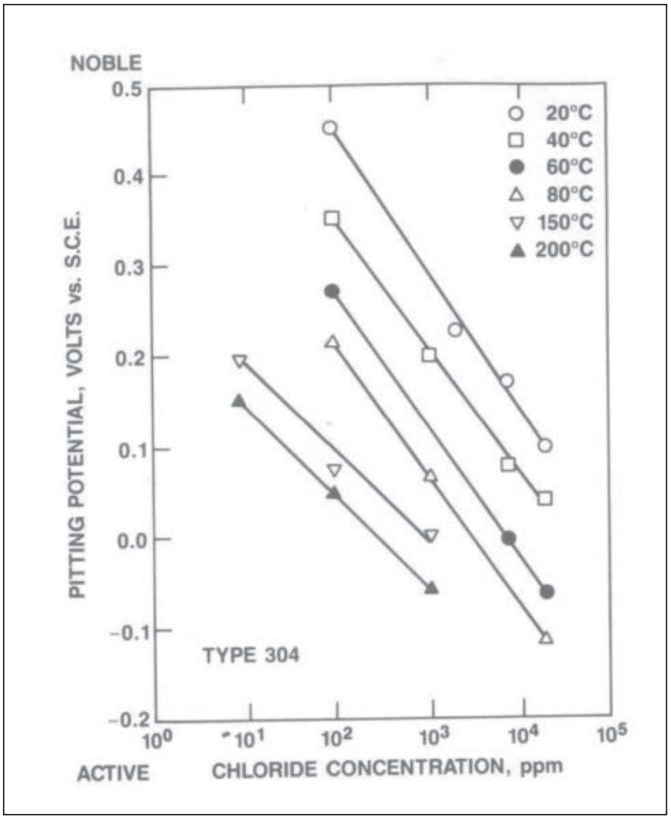
Pitting is an insidious localized form of corrosion that occurs on passivated metallic surfaces exposed to relatively specific aggressive environments. Small defects or discontinuities such as scratches, inclusions, or slight compositional variations in the passive film may selectively be attacked by the corrosive media and initiate a pit. Figure 5 shows the autocatalytic processes occurring in a corrosion pit. Pitting is influenced by temperature and is associated with velocity of the corrosive medium. Local aggressive chemistries develop in regions where stagnant conditions exist and mixing with the bulk solution is low. Once a pit has initiated, an aggressive chemistry quite different from the bulk solution develops within the pit and may lead to rapid autocatalytic growth of the pit (in depth).

Pitting is expected to occur most likely through the presence of chloride ions. These chlorides ions would be a contaminant in the piping. Material properties affect the pitting resistance in stainless steel. These properties include the presence of manganese sulfides, sensitization of the metal, surface condition and the effects of cold work. The effects of cold work have been found to either increase or decrease pitting resistance but this effect is small.

The presence of manganese sulfides is probably the most important factor contributing to the pitting resistance since the sulfides are sites of pit initiation.[17] The sulfides dissolve, especially in chloride bearing solutions, at the corrosion potential of stainless steel. A small pit without a protective oxide and containing an acidic environment is left for the dissolution of the base metal and propagation of the pit. The effectiveness of a sulfide inclusion as pit initiators is dependent on its shape, size and chemistry.

Welding of the piping can lead to sensitization of the base metal, which is the formation of chromium carbides that result from a thermal transient into a critical temperature range as discussed previously. These sites are more favored than the manganese sulfides. For 304, the manganese sulfides in the weld metal redistribute and provide a superior pitting resistance than the base metal.

Figure 6. Effects of chloride concentration and temperature on the pitting potential of 304 stainless steel[18]

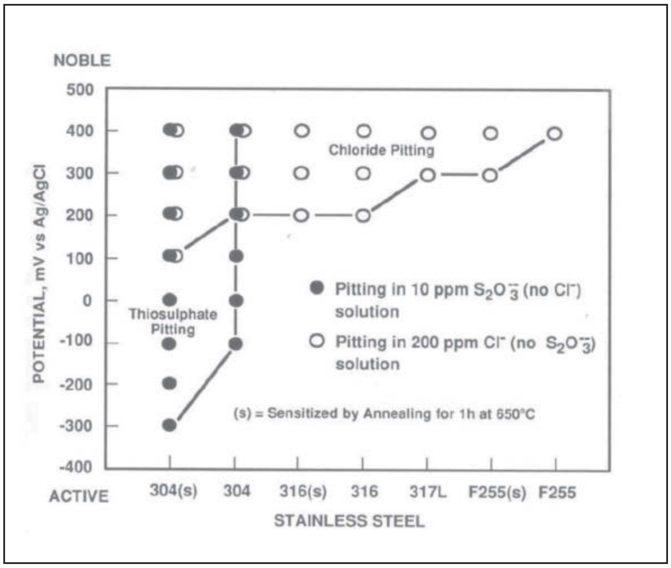


The surface condition of stainless steel can alter the pitting resistance.[17] Heat treatments, grinding, and abrasive blasting tend to decrease the pitting resistance. Pickling and passivation are beneficial due to the removal of manganese sulfides, embedded iron particles and the outer oxide layer which can be depleted in chromium.

The pitting process is also affected by the environment including the temperature, concentrations of aggressive species, oxygen, and hydrogen ion (pH) concentrations. Aggressive species include chloride, thiosulfate (from manganese sulfides), mercury, and permanganate. For stainless steel the susceptibility to pitting increases with chloride concentration. A measure of this susceptibility is the pitting potential. The pitting potential is an electrochemical measure at which pitting is found to initiate and propagate in a given solution. As the concentration of chloride increases the pitting potential decreases logarithmically and pitting becomes more likely. The effect of chloride and temperature for 304 is shown in Figure 6.[18] At a given chloride concentration, the pitting potential decreases and pitting susceptibility increases with a rising temperature. These electrochemical changes are a manifestation of the change in the protective nature of the oxide film.

Even in the absence of chloride, pitting can occur due to the dissolution of manganese sulfides as discussed above. This dissolution leads to a local acidification and the formation of thiosulfate ions. For 304, pitting readily occurs in a solution (pH = 4.5) with 10 ppm thiosulfate at a temperature of 50°C (122°F) as shown in Figure 7. The 304 pitted at potentials even in the active range, i.e., less than 100 mV, which is well below the normal corrosion potential for stainless steel.

Figure 7. Pitting of stainless steels in chloride containing and thiosulfate containing solutions at twenty-four-hour potentiostatic tests[17]



The mercury and permanganate ions all act as cathodic depolarizers, i.e., they accelerate the cathodic reaction for the corrosion process.[17] This acceleration results from either increased efficiency of cathodic areas or as an additional cathodic reaction. The increased efficiency results from metal ions that deposit on the stainless steel surface which have a smaller overpotential for the cathodic reaction, which is oxygen reduction at neutral and alkaline pH water or hydrogen reduction in acidic water. For mercury, the concentration must be greater than 0.5 ppm to aggravate the corrosion due to the amalgamation of the stainless steel surface.[20]

Experimental evidence shows that although pit depths increase with time, pitting rates decrease. Because of the uncertainties in predicting the growth rate of the deepest pits, pitting control measures often depend upon the establishment of conditions under which pits do not initiate.

For H-canyon piping, mitigating actions for pitting include rinsing of the lines between changes in service, monitoring of chloride concentrations in feed water for steam system, and selection of low-chloride bearing non-metallic materials to be in contact with process equipment. Pitting attack of austenitic stainless steel is inhibited by the presence of nitric acid (i.e., nitric acid promotes the formation of a passive film layer on types 304 and 304L stainless steels), so using a low molar nitric acid rinse is beneficial.

Figure 8. Schematic representation of crevice corrosion[20]

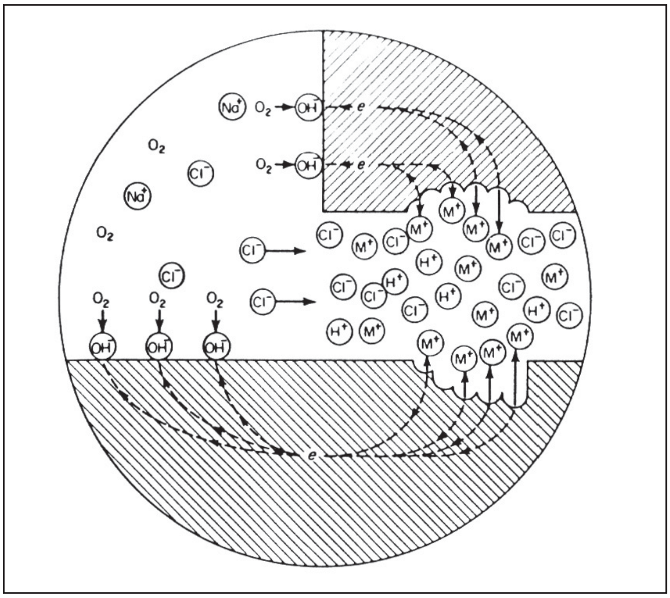
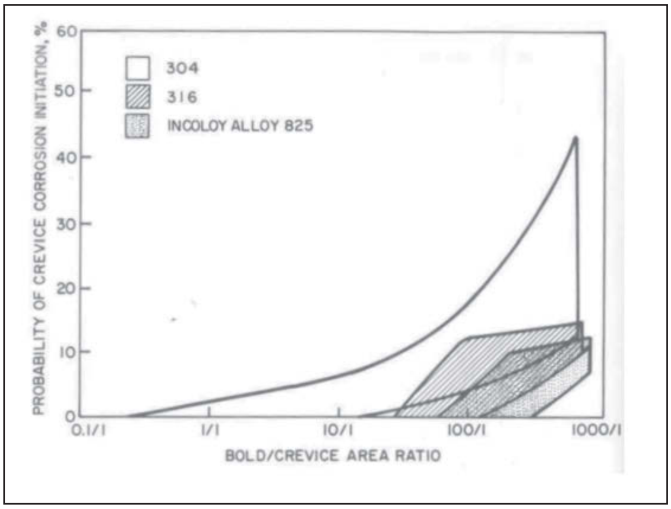


Figure 9. Probability of crevice corrosion initiation as a function of bold/crevice area ratio[17]



Crevice Corrosion

Crevice corrosion occurs at shielded locations with a stagnant solution such as under deposits (scale, corrosion products) or inside crevices (weld defects). These crevices can be at mating metal surfaces or where metal and non-metal surfaces are in contact. Concentration-cell attack is also used to describe this type of corrosion, although differences in metal ion or oxygen concentration are only part of the initiation and growth process. Crevice corrosion can be an autocatalytic process, similar to pitting where metal dissolution is followed by water hydrolysis and the migration of chloride ions into the crevice. For the embedded piping, the source of chloride would be either non-metallic materials in contact with process equipment or introduced through chloride contaminated chemicals. Since the corrosion resistance depends upon the oxide film, which is destroyed by high concentrations of chloride and hydrogen ions, austenitic stainless steels are susceptible to crevice corrosion. This form of attack is shown schematically in Figure 8.

Crevice corrosion may initiate in stainless steel by several mechanisms.[17] For 304 in neutral low-chloride solutions, the dissolution of manganese sulfide inclusions is the probable cause of crevice corrosion. As the manganese sulfide dissolves, the solution becomes acidic with the generation of hydrogen ions in addition to manganese and thiosulfate ions.[21] As the pH drops, the thiosulfate breaks down and anodic dissolution of the stainless surface commences. The corrosion products, especially chromium, cause water hydrolysis, leading to further acidification of the water and migration of chloride ions into the crevice. This increased aggressiveness leads to general breakdown of the passive oxide.

In a higher chloride solution, the passive film could breakdown due to changes in the electrochemical nature of the passive film. This level will be influenced by temperature, the opening and depth of the crevice, as well as other constituents in the solution. Mathematical modeling of the crevice corrosion process has been developed and with experimental inputs has been used to define predicted resistances to crevice corrosion of stainless steels in chloride-bearing waters.[19] For 304, exceptional resistance is obtained at levels near 200 ppm. Others have reported a safe chloride limit of 100 ppm for 304.[21] Crevice corrosion and pitting are affected similarly by these variables because the mechanisms are similar. The effect of the solution constituents and temperature was discussed previously.

As referred to above, crevice size is a factor that contributes to the probability or likelihood of crevice corrosion occurring. Mathematical modeling has shown that the deeper the crevice and the narrower the opening or gap the more likely crevice corrosion will be to occur. The crevice size also affects the ratio of the cathode area to the anode area. Simplistically, the anode area is the active corroding portion of the crevice where the dissolution or anodic reaction is occurring. The cathode is generally the area surrounding the crevice on the exterior. As this ratio increases or the cathode size increases, the probability of crevice corrosion increases as shown for stainless steels including 304 in Figure 9. The exposure was in flowing ambient temperature seawater for thirty days. The bold/crevice area ratio is the same as the cathode/anode surface area. However, the implication for embedded piping is still the same; crevice corrosion has a significant probability since the interior surface of the pipe can be the cathode.

Mitigation of crevice corrosion for the embedded piping would consist again of a thorough flush of chemicals that may increase cathodic depolarization such as manganous or permanganate ions and the minimization of chloride contamination. The low temperature of operation will aid in minimizing crevice corrosion.

Intergranular Corrosion

Intergranular corrosion (IGC) occurs when grain boundaries are attacked preferentially in a corrosive oxidizing solution. In IGC, the grain boundary is active whereas the grain is passive. Sensitization is the common cause of IGC especially in heat-treated or welded austenitic stainless steels. As discussed previously, sensitization of the metal structure occurs due to the formation of chromium carbides on the grain boundaries and depletion of chromium from the adjacent grain. This chromium depletion creates an oxide film on the surface next to the grain boundary susceptible to corrosion. Figure 10 depicts a schematic representation of carbide particle precipitation at the grain boundary during sensitization to IGC in stainless steel. Low carbon (<0.3 percent) grades of stainless steel are made to minimize the occurrence of sensitization since an increasing amount of time is required for carbides to form as the carbon content is reduced.

Sensitization of austenitic stainless steels during welding is known as weld decay. Intergranular corrosion, the classic form of weld decay, is more evident at elevated temperatures as documented from the failure of several of the batch evaporators in the separation areas.[22] The "weld decay" area in most cases is removed from the weld metal as shown in Figure 11 and depends on the time within the sensitization range (500-850°C, 932-1,562°F). Because of microstructural inhomogeneities and temperature variations during the multi-pass weld, totally uniform through-wall attack is not anticipated. The degree of sensitization in a weld heat-affected zone (HAZ) would determine the depth of attack.

Other factors that affect IGC include the material composition, microstructure, cold work, and exposure to radiation. Radiation increased chromium depletion at the grain boundaries without the precipitation of chromium carbides although a large neutron fluence is required.

Knife line attack occurs in "as welded" 347, 348, 321, 309Cb and any other columbium or titanium stabilized grade stainless steel when sensitized in the temperature range of 500-850°C (932-1,562°F). This is a special form of intergranular attack and occurs in sensitized regions near welds.[32] These regions are very thin (knife-line thin). Knife line attack is not a common degradation mechanism but has occurred at the site. An Area Metallurgical Report filed in February 1956, describes the inspection of a 309Cb slag and crucible dissolver coil which showed 0.0625 in (0.16 cm) deep attack at the outer edge of the weld joining the coil to the riser.[30] Knife line attack was shown to have occurred beside the weld. Another failure in November 1956 was reported as knife line attack of longitudinal welds of two 309Cb 3-in (7.6 cm) O.D. Schedule 40 welded pipe risers.[31,32] Severe knife line attack was noted along the length of the riser on either side of the girth welds. These examples of knife-line attack are given primarily to illustrate the potential for such degradation and to demonstrate that long term record keeping may add value to any process. The use of Cb stabilized steel was discouraged because of the potential for knife line attack.

Figure 10. Schematic representation for stainless steel sensitization with a carbide precipitation zone along grain boundaries and the resulting intergranular corrosion (dissolved metal)[13]

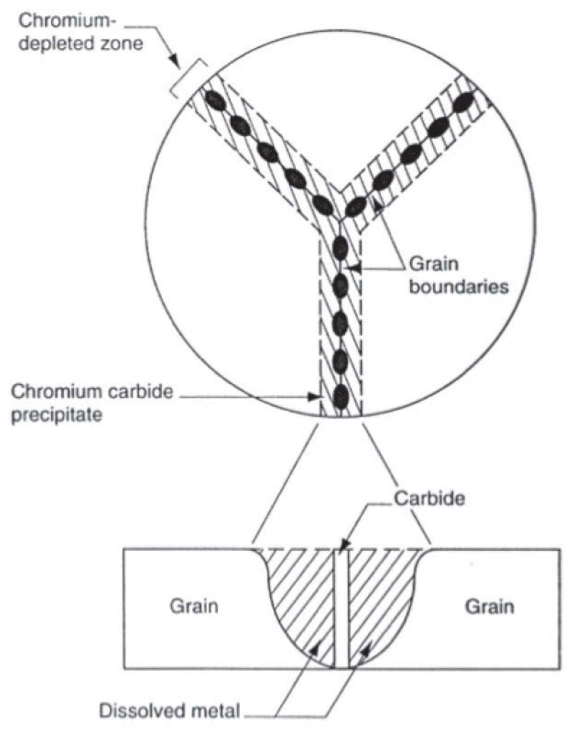
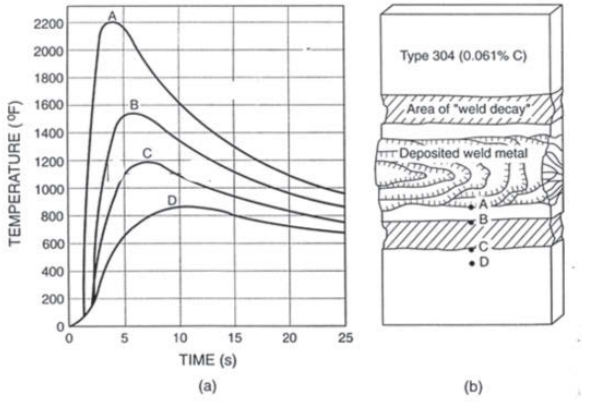


Figure 11. Thermal transients producing weld decay during welding of austenitic stainless steel: (a) temperature-time relationships for location within and near the weld as shown in b[13]



End grain attack, a form of IGC, is a type of corrosion that preferentially attacks defects (inclusions, stringers, etc.), and grain boundaries which are oriented parallel to the rolling direction of the material. Since there is an increased number of sites favorable for the initiation of corrosion in the longitudinal direction compared to that of other rolling orientations, this region is prone to increased corrosive attack. End grain attack is of primary concern in concentrated nitric acid or nitric/HF solutions. End grain attack was observed in thermowells for low activity waste evaporators due to an incorrect material chosen for the end tip as well as exposed end grains in pipes and nozzles. To combat this form of degradation, all components are required to have any surface with exposed end grains weld overlaid. End grain attack in weld overlaid material has not been observed.

There have also been other documented cases of IGC in the canyons. A 0.5-in (1.27 mm) 304 stainless steel tube, which was welded to a draw-off line for a 304 ELC nitric acid absorber, showed intergranular attack at the weld.[23] Another instance of intergranular corrosion of the HAZ involved a 2-in (5.1 cm) Schedule 80, 304 stainless steel nozzle removed from the bottom of an HNO_3 tank.[24] The thickness away from the HAZ ranged from 0.210-0.218 in (0.53-0.55 cm) while the minimum thickness at the heat affected zone was 0.070 in (0.18 cm).

IGC is not expected to lead to failure and is most likely to occur in embedded piping that carries the more concentrated nitric acids and only if other oxidizing species are present such as chromium or manganese ions. Again, rinsing piping prior to change in service will assist in minimizing this type of corrosion. IGC is believed to be the cause of failure in several small dissolvers which leaked near welds; confirmatory failure analyses were not possible.

The incidences of intergranular corrosion have now been essentially mitigated by using a selection process for austenitic stainless steels and other austenitic alloys that required a corrosion acceptance test, as summarized in Reference 6, which is included in this issue of the *Journal of Nuclear Materials Management.* When specified, the acceptance testing is performed prior to delivery of materials to the site or contractors for fabrication.

Corrosion Fatigue

Fatigue is the failure or fracture under repeated cyclic loads at stress levels below the yield point. Surface discontinuities such as notches, sharp corners, or surface roughness act as stress raisers and serve as crack initiation points. Corrosion fatigue (CF), which is defined as the reduction in fatigue resistance due to exposure to a corrosive medium, results from the combined deleterious effects of cyclic stresses and a corrosive environment. Stainless steels possess a good corrosion fatigue resistance in water systems but may be susceptible to CF depending on oxygen content, temperature, pH, and composition of the exposure environment. The susceptibility is also markedly affected by stress-cycle frequency and is more pronounced at low frequencies.

Corrosive mediums that produce pitting are most prevalent to CF such as in chloride bearing environments. Pit sites are regions where aggressive environments may concentrate. The combined effect of a locally aggressive environment with cyclic stresses promotes the propagation of CF cracks. One of the embedded piping liner failures in a canyon building was associated with CF. The cycling was associated with the thermal cycling of the on/off use of the steam line.[25]

A Type 309 stainless steel shaft exposed to an environment of acidified condensate containing 0.16 percent HNO_3 failed by corrosion fatigue.[33] Fracture was noted to have begun at the edge of the keyway and crack growth was enhanced by the presence of the aggressive environment.

Erosion Corrosion

Erosion corrosion results when abrasive particles or fluids flowing at a high rate impinge on the metal surface and remove the protective oxide layer. The nascent (bare) metal surface then reacts with the corrosive environment forming a new protective oxide layer. This cycle is repeated and rapid metal loss occurs.

An example of erosion corrosion is a return piping weld in a stainless steel evaporator column.[22] The return piping was contained within the vessel and was 50 percent to 75 percent eroded. The erosion-corrosion attack occurred from the inside out but, unfortunately, the contents of the tanks and the time in service could not be accurately established. The lack of all the information required to effectively address a corrosion problem is common in industrial/production situations and can inhibit mitigating the observed failure process. Fortunately, even though the exposure conditions were not conclusively established, a basic knowledge of the operating conditions (fluid flow, aggressive environment, and turbulence) was sufficient to identify the erosion-corrosion process. Another important factor contributing to maintaining system integrity was that the eroded area was identified through routine examination of an operating system.

Microbiologically Influenced Corrosion

Microbiologically influenced corrosion (MIC) may result when structural materials are exposed to stagnant or low flow aqueous environments (particularly untreated water) for long periods of time. This type of corrosion is observed in regions of a piping system, especially welds, where flow rates of less than 3 feet/sec (0.91 m/s) exist. Stagnant systems promote the growth of various microbiological organisms which can form films and deposits on exposed metal that accelerate attack of the material. MIC would affect the inside of the pipes or vessels where flow may be reduced or in low points where water collects when the components are out of service for an extended period of time.

Microorganisms are present in virtually all natural aqueous environments; however the presence of bacteria does not necessitate their involvement in the corrosion process. Specific bacteria have been identified that lead to localized corrosion of stainless steel. Bacteria include iron and manganese oxidizing bacteria and sulfate reducing bacteria. Bacteria attach to surfaces and develop biological films or colonies, which contain both aerobic and anaerobic bacteria, where bacteria can have synergistic relationships. Bacteria affect the corrosion process by changing the local environment including pH, oxidizing power and concentration of aggressive species (Cl- , Fe+3). Along with these environmental changes, the presence of a non-continuous film leads to the development of oxygen and chemical concentration cells. The oxygen depleted regions are where the protective oxide breaks down and initiates the localized corrosion.

For stainless steels, welds and heat-affected zones are a frequent location for MIC, which is manifested as pitting[17]. The pits have a characteristic morphology with a minute pinhole penetration with large subsurface cavities. On the surface there are deposits which are generally discrete mounds with colors distinctive to the type of bacteria, such as the red tubercles associated with iron-oxidizing bacteria (*Gallionela*). The pits are enriched with chromium and chloride. With chloride present, cracks can radiate from the pits depending on the surrounding stress field. The reasons that films or colonies develop are insufficient biocides and poor practices after hydrotesting including leaving standing impure water.

The bacteria growth and proliferation occurs over a broad range of conditions. Optimal conditions for bacteria associated with MIC are (parenthetic values show the range extremes) for temperature, 15 – 45°C (0 – 99°C, 32 – 210°F) and pH, 6 – 8 (0 – 10.5). The energy sources also cover a broad range including oxygen, nitrate, carbon dioxide and sulfate. The storage of heavy water in drums at warm temperatures (30 – 40°C, 86 – 104°F) without biocides and some amount of chloride makes it favorable for the development of biofilms if bacteria associated with MIC are present.

Microbiologically induced corrosion damage was discovered as a result of leaks which developed in two parallel 16-inch carbon steel piping systems between 1972 and 1976.[26] This section of pipe was replaced with schedule 10S stainless steel pipe during a period when process operations were suspended. New leaks began to appear in this new section of pipe in 1991 due to low laminar flow (estimated at 2 gpm (9092 cm^3/min) conditions. A 1-inch (2.5 cm) layer of mud which proved to contain anaerobic, sulfate reducing, and acid-producing types of bioorganisms covered the inside surface of the pipe.

Radiation Embrittlement

Type 304L stainless steel is an extremely ductile and tough material even after irradiation. Experimental tests were performed to evaluate the fracture behavior of irradiated Type 304 and Type 304-L stainless steel at high radiation exposure levels for evaluating the structural integrity of the SRS reactor tanks.[27, 28] Test results showed that some loss of fracture toughness occurs at exposures of 0.1 displacements per atom (dpa). The materials have high fracture toughness and the structures do not become embrittled threatening structural integrity even after exposures to 6.4 dpa. Canyon process vessels and piping would be exposed to high radiation fields (primarily gamma radiation) that would lead to displacement damage, but the lifetime exposure (100 years) would result in exposures roughly estimated to be much less than 0.1 dpa.

Conclusions

The discussion of mechanisms that could cause degradation of the austenitic stainless steels used for fifty-plus years in the SRS chemical separation facilities has illustrated:

- Corrosion-induced degradation of the austenitic stainless steels used in nuclear materials extraction and separation processes is not unique but is common to systems handling nitric acid solutions.
- General corrosion of austenitic structures by nitric acid solutions can be avoided because its behavior in many environments is predictable from data available in the literature.
- The potential for stress-corrosion cracking can be reduced by a chloride exclusion program that required that materials with leachable chlorides (250 ppm max, total chloride is the requirement, not leachable, conservatively assumes that all chloride could be released due to material degradation) be excluded from use in austenitic stainless systems.
- The potential for intergranular corrosion can be significantly reduced by a materials selection program that requires a steel pass a corrosion release or acceptance test before use in a wetted system.
- End grain attack can be avoided by placing a weld overlay on surfaces which have exposed end grains.
- MIC can occur even when the exposure environment is radioactive so leaving water laid up in systems (or low flow, intermittent stagnant periods, etc.) should be particularly avoided.

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Intergranular Corrosion Evaluation of Stainless Steels and Higher Alloys at the Savannah River Site

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Abstract

The Savannah River Site has, for more than fifty years, evaluated the susceptibility of austenitic stainless steels and other corrosion-resistant alloys to intergranular corrosion prior to use in critical site applications, including radioactive waste processing environments. Screening of alloys for sensitization and the potential for intergranular corrosion in certain environments is critical to avoiding corrosion-induced in-service failures. In radioactive systems, the consequences of such failures can be more significant than similar failures in non-radioactive environments. Early DuPont experience in using nitric acid in chemical plants and at the Savannah River Site led to the development of several test protocols that have been adopted in ASTM A262 and G28 standards and can be used to screen materials for service in potentially corrosive environments. This paper provides an overview of the approach used at the Savannah River Site to screen materials for intergranular corrosion susceptibility in order to minimize intergranular corrosion in chemical and radioactive waste processing systems.

Introduction

In 1950, E. I. DuPont de Nemours & Company was formally asked by President Harry S Truman to design, construct and operate the Savannah River Plant (SRP) near Aiken, South Carolina, USA, now the Savannah River Site (SRS). The original purpose of the plant was to produce nuclear materials critical to national defense. Over the years, new facilities have been constructed for new missions and many existing facilities have operated well beyond initial design lifetimes. At the time of the presidential request, DuPont was uniquely qualified to lead the design and construction of many of the chemical separations and waste processing facilities at the SRS, particularly those which required the handling and transfer of nitric acid solutions and/or the exposure of corrosion resistant materials to wetted environments. Materials of construction for processing equipment in the SRP facilities were predominantly TP304/304L grades of austenitic stainless steel, or the cast equivalent.

Intergranular corrosion (IGC) was known to be a primary and aggressive failure mode in type 304/304L stainless steel exposed to wetted environments, thus DuPont and SRP personnel established early test protocols to screen alloys to minimize susceptibility to IGC in process environments. A culture of interaction and cooperation between design, operations, procurement, and the testing laboratory developed as a result of the screening protocols. The testing, when required, became incorporated into site piping codes, drawings, and procurement specifications. The screening protocol coupled with the emergent culture has minimized IGC induced failures in SRS facilities. The SRS Corrosion Evaluation (CE) program is conducted as part of the materials/component procurement activity. This failure avoidance program is basically applicable to the procurement of any alloy that may be susceptible to service induced IGC. This paper summarizes the SRS Corrosion Evaluation (CE) program, test methods employed, design criteria, historical test data and project examples.

Test Methods

The test methods used at the SRS to screen alloys for IGC principally follow ASTM A262 for austenitic stainless steels and ASTM G28 for wrought, Ni-rich, Cr-bearing alloys.[1,2] Some of these tests were in fact developed by DuPont researchers, during the early years of SRP construction and operation. At the SRS, ASTM A262 Practices A, B, and C are routinely used, while Practices E and F are not used. The methods and their historic basis are briefly discussed.

ASTM A262 Practice C (widely known as the Huey test) was developed in the 1920s at DuPont as a process simulation test to quantitatively detect performance variations in alloys intended for nitric acid service. This test (65 percent boiling nitric acid, 240 hours, multiple immersion stages) was the leading method for acceptance testing of stainless steels in the United States for many years, particularly for nitric acid service.[3]

The test duration and hazards associated with Practice C later led DuPont researchers (M. Streicher et. al.) to develop the oxalic acid etch (now ASTM A262 Practice A) as a rapid screening test for acceptance of austenitic and ferritic stainless steels.[3,4] This test, which requires only a few hours to perform, is used for material acceptance based on microstructural classification. Samples are prepared and rated as defined in ASTM A262 Practice A. Examples of Dual (acceptable) and Ditch (not acceptable) microstructures are given in Figures 1a and 1b. End Grain Pitting I and II examples are given in Figures 2a and 2b. Per ASTM A262, samples rated as End Grain Pitting II may or may not

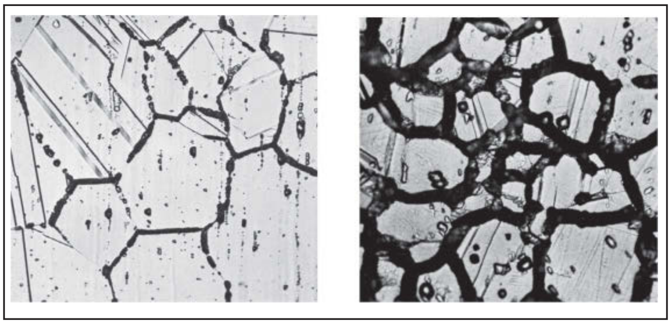


Figure 1a-b. Dual structure (left, 250X), Ditch structure (right, not acceptable), 250X

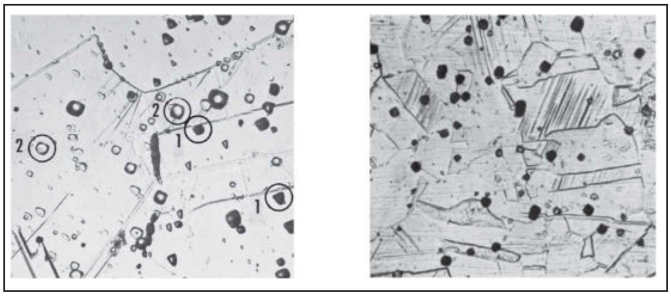


Figure 2a-b. End Grain Pitting I (500X), left, with few deep grain pits (1) and shallow etch pits (2), End Grain Pitting II (500X), right, not acceptable when screening for Practice C

be acceptable depending on the immersion test being screened. Practice A cannot be used to screen Mo-bearing grades for Practice C, as sigma phase may be present but not visible in the etch structure. Materials that fail Practice A are subjected to one of the other evaluation tests and may still be acceptable, depending on the test results.

The ferric sulfate-50 percent sulfuric acid test (Practice B in ASTM A262, Method A in ASTM G28) was developed by Streicher to screen Mo-bearing stainless steels (316/316L, 317/317L) for IGC susceptibility due solely to chromium carbide precipitation. This test was primarily developed as an alternative for alloys sensitive to sigma phase attack and end grain corrosion in the Practice C test, and that are not intended for nitric acid service. Practice B (120 hours) is shorter than Practice C and insensitive to the build-up of hexavalent chromium ions (Cr^{+6}) in the test solution, thereby allowing continuous exposure during the test period and avoiding the solution changes associated with Practice C. Note that Practice B will detect intergranular corrosion related to sigma phase in cast alloys CF-3M and CF-8M. In ASTM G28, Method B (Manning) was developed for certain alloys (N10276, N06022, N06059, and N06455) as the high overall corrosion rate obtained by Method A may mask the intergranular corrosion component.[5] However, this method is not currently used at the SRS.

The copper sulfate-sulfuric acid test (ASTM A262 Practice E) is often performed by production mill and supplier laboratories. Practice A may be performed as a screening test for Practice E. Certified Material Test Reports (CMTRs) for materials usually indicate acceptable Practice E (or A) results. However, the SRS program does not consider Practice E adequate for screening plant materials for IGC susceptibility, particularly for nitric acid service. Therefore, supplier documentation of Practice E (or A) results are not accepted. In several instances, materials with acceptable vendor Practice E results have shown failures in SRS testing.

The SRS Corrosion Evaluation Program

Corrosion Evaluation (CE) testing has long been specified at the SRS based on a combination of historical experience and input from site materials experts. When specified, materials are submitted directly to the laboratory by suppliers for testing prior to site acceptance. This is critical to prevent substandard material from being placed into site inventory or used for component or system fabrication.

The SRS CE program principally follows ASTM A262 and G28 standards. However, there are several testing aspects that are not addressed in the standards. A key aspect is that ASTM A262 only provides acceptance criteria for Practice A and E examinations, but not for immersion tests. The individual company or end-user is therefore responsible for establishing their own acceptance criteria. Based on early testing of many samples, DuPont established acceptance criteria for various alloys that have since been adopted by many industries and testing laboratories.[3,4] The CE criteria for the primary alloys used at the SRS are provided in Table 1.

Additional key aspects of the SRS CE program are summarized below:

- Materials are submitted directly to the site laboratory for testing prior to acceptance by site procurement or subcontractors for fabrication. The testing laboratory provides acceptance certificates to suppliers before delivery or fabrication can proceed.
- Involving the site laboratory early in the procurement process reduces concerns over approval delays. Consolidation of material heats and production lots to be used in fabrication can reduce testing needs. In some cases, the site laboratory has identified previously tested material that can be used without additional testing.
- The site laboratory closely examines the material and documentation provided to ensure that the salient features are correct and the item is properly marked. On several occasions, the site laboratory has identified documentation errors, improper markings and suspect/counterfeit parts.
- The use of strategic source suppliers that know test and quality requirements in advance minimizes quality issues, nonconformances and repeat tests due to failures.
- Different sizes and production lots of the same heat are required to be tested as the variation in working conditions

Table 1. SRS acceptance criteria for ASTM A262/G28 tests

Alloy	UNS Number	Sensitizing Treatment	Test Method*	Exposure Time (hr)	Corrosion Rate, max (inches/month)
304L	S30403	1 hr @ 663 +/- 14°C	A262-A A262-C	N/A 240	0.0020
316L	S31603	1 hr @ 663 +/- 14°C	A262-A A262-B	N/A 120	0.0040
Alloy 20 (20Cb3)	N08020	1 hr @ 663 +/- 14°C	G-28 Method A	120	0.0020
G30	N06030	None	G-28 Method A	120	0.0013
600	N06600	1 hr @ 663 +/- 14°C	G-28 Method A	24	0.0020
625	N06625	None	G-28 Method A	120	0.0030
690	N06690	1 hr @ 538 +/- 14°C	A262-C	240	0.0010
C-4	N06455	None	G-28 Method A	24	0.0170
C-22	N06022	None	G-28 Method A	24	0.0400
C-276	N10276	None	G-28 Method A	24	0.0400

*Immersion tests are only performed if samples fail Practice A.

and annealing practices for specific product forms may influence material response.

- Materials are tested by the site laboratory regardless of vendor documentation. On-site testing provides consistency in material evaluations for site projects and facilities, as well as ownership in the acceptance process.

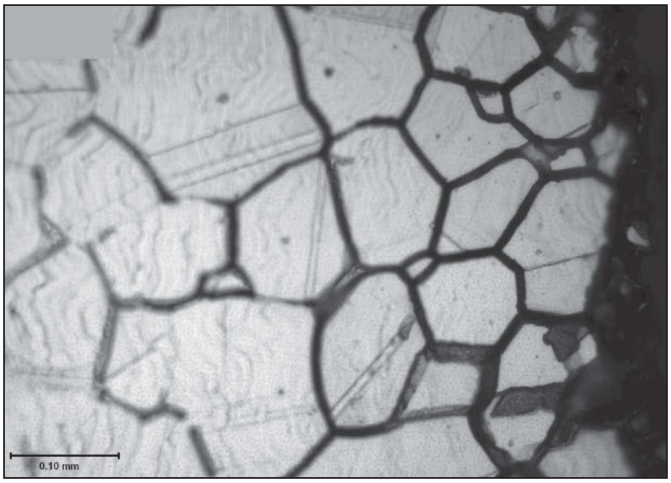
Consistency in sample preparation and evaluation is critical for proper screening of materials. The Practice A examination is not a trivial exercise, as sample microstructures do not always readily fall into the classical definitions given in ASTM A262. Proper sample preparation and laboratory personnel experience are critical to obtaining correct and consistent results. The Practice A screening test is subjective and is therefore used for acceptance only, not final rejection.

For example, ASTM A262 defines a Dual structure as having *no single grain* completely surrounded by ditching at the grain boundaries. For many samples, the Dual rating is quite evident. However, samples often require extensive review before ruling out a Ditch (unacceptable) rating. A single enclosed grain at 250-500X is technically sufficient to fail Practice A, justifying subsequent immersion testing. Similarly, the rating of structures as End Grain Pitting I or End Grain Pitting II is subjective. Variation in the degree of conservatism and level of scrutiny imposed by different laboratories and examiners during Practice A examinations can lead to varying results. The conservative and prudent approach is to subject any questionable material to immersion tests prior to final acceptance. Conversely, being too conservative can result in excessive Practice A failures, unnecessary delays and increased costs.

In any case, material that has been properly examined per Practice A should not fail immersion tests. Samples with acceptable vendor Practice A results usually pass SRS Practice A examination, but failures are observed. The majority of samples that fail SRS Practice A do pass subsequent immersion tests. However, a number of cases have occurred where materials with acceptable vendor Practice A results failed both SRS Practice A and immersion tests. In the case of immersion test failure, the supplier has the option of retesting or submitting an alternate heat of material. The causes in such cases are varied but likely depend on the experience of the testing laboratories and examiners involved as well as the level of scrutiny imposed. This is not to say that vendor or third-party laboratories and examiners are inherently flawed or less qualified. In fact, no laboratory or examiner is infallible. However, this is further justification for performing on-site testing to consistently screen materials for plant use, rather than simply accepting vendor documentation.

An example of 304L stainless steel pipe that passed a supplier's Practice A examination is shown in Figure 3. However, this material failed SRS Practice A as a result of localized grain boundary attack or *ditching* in the ID region. The bulk pipe microstructure shows *Dual* characteristics but uniform ID sensitization was judged to fail the Practice A criteria per ASTM A262 with a Ditch rating. The sample subsequently failed Practice C by a significant

Figure 3. Localized sensitization of 304L stainless pipe ID, Practice A failure (Ditch)



margin, with repeat tests confirming initial results. Examination of as-received surfaces and as-polished cross-sections in both the non-sensitized and sensitized conditions confirmed localized ID attack and eliminated possible errors in sample preparation. Mechanical cleaning and solution annealing steps showed improved corrosion rates. The cause of ID sensitization in this piping is unknown, possibly due to a drawing lubricant or other contaminant in the production process. The basis for vendor Practice A acceptance of the material is also unknown. This is shown as an example of how important it is to have consistent screening practices to avoid failures in critical processes where IGC is a concern.

The SRS CE program principally follows ASTM A262 and G28 standards. However, some differences have evolved over time based on plant experience and the nature of some operating facilities (Table 2). In earlier years at the SRP, Mo-bearing austenitic alloys such as type 316/316L were screened by Practice C for corrosive service. Note that ASTM A262 currently requires that stabilized and Mo-bearing grades intended for nitric acid service and all grades subject to end grain corrosion in nitric acid service must be tested per Practice C, though no acceptance criteria are identified. However, broad use of this approach led to many test failures that were not necessarily a service problem. Therefore, these alloys are currently screened via Practice B (if fail Practice A). In addition, the preferred use of type 304L or cast equivalent alloys in nitric acid service minimizes the risk of failure of Mo-bearing alloys due to lower chromium content and possible sigma phase attack.

When to Evaluate for IGC Susceptibility

Testing is not required for all services or environments at the SRS, and the use of such testing has been reduced over the years, lowering cost and schedule impacts. Intergranular corrosion is a particular form of corrosion that is only known or anticipated to occur in certain environments, notably nitric acid. However, the risk of process equipment failures in radioactive waste processing facilities can be quite significant, and well beyond that which might occur in a non-radioactive system. Therefore, even in systems where the probability of IGC is considered low, the need to perform on-site IGC screening tests is still given significant consideration.

Table 2. Variations between ASTM A262 and the SRS CE program

ASTM A262	SRS CE
End Grain Pitting II — acceptable if screening for Practice B but not for Practice C	End Grain Pitting II - not acceptable, regardless of the immersion test.
Dual structures allowed for Mo-bearing alloys when screened for Practice B	Mo-bearing alloys with Dual structures require Practice B
Practice C required for Mo-bearing grades and stabilized grades intended for nitric acid service (no criteria identified, aggressive test)	Mo-bearing grades screened via Practice A and B Type 304L or cast equivalent alloys are generally specified for nitric acid service

A site engineering guide was developed to assist design authorities in determining when testing is required or recommended, often with input from site materials experts. Key aspects of this guidance are summarized:

- Testing is recommended for corrosive or radioactive processes in which the consequences of failure are considered high, or in cases where the service environment is suspected to cause IGC and where the as-received material condition can influence IGC susceptibility. Performing the test assures that the as-received material is in the correct condition (i.e., solution annealed) prior to fabrication.
- In critical service or safety-related systems, testing is recommended even if the probability of IGC may be considered low. An example is high-level radioactive waste (HLW) transfer lines that normally carry alkaline radioactive waste solutions. The normal service environment may not have a high risk for IGC, but these lines provide primary HLW containment and must maintain the highest integrity. Process changes may also be required on occasion such as cleaning with nitric acid or other chemicals with higher risk of IGC, thus warranting the need for testing.
- In some facilities, process conditions may have changed such that testing is no longer required. However, a thorough review by site material experts is recommended before the test requirement is waived. All service conditions, including off-normal scenarios, must be considered.
- Passing the test does not guarantee against failure. However, performing the test is more defensible than justifying why the test was waived or not required after a failure occurs, especially if the failure is determined or suspected to be IGC-related.

- Possible changes in the operating life of the facility, process conditions, spare equipment availability, consequences of failure and other aspects must be considered. Facilities often operate longer than initially planned. Testing is recommended when repair or replacement is very difficult if not impossible without significant cost/schedule impacts and risk to personnel.
- The absence of failures in a given system where testing has been required does not inherently mean that the test was not worth performing or that the requirement can be waived for that system or similar systems being designed or constructed. Though difficult to prove, failures have likely been avoided because the screening test was required.
- A graded approach may be considered for large projects and systems, particularly for components that will not be exposed to wetted environments known or anticipated to cause IGC. Non-critical items, non-wetted components and other categories can possibly be eliminated from testing. However, knowledgeable materials/corrosion experts should review such decisions. Such reviews should also account for unplanned or off-normal events or infrequent flushes, including possible exposure to decontamination agents and other chemicals that may cause IGC.
- Corrosion tests such as ASTM A262 only evaluate the susceptibility of certain alloys to IGC, not other forms of degradation such as crevice corrosion, pitting corrosion, chloride-stress corrosion cracking, or microbiologically-induced corrosion (MIC). Material that passes IGC screening tests could readily fail in service if the wrong material is selected, the design is flawed or if the complete service environment is not evaluated, including media used for system flushes, cleaning or decontamination solutions, hydrostatic testing and other purposes.
- The use of low-carbon grades of austenitic stainless steels reduces but does not eliminate sensitization and IGC in certain environments. For critical or hard to replace components, the use of extra low carbon grades and specialty grades (NAG, nitric acid grade) of stainless steels and alternative alloys can further reduce the risk of IGC, but the availability and cost of alternative materials may pose procurement and schedule issues.

Program Data

Since 1987, corrosion test data have been entered into an electronic database. Prior to 1987, corrosion data were recorded manually in logbooks. From 1987 to present, the SRS laboratory has tested over 20,000 samples (average ~800 per year), with approximately 2,400 failures, for an overall failure rate of approximately 12 percent. Many different wrought and cast products of various alloys have been tested, with the majority being 304L and 316L austenitic stainless steels, followed by nickel-base C-276 alloy (UNS#N10276) and other alloys tested to lesser extent. Table 3 provides failure rates for samples made from these alloys tested in years 1993 to 2010. These data are shown due to more consistent data entry. This subset of the total data would imply an average failure rate of approximately 8.7 percent. Failure rates also tend to vary with product form, wall thickness and fabrication method.

Table 3. Summary of SRS IGC screening test data (1993-2010)

Alloy	Samples Tested	Number of Failures	Failure Rate	Test
304L	5533	509	9.20 percent	A262 Practice A and C
316L	657	50	7.60 percent	A262 Practice A and B
C-276	255	2	0.80 percent	G28 Method A

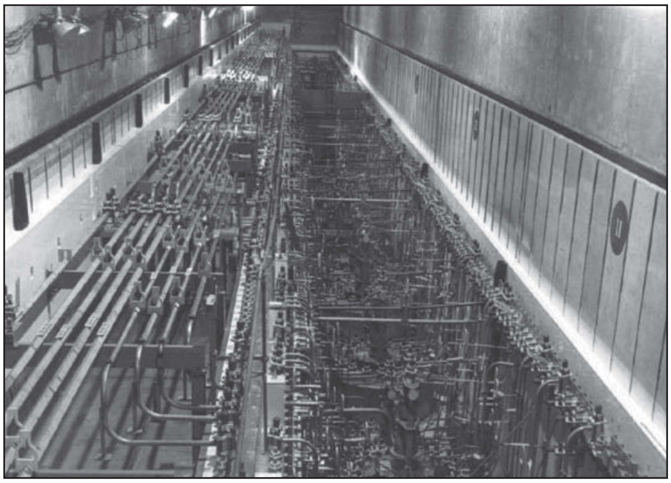
SRS Project/Design Examples

Early examples of components screened for IGC susceptibility include critical process equipment (evaporator pots, vessels) and many lengths of jumper piping used in the F & H-Area separations facilities known as *canyons* (Figure 4) and later in the Defense Waste Processing Facility (DWPF, Figure 5). The alloy principally used in the separations facilities is 304L stainless steel, with both 304L and C-276 alloys used in the DWPF. Inconel® 690, G3, G-30 and other nickel-base alloys are used to a lesser extent in these facilities to handle mixed nitric/HF acids and other aggressive solutions.

Early Hanford and SRS design philosophy led to the use of jumpers and specialized connectors to facilitate equipment replacement and process changes as needed. Though such efforts are not trivial, this approach offers some significant advantages over the "black cell" concept in which all equipment and piping installation is essentially permanent. Though many SRS components can be remotely replaced, the IGC screening process is still used to minimize IGC-induced failures. Such testing would be even more prudent for materials installed in black cell or no-entry type facilities to minimize failures.

In the HLW facilities, primary waste transfer lines are made of 304L stainless steel that is screened for IGC susceptibility. The alkaline waste environment does not pose a high risk for IGC, but these lines provide primary HLW containment and are difficult to access in the event of a leak. Jacket lines, typically made of carbon steel, serve as secondary containment, but the primary lines are critical. Infrequent process changes such as cleaning with nitric acid or other chemicals with higher risk of IGC may potentially be required, further warranting the need for testing.

Figure 4. SRS Separations canyon facility equipment (Corrosion Evaluated)



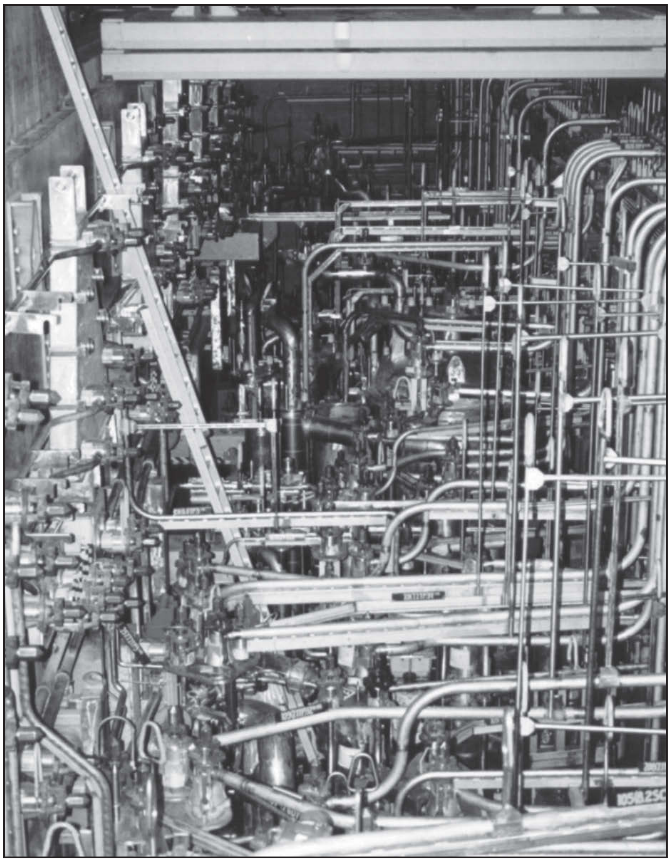
During the 1980s, the Defense Waste Processing Facility (DWPF), the largest waste vitrification plant in the world, was constructed at the SRS. A significant corrosion testing program was initiated to identify the most suitable alloys for the DWPF. Once materials of construction were selected, many components were subject to IGC screening tests (CE) prior to fabrication. Due to the large sample volume, testing was performed at both corporate DuPont and SRS laboratories.

In the early 2000s, CE testing was performed on many materials used in the Highly Enriched Uranium (HEU) Blend Down Project developed to blend weapons-grade, highly enriched uranium with natural uranium, creating a solution for off-site shipment to Nuclear Fuel Services in Erwin, Tennessee, USA. The solution was then prepared for fabrication into a fuel for use in commercial nuclear reactors at Browns Ferry. Approximately 290 trailer shipments were made, with SRS blending down approximately 11.9 metric tons of HEU into 179 metric tons of low-enriched uranium (LEU).

More recently, the Savannah River National Laboratory (SRNL) has performed IGC screening tests on many materials being used in the Waste Solidification Building (WSB) currently under construction at the SRS (Figures 6 and 7). The WSB facility will receive acidic wastes from the Mixed Oxide (MOX) Fuel Fabrication Facility (MFFF) also being constructed nearby at the SRS to convert weapons-grade plutonium into MOX fuel that will be utilized in commercial power reactors.

The WSB will treat transuranic waste and low level radioactive waste generated from the MOX plant, converting these wastes into a cement form. Resulting transuranic waste will be packaged and sent to the Waste Isolation Pilot Plant (WIPP) in New Mexico. Resulting low-level waste will be packaged and sent to low-level waste disposal facilities. The WSB is a ~33,000 foot^2 single story hardened concrete structure with low- and high-activity liquid waste process rooms, laboratory and cementation process rooms.

Figure 5. DWPF Canyon jumper piping and vessels (Corrosion Evaluated)



As in the MOX plant, much of the WSB process chemistry is based on nitric acid. Therefore, the majority of WSB process piping and components are made of corrosion-evaluated 304L alloy. For systems such as laboratory drains that will see a broader chemistry range including halides, more corrosion-resistant alloys such as G-30 or 690 alloys are specified. Such alloys are particularly well suited for systems that are not readily accessible for repair. This is based in part on previous failures of austenitic stainless steels in older laboratory drain systems at the SRS. Below-grade transfer lines (primary and secondary) to carry the acidic wastes from the MOX plant into the WSB facility were also screened for IGC susceptibility.

To date, SRNL has tested approximately 500 samples for the WSB, with an overall test failure rate of ~8.2 percent. SRNL has also tested nearly 200 samples for the MOX facility. Note the majority, if not all, of these materials previously passed ASTM A262 Practice E (or A) at supplier or third-party laboratories. It is impossible to know whether any of the materials that failed the SRS screening test would have ever failed in service, but it is clear that such testing is needed to minimize the risk.

Figure 6. Waste solidification building (WSB) under construction at the SRS

Figure 7. Header for WSB entrainment column (Corrosion Evaluated)

Summary

The Savannah River National Laboratory at the SRS has performed on-site corrosion testing on materials and components for IGC susceptibility for more than fifty years. This materials management practice has significantly minimized the risk of using IGC-susceptible alloys and components in environments that could cause IGC-induced failures. This approach is particularly needed and recommended for radioactive or hazardous solutions, especially in long design-life facilities and for components and systems that are critical in nature or difficult to replace. For these processes, material acceptance based solely on manufacturer or supplier documentation is not considered sufficient. The SRS CE program has been and continues to be an asset for the safety, procurement, construction and management of many facilities at the Savannah River Site. On-site testing prior to delivery or fabrication ensures that plant materials are properly and consistently screened for intergranular corrosion susceptibility. This results in improved material quality, personnel safety, system performance and environmental stewardship in SRS facilities.

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Management of High-level Waste at the U.S. Department of Energy's Idaho Site Past, Present, and Future

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Abstract

A byproduct of the development and application of processes to recycle useful isotopes from irradiated nuclear fuels is highly radioactive wastes that require permanent isolation from the environment. Liquid, high-level waste was produced directly from the reprocessing operations at the U.S. Department of Energy's (DOE) Idaho Site. Beginning in 1953, these reprocessing liquids were stored in stainless steel tanks, each tank having a 300,000 gallon capacity. In 1963 the Idaho Site began to convert the liquid waste to granular solids by evaporating the water and other volatile components. This process, termed calcination, produces a more manageable nuclear material and has been basically completed. The granular solids or calcines that were produced are currently stored in stainless steel bins. The calcine will ultimately be treated by the Calcine Disposition Project that will retrieve and treat the calcine for shipment to a repository by a target date of 2035.

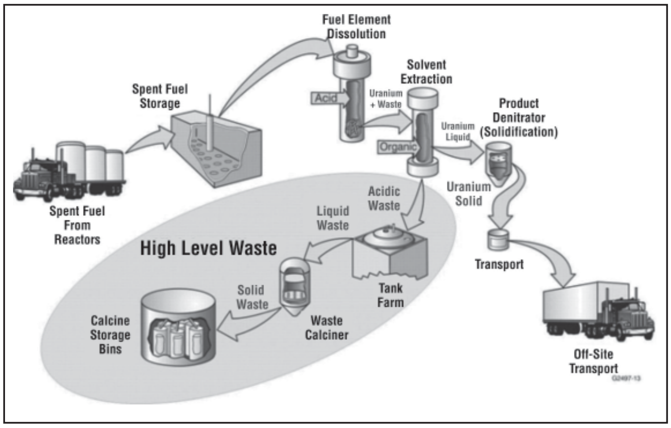
Introduction

The U.S. Department of Energy's (DOE) Idaho Site, located in southeastern Idaho, is 890 square miles of high desert sagebrush, neighboring dormant volcanic buttes and the mountains of the Lost River Range. The Idaho Site is where fifty-two nuclear reactors were developed and built and remains one of the leaders for nuclear research in the United States. In addition to developing nuclear materials production processes, workers at the Idaho Site investigated the application of nuclear reactors for electric power and continue to develop applied technologies for the decommissioning and decontamination of nuclear facilities. Additionally, the Idaho Site is involved in the management of the nuclear wastes that result from the recycling of spent nuclear fuel. The paper outlines the past, present, and future strategies that Idaho Site workers used and will use to handle highly radioactive nuclear wastes.

High-Level Waste — A Nuclear Materials Management Issue

The highly radioactive nuclear waste produced by recycling spent nuclear fuel is a material that must be managed to protect the workers, the public, and the environment. One of the many nuclear missions conducted at the Idaho Site was to discover, develop, and apply processes to recycle useful components from irradiated (spent) nuclear fuel. Many fuel designs and types were irradiated in the Idaho National Laboratory (INL) reactors and these irradiated fuels were reprocessed (recycled) to recover uranium, lanthanum, neptunium, krypton, and other isotopes for the DOE and its predecessor organizations. The highly radioactive byproduct from irradiated fuels reprocessing is termed high-level waste. High-level wastes include the liquids produced directly from the reprocessing and the solids derived from those liquid wastes. These wastes contain fission products in sufficient concentrations to require permanent isolation from the environment[1] and therefore present the management issues generally associated with nuclear materials.

Figure 1. Process flow diagram for the Idaho Nuclear Technology and Engineering Center



The Idaho Chemical Processing Plant, now known as the Idaho Nuclear Technical and Engineering Center (INTEC) had numerous missions associated with the safe handling of spent nuclear fuel. These missions included reprocessing the fuel, recovery of useful isotopes, and the management of the resulting high-level waste. The process flow diagram for these missions is outlined in Figure 1 and involves initiatives that take the spent fuel from the reactors and carry it to calcination and ultimately to offsite disposition of the high-level waste product.

Tank Farm and Calcination

The irradiated nuclear fuels removed from the reactors were first stored underwater in large pools. The pool water serves as shield-

Figure 2. Pour in place concrete vault (left) and pillar and panel concrete vault (right)

ing for fuel handling processes and as a coolant to remove the decay heat. After the fuel had cooled sufficiently, it was transferred to a fuel element dissolver where acidic solutions were used to dissolve the fuel and ^{85}Kr (Krypton-85) was recovered. The acidic solutions underwent solvent extraction processes to remove the useful isotopes. The remaining acidic waste was then transferred into stainless steel tanks in a "tank farm." The tank farm consists of fifteen stainless steel storage tanks; the largest tanks (300,000 gal.) are contained in concrete vaults and the smaller tanks (30,000 gal.) are direct buried.

The tank farm facility was constructed during the 1950s and 1960s to manage the acidic, liquid high-level reprocessing wastes. See Figure 2.

From 1953 to 1992, a variety of spent nuclear fuel was routinely processed at INTEC resulting in two basic types of reprocessing wastes: aluminum rich and zirconium rich. The composition of the waste depended on the type of fuel being processed. The aluminum-rich wastes were from the reprocessing of fuels clad with aluminum alloys while the zirconium-rich wastes were from the reprocessing of fuels clad with zirconium alloys. Liquid wastes from incidental activities were also stored in the tank farm. These wastes were typically high-sodium wastes from second and third cycle refinement processes and from decontamination operations at INTEC. The term "sodium-bearing waste" is used to emphasize the waste's high concentration of sodium ions that are problematic to calcination, primarily because sodium increases the potential for bed agglomeration. The high levels of sodium are a result of processing and decontamination activities that use sodium based chemicals such as sodium hydroxide and sodium carbonate.

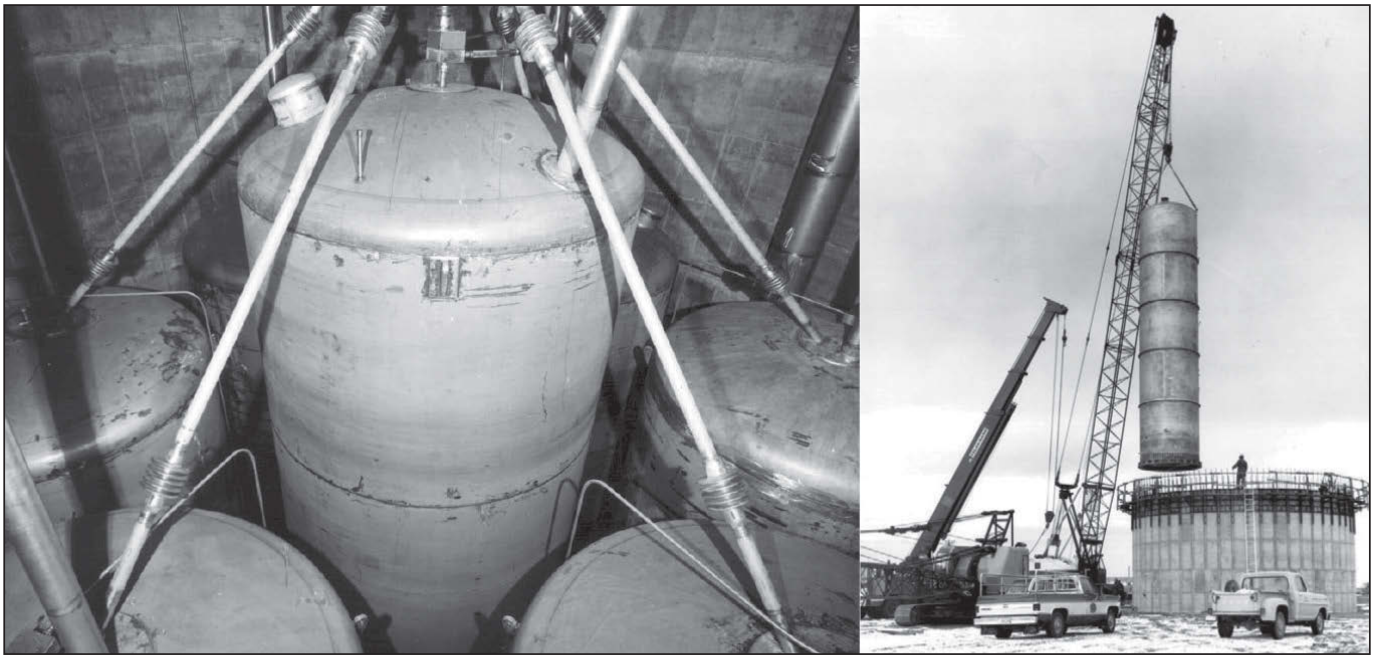
Liquid waste removal from the tanks and solidification by calcination began in 1963. The calcination processes were conducted in the original Waste Calcining Facility which was used until 1981. The New Waste Calcining Facility (NWCF) began operations in 1982 and continued operations until February 1998. Calcination evaporates the water and other volatiles from the liquid waste and converts the remaining materials to dry granular solids. The solids produced by this process are termed *calcine* and are stored in specially designed stainless steel storage bins that are contained in reinforced concrete vaults. The bin/vault combination is referred to as calcined solids storage facilities (CSSFs).

The CSSF shown is CSSF IV (see Figure 3) and is one of seven such facilities at the Idaho Site. Although the various CSSFs have different designs, all are basically welded stainless steel tanks that provide the primary containment vessels for the calcine and concrete vaults that provide radiation shielding.

Reprocessing of spent fuel was discontinued in 1992 when the DOE announced that spent fuel would no longer be reprocessed in Idaho. This directive forced the shutdown of the reprocessing facilities at INTEC and since that time no more high-level waste has been generated from spent fuel reprocessing. However, sodium-bearing waste generation continued on a reduced scale as a result of spent fuel storage, waste management, off-gas cleanup and the decontamination and decommissioning of unused facilities. On February 20, 1998, the last of the liquid high-level waste that was stored in the tank farm was calcined.[2]

The tank farm currently operates under interim status via a consent order and a Resource Conservation and Recovery Act (RCRA) Part A permit for storage of hazardous waste. The Notice of Noncompliance Consent Order states that cease-use of the pillar-and-panel and panel-vaulted tanks will occur on or before June 30, 2003.[3] The cease-use process was accomplished as of January 9, 2002.[4] Closure involves removing the residual heels of the tanks, cleaning the empty tanks, and grouting the cleaned tanks. Closure activities have been completed for seven of the 300,000-gallon tanks and four 30,000-gallon tanks at the tank farm. Only four tanks remain active: three containing sodium-bearing waste and one spare. No newly generated liquid waste has been sent to the tank farm since September 30, 2005, although

Figure 3. Interior of Calcined Solids Storage Facility III (left) and bin placement in Calcined Solids Storage Facility IV (right)

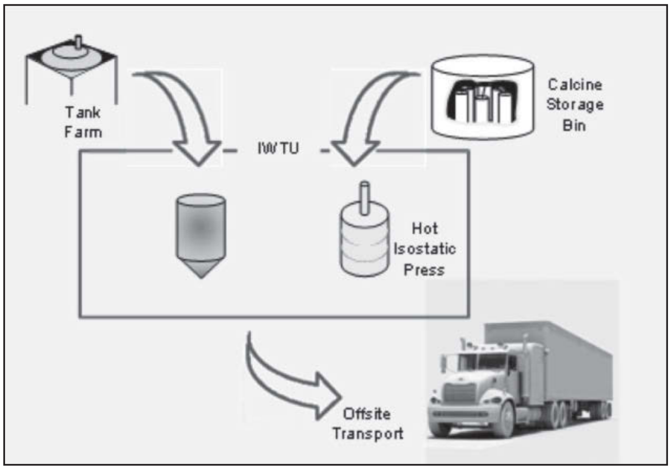


concentration of the stored wastes continues. After the existing waste is removed and converted to a solid form, closure activities are anticipated for the remaining four tanks.

To ensure the continued safe storage of sodium-bearing waste in the tank farm and the calcine in the CSSFs, the INTEC Structural Integrity Program was instituted. This program follows the Brookhaven guidelines for high-level waste and is based on the program outlined in DOE G 435.1-1, "Implementation Guide for Use with DOE M-435.1-1."[5] and the Brookhaven National Laboratory's *Guidelines for Development of Structural Integrity Programs for DOE High-Level Waste Storage Tanks*.[6] The Brookhaven guidelines specify criteria for developing programs that meet the directives of DOE Order 435.1.

CH2M-WG Idaho has, since 2005, been contracted by DOE to build and operate a treatment facility where the remaining liquid sodium-bearing waste will be treated. This facility is called the Integrated Waste Treatment Unit (IWTU). The IWTU will be retrofitted with a new set of systems and a new packaging annex to treat the calcines in the CSSFs after the remaining sodium-bearing wastes in the tank farm have been treated, see Figure 4. The IWTU has passed the construction phase of the project and is currently tasked to meet a new Idaho Department of Environmental Quality deadline to have the remaining liquid sodium bearing wastes removed from the tanks and converted to solids by the second quarter of 2014.[7] The IWTU will use a patented steam reforming technology to reduce the liquid sodium-bearing wastes into a carbonate granular form similar to calcine in terms of a solid material.

Figure 4. Process flow diagram for waste management at the INTEC



The calcine solids currently stored at the Idaho site will be processed for disposal using a retrofitted IWTU. The Calcine Disposition Project, currently in the planning phase, will retrieve and treat approximately 4,400 cubic meters of high-level granular solid waste. The preferred option is to treat the calcine by hot isostatic pressing (HIPing), which will create a glass/ceramic waste form and then package the result for interim storage and eventual shipment to a repository. This activity will ensure that all high-level waste at the Idaho Site is treated and ready to be transferred for final disposal by a target date of December 2035. This date is in accordance with the Settlement Agreement between the state of Idaho, DOE, and the Environmental Protection Agency.[8]

Conclusion

The treatment and storage of high-level radioactive wastes at the Idaho Site has evolved over the fifty-plus years of site operations. Initially, the bulk of the wastes were stored as acidic liquids, in stainless steel tanks. These liquids were subsequently treated by calcination to form a granular solid, termed calcine, which is contained in welded stainless steel bins and concrete vaults. The liquids remaining in the tank farm and the calcined solids stored in the CSSFs will be treated in the IWTU and new calcine disposition project HIPing facility and prepared for final disposal in a repository.

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Structural Integrity Program for Calcined Solids Storage at the U.S. Department of Energy's Idaho Site

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Abstract

The calcined, high-level radioactive wastes at the U.S. Department of Energy's (DOE) Idaho Site are stored in stainless steel bins that are contained in concrete vaults to isolate the bins from the atmosphere. The storage facility is termed the Calcined Solids Storage Facility (CSSF) and contains approximately 155,300 feet^3 of calcine. Safety analysis information, including seismic and tornado evaluations, are coupled with corrosion evaluations and corrosion monitoring to demonstrate that the CSSF is currently structurally sound and should be fit for service for at least 500 years. This paper summarizes the structural integrity program for the CSSF.

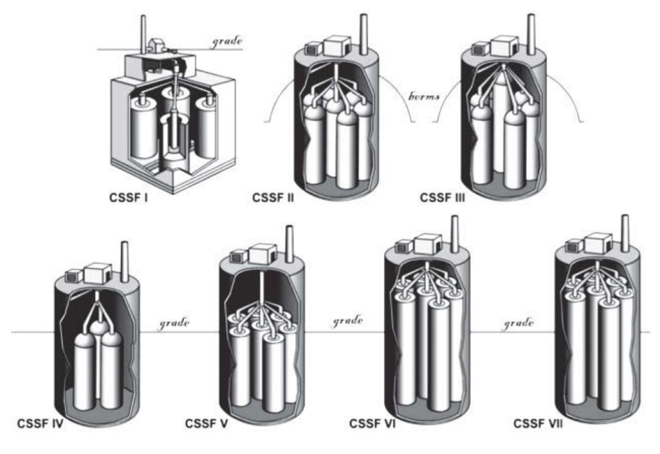
Introduction

Solidified, high-activity radioactive wastes have been stored at the Idaho Site for nearly fifty years. This high-level waste is managed, in part, through activities of the structural integrity program at the Idaho Nuclear Technical and Engineering Center (INTEC). The activities follow the U.S. Department of Energy's (DOE) requirements[1,2,3] and focus on the structural integrity program for safe management of the structures housing solidified high-level wastes. This paper is based on two Idaho Site reports — Structural Integrity Program for the Calcined Solids Storage Facilities[4] and Calcined Waste Storage.[5] These reports are publically available and should be consulted if additional information be desired.

Background

Spent nuclear fuel reprocessing at INTEC produced aqueous, highly radioactive wastes that were temporarily stored in stainless steel tanks at the site's tank farm. The liquid wastes have been converted into a solid, granular form called calcine. Solidification of the liquid wastes began in December 1963 and continued until May 2000. The liquid-to-solid conversion was completed in two fluidized-bed calcination facilities. The principal reactions during calcination were evaporation and thermal decomposition of the radioactive liquids to form metallic salts, water vapor, and nitrogen oxides. The solids produced contained the bulk of the radionuclides, which were present as metallic salts, termed calcine. The material produced is designated alumina-, zirconia-, or sodium-calcine, depending on the liquid waste source used in its production. In addition, calcination of the various blended liquid wastes produced blends of various compositions, with the most common being zirconia-sodium. Finally, calcine produced at higher temperatures during the last operating campaign is termed high-sodium calcine.

Figure 1. Artist's depiction of the Calcined Solids Storage Facilities[4]



The Waste Calcining Facility (WCF) operated from November 1963 to March 1981 and converted 4,091,000 gallons of aqueous radioactive waste into 77,300 feet^3 of calcined solids. The WCF was replaced by the New Waste Calcining Facility, which operated from August 1982 through May 2000 and converted 3,642,000 gallons of aqueous waste into 78,000 feet^3 of calcined solids. The 155,300 feet^3 of calcine produced in the two facilities is stored, on an interim basis, in the CSSF.

The calcine is placed inside stainless steel bins with sets of three, four, or seven bins placed inside a single concrete vault enclosure, see Figure 1. Each set of bins and its associated enclosure is termed a bin set or a Calcined Solids Storage Facility (CSSF). There are currently seven CSSFs at INTEC although only six (I through VI) contain calcine. The vaults are partially below grade or partially covered with an earthen berm (lines in Figure 1 depict grade or berm levels). The CSSFs were constructed as additional storage was required and the design evolved with experience. The prime design consideration was control of the calcine storage temperature by removal of the radioactive decay heat. The basic designs were modified to promote the release of the decay heat through natural convection and include welded construction of the stainless steel bins, reinforced concrete enclosures, natural convection cooling and filtered off-gas venting.

Chemical and radiological composition data for the calcines are required for regulatory compliance (permitting, waste disposal under the Resource Conservation and Recovery Act, etc.) for interim waste storage, for retrieving the calcine for future treatment, and for shipping to off-site facilities (a geologic repository, for example). The calcine compositions vary significantly among the CSSF storage bins and because of radiological processes, with time. Therefore, characterization of the calcines entail garnering bin specific information from spent fuel dissolution processes, tank farm storage operations, operating data, such as the volume of the liquid waste used to produce the calcine, liquid waste composition data from sample analyses, operational data from the CSSF and time. The information relative to calcine chemistry is developed as required for the specific activity involved.

Structural Integrity Program

An effective structural integrity program that meets the requirements of DOE M 435.1-1 is in place at the Idaho Site. Elements of the program include verifying the leak tightness of the CSSFs, assuring that the CSSFs are structurally adequate, identifying potential degradation mechanisms, and quantifying the presence or absence of degradation. Techniques used to quantify degradation and to manage the CSSFs include monitoring for corrosion, performing non-destructive examinations, and lifecycle management.

Verifying Leak Tightness

The vault and bin design for the CSSFs provides a double containment system for the radioactive calcine so a leak from any of the bins would be contained in the vaults.[6] Each vault is a reinforced concrete structure built on basalt bedrock. The below grade, vertical portions of the concrete containment vaults for CSSF II through VII are coated with pitch to provide a water tight seal, and the continuing quality of that seal is monitored. Continuous vault sump level readings are taken to detect any in-leakage of groundwater. Radiological monitoring of the vaults is achieved through continuous air monitors (CAM), which provide a means of detecting airborne radioactivity. If calcine should leak from a bin the CAM would provide a signal to an alarm that would sound in a manned control room. No such leaks have ever occurred in any CSSF.

Verifying Structural Integrity

Design requirements to assure against structural failure under postulated events (earthquakes, floods, tornados, etc.) have evolved significantly since CSSF I was built in 1955. The CSSF I vault was constructed in 1955 and was designed to the requirements of the version of the Uniform Building Code then in effect. Prior to 1970, the Idaho Site was in Seismic Zone 2[7] and seismic design evaluations considered a static lateral ground acceleration of 0.1 g. However, subsequent seismic evaluations meeting the requirements of the commercial nuclear Regulatory Guide 1.60,[8] have been performed for CSSF I. The first of these evaluations was by EQE Engineering in 1989,[9] Raytheon performed the second[10] with a third[11] evaluation in 1995. These evaluations considered ground accelerations up to 0.24 g and concluded that CSSF I may be over stressed, but should not collapse under earthquake loads.[9,10] However, one evaluation suggested that cracks would develop along the walls under static soil pressure loads from the adjacent berms. A video inspection of the portions of the walls available for such inspection (essentially the top half of the walls) showed no evidence of structural cracking.[12] In 2002, a structural evaluation[13] of the CSSF I vault was performed in accordance with DOE Performance Category (PC) 2 requirements as described in DOE-STD-1020-2002.[14] Based on this evaluation, the CSSF I vault meets the requirements for a PC-2 structure.[15] The Idaho Department of Environmental Quality concurs with the conclusions of the 2002 analysis.

The safety analysis for CSSF II and III provides seismic analyses that confirm the adequacy of the design to withstand the maximum credible earthquake at the Idaho Site.[6,16] The safety analysis for CSSF IV indicated that the facility can withstand an earthquake with a bedrock acceleration of 0.33 g and a tornado with a maximum wind speed of 175 mph without releasing calcined material to the environment.[6,17] The safety analysis for CSSF V noted that the bins, anchors, and all connecting components are designed for resistance to a maximum bedrock acceleration of 0.33 g horizontal and 0.22 g vertical. The CSSF V is also designed with tornado protection features to prevent unacceptable radiological consequences if struck by a design basis tornado.[6, 18] The design specifications for CSSF VI required a dynamic seismic analysis using the horizontal and vertical bedrock response spectrum curves specified in Regulatory Guide 1.60 scaled to a 0.24 g horizontal and 0.16 g vertical acceleration.[19]

Identification of Degradation Mechanisms

The Brookhaven guidelines[20] identify several possible age-related degradation mechanisms but evaluation of the proposed processes suggests that none are significant for the CSSFs, especially since the bins are planned to be empty by 2035.[21] The weld-sealed stainless steel bins containing the calcine are exposed to a warm, dry environment and, without water ingress into the vault, should not be susceptible to significant corrosion. Stress-corrosion cracking has occurred in stainless steel components exposed to relatively dry environments when a thin film of water dissolves chlorides from contained salts but, if such a film were to develop, dissolution of the calcine would produce a basic solution rather than an acidic solution known to promote stress-corrosion. Stress-corrosion cracking and other age-related degradation mechanisms are nucleation and growth processes and if the time for nucleation were extensive and crack growth rates rapid, cracking might occur at some future date. However, the stainless steel is a tough, ductile metal and the primary stresses on the bin walls are residual thus any cracking would be self-limiting and crack openings minimal. Additionally, even if unexpected cracking were to occur, release of radionuclides would be detected by the CAMs.

The vault/bin temperatures are not high enough to promote sigma phase formation in the steel or lead to other deleterious microstructural evolution processes and there is no creditable mechanism for the development of cyclic stresses that might cause fatigue. However, the concrete in the vaults may be susceptible to degradation from the thermal exposures and from chemical attack.

Concrete, exposed to elevated temperatures, begins to experience reactions that cause a loss of absorbed and combined water from the cement paste.[22] This loss results in reduced compressive strength and stiffness thus the design features of the CSSFs allow for convective cooling to minimize heat buildup and reduce the temperature of exposure to the point that heat induced degradation is not anticipated, especially if the calcine is removed by 2035.

The conditions that the concrete and stainless steel experience change during the exposure period. During the initial exposure period, the heat from radioactive decay produces a relatively hot, dry environment. The exposure temperatures decrease with time and during the later storage periods a water film might form on the exposed surfaces if the humidity is high or water ingress occurs. These conditions are not anticipated. For example, analysis has demonstrated that there is no credible scenario for the introduction of water into the bins.[6] Additionally, water ingress to the concrete is not expected to lead to degradation because neither the soil nor the calcine contain sufficient quantities of aggressive species (e.g., chloride). Chemical attack from the outside of the vaults from soils and groundwater is also minimized because the underground portions of the outside walls of all the vaults except CSSF I, are protected by a coating of pitch. Visual inspection of CSSF I in 1995 (approximately forty years of exposure) provided no evidence of structural defects, damage, or degradation of the storage vault walls.[12]

Quantifying Degradation

The reinforced concrete vault and the welded, stainless steel bins in the CSSFs provide double containment for the radioactive calcine. The CAMs, continuous vault sump level monitors and routine visual inspections combine to monitor for the unexpected occurrence of large scale degradation. In order to quantify the performance of the bin materials, with the exception of CSSF I, corrosion coupons were installed in all CSSF bins during construction and laboratory testing has been performed to characterize bin material behavior in simulated CSSF calcine. Some of the corrosion coupons have been removed and evaluated.

Analysis of Coupons Retrieved from CSSF II

One-hundred sixty corrosion coupons were hung on ten stainless steel cables in two bins in CSSF II during January 1966. After the coupons were hung, one of the bins received zirconia calcine and the other bin received alumina calcine. Each cable supported a statistically significant set of Type 405, 304, and 304L stainless steel coupons and of AISI 1025 carbon steel. The coupons were cylinders and plate of mill-certified steels and contained welds made using the tungsten inert gas process with the appropriate electrode for the different steels.

One set of coupons was retrieved from each bin during October 1973. The exposure temperature, as determined from the average readings from a thermal well near the coupons, was 60°C for the coupons exposed in an alumina containing bin and 58°C for those exposed in a zirconia containing bin. The temperature averages were based on data obtained from 1971 through 1973. The bin containing zirconia calcine was filled in 1973 while the bin containing alumina calcine was filled four years earlier. The coupons were decontaminated in a boiling alkaline permanganate solution for forty-five minutes followed by fifteen minutes in alternating nitric acid and water rinses. The effect of decontamination was subtracted from the observed corrosion.[23] The results of the evaluation of each alloy in each bin showed the corrosion induced degradation was nil.

The major conclusion drawn from the analyses of the corrosion coupons was that corrosion would not cause significant degradation of the bins over their design life. The bins were designed for up to 500 years of service and the corrosion results demonstrated the bin suitability for alumina and zirconia calcine storage over such time frames. Also, due to the very low corrosion rates, the recommended schedule for retrieval of the remaining coupons was modified to delay the retrievals for decades.

Laboratory Scale Zirconia Calcine Corrosion Evaluations

Laboratory scale tests were initiated in October 1966 to determine the long-term corrosion effect on bin materials exposed to zirconia calcine.[24] Welded coupons fabricated from Types 405, 304, 304L, 316L, and 347 stainless steel, AISI 1025 carbon steel, and 6061-T6 aluminum were exposed to nonradioactive zirconia calcine produced in the calcine pilot plant. The test coupons and calcine were placed in a test vessel that was then loaded into a tube furnace. The temperature of the tube furnace was varied over seventeen years of testing to determine the impact of temperature on corrosion. After each year of exposure, the coupons were removed from the test vessel and cleaned to remove any loose oxide on the sample surface. The following process was used to clean the coupons: ultrasonic cleaning in distilled water for fifteen minutes, followed by a distilled water rinse, then dipped in isopropyl alcohol and dried in an oven at 100^{0}C for thirty minutes and air cooled.[24]

The average temperature inside the vessel during the first two years of exposure was 201^{0}C, ranging from 154^{0}C at the bottom to 206^{0}C at the top of the vessel. During this exposure period, all samples increased in weight. The increase was presumed to result from oxidation of the coupons and is consistent with the development of surface discolorations, indicative of oxide film formation.[24]

The temperature of the vessel was increased for the next fifteen years of exposure. The average temperature inside the vessel was 301^{0}C with the top being at 343^{0}C while the bottom was at 204^{0}C. During this period many of the samples ceased to gain weight and weight decreases began at different times for the different alloys placed at various locations. However, the weight changes were minimal and essentially no corrosion was observed. No correlations were apparent between the weight gain behavior, the temperature or the increase in temperature. Some of the 6061-T6 aluminum coupons gained weight throughout the test[24] and after seventeen years of exposure most of the samples increased in weight. The exception to the weight increases were the Types 304, 304L, and 347 stainless steels. To compare the estimated 500-year corrosion behavior of the laboratory scale coupons with the in-bin coupons, the laboratory coupons were cleaned in a similar manner to those from CSSF II. The CSSF II behavior removes the loose and adherent oxide films while the less aggressive ultrasonic cleaning only removes loose oxide films. When the results of the corrosion studies on laboratory samples were compared, the 304 and 304L results were basically identical and were too low for realistic extrapolation. This observation is significant because the bins are fabricated from 304L stainless steel and the fact that the corrosion rates were essentially nil demonstrates that corrosion induced degradation of the bins should not occur during a 500-year storage period.

Laboratory Scale High-Sodium Calcine Corrosion Evaluations

The high-sodium calcine is highly alkaline, relative to the alumina and zirconia calcines; therefore laboratory corrosion tests were conducted (tests began in 2000) to determine the effect of exposure to the high sodium calcine on Type 304L stainless steel. Welded, Type 304L stainless steel coupons were placed in containers of non-radioactive high-sodium calcine that had been prepared in several pilot plant tests.[25] The coupons included plate corrosion samples to determine the general corrosion rates and U-bend samples to determine the susceptibility to stress-corrosion cracking. The containers of calcine with the coupons were placed in an environmental chamber at a set temperature of 32^{0}C and 60 percent relative humidity for two months. The coupons were removed from the chamber and cleaned after the exposure. The cleaned samples were weighed and visually examined using a microscope. The maximum rate of corrosion observed on any sample was 0.0208 mils per year, which corresponds to a penetration of 10 mils after 500 years. The design corrosion allowance for the CSSF VI bins where the high sodium calcine is stored is 20 mils after 500 years. The U-bend coupons showed no corrosion or cracking and no evidence of pitting or other forms of localized corrosion were noted. The conclusions from these tests is that the Type 304L bins will experience minimal general corrosion over the postulated 500-year exposure to high-sodium calcine and that degradation by localized corrosion processes will not occur.[25]

Non-Destructive Examination

The high radiation levels within the CSSFs make direct visual inspection of the vault interiors or the storage bins difficult. However, despite the difficulty, periodic inspections of the bins are required by the regulatory hazardous waste permit[6] for the facilities. This requirement is met by using remote visual and video inspections to detect incipient degradation. Remote visual inspection of the upper half of the CSSF I vault was performed in 1995,[12] after twenty-two years of service. No degradation was detected by this inspection. Video inspection of the vault interiors was performed again in 2007 and no degradation was detected.[26] Comparing the results of the two inspections revealed little or no changes in the vault surfaces during the twelve-year period. Similar remote inspections of CSSFs II through VI detected no deterioration or structural issues with the bins, the exposed stainless steel piping or the vaults. Manned entry into the CSSF VII (an empty facility that has not contained calcine) showed that the vault, concrete walls and floors, the stainless steel bins and piping and the sump were in excellent condition. These results demonstrate the continuing integrity of the CSSFs and lead to the conclusion that the radioactive calcine continues to be stored in a leak tight double containment system.

The lack of observable degradation in the CSSFs has led to a biennial inspections schedule for the three oldest systems, CSSFs I, II, and III, and an every five-year schedule for CSSFs IV, V, and VI. The empty facility, CSSF VII, is inspected annually because ALARA (as low as reasonably achievable) considerations permit such inspections. The inspection results to date provide the visual evidence necessary to recommend that no additional non-destructive testing is necessary. However, further inspections may be conducted if the visual inspections reveal indications of damage and when the vaults are emptied to assure that no hidden damage is occurring.

System Life Projection

The CSSFs are designed, constructed, and operated to prevent any leakage of the stored calcine to the environment. Double containment by the welded stainless steel bins and the reinforced concrete vaults is an essential component of the radioactive waste storage system. However, even though the vaults provide a secondary containment system, the preferred operational option is to maintain the bins in a fit for service condition (uncompromised) throughout the operating life. The probable effects of corrosion on the long-term serviceability of the bins have been projected by comparing the results of the corrosion evaluations with the design-based corrosion allowance. A corrosion allowance is the amount of material that can be lost, evenly from the material surface, before the structure becomes structurally inadequate to perform its intended function. The smallest corrosion allowance for a bin is 0.016 inch for bins in CSSF IV, although no corrosion allowance was identified for CSSF I.[17] The highest corrosion rate for any Type 304 corrosion coupon recovered from CSSF II was approximately 0.000012 inch per year. Based on these data, the bounding service life of the bins in the CSSFs is projected to be about 1,300 years. This projection is based on the fact that little or no general corrosion was observed in the coupon testing programs and that no localized corrosion has been observed in the corrosion studies. If localized corrosion were to occur, it could shorten the projected life and will be included in the projections if such corrosion is detected in the corrosion studies or by the remote inspections.

Conclusion

The conclusions of the structural integrity analysis of the CSSFs at the Idaho Site are that the systems are structurally sound, the radioactive calcine is doubly contained and the systems will remain sound into the projected future. Storage of the calcined solids in the CSSFs is a passive operation with very little opportunity for release of the radionuclides. If release of the calcine from the stainless steel bins to the concrete vault were to occur, the vault is isolated from the atmosphere to prevent release of contamination to the environment. By combining safety analysis information from the seismic and tornado evaluations with the bin corrosion evaluations, design corrosion allowances and projected system lifetimes, the continuing structural integrity of the CSSFs was demonstrated. Based on the continuing visual/video examinations, the retrieval of coupons from the CSSFs after 50, 100, 250, and 450 years of exposure to stored calcined wastes and the projected results of those evaluations, the CSSFs will remain structurally sound for more than 500 years. However, the Settlement Agreement between the state of Idaho and the DOE requires DOE to treat all high-level waste at the Idaho Site so that the waste is ready for removal from Idaho and disposal by a target date of 2035.[27] Under the Environmental Management Performance Management Plan for Accelerating Cleanup of the Idaho Site, the calcine is to be retrieved, stabilized and packaged in a facility that will be constructed by 2020 and the calcine will be ready for shipment to a federal repository by 2035.[22]

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The Use of Polymers in Radioactive Waste Processing Systems

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Abstract

The Savannah River Site (SRS), one of the largest U.S. Department of Energy (DOE) sites, has operated since the early 1950s. The early mission of the site was to produce critical nuclear materials for national defense. Many facilities have been constructed at the SRS over the years to process, stabilize and/or store radioactive waste and related materials. The primary materials of construction used in such facilities are inorganic (metals, concrete), but polymeric materials are inevitably used in various applications. The effects of aging, radiation, chemicals, heat and other environmental variables must therefore be understood to maximize service life of polymeric components. In particular, the potential for dose rate effects and synergistic effects on polymeric materials in multivariable environments can complicate compatibility reviews and life predictions. The selection and performance of polymeric materials in radioactive waste processing systems at the SRS are discussed.

Introduction

Approximately 36 million gallons of liquid radioactive nuclear waste are now stored in forty-seven underground carbon steel tanks at the SRS. The waste chemistry is controlled to minimize corrosion of the carbon steel waste tanks. The waste is processed through evaporators to condense the high-level radioactive waste volume. The vast majority of the high-level waste (HLW) will be vitrified at the Defense Waste Processing Facility (DWPF) into a stable glass form with the radionuclides incorporated into the glass structure. The glass waste is melted and poured into stainless steel canisters that are stored in specific facilities (glass waste storage buildings). The DWPF is currently the largest radioactive waste vitrification plant in the world, beginning radioactive operations in March 1996 and is currently projected to produce ~6,000 canisters by year 2019.

The liquid nuclear waste in SRS tank storage exists in three forms: supernate, sludge and salt. The supernate is basically a sodium salt solution and is passed through evaporators to reduce the volume. The DWPF is designed to treat the salt and sludge from the HLW storage tanks and produce a glass that incorporates the radioactive nuclides in the stable glass structure. The sludge, which comprises ~10 percent of the waste volume, contains about half of the radioactivity. The salt, which readily dissolves in water, comprises about 90 percent of the volume and contains the balance of the radioactivity. Before being sent to the DWPF, the majority of the salt waste will be treated at the Salt Waste Processing Facility (SWPF) currently under construction at the SRS. Until the SWPF is operational, interim salt waste processing is conducted via the Modular Caustic Side Solvent Extraction (MCU) Unit and the Actinide Removal Process (ARP) in H-Area.

Low-level radioactive waste (LLW) is sent to the Saltstone facility where it is mixed with specialized grout formulations and transferred into large disposal units at the Saltstone Disposal Facility. SRS is the first site in the U.S. Department of Energy (DOE) Complex to disposition salt waste. Removing waste from the tanks will result in the permanent closure of the Site's high-level waste tanks, a high priority for the DOE.

Polymeric Materials and Components

The majority of process equipment in radioactive waste processing facilities is made of metal alloys and structures are predominantly made of reinforced concrete. However, as a practical matter, polymeric materials are inevitably used as seals, pump/valve components, hoses, piping/tubing, electrical and thermal insulation, personal protective/safety equipment, coatings/linings and other components. Such components are often designed for replacement, as degradation over time is expected. However, regardless of service duration, polymeric materials must meet certain requirements and exhibit sufficient resistance to the service environment. For critical service or long-life components, testing is often recommended and necessary.

Polymers are known to be sensitive to ionizing radiation. However, in many radiological applications, polymeric materials can be used, either because dose rates are sufficiently low or the exposure duration is limited thus minimizing degradation. Systems, especially those that contain polymeric materials, should be designed to allow component replacement wherever practical. However, some components must remain functional for the design life of the facility which might range from a few years to several decades. Standard vendor equipment may require modifications or upgrades, particularly for critical or safety-related systems. This paper discusses the selection, use and performance of polymeric materials in radioactive waste processing facilities at the SRS.

Sealing Components

A major use of polymers in radioactive waste processing systems is for sealing components. Metal or ceramic seals may be required in some cases, but polymers are frequently used due to common design, low cost, compliance and lower sealing stresses. Most polymer sealing applications such as gaskets involve elastomers such as EPDM (ethylene-propylene diene monomer) or certain thermoplastics such as Teflon™ PTFE (polytetrafluoroethylene). Stiffer polymers such as ETFE (ethylene-tetrafluoroethylene) co-polymer, UHMWPE (ultra-high-molecular weight polyethylene) or PEEK (polyetheretherketone) may be used as valve seats. Flexible graphite is not technically a polymer, but an organic material often used for gasket and seal ring applications.

In several SRS facilities (Figure 1), piping jumpers are fabricated with unique connection devices (Hanford connectors). Early wisdom by DuPont engineers at Hanford and later at SRS led to such designs to provide system flexibility and account for possible failures and equipment replacement. The Hanford connector (Figure 2) is a stainless steel block with flow ports and a large threaded stud with an ACME nut that tightens a jaw assembly against process vessel or wall nozzles. Jumpers are lifted and moved as needed by overhead cranes and the connector is engaged by a remotely operated impact wrench.

The SRS jumper connectors have historically been sealed with gaskets made of Teflon PTFE-asbestos fabric. The gaskets are held in place with a snap ring installed in the sealing face of the connector block. In the SRS separations facilities, process solutions are primarily based on nitric acid, thereby requiring high chemical resistance.

The original jumper gasket material was constructed of finely-woven crocidolite (Blue African) asbestos dipped with a Ludox® dispersion and blended with 30 wt percent Teflon PTFE. The fabric was then calendered and sintered. In the 1980s, the material was changed to use chrysotile (Canadian White) asbestos due to limited crocidolite availability and a decreasing number of asbestos suppliers. Teflon/asbestos gaskets are still used to seal many process jumpers at the SRS.

Teflon™ PTFE is well-known to exhibit low resistance to ionizing radiation. However, in the jumper gasket, the woven asbestos provides continuous reinforcement and durability with the PTFE binder providing sealability. The high compressive load and sealing stresses imposed by the connector also significantly contribute to gasket performance.

Over the years, different materials have been evaluated for the jumper gaskets to minimize reliance on asbestos-containing materials. However, due to the salient features required, no single commercially-available, non-asbestos gasket material has yet been found suitable. Flexible graphite is resistant to many process streams, but not to nitric acid solutions. The sealing stress imposed by the connector is quite damaging to flexible graphite and other materials, particularly where multiple uses are required. Compressed non-asbestos gaskets with EPDM binder have been successfully used in neutral or high pH service in some facilities but they cannot be used for acid service.

Figure 1. Canyon jumper piping, sealed with Hanford connectors and jumper gaskets

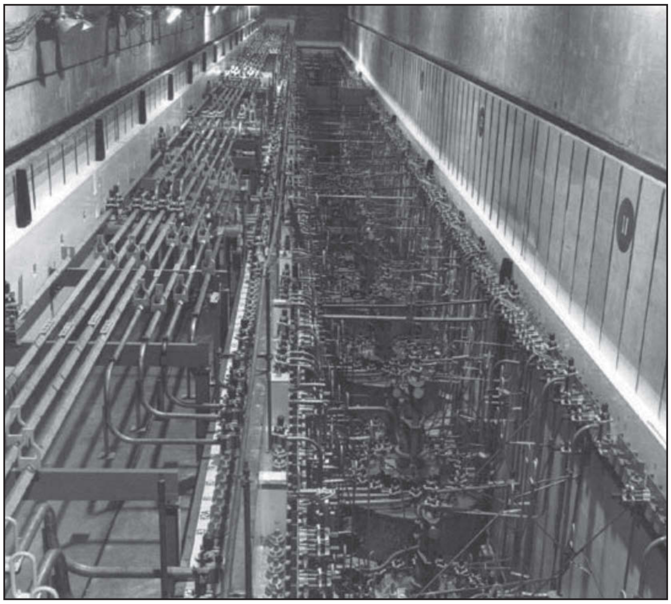
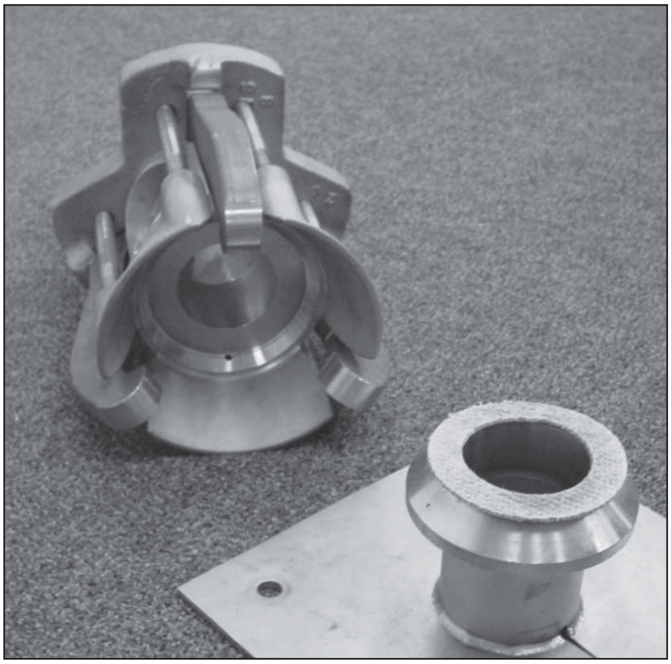


Figure 2. Hanford connector block and demo nozzle with Teflon/asbestos gasket



In many systems, Site piping codes dictate what materials are used for specific process conditions. PTFE or reinforced PTFE is typically excluded from highly radioactive solutions due to known radiation sensitivity (jumper gaskets excluded), but it is widely used in non-radioactive systems. PTFE can be used if dose rates are sufficiently low or service periods are such that radiation-induced degradation is avoided.

For acid and/or elevated temperature service in aqueous environments, FKM fluoroelastomers (Viton® or similar) are often specified. General-purpose grades (copolymer A-type) are widely used, but terpolymer grades (B, F, GF, GLT, GFLT types) may be needed for superior chemical resistance and other properties. Older compounds often contained lead oxide (litharge) as an acid acceptor, but newer formulations based on peroxide cures are superior.

FFKM-type perfluoroelastomers (Kalrez® or similar) offer the broadest range of resistance to heat and chemicals, although radiation resistance is moderate and these elastomers can be less dynamically resilient than more conventional elastomers. Thermal expansion characteristics must be considered when alternative elastomers are needed. Simply changing the seal material in a given design to improve chemical or radiation resistance can result in premature failure if thermally-induced dimensional changes are not considered. Consultation with seal manufacturers is recommended before an alternate sealing material is selected.

Neutral and alkaline waste processes tend to be less chemically aggressive than acidic solutions toward most polymers. Many of the common elastomers such as EPDM, FKM/FFKM fluoroelastomers, neoprene, butyl rubber, nitrile butadiene rubber (NBR), styrene-butadiene rubber (SBR), CSPE (chlorosulfonated polyethylene), silicone, polyurethane and even natural rubber can possibly be used depending on specific conditions.

EPDM elastomers can provide an excellent balance of resistance to aging, chemicals, ionizing radiation and thermo-oxidative degradation within limits. EPDM is sensitive to certain chemicals, notably hydrocarbon-based fluids and certain acids (particularly nitric). EPDM is often a *preferred* elastomer for applications in contact with stainless steel due to low chloride content, reducing concerns over chloride stress-corrosion cracking. The SRS limit for chlorides in materials in contact with austenitic stainless steel at certain conditions is 250 ppm (total), which can limit material options in certain environments.

FKM elastomers have been used in alkaline service (evaporator seals) due to elevated temperature requirements but resistance to strong alkaline solutions is limited. However, newer base-resistant grades of FKM elastomers are now available when EPDM or other elastomer types are not suitable. FFKM types may be needed for higher temperatures.

Elastomers are often used to seal containment vessels in radioactive material packages. As an example, O-rings based on Viton® GLT (now GLT-S) are used to seal the stainless steel containment vessels in Model 9975 shipping packages designed for transportation of plutonium-bearing materials. Designed for transportation, robust 9975 packages are also being used for safe interim storage of Pu materials in the K-Area Materials Storage (KAMS) facility at the SRS (Figure 3). The aging behavior of the O-rings and fiberboard insulation in the packages is being studied to develop life prediction models for the storage facility.[1,2] Polyurethane foam is also used in certain packaging designs for thermal insulation and impact protection.

Figure 3. Model 9975 shipping packages used for interim Pu storage at SRS (internal containment vessels sealed with GLT/GLT-S fluoroelastomer O-rings)

Figure 4. ETFE copolymer ball valve seats used in HLW transfer systems

Valve seats are another application of polymers in radioactive waste processing systems. In the HLW tank storage facilities (tank farms), HLW is transferred via underground piping made of austenitic stainless steel with carbon steel jacket lines for secondary containment and leak detection. In diversion boxes (pump/valve pits), the process flow can be diverted as needed. Transfer line ball valves contain seats made of Tefzel® ETFE (ethylene-tetrafluoroethylene) copolymer (Figure 4). Carbon-graphite seats are highly resistant to the waste chemistry and radiation, but exhibited limited toughness and installation difficulty (cracking problems). ETFE seats have not been formally examined after service in HLW but have been used successfully for years.

ETFE fluoropolymer valve seats are also specified for use in the waste solidification building (WSB) currently under construction at the SRS. The WSB will receive and process the liquid waste generated by the mixed oxide fuel (MOX) facility also currently under construction at the SRS. For the WSB facility, the combined resistance of ETFE polymer to nitric acid at elevated temperature and ionizing radiation was investigated. Cracks in a ETFE polymer sample after exposure to gamma radiation and 8M boiling nitric acid are shown in Figure 5. Moderate degradation was observed in mechanical properties after a dose of 150 Mrad (1.5 MGy) exposure, with severe embrittlement occurring at 500 Mrad (5 MGy).

In the WSB, the valve seats will primarily see alpha radiation with some beta/gamma exposure. The bulk (beta/gamma) radiation dose rate for the valve seats is estimated at 1 Gy/hr during processing, with an bounding alpha (surface) dose rate of 177 Gy/hr. Service temperatures are bounded at ~113°C, with the majority of process streams being limited to 60°C. Maximum service life is desired to avoid personnel exposure and facility downtime as a result of valve maintenance. The design life of the WSB is thirty years. At 1 Gy/hr, the thirty-year bulk dose to the valve seats is ~0.26 MGy. At 177 Gy/hr (alpha), a thirty-year surface dose is ~47 MGy. This dose would principally apply to sealing surfaces subject to constant exposure.

As a result of PTFE valve seat failure in a DOE plutonium processing facility, studies were performed to show the susceptibility of PTFE polymer to alpha (heavy ion) radiation.[3, 4] These studies showed that surface doses of 10^{10} rad (10^{8} Gy) or greater were required for significant surface degradation. Similar studies have not been performed for ETFE polymer, but similar if not greater resistance to alpha surface degradation is expected. At 177 Gy/hr, such doses will not be reached in WSB applications until approximately sixty-five years.

Backflush valves used in the HLW tank farms are three-way plug valves with carbon-graphite seats (Figure 6). These valves are operable but have posed binding problems, primarily attributed to thermal expansion issues and the two-piece seat design. Binding during operation can cause processing delays and require removal of the entire assembly from the tank and transfer to a decontamination facility for maintenance. Such efforts are obviously undesirable. ETFE and PEEK polymers were investigated as possible seat alternatives. ETFE was investigated based on successful use in HLW transfer line valves, with PEEK investigated due to known chemical, heat and radiation resistance.

Figure 5. ETFE copolymer after irradiation to 500 Mrad (gamma)

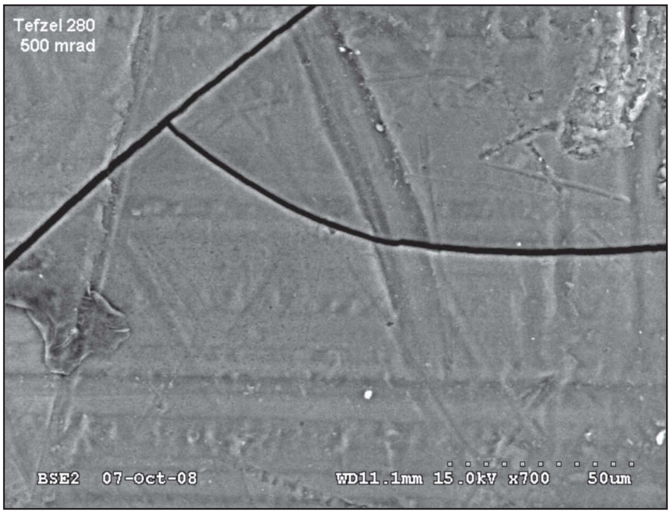
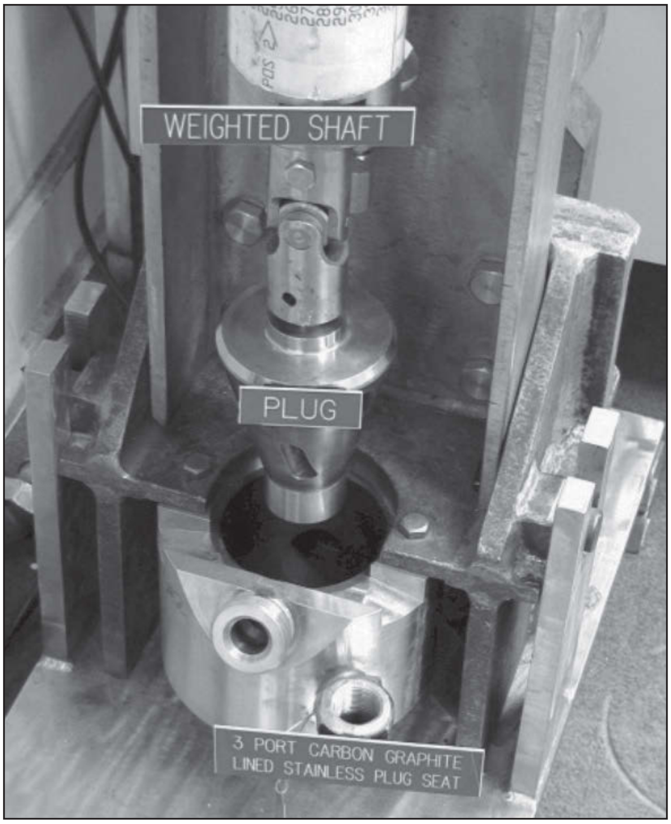


Figure 6. Backflush valve with three-way carbon-graphite plug seat



ETFE and PEEK polymers were subjected to gamma radiation doses of 2 MGy and 5 MGy followed by a 14-day exposure to 50% NaOH at 142 °C. Radiation doses were selected to bound a 10-year service period. PEEK 450G showed essentially no significant change in tensile properties with only a slight color change occurring during exposure. Conversely, ETFE copolymer was significantly degraded at the prescribed test conditions. ETFE polymer may be suitable for shorter service periods or less conservative conditions, but these have not yet been evaluated. Though PEEK shows significant resistance to degradation, a limitation of PEEK in valve seat applications is its relatively high stiffness and limited compliance so functional testing was recommended. Additionally, valve redesign could possibly allow remote replacement of components, reducing the service life required.

Electrical Systems

Polymers are often needed in electrical systems for dielectric/insulation properties. An example is in the electrical jumpers used in several SRS facilities to carry electrical power and instrumentation signals. The jumpers use 10-40 percent glass-filled polycarbonate insulator blocks that isolate gold-plated connector pins in various configurations (Figure 7). Polycarbonate is used for its combined mechanical and electrical properties as well as reasonable resistance to the facility environment.

Figure 7. Electrical jumper connector block (40% glass-filled polycarbonate)

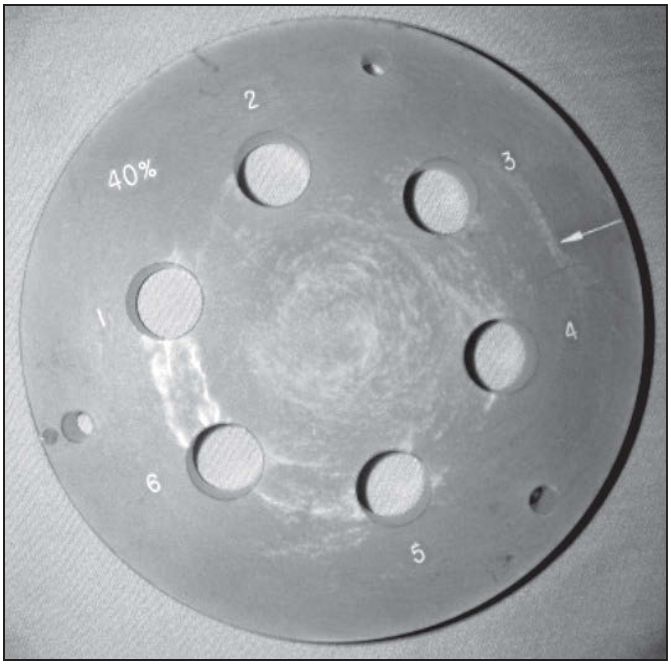


Figure 8. Class 1E nuclear cable (XLPE insulation, CSPE jacket)

Electrical cables, motors and other instrumentation in some SRS facilities are specified to meet IEEE Class 1E requirements, at least for radiation tolerance purposes.[5] Such cables (Figure 8) are typically insulated with fire retardant cross-linked polyethylene (FR-XLPE), cross-linked polyolefin (XLPO) or EPR (ethylene-propylene copolymer), with jackets made of CSPE (chlorosulfonated polyethylene), EPR, EPDM, XLPE/XLPO or EVA (ethylene-vinyl acetate) copolymer.

PVC is a common insulation, particularly in older cables or in cables used in low radiation areas, but it is not preferred due to the potential generation of HCl during radiolysis or fire scenarios. Plasticizer migration has also been observed in PVC-insulated cables. Low-halogen or zero-halogen cable insulations are now more commonly specified.

Cables with polyimide (Kapton®) or PEEK insulations are sometimes specified for high radiation resistance. Commercial nuclear-qualified cable products are typically rated to total doses of ~200 Mrad (2 MGy), which accounts for normal service dose (50 Mrad) plus the dose incurred (150 Mrad) during a LOCA (loss-of-cooling accident). Depending on the actual dose rates involved, even such ratings may not be sufficient. Shielding or other methods may be needed to reduce dose rates. It is important to note that qualification protocols for nuclear components generally involve high dose rate exposures that may or may not represent actual service conditions. Dose rate effects can influence material behavior. In addition, electrical equipment must be specified based on all relevant properties, not radiation resistance alone.

An important property of amorphous polymers is the glass transition temperature (T_g). The T_g value is the temperature at which the polymer structure transitions from elastic to rigid or "glassy" behavior, often with a change in specific volume. It is important to ensure that such temperatures are not reached within normal service, or if such transitions occur, the effects of the transition are acceptable. Studies have shown that the glass transition temperature of PEEK and other polymers can be affected by radiation and thermal aging.[6] This may also vary with the dose rate and level of oxygen in the environment.

Thermal transitions are important at both high and low temperatures. For example, the low temperature performance of elastomers is greatly dependent on the T_g value. Ideally, the T_g of elastomers should be at or below the minimum service temperature. Elastomeric seals may function at or even below the glass transition temperature, but the lower the service temperature relative to the T_g value, the more likely the performance will be affected. Therefore, the glass transition temperature of amorphous polymers, including elastomers, should be carefully considered.

Hose-in-Hose Systems

Hose-in-hose (HIH) systems have been used for radioactive waste transfer operations at the SRS and Hanford sites. These systems are intended to provide design flexibility at lower cost than hard-welded piping systems. These systems typically involve use of heavy-duty chemical transfer hoses made of EPDM or other elastomers, reinforced with steel wire and inorganic/polymeric fibers. Some hoses may be lined with cross-linked polyethylene (XLPE), ultrahigh molecular weight polyethylene (UHMWPE) or other polymers.

Some hose systems have been developed on-site using commercial products, while others have been developed and marketed by vendors specifically for hazardous material and radioactive waste transfer. Although such systems have been successfully used, the long-term effects of radiation, thermal aging and chemical exposure are not completely understood. Synergistic effects and dose rate effects are difficult to predict. For that reason, accelerated-aging tests and post-service examination of hoses have been recommended.

One commercial chemical transfer hose was evaluated for use as an emergency flexible HLW jumper (< 6 months service).[7] The wire/fiber-reinforced hose with an EPDM cover and a modified XLPE liner (Figure 9) was investigated for the effects of radiation dose to 2 MGy and 50 percent NaOH solution at 93°C. Over a six-month service, the hose will likely see less than 0.50 MGy, but higher doses were evaluated for margin and to determine the hose limits. The effects of radiation at 0.5 MGy were minor, with more severe effects at higher doses. Dose rate effects were not evaluated for the short service period. The hose has not yet been put into service as a flexible HLW jumper.

An aboveground, low-level HIH system has been used for several years at the SRS to transfer low-level HEU solutions. This system consists of the same robust chemical transfer hose evaluated above, inserted inside a larger EPDM water discharge hose. The service conditions for this hose system are less severe than evaluated for the emergency HLW jumper. The bounding radiation dose rate for the core transfer hose during transfers is ~7 rad/hr. The dose rate to a limited section of hose inside the receipt tank is 660 rad/hr. Approximately 600 feet of this HIH system has been in operation for several years without reported degradation. Post-service evaluation of the hose condition after service has been recommended.

Figure 9. Cross-section of chemical transfer hose evaluated for HLW transfer (steel/fiber-reinforced with modified XLPE liner and EPDM cover)

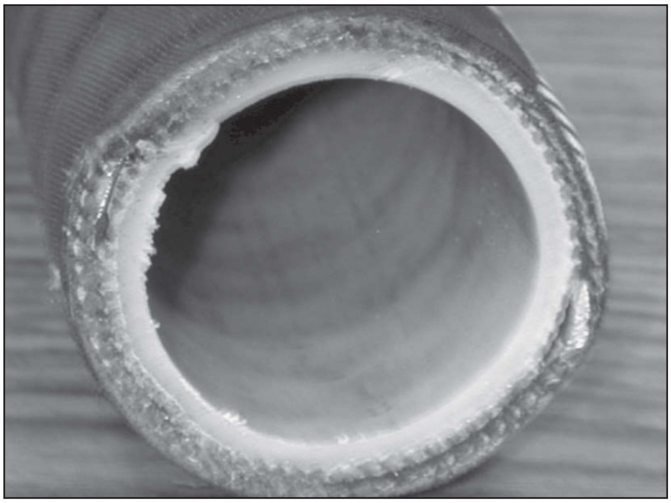
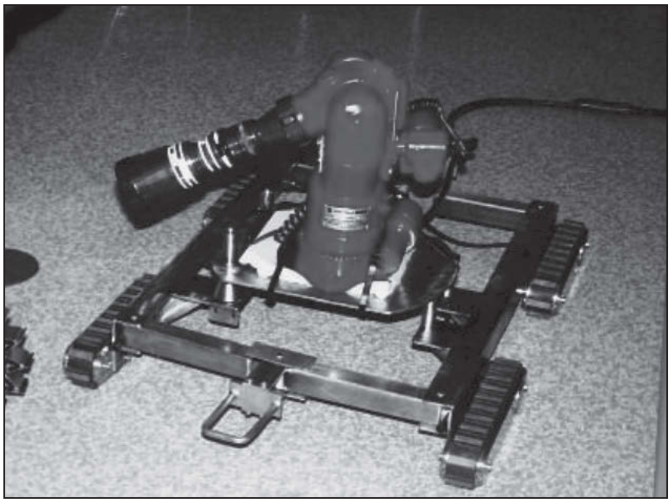


Figure 10. Tank crawler developed by SRNL for HLW tank cleaning



In-Tank Equipment

Submersible mixing/transfer pumps, tank crawlers and other equipment has been designed for operation within the HLW tanks (Figure 10). The service life range for such components can vary from a few months to several years. Internal components (such as motor insulation) will see radiation only but other components (seals) may be in direct contact with the waste, requiring resistance to the waste chemistry as well the heat and radiation involved. The radiation dose to direct contact components is likely higher due to alpha/beta contributions. Therefore, the actual dose rates to such components should be determined. Overly conservative dose rate estimates can limit material selection or complicate design efforts.

Polymers such as PTFE, acetal (polyoxymethylene), polypropylene, acrylic and butyl rubber are usually excluded due to low radiation tolerance. Polycarbonate and several other amorphous polymers are usually excluded due to limited resistance to strong alkaline solutions. PVDF (polyvinylidene fluoride) fluoropolymer is relatively resistant to radiation and many chemicals, but is sensitive to strong alkaline solutions. Fiberglass reinforcement in some materials may also be subject to attack by alkaline waste. Several elastomer types may be suitable, though EPDM elastomers are generally preferred for direct waste contact.

MCU/SWPF

The SRS deploys two physical processes for decontaminating the radioactive salt solutions typical of the waste tanks: actinide and strontium adsorption on an inorganic sorbent (monosodium titanate, MST) and cesium absorption into a calixarene-crown ether molecule in a solvent extraction process using centrifugal contactors. The facility housing this operation is the Modular Caustic Side Solvent Extraction Unit (MCU).

The concentrate stream created in these processes includes caustic, radioactivity and organic from the solvent extraction. Early in MCU construction, polymeric materials were selected based on expected resistance to process conditions and commercial availability. No testing was initially performed. Polyolefins such as EPDM, UHMWPE and HDPE were initially excluded due to concerns over solvent compatibility and possible swelling (primarily due to the Isopar® L). Table 1 shows the initial CSSX composition. Testing was later performed to evaluate the resistance of certain polymers in the MCU to the initial and improved solvent compositions. The polymers tested included Tefzel®/ETFE, Isolast® and Kalrez® FFKM, carbon-filled PEEK, flexible graphite and chlorinated polyvinyl chloride (CPVC). In those tests, only the ETFE polymer swelled slightly in the presence of the modifier.

In the MCU, Kalrez® seals were found to have suffered dehydrogenation and defluoronation due to exposure to caustic solution and friction heat from the shaft that drives the centrifugal contactors. This is believed to have been more of a design issue rather than a materials degradation problem. FFKM fluoroelastomers have a relatively high thermal expansion coefficient, which can cause problems with shaft seals and other applications if such behavior is not accounted for.

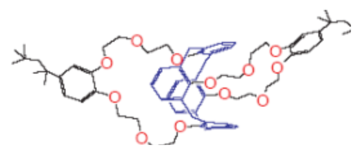
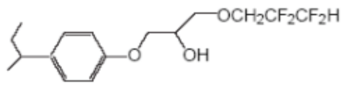
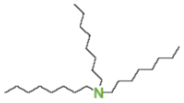
Another polymer used at MCU for coalescing oil carried over by the treated salt solution is nonwoven polyphenylene sulfide (PPS). PPS is an aromatic thermoplastic highly resistant to alkaline environments, non-oxidizing mild acidic environments and ionizing radiation. Literature data suggest that gamma radiation doses > 450 Mrad (~15 years service in the MCU) are required to affect performance of PPS polymer via oxidation of sulfide to sulfone or sulfoxide groups. Dose rate effects on PPS polymer in this application have not been studied, but thus far the MCU service environment has had no discernible effect on the performance of PPS polymer.

Protective Coatings & Linings

Polymeric coatings and linings are often used in radioactive waste processing facilities to prevent corrosion, provide secondary containment and allow decontamination and clean-up. In limited cases, the linings may be required to be in direct contact with waste solutions for extended periods of time (e.g., Saltstone vault linings).

Coatings and tape wraps are used to protect buried carbon steel piping, including waste transfer jacket lines, from corrosion. Protective coating types that have been used include coal-tar emulsions, coal-tar epoxies, inorganic zinc with hydrophobic powder, epoxy-phenolic, extruded polyethylene, copolymer tape-wraps, and bituminous coatings with asbestos felt and kraft paper. Coal-tar epoxy coatings have been used successfully for years for below-ground piping protection. Epoxy-phenolic coatings with micaceous iron oxide are now more commonly specified due to health concerns related to coal-tar epoxy application. Stainless steel waste transfer lines and below-grade process piping in the WSB facility were recently coated with epoxy-phenolic (Figure 11).

Table 1. Initial CSSX Composition

Component	CSSX
BoBCalixC6	 7 mM
Cs-7SB Modifier	 29 wt %
TOA (trioctylamine)	 0.12 wt%
Isopar® L	Linear/branched C12 69 wt %
MaxCalix	0 wt %
LIX® 79 (Guanidine)	0 wt %

A primary limitation of coatings is that performance is strongly dependent upon proper selection, substrate preparation and application. Even the most robust coating can fail if improperly applied. Failure of a carbon steel waste transfer jacket line attributed to adjacent steam leaks and coating degradation is shown in Figure 12.[8]

Secondary containment linings are used in radioactive waste processing facilities to provide containment in the event of a catastrophic break, protect the substrate from degradation and facilitate decontamination. Linings should be selected based on bounding anticipated exposures even though the lining may never be challenged. Many factors should be considered, primarily the process chemistry (including possible decontamination agents), solution temperature, radiation resistance, UV light resistance, duration of exposure, equipment traffic and access for inspection/repair.

Secondary containment linings generally fall into two categories: liquid-applied systems and sheet linings. Liquid-applied systems usually consist of epoxy, novolac epoxy, elastomeric polyurethane, polyurea and vinyl ester systems. Within each general polymer type, the formulation and properties can vary significantly. Linings may be mat-reinforced or non-reinforced systems, varying in thickness. Vinyl ester linings are generally

Figure 11. WSB process drain piping coated with epoxy-phenolic

Figure 12. Carbon steel waste transfer jacket line failure due to coating degradation

limited to facilities handling strong caustic or nitric acid solutions. Linings may also contain graphite or other low surface-energy additives to facilitate decontamination. Flexible base layers may be needed for crack-bridging capability. Moisture vapor barrier systems are highly recommended below containment linings, particularly if below-grade, to prevent failure due to moisture vapor transmission.

Sheet linings may be adhesive-bonded, hot-air welded or loose laid systems that are mechanically fastened. Material options consist of thermoplastics such as HDPE or PVC or elastomers such as EPDM, EVA, or CSPE. Containment linings should be installed by qualified and experienced applicators, with appropriate inspection hold points.

Radiation resistance is usually not the most critical aspect for secondary containment linings but it should still be considered. The dose to the coating/lining system during normal service plus any off-normal events should be determined. Most thermosetting polymers are relatively resistant to radiation. As an example, certain coatings used in nuclear power plants are qualified to 1000 Mrad (10 MGy) at very high dose rates per ASTM D4280.[9] However, coatings with this pedigree may not be suitable for radioactive waste/material processing environments and many containment linings for chemical service have not been tested to this standard. Dose rate effects in coatings have not been widely studied. Therefore, actual service conditions should be reviewed.

In DOE nuclear facilities, coatings and linings may be required to meet NFPA 801.[10] This standard requires that interior wall and ceiling finishes have Class A flame spread ($\leq$25) and smoke development ratings ($\leq$450), as tested per ASTM E84 (or NFPA 255). Floor coatings must have Class I critical radiant flux (CRF) values ($\geq$ 0.45 W/cm^2) as tested per NFPA 253 (or ASTM E648).

Unfortunately, many coatings have not been tested to these standards, with even fewer systems tested to the floor requirements, as such requirements were initially developed for floor covering materials. Therefore, facility owners, design engineers, architects, and fire protection and coatings/materials engineers should discuss requirements before selecting a coating/lining system. If NFPA 801 compliance is required and a compliant coating cannot meet all other requirements, testing of alternate coatings is required. Recently, a major coatings manufacturer and strategic supplier at the SRS had several coatings tested to meet NFPA 801 requirements for site projects.

Safety/Contamination Control

Polymers are widely used for contamination control and personal protection during maintenance or decommissioning activities. Personal protection equipment includes plastic suits, respirators, safety glasses and other safety-related items. The SRS containment fabrication group uses huts, windbreaks, tarps, and covers constructed from PVC-laminate material with a woven nylon scrim. Glovebags, catch containments, and containment huts are custom made of PVC, polyurethane or nylon 6+6 copolymer material depending on service conditions (Figure 13).

Polyurea coatings and other types have been used to fix contamination in place and to rollback previously contaminated areas (Figure 14). Though such activities have been successful, surface preparation is often limited or restricted. A limitation of fast-cure coatings such as polyurea is that rapid curing may not result in good adhesion. Early marketing claims and misapplication of such coatings have led to site and industry failures. These issues have largely been resolved by formulation changes, the use of primers and renewed emphasis on adequate surface preparation.

Figure 13. Fabricated containment hut at SRS containment fabrication facility

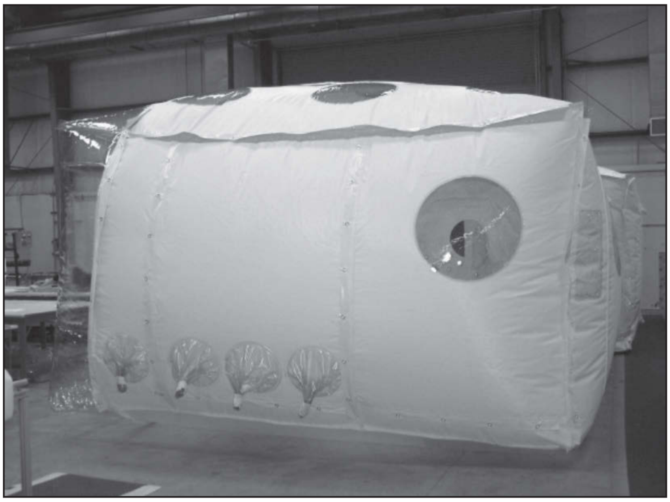
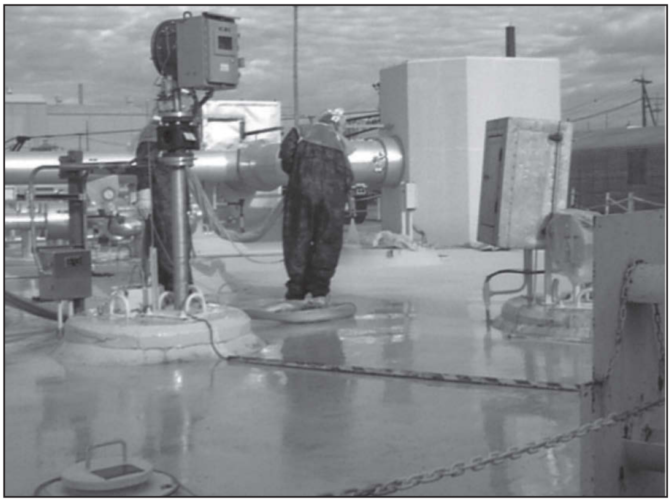


Figure 14. Polyurea coatings applied on tank tops for contamination control



Radiation Data Limitations

A challenge in evaluating the radiation resistance of polymers is that most historical data from the 1950s to the 1970s came from very high dose rate exposures. Polymers are now known to be potentially sensitive to the dose rate, thus complicating service life predictions. Predictions based on high dose rate exposures have often been shown as non-conservative.

One of the first industry examples of this behavior was observed in the SRS K-reactor in the mid-1970s.[11] PVC/polyethylene insulated cables qualified for service based on high dose rate data were found to be significantly degraded after only twelve years at much lower dose rates. Subsequent testing confirmed that dose rate effects were significant. Such effects are generally attributed to diffusion-limited oxidation but variation in degradation mechanisms can also occur. This observation led to many investigations into the potential for dose rate effects in nuclear cable insulations and other components.[12] As a result, nuclear qualification protocols now acknowledge the potential for dose rate effects. Condition monitoring programs are often implemented to address limitations of accelerated-aging test methods.

Dose rate effects are likely less important for components that can be readily replaced or those that only need to function for short periods. Dose rate effects are also likely less critical in non-oxygen bearing environments but oxygen is difficult to completely exclude. For critical or long-life components, particularly those in oxygen-bearing environments, dose rate effects should be evaluated and testing may be required. The effects of temperature and other variables should also be considered.

Another limitation is that literature data often quote damage threshold values for various polymers and properties (ex. dose to cause 25 percent change in elongation). These values allow comparison of materials at the same level of damage, but they are not very useful for service life prediction. Such values are arbitrary and the properties evaluated may not be the most relevant for a specific application. In many cases, the dose to failure or unacceptable performance for specific components is unknown.

Chemical/Thermal Data Limitations

Chemical resistance data from polymer/component manufacturers and general literature sources are often sufficient to determine compatibility. However, not all chemicals have been widely studied and there are several aspects to consider when interpreting such data. Compatibility data are often based on relatively short-term exposures to *pure* chemicals of specific concentrations at certain temperatures. While such data might rule out highly incompatible materials, prediction of long-term effects of the same chemical (or mixtures) at different concentrations and/or temperatures is complex. Service history may be sufficient to determine compatibility, if similar conditions are anticipated.

Chemical compatibility should not be based solely on the primary waste stream components. Even minor constituents in the process can affect material performance. An example is tributyl phosphate (TBP), an ester of orthophosphoric acid, which is present in certain systems. The presence of TBP in a process stream, even in low concentrations, may lead to polymer degradation. TBP is used for many purposes including anti-foaming and solvent extraction but it is also a strong polar solvent used in the production of many synthetic resins and as a flame-retarding plasticizer. FKM fluoroelastomers are acid-resistant, but they are sensitive to TBP. Conversely, EPDM seals are very resistant to TBP but have limited acid resistance. For combined acid/solvent resistance, FFKM perfluoroelastomers may be required. The presence of TBP is known to have caused significant damage to CPVC piping in one SRS facility. Therefore, the compatibility of all constituents in a process stream should be evaluated.

Thermal aging data also have significant limitations. An example is the use of *continuous* service temperatures. Such limits are often based on undefined criteria and limited time periods that may not match service conditions. Most polymers are susceptible to oxidation, which is a diffusion-related process. The consumption of antioxidants over time is another mechanism that can result in premature failure. Even accelerated-aging tests at elevated temperature can overlook such mechanisms and produce non-conservative life estimates.

The general upper service limit for FKM fluoroelastomers is often quoted as 204°C. Seal manufacturers typically base this temperature on the near-complete loss of sealing force as measured by compression stress-relaxation (CSR) behavior after 1000 hours or similar data.[13] Depending on the seal design and service conditions, this level of relaxation may still be acceptable but the seal is no longer pushing back against mating surfaces. Therefore, such thermal ratings should not be interpreted as applicable for longer time periods.

For example, SRS testing of GLT-based fluoroelastomer seals has shown that leakage failure (>1E-07 cm^5/sec) can occur in a specific radioactive material packaging design after aging at 177°C for less than one year and at 149°C in 2.8 years.[2] No leak failures have yet been observed after ~6 years at 93°C, which is bounding for the service environment. Accelerated-aging tests using time-temperature superposition techniques predict several decades of service life at realistic service temperatures. However, in other applications, seal life could be significantly reduced, even if technically below the *continuous* service limit. Thermal limits may also be reduced by radiation or chemical effects.

Summary

As a practical matter, polymeric materials are inevitably used in radioactive waste processing systems and facilities. Polymers can be successfully used within their limits but resistance to all potential environmental factors must be evaluated. A primary limitation of polymers is their relative susceptibility to damage by ionizing radiation. Dose rate effects can significantly reduce service life compared to predictions based on high dose rate data. In chemical environments, even minor process constituents can lead to unexpected degradation. The use of *continuous* thermal limits based on short-term data should be viewed with caution. Material selection should therefore be carefully reviewed. For critical, long-term or difficult to replace components, testing may be needed to verify compatibility or for service life prediction.

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The Value of Using Independent Technical Experts to Enhance the Management of High-level Nuclear Waste

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Abstract

The use of expert panels and other consultants to enhance and supplement technical and managerial expertise within organizations is a well-accepted practice. This paper highlights the engineering and scientific contributions of such panels to the management of nuclear waste storage within the U.S. Department of Energy complex. The value added through exchanges with such panels is demonstrated by recommendations and responses that have resulted from specific exchanges.

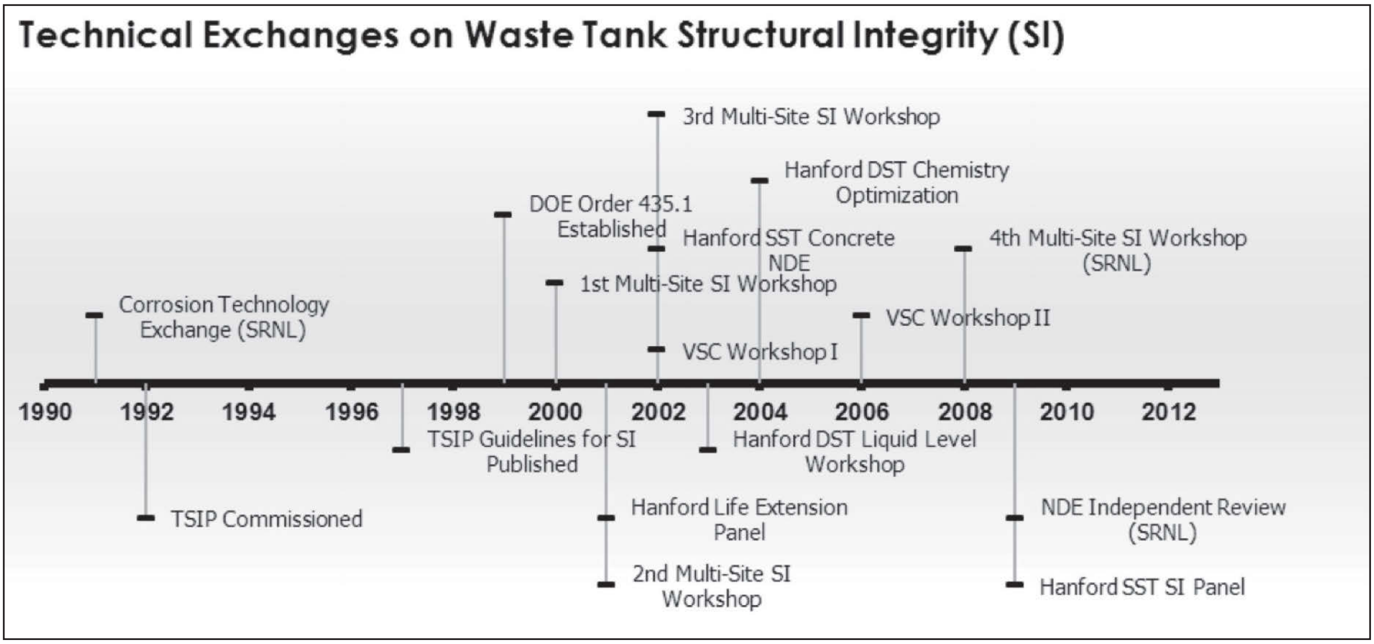
Introduction

Technical experts have been employed in the nuclear materials field, since the days following the Manhattan project, to enhance the workforce, evaluate alternative technical approaches, and to assist in defining the direction of actions taken by the U.S. Atomic Energy Commission and its successor government agencies, the U.S. Energy Research and Development Administration which was later incorporated into the U.S. Department of Energy (DOE). This is particularly true at sites which have high-level radioactive liquid waste storage tanks including: the Savannah River Site in Aiken, South Carolina, USA; the West Valley Demonstration Project in West Valley, New York, USA; the Idaho National Laboratory in Idaho Falls, Idaho, USA; and the Hanford Nuclear Reservation in Richland, Washington, USA. In recent years the use of elite scientists, engineers, and researchers to assess programs at these sites has become a regular occurrence and, in the area of waste tank structural integrity assessment, this practice has become quite prevalent. This paper will review some of the highlights from the major interactions since 1990. A timeline of some of the key expert panel evaluations of high-level nuclear waste programs across the DOE complex is provided in Figure 1. A brief summary of selected expert panel discussions is presented to demonstrate various ways that panel participation generally adds value to ongoing programs.

Summary of Major Technical Exchanges

In September, 1990, the U.S. Department of Energy, Office of Environmental Restoration and Waste Management, created a task force to assess the design, operations, and analyses of the high-level radioactive waste (HLW) tanks in the DOE com-

Figure 1. History of tank farm structural integrity technical exchanges



plex.[1] This task force established a multi-organizational panel of experts, led by Brookhaven National Laboratory, consisted of members from academia and national laboratories. Eight experts representing relevant disciplines gathered information from technical personnel at each of the sites and held eighteen meetings over a six-year period to discuss and examine emergent issues. One of the first items of business was to identify the group as the Tank Structural Integrity Panel (TSIP) and suggest that a corrosion technology exchange be held in 1991.

Corrosion Technology Exchange (1991)

The recommended corrosion technology exchange was held and provided collaboration on waste tank corrosion among the DOE sites dealing with high-level waste (HLW) storage and management. The workshop brought together a diverse group of twenty-six individuals representing each of the main storage sites. The TSIP members also participated in this exchange and were introduced to the different individual site practices and to the differing processes performed at each site. This meeting served to enhance cooperation and exchange among the technical and managerial experts at the various sites and ultimately led to additional technical/managerial exchanges. Such exchanges increased cross site awareness of existing and emergent problems and improved the foundation from which corrosion experts at the various sites could construct programs to address multi-site rather than basically local issues.

Tank Structural Integrity Panel (1992-1997)

The TSIP was commissioned by DOE to prepare a guideline document for the development of structural integrity programs at the HLW storage sites.[2] A structural integrity program that is consistent with the guidelines includes a (1) definition of appropriate loads; (2) collection of data for possible material and geometric changes; and (3) assessment of the tank structure. Appropriate loads are defined according to the applicable national codes and standards and specific guidelines for structural evaluation including loading, analytical techniques and acceptance criteria are discussed. Possible age related degradation mechanisms are also explored and evaluated. The conditions required for potentially active mechanisms to be operative and damaging were identified and effects estimated. The desirability of controlling waste chemistry to minimize degradation of tank materials, and of monitoring for corrosion-induced degradation was also stressed. Important elements of the structural integrity plan also included a leak detection system and a reliable non-destructive examination (NDE) program extracted from the applicable ASME Code Sections and commensurate with the physical conditions in the waste storage tanks. These guidelines have provided the basis for tank in-service inspection programs at DOE HLW sites.

DOE Office of Environmental Management, Office of Science and Technology — Tanks Focus Area

The DOE Office of Environmental Management (EM) created the Tanks Focus Area (TFA) in 1994 to concentrate on the science and technology applicable to tank waste remediation. An integral part of the TFA was formation of an oversight group, consisting of retired senior members from DOE HLW sites, as well as members from academia and industry. This Technical Advisory Group assured that the science and engineering being developed as part of the many technologies being investigated, was applicable to waste storage tanks.

The TFA's mission was to fund and deliver integrated technical solutions that enable tank waste remediation to be successful across the DOE complex. To do this, the TFA assembled users and technical experts to define and execute the mission; integrated the work across the sites and other funding organizations; and, built teams of users and providers to deliver and deploy technical solutions to complex tank related problems.

In September 2000, the TFA identified the development and coordination of new and improved technologies for tank integrity assessment as a high priority. To that end, TFA contracted with the Center for Non-destructive Evaluation at Iowa State University, one of the National Science Foundation's Industry/University Cooperative Research Centers. This center operated in close collaboration with the Ames Laboratory, and provided overall technical guidance and leadership in tank integrity related issues. The program coordinated and implemented an activity that involved collaborations among the five main waste storage sites, regulators, and oversight organizations. Three workshops, jointly sponsored by the TFA and the Characterization, Monitoring and Sensor Technologies Crosscutting Program of the Office of Environmental Management, DOE, were held.

First Multi-Site Structural Integrity Meeting (2000)

A Tank Integrity Workshop was held in Atlanta, Georgia, on October 31 and November 1, 2000, to identify technology issues, foster inter-site communication, and refine plans for technical activities to support NDE needs of the sites.[3] The workshop brought together a diverse group of twenty-six individuals from the five main storage sites; Savannah River, Los Alamos, Oak Ridge, and Idaho National Laboratories (SRNL, LANL, ORNL, and INEEL); the Defense Nuclear Facilities Safety Board (DNFSB); DOE Headquarters; TFA; the Characterization, Monitoring and Sensor Technology (CMST) cross-cutting program, Iowa State University; and other involved organizations and institutions. Two primary goals existed for this workshop. The first goal was to identify any significant impediments to the safe operation and management of the storage tanks, particularly those common to multiple sites. The second goal was to establish groundwork for collaborative efforts aimed at eliminating these impediments, including the development of preliminary action plans and the improvement of networking among individuals at the various sites.

A significant amount of time was spent discussing DOE Order 435.1, *Radioactive Waste Management*. The order mandated the inspection of the tanks but the participants discovered that there wasn't a perfectly common interpretation of the extent of that inspection requirement. In addition to the proceedings of the workshop, the final report from this meeting included a compendium of information about tank integrity activities related to large underground tanks used to store radioactive waste and issues at each of the five main storage sites. This information was primarily collected during visits to the five facilities between September 18 and 29, 2000.

Hanford Double-Shell Tank Life Extension (2001)

An expert workshop was held in Richland, Washington, May 1–4, 2001, to review the Hanford Double-Shell Tank Integrity Project and make recommendations on how to extend the life of the double-shell tanks. The scope of the workshop was limited to corrosion of the primary tank liner, and the main areas reviewed were waste chemistry control, headspace and annulus humidity control, tank inspection, and corrosion monitoring.

Participants included corrosion experts from Hanford, the Savannah River Site, Brookhaven National Laboratory, Pacific Northwest National Laboratory, and several experts from industry.

The workshop developed seventy-three specific recommendations to improve the tank integrity program. A senior review committee, selected from the initial workshop participants, later grouped and sorted this list into twenty-seven high-priority recommendations. The current state of the program, the final recommendations of the workshop, and the rationale for their selection were summarized and many of the recommendations have been put in place at the Hanford site.

Second Multi-Site Structural Integrity Meeting (2001)

Twenty-five people, including representatives of the five major DOE HLW tank sites; National laboratories (SRNL, LANL, ORNL and INEEL), the DNFSB, the DOE Office of Environmental Health, the DOE Office of River Protection, TFA, and CMST attended the second Tank Integrity Workshop in Las Vegas, Nevada, USA, on November 13-15, 2001.[5]

The application of nondestructive evaluation techniques to validate the integrity of DOE HLW tanks was the major focus of the meeting. Attendees shared experiences at the various sites, gained valuable insights from the DNFSB representatives, and prioritized future activities in this area. Particular attention was directed to integrating the electrochemical noise corrosion probe into tank operations at multiple sites (Hanford, Savannah River, and Oak Ridge); leak integrity vs. structural integrity; the potential use of electromagnetic acoustic transducer technology (EMAT) as a rapid screening tool to increase the surface area of the tanks that could be scanned for flaws in a given period of time; and DOE headquarters' interest in tank structural integrity concerns. The concerns about potential structural flaws were basically driven by the early and continuing observations that stress corrosion cracking has occurred in non-stress relieved welds exposed to waste tank solutions and the associated questions about the potential for similar flaw development in the stress relieved tanks.

Extensive discussion of potential concerns for flaw development expanded the areas of concern to include the vapor phase and liquid-air interface regions of the tanks. These discussions concluded that corrosion was not limited to regions exposed to supernate-salt-sludge regions and determined that additional research was needed to understand the mechanisms of vapor phase and water line corrosion. A multi-site team, working together with TFA, agreed to organize a meeting of corrosion subject matter experts in March 2002 to discuss strategies for closing this knowledge gap.

Vapor Space Corrosion Meeting (2002)

Corrosion in the vapor space and at the liquid-air interface of HLW Tanks made of low carbon steel emerged as potential degradation mechanisms during the Multi-Site Structural Integrity Meetings.[6-8] Even though the bulk liquid waste is inhibited, the chemistry of solutions at the water/air interface and within the vapor phase may not be inhibited and corrosion in these areas remains a concern. A workshop sponsored by the TFA was held at the Savannah River Site March 26-27, 2002, to address the potential for such mechanisms to occur. An expert panel consisting of staff from Los Alamos National Laboratory (LANL), Iowa State University (ISU), Savannah River Technology Center (SRTC), and the TFA Technical Advisory Group (TAG) reviewed the operational and corrosion history of the HLW tanks. The participants/presenters included individuals from the Savannah River Site (SRS) and the Hanford Site. Observers included staff from the DNFSB.

The focus of the workshop was on the development of a basic understanding of the important corrosion parameters in context of vapor space and the liquid-air interface at the tank wall corrosion. Each of the participating sites presented a history of their HLW tanks including design, fabrication, operational history and conditions, waste chemistry and corrosion control chemistry, and experience with degradation. The expert panel, participants, and observers discussed the potential for corrosion induced degradation mechanisms within the context of the chemistry and operational conditions presented. The vapor space corrosion programs discussed were largely experimental in nature and focused on three degradation mechanisms: 1) pitting corrosion, 2) general (uniform) corrosion, and 3) stress corrosion cracking. To further advance these areas, the Panel recommended that the program include efforts to: establish the surface chemistry on steels exposed in the vapor space; define tank conditions (ventilation and temperature) that promote condensation; understand how

Table 1. Importance of identified options as seen by experts and site personnel

Option	NDE Experts	Site Experts
Load test	1	3
Measurement criteria specification	3	2
Dome sample analysis	1	1
Rapid global screening test	5	4
Specified problems/solutions	3	2

the evolution of surface chemistry leads to pitting, wall thinning and/or other corrosion process; and, develop surface chemistry controls by altering waste tank chemistries and/or tank operating conditions to mitigate vapor space corrosion.

Workshop on NDE of Concrete in Single-Shell Tanks (2002)

The initial efforts of the expert panels focused on the conditions of the carbon steel in the tank structures. However, discussion of waste transfer and removal processes brought increased attention to the structural integrity of the concrete in the tanks, especially the concrete domes that provide the top cover for the tanks. An initial engineering analysis of single shell tanks, including survey data for the concrete, suggested that the structure is sound for current loads. However, some waste retrieval operations might increase dome loads and issues regarding the possible degradation of steel rebar and resultant impacts on tank structural integrity were identified. Stress corrosion cracks may have penetrated the carbon steel liner and led to corrosion induced degradation of the steel-reinforced concrete outer shell. Hence, there was a desire to examine the possible NDE measurements that might be made to more fully evaluate the load bearing capacity of the concrete. Particularly challenging was the limited access to the tank structures. The domes are covered by seven to eight feet of soil and access to the inner surface is only possible through risers of various diameters ranging from four to forty-two inches. Additionally, not all risers are readily available for access and may require the removal of equipment (e.g., pumps, thermocouple trees, liquid level gauges, etc.) before access can be obtained.

A workshop that focused on this problem was held on September 16, 2002, in Richland, Washington, USA. Experts from Iowa State University, Sonic Sensors, Pacific Northwest National Laboratories, Los Alamos National Laboratory, TFA, CMST, and the National Institute of Standards and Technology familiar with the NDE of concrete were asked to review the particulars of these structures and recommend the most promising NDE approaches.[8] The NDE experts identified five major options/possible actions that could be carried out: perform a dome load test; more clearly specify what must be measured by NDE and against what criteria it should be evaluated; collect a local dome sample and perform materials integrity test; develop a rapid global test for screening; and, attack specific problems/solutions. The meeting attendees could be divided into two subgroups (NDE experts and site experts) and each group was asked to rate the options according to perceived importance. The response of these groups is summarized in Table 1, with 1 indicating the highest priority and 5 indicating the lowest priority. It is noteworthy that both groups evaluated the analysis of a dome sample as the most important path forward.

In evaluating the workshop, site personnel benefited from exposure to the views of experts, while the NDE experts were made aware of the great challenges associated with implementing even well established NDE techniques in an operating nuclear environment. The sentiment was expressed that an important community had been established and that if events demand that increased attention needs to be given to NDE of the concrete, an expert group could be readily reassembled.

Third Multi-Site Structural Integrity Meeting (2002)

The third Multi-Site Structural Integrity Meeting was held December 11-12, 2002, in Ames, Iowa, USA. Attending were representatives of the five major DOE HLW tank sites, the national laboratories, the DNFSB, the DOE Office of Environmental Health, the DOE Office of River Protection, the DOE Savannah River Operations Office, the DOE West Valley Field Office, the DOE Office of Integration, SRNL, LANL, ORNL, INEEL, CMST, and the CNDE.[10] Despite the contributions from TSIP/TFA collaborations, funding for the TFA and TSIP were discontinued when DOE restructured and closed the TFA.

The application of nondestructive evaluation techniques to validate the integrity of waste tanks was the subject of intense discussion at the Iowa meeting. Attendees shared experiences, gained valuable insights from the DNFSB representatives, and discussed the potential application of several emergent NDE technologies to inspecting various portions of the tank walls.

One of the unfortunate results of the demise of the TFA was that a number of sites interested in continuing regular structural and leak integrity interactions was reduced to Hanford and the Savannah River Site. Interactions among these two sites have continued because of the similarities in waste chemistries, waste handling operations, tank configurations, and materials.

Expert Panel Workshop for Hanford Double-Shell Tank Waste Level Increase (2003)

An expert panel workshop was held in Richland, Washington, USA, October 14-16, 2003, to review issues associated with raising the waste levels of the Hanford double-shell tanks (DSTs) above the original design basis and to make recommendations to safely accomplish this new service rating.[11] The scope of the workshop was to provide a thorough assessment of the Hanford DST integrity basis for support of the waste level increase. The expert panel was to provide recommendations for maximum waste fill height, using recommended fill controls and additional testing. The desired outcome of the Workshop was to provide a credible, validated, technical basis for DST waste level maximums, with technical information and justification to support the independent qualified professional engineer (IQRPE) certifications of DST adequacy.

Participants included structural, non-destructive testing, statistical, mechanical, metallurgical, and corrosion experts from Hanford, the Savannah River National Laboratory, Brookhaven National Laboratory, Pacific Northwest National Laboratory, Ames Laboratory, Los Alamos National Laboratory, and several experts from industry. The workshop developed specific recommendations and suggested controls to allow the DST waste height to be raised in selected tank farms.

The expert panel workshop participants recommended a maximum design waste level height of 460 inches with a maximum operating limit of 449 inches (451 inches minus the 2-inch design tolerance), in four double-shell tank farms (two tank farms' waste heights were not changed due to their unique design elements).

Expert Panel Workshop for Hanford Site Double-Shell Tank Waste Chemistry Optimization (2004)

Hanford's waste chemistry controls were established in the 1970s for DSTs, in response to failures in the older, non-stress relieved tanks at SRS. These failures were attributed to nitrate-induced stress-corrosion cracking (SCC) of the carbon steel liner. Due to the limited amount of laboratory work done at that time and the stochastic character of SCC initiation, what appeared to be very conservative chemistry limits were established.

The chemistry control program verifies that the waste remains in compliance with the waste chemistry specification limits established for nitrate, nitrite, and hydroxide concentrations, all of which play important roles in tank corrosion. Periodic sampling and analysis of both the supernate and the sludge provide verification of compliance with waste chemistry controls. When sampling and analysis indicates an actual or imminent deficiency in the concentration of inhibitors (hydroxide and nitrite) relative to the nitrate composition, the inhibitors are added to the supernate to bring the bulk composition to the level required by the waste specifications.

Waste volume projections have shown that maintaining sufficient DST space is one of several factors important to the SST waste retrieval schedule and to the ability to safely optimize DST corrosion chemistry. Additionally, the panel addressed, in two workshops, potential initiatives to increase the flexibility available to operate outside waste chemistry control guidelines. These initiatives were to:

1. Define an acceptable time period during which double-shell tanks can be safely operated outside the established chemistry control limits without risking the integrity or mission life of the primary tank.
2. Identify an approach for reducing or eliminating the number of sludge core samples taken from the double-shell tanks without risking the integrity or mission life of the primary tank.
3. Revise the conservative chemistry control limits based on currently available information with respect to general and localized corrosion and confirm an accelerated stress corrosion cracking experimental program.

The workshops were held in Richland, Washington, USA on April 14-16 and July 13-15, 2004.[12] The first workshop addressed the first two initiatives and the second workshop addressed the third initiative. Both workshops reviewed the assumptions, methodology, and conclusions associated with proposed revisions to the Hanford Site DST corrosion chemistry program.

Participants included metallurgists, materials scientists, electrochemists, chemists, corrosion experts, and chemical and mechanical engineers from academia, industry, the Savannah River National Laboratory, and Brookhaven and Pacific Northwest National Laboratories. The workshop developed specific recommendations and offered additional technical guidance to enhance the conduct of the site chemistry control program.

The panel made recommendations for experimental and analytical programs to address some of the proposed adjustments to the established chemistry control program at the Hanford Site. However, the panel also declined to support other proposed programs.

An additional outcome from the these meetings was the formation, by CH2M Hill, of the Double-Shell Tank Corrosion Monitoring and Testing Expert Panel Oversight Committee (EPOC) to provide ongoing, independent, guidance on the implementation of the panel recommendations and to address other issues as requested. The EPOC consisted of five selected members of the original panel with expertise in materials science, pitting, chemistry, and stress corrosion cracking. In 2011 one of the original members was replaced and in 2012 the EPOC chairman and another member were replaced. Generally, the EPOC met every other week by phone and two face-to-face meetings were held annually. To date, the EPOC has published about thirty letters of evaluation, clarification, direction, and recommendation to the Hanford tank farm operating contractor. External organizations such as the DNFSB, the DOE Office of River Protection, and the Washington State Department of Ecology have expressed high regard for the benefits of the EPOC.

Expert Panel Workshop on Double-Shell Tank Vapor Space Corrosion Testing (2006)

An expert panel workshop was held in Richland, Washington, USA, on July 10-12, 2006, to provide an assessment of Hanford and Savannah River Site vapor space and liquid-air interface corrosion programs and, to develop credible, validated technical bases for corrosion and chemistry monitoring in the waste tanks, and corrosion testing in simulated tank environments.[13]

Panel members included metallurgists, electrochemists, chemists, corrosion engineers, and chemical and mechanical engineers from academia, industry, the Savannah River National

Laboratory, and Pacific Northwest National Laboratories. The core of the panel consisted of members of the EPOC so continuity with other corrosion testing efforts was maintained. Individuals from the Defense Nuclear Facilities Safety Board, Washington State Department of Ecology, U.S. Department of Energy, Office of River Protection, CH2M HILL Hanford Group, Inc., and private industry also participated. The workshop developed specific recommendations and offered additional technical guidance to enhance the conduct of corrosion testing in vapor space and liquid/air interface environments.

The purposes of the expert panel workshop were to provide an assessment of corrosion in the vapor space and at the liquid-air interface in double-shell high-level radioactive liquid waste tanks at the Hanford and Savannah River sites; to assess the practicality and validity of various approaches for corrosion and chemistry monitoring in the waste tanks; to assess the potential need for and possible mitigation strategies for vapor space corrosion; and to develop a test plan to address unresolved issues.

The panel determined that the available information about the chemical compositions of the liquid and solid deposits on the walls and in the ventilation lines was incomplete, but that there was adequate information about the chemical composition of the condensate collected from the 241-AZ-702 tank ventilation system at Hanford to design simulants for corrosion testing. The necessary information was not yet available for simulating the other waste types. Consequently, there was not yet sufficient technical information for a comprehensive evaluation of the propensity for vapor space corrosion, for the design of simulants for corrosion testing, and for the desired determination of the relationship between changes in waste chemistry and corrosion in the vapor space.

Panel recommendations also led to thermodynamic modeling and experimental investigations of the compositions of evaporating solutions of Hanford Site wastes by scientists at Pacific Northwest National Laboratory. The compositional changes that occur during the evaporation of seven different DST simulants, which contained more than ten different chemical substances, were investigated to obtain insight concerning the corrosion propensity of the concentrating solutions that might be formed, for example, by the spattering of waste on a steel wall or the deposition of waste in a crevice on the wall during waste transfer operations. The results of the investigations were then confirmed by waste simulant testing at the Savannah River National Laboratory.

Fourth Multi-site Structural Integrity Meeting (2008)

As a follow-up to previous meetings, a High-level Liquid Waste Tank Integrity Workshop was held in Aiken, South Carolina, USA, May 13-15, 2008.[14] The workshop brought together a diverse group of forty individuals from the Savannah River and Hanford Sites, the DOE Office of Engineering and Technology, the Defense Nuclear Facilities Safety Board, private industry, the national laboratories, and academia. Most of the participants had been involved in previous meetings on the same topics held in early 2000. All formal presentations made at the workshop were webcast in real time, a first for a meeting of this type. More than thirty hits for the webcast were received implying that there was considerable viewing from web participants. The focus of the meeting was to discuss DOE HLW tank integrity technology needs, based on the evolving waste processing and tank closure requirements. Following over a dozen, in-depth, interactive, presentations, related to the structural integrity of the tanks at Hanford and Savannah River, facilitated sessions were conducted utilizing three small groups and full group participation. The workshop was sponsored by the DOE and hosted by the Savannah River National Laboratory in collaboration with the Liquid Waste Organization of the Washington Savannah River Company.

Non-destructive Examination Independent Review (In-service Inspection) (2009)

The High-level Liquid Waste Tank Integrity Workshop, held in Aiken, South Carolina, USA, during May 2008 identified the need for a meeting that focused on non-destructive evaluation (NDE) techniques for application to high-level radioactive liquid waste tanks. The Non-destructive Evaluation Independent Review, held in Atlanta, Georgia, USA, on August 25-27, 2009, responded to that need.[15] All formal presentations made at the workshop were webcast in real time. Numerous hits for the webcast were received and questions were received from online viewers. Representatives from the Savannah River and Hanford sites were joined by participants from the National Laboratories, the DOE Office of Engineering and Technology, the Defense Nuclear Facilities Safety Board (DNFSB), industry and academia to discuss NDE applications to waste storage tank liners and concrete structures as well as the application of statistics to tank NDE. The review panel consisted of industry and academic experts in the fields of NDE and statistics. The organizers established the following three primary goals for the workshop:

- Identify techniques to collect data at a faster rate while maintaining the necessary resolution to make accurate assessments.
- Determine how much tank inspection area is adequate to provide information on the condition of the tank on a qualitative basis.
- Define an evaluation of statistically based, risk-informed, inspection strategies that should be performed to determine their potential application for the waste tanks.
- Fill a gap in technology for effectively surveying the condition of the tank concrete vault.

Based on its deliberations, the panel recommended the following:

Guided Wave Technology

Recommendation 1: Develop and deploy guided wave technology to increase the area of the tank wall from which information can be obtained.

Recommendation 2: Explore opportunities for applying guided wave technology to the tank bottom balanced with risk based barrier confinement.

Concrete Vault Surveillance

Recommendation 3: Develop and implement a comprehensive condition assessment plan that includes structural analysis of the tanks that will indicate critical areas for inspection.

Recommendation 4: Develop mockups of the critical locations with damage and use them to evaluate the capability of NDE techniques when applied *in-situ.*

Recommendation 5: Develop procedures and sampling plans for implementing NDE for condition assessment of the tanks, based on the results of (3) and (4) above.

Sufficiency of Tank Inspection

Recommendation 6: Reformulate the exact technical problem associated with the tank inspection program that will lead to an accurate assessment of tank corrosion rates.

Recommendation 7: Develop a truly random or stratified (e.g., plates or panels) random sampling plan for measuring waste tank corrosion rates and tank life expectancies.

Recommendation 8: Evaluate (SRS and Hanford) the tradeoffs between:

1. the development of new sampling technology that will preserve the intended scope of inference of the entire tank wall surface area within each waste tank, versus
2. the use of current technology under non-statistical assumptions that may adequately address the intended scope of inference on condition that the assumptions apply.

Recommendation 9: Continue the positive collaboration displayed among colleagues at both SRS and Hanford in order to achieve a sampling methodology that provides comparability between sites.

Risk-Informed Inspection

Recommendation 10: Develop a risk-informed approach using all aspects of structural integrity management, such as those captured in the SRS and Hanford Structural Integrity Charts, and not isolated to just NDE concerns.

Additional Observations

Recommendation 11: Create an NDE measurement technique performance assessment program to quantify the expected performance of the techniques employed under field conditions. This should include both assessment of both Probability of Detection and Measurement Uncertainty. The results are needed to quantify the accuracy of data driven, risk-informed, decisions so that the decisions are based on a sound foundation.

These recommendations provided guidance to the Savannah River Site for improving their In-Service Inspections and have been incorporated into their programs.

Hanford Single-Shell Tank Integrity Project Expert Panel (2009 and 2010)

Two expert panel workshops were held on leak and structural integrity of single-shell tanks at Hanford. The goal was to provide recommendations to Washington River Protection Solutions, LLC for implementation of an enhanced single-shell tank integrity project. The panel focused on four key elements for the tank integrity project:

- Confirmation of structural integrity of tanks
- Assessment of the likelihood of future degradation of tank liners
- Identification and prevention of leaks
- Mitigation of subsurface contaminant migration

The workshops were held in Richland, Washington, USA, on January 26-29, 2009, and April 29-May 1, 2009. The expert panel consisted of the EPOC, a member of the original TSIP, a technical representative from the Savannah River Site and the parent company to Hanford Tank Farm Operating Contractor as well as industry experts. Additional participants included representatives from the State of Oregon, the Washington State Department of Ecology, the DNFSB, the Hanford Advisory Board, Tribal Nations, and others. In the first workshop, the panel received presentations outlining the history and current status of Hanford Site's single-shell tank farms and related projects. The second workshop focused on additional clarification of issues and development of panel recommendations.

The panel provided recommendations regarding; (1) confirmation of tank structural integrity (SI), (2) assessment of the likelihood of future tank liner degradation (LD), (3) leak identification and prevention (LIP), and (4) mitigation of contaminant migration (MCM).[16]

Shortly after the release of the panel's first report, the Department of Energy Office of River Protection (DOE-ORP) sent a letter to WRPS requesting additional commentary from the Panel. WRPS, in turn, requested the Panel provide such commentary in four areas outlined in the DOE letter: (1) evaluation of the existing known conditions of the SSTs; (2) evaluation of the proposed future use of the SSTs; (3) recommendations for critical modifications and associated schedule aimed at preventing or minimizing further degradation of SST integrity; and (4) recommendations for additional evaluations and program elements that would improve existing understanding of SST integrity.[17]

The panel participated in a third workshop in January 2010 in which panel members were updated on the ongoing work by WRPS to implement the recommendations of the first report. In response to the inquiry from DOE-ORP, the Panel responded with specific guidance and clarification of prior recommendations.[18]

WRPS prepared an implementation plan to address the panel recommendations in June of 2010 and has been actively following the plan.[19]

Conclusions

The summaries of selected expert panel meetings discussed in the paper illustrate how such panels add value to both managerial and technical programs. Participation in panel discussions requires preparation which generally involves review, discussions, summarizing information and developing a clear message to present to the panel. Even without panel input, the preparation alone adds value to most programs. Further value is added by the interactions with personnel from other organizations which generally expands the knowledge base and increases the expertise being applied to a program. Various panel members may question details of ongoing programs and, as a result of the questions the program may be altered and become more productive. Panel members may suggest emergent science and technologies that were not recognized before the suggestion. Multi-site cooperation generally broadens the resources available for specific programs and "been there, done that" revelations can significantly alter ongoing programs. The panels may make specific technical or managerial recommendations and review, approval and oversight boards generally respond well to expert panel conclusions and recommendations. The programs discussed in this paper are large scale, high value, programs that address unique, billion dollar systems. However, the use of expert panels to improve managerial and technical progress on programs requiring significantly less resources is a valid approach that should be considered whenever programs appear to stall or multi-site cooperation could occur.

After having participated in the formation and selection of numerous expert panels as well as having chaired and facilitated many more over a period of twenty-five years or so, the following observations are also pertinent.

URS Corporation, parent company to the tank farm operating contractors at both Hanford and the Savannah River Site (Washington River Protection Solutions LLC at Hanford and Savannah River Remediation LLC at Savannah River) has benefitted immeasurably by having Expert Panels that have looked both sites of many issues. Although the waste chemistries and management practices are somewhat different at the two sites, they are enough alike so that many decisions made for one site may be applicable to the other. The result is that management of the tanks is facilitated and technical bases are strengthened.

Generally, a panel is only as successful as its least productive member. Great care must be taken when selecting panel members. In order to gain consensus and agreement to accept the issue at hand, all members must be active and timely in their responses.

Panels must have broad representation, but not so broad that they are unmanageable. An expert panel that is too large becomes extremely difficult to manage and too many members make it extremely difficult to come to closure on complex issues. This can greatly prolong the amount of time it takes to produce recommendations or even a meeting summary. Strong but understanding expert panel leadership is crucial to the success of panel performance. Without such guidance, a panel is likely to produce incomplete or ineffective recommendations and advice and the panel may even fall apart completely.

There is a significant investment in bringing a panel up to speed on the complex issues. Consequently, it is of benefit to utilize established panel personnel whenever possible. Keeping a group of experts engaged over a long period of time will strengthen the technical position with regulators, and oversight organizations.

Having technical representation from the one site on another site's expert panels, and vice versa, will strengthen the projects at both sites and is highly encouraged.

A knowledge retention plan should be developed and established. The last member of the original TSIP passed away in 2011. He had also served on numerous other DOE sponsored panels during his career. With his passing, the "boxes of history" he had kept in his office for decades were lost to posterity. The plan should establish a mentoring/training program, a knowledge center for documentation, and a college recruitment program.

When expert panel members are asked to put their professional reputation on the line, they are more likely to do so when their understanding of the technical issues is enhanced by regular meetings and extended involvement. For example, the technical and managerial benefits gleaned from the long-term involvement of the EPOC at the Hanford site have provided millions of dollars in cost avoidance and has been acknowledged to be of significant value-added benefit to the High-Level Liquid Waste Project.

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Taking the Long View in a Time of Great Uncertainty

As the World Turns…Toward a More Dangerous Place

By Jack Jekowski
Industry News Editor and Chair of the Strategic Planning Committee

For almost three years we have explored many issues in this column that impact the nuclear materials management world that we all live in. Occasionally there have been glimmers of hope as a growing international consensus builds toward addressing the long-range threats to nuclear security and safety posed by both state and non-state actors seeking to use nuclear technology and materials for nefarious purposes. We have also seen the world powers rally to support the people of Japan as a result of the Fukushima event, sharing lessons learned and working together to strengthen safety systems to avoid future incidents, despite their rarity. And, we have seen from those lessons learned, an increased focus on the vulnerability of nuclear plants and their spent fuel storage.

However, in the months since our last column, *as the world turns,* there has emerged an ominous and foreboding nuclear threat from three disparate parts of the world: the growing intransigence of Iran to economic pressures to halt its surreptitious uranium enrichment and ballistic missile programs; the increased hostile rhetoric of North Korea's new leader, Kim Jong-un, including threats to use its nuclear weapons against the U.S.; and a re-emergence of non-nation state terrorist groups world wide as the U.S. prepares to withdraw from Afghanistan. With regard to the latter issue, as this column goes to press, law enforcement and counter-terrorism experts are sifting through the debris of the bombings at the Boston Marathon — perhaps a harbinger that this terror method that has been used so often in many other countries over the past decade has now reached the shores of the U.S. It is almost unimaginable to think of how disruptive such an event would be if nuclear materials were used in the explosive device.

So intense has the rhetoric become that many in the literature have turned the conversation to not *if* we will see a nuclear exchange, or nuclear dispersal event in our life time, but *when it will* occur. The ominous question becomes what path will the world take and how prepared will we be if that path is taking us to a more dangerous place. These are vital questions to the Institute because so many of our members and affiliated organizations provide the technical expertise as well as policy guidance to assist in the preparation for such a dangerous future.

The Glimmers of Hope

There are glimmers of hope, but they require a long-range, optimistic vision of the future. This path has been facilitated by President Obama's leadership in convening International Nuclear Security Summits,[1] and in his continued pursuit of the goals set forth in the now-historic Prague speech of April 5, 2009.[2] These goals are built upon the optimistic vision that mankind understands the importance of working together to improve the security, safety and quality of life of all citizens, as stated in the 2010 U.S. National Security Strategy:[3]

> *"…we must focus American engagement on strengthening international institutions and galvanizing the collective action that can serve common interests such as combating violent extremism; stopping the spread of nuclear weapons and securing nuclear materials; achieving balanced and sustainable economic growth; and forging cooperative solutions to the threat of climate change, armed conflict, and pandemic disease…The international order we seek is one that can resolve the challenges of our times…"*

Much continues to be written in the literature of the goals set by President Obama in 2009, and what, if any accomplishments have been made since then. However, with his reelection to a second term, and a new national security team in place[4] Obama appears to be poised to continue driving this policy initiative forward.

At the same time, the "Four Statesmen" (George Schultz, William Perry, Henry Kissinger, and Sam Nunn) have also recently collaborated on a new *Wall Street Journal* editorial (the fourth in a series since 2007) titled "Next Steps in Reducing Nuclear Risks,"[5] that continues to raise this issue in an international forum.

Internationally, the focus of a more secure nuclear future has been promoted by the United Nations' International Atomic Energy Agency (IAEA),[6] as well as other organizations such as the Nuclear Threat Initiative,[7] the Arms Control Association,[8] the Federation of American Scientists,[9] and the Global Zero Initiative.[10]

Moving to a More Dangerous Place

But amid all of these positive steps, as this column goes to print, there are dark clouds forming as indicated by some of the headlines from newspapers in the U.S.:

> *"North Korea Tests Nuke, Defies Warnings from West"*
>
> *"New U.N. Sanctions Hit North Korea After Nuke Test"*
>
> *"North Korea Threatens Guam, Hawaii, Rest of U.S."*
>
> *"Report: North Korea Likely Can Put Nuke on Missile"*
>
> *"Iran, IAEA Remain Deadlocked on Nuclear Probe"*
>
> *"Iran Warns Terrorism Coming to Washington"*

Under the current administration, we have seen an increased emphasis to resolve these situations through international diplomacy and collaboration. From President Obama's 2010 National Security Strategy, we have seen the use of diplomacy elevated in its status:

> *"We must build and integrate the capabilities that can advance our interests, and the interests we share with other countries and peoples. Our Armed Forces will always be a cornerstone of our security, but they must be complemented. Our security also depends upon diplomats who can act in every corner of the world, from grand capitals to dangerous outposts; development experts who can strengthen governance and support human dignity; and intelligence and law enforcement that can unravel plots, strengthen justice systems, and work seamlessly with other countries….Diplomacy is as fundamental to our national security as our defense capability. Our diplomats are the first line of engagement, listening to our partners, learning from them, building respect for one another, and seeking common ground."*

Thus we have seen an extraordinary effort by this administration to use the diplomatic route first toward solving these seemingly intractable problems. With the new national security team, we have a renewed vigor in this pursuit, but one wonders with the growing disconnects, at what point even they will throw up their hands.

Such is the dichotomy of our times.

Divergent Paths to the Future

In previous columns[11] I have mentioned that scenario planning provides a tool to look at very different future worlds, driven by critical uncertainties. Scenario planning, in fact, is a method by which organizations can prepare for uncertain futures by rehearsing those futures, speculating on the events that might lead to them, and identifying strategies that may either change those paths (if it is undesirable) or, at least, better prepare the organization to survive and thrive in those futures. In the headlines we see at least two very different futures ahead for the world and things nuclear…one full of optimism and one that is more dark and dangerous. One of the critical uncertainties we are dealing with is how strong the resolve of nations will be to stem the tide of improper use of nuclear technology, and another is how successful our scientists, engineers and policy makers will be in creating a safe and secure environment for the peaceful uses of nuclear energy. The creation of scenarios in such an uncertain environment is a nontrivial exercise that will be explored in more detail in future *Taking the Long View* columns.

The Role of INMM

As an international organization, the INMM is poised to help the world meet the challenges of the new millennium. Recent efforts led by the Executive Committee have identified more than fifty organizations, many of them international in their reach, with similar missions and objectives to the Institute. Some of these have well-established formal relationships with the INMM: American National Standards Institute — ANSI; European Safeguards Research and Development Association— ESARDA; the Nuclear Infrastructure Council — NIC; the Nuclear Material Control Center — NMCC; and the World Institute for Nuclear Security — WINS). Other organizations identified have existing working relationships with the Institute, but we may not have fully exercised the collaborative potential. As the EC and the Institute work to broaden our reach to these organizations, we may find our role grow significantly in solving the dichotomy that the world faces today.

The challenges faced by our membership can at times be overwhelming. It is important that in the midst of all of this, we also keep in mind the historically successful role the Institute has had in bringing the global nuclear community together to ensure the knowledge and skills needed to address these national and global issues are available, and can be passed on to the next generation. Each member should work as diligently as possible within their sphere of influence to continue this legacy.

We encourage JNMM *readers to actively participate in these strategic discussions, and to provide your thoughts and ideas to the Institute's leadership. With your feedback we hope to explore these and other issues in future columns, addressing the critical uncertainties that lie ahead for the world and the possible paths to the future based on those uncertainties. Jack Jekowski can be contacted at jpjekowski@aol.com.*

End Notes

1. See http://www.state.gov/t/index.htm for general information on the Under Secretary for Arms Control and International Security and http://www.state.gov/t/isn/nuclearsecuritysummit/ for direct links to each of the two previous Nuclear Security Summits in 2010 and 2012.
2. See http://www.whitehouse.gov/the_press_office/Remarks-By-President-Barack-Obama-In-Prague-As-Delivered.
3. See http://www.whitehouse.gov/sites/default/files/rss_viewer/national_security_strategy.pdf.
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- Numbered references in the following format:
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  112–118. 2. Jones, F.T. 1976. ***Title of Book***, New York: McMillan Publishing.
- Author(s) biography

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Book Review

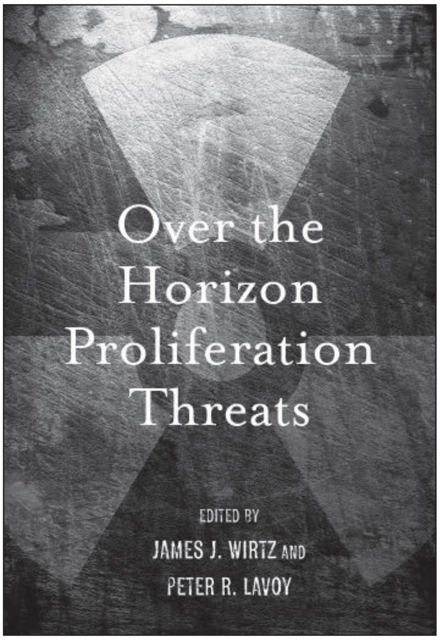
By Mark L. Maiello
Assistant Book Editor

Over the Horizon Proliferation Threats
2012, 316 pages, soft cover, $29.95
James J. Wirtz and Peter R. Lavoy
Stanford University Press, Stanford, CA
ISBN 978-0-8047-7401-7

By Mark L. Maiello, Ph.D.
Associate Book Review Editor

This intriguing volume peers into the near future (the world of 2020 to be exact) and attempts to assess the state of nuclear and biological weapons proliferation at that time. The assessments are done in some cases regionally and in other cases nation by nation. What maybe surprising to some readers and that were certainly enlightening to this reviewer were the nations and regions analyzed. Burma, Japan, Taiwan, the Middle East, Southeast Asia, and Ukraine among others are considered in Part 1 of the book. Notably and deliberately left out were the near-term issues regarding North Vietnam and Iran though these are considered in the context of their regional neighbors that were covered.

Each chapter is a thoughtful, reasoned analysis of the motivations and concerns that could restrain or propagate proliferation. The editors called upon fifteen experts to accomplish this including overseas specialists for first-hand assessments of South Africa, Japan, and Taiwan. These contributors may not be household names (many readers of this journal will recognize Etel Solingen of the University of California), but each is an accomplished authority who contributed an extremely readable, highly accessible account. Indeed, one of the hidden assets of this book is how well-written it is — no mean editorial accomplishment considering that it is an ensemble effort. Another feature contributing to the book's readability is the comfortable length of each chapter. In most cases this is an efficient twenty pages or less including notes (references). Each of the fifteen chapters is also graced by a conclusion or "final thoughts" that ties the bow on the preceding analysis. The book is supported by a nine-page index.



Although it has been said many times that predictions of the future are rarely accurate, one feels very comfortable that the short, seven-year horizon of this book and the expertise of its authors and editors provides a solid basis for the considerations made therein. If fact, the contributors do not for the most part predict. They reflect and analyze. They are reasoned about their assessments.

Why investigate these regions and the nations therein? The consideration of the nuclear option always provides data for policy makers — the reasons for choosing or not choosing to go nuclear — that can later be considered in future policy-making or future decision-making if a nuclear crisis develops. Another more obvious reason is that these regions and nations are not normally considered as proliferation candidates. Argentina and Saudi Arabia, Burma and Brazil, Vietnam and Venezuela, all have a nuclear infrastructure of some sort and have considered furthering the technology. The book considers what these respective governments discuss when they consider advancing the field. These include traditional concerns of domestic security, the financial costs of going nuclear, the political nature of the particular nations, and existing security agreements, among many factors. What this book does so well is to elucidate these issues in terms that novices to the field can easily understand. It also highlights a little known or overlooked aspect of national debates about the nuclear option: that there are *always* factions in these nations that consider it viable and when circumstances permit can succeed at floating it and perhaps succeed at making it a national policy.

In Part 2, proposals to foster nonproliferation are proffered. These include "finding the silver lining" in proliferation shocks such as an Nonproliferation Treaty (NPT) withdrawal by a state party, the theft of a nuclear weapon, or the detonation of a radiological dispersal device. The disruption so produced can be leveraged into motivating policy makers and politicians to bolster nonproliferation norms. Another chapter examines the effects of security assurances — the agreements of varying formality made regionally or between two nations where one promises to protect another with nuclear weapons if so threatened or attacked (a positive assurance) or where one promises not to attack another with nuclear weapons (a negative assurance) and includes a lucid discussion of the advantages and drawbacks of each. Another chapter neatly covers the contributions of intelligence gathering and interdiction to nonproliferation efforts. Ironically, the most enlightening chapter in this section is that covering chemical and biological weapons (CBW) proliferation written by Michael Moodie, assistant director of foreign affairs, defense and trade at the Congressional Research Service (in what is probably an oversight, Moodie's biography is not included in the book). Moodie's overarching message is that unlike nuclear technology, which when proliferated follows a well-known, nationally-backed, more or less straight line path from enrichment to weapons, CBW proliferation is embedded in the academic and commercial world of scientific research. The knowledge, information, and technology to alter genes and create toxins or infectious diseases can and often does reside at the bench-top of common laboratories — many located in nations that do not share the security concerns of the United States. The commercial world represents a very interesting case. Here, globalization of corporations can put such bench-top knowledge anywhere on the planet. Firms that do not succeed can in fact sell their knowledge to the highest bidder whether scrupulous or not, in order to escape financial loss and bankruptcy. The means to regulate or to monitor the efforts of this research are difficult enough without considering that the basic knowledge of genetic research is so commonly accessible and more importantly, so quickly changing. Obviously, it does not lend itself to conventional means of nonproliferation oversight. Moodie offers several means to build a credible defense including acknowledging that governments cannot do the job alone. It is necessary to bring together representatives from industry, the military, public health, and academia among others to exchange information. Individual governments should conference with life scientists to create accepted norms prohibiting chemical and biological weapons development. Ultimately he advocates a *networked* approach to security but admits that currently does not exist and provides little detail as to what its nature might be. Though these approaches to security are somewhat divorced from the more linear and traditional nuclear non-proliferation efforts, chemical and biological weapons production can be a counterweight to a nuclear weapons threat and thus are related. Syria's production of chemical and perhaps biological warfare agents is such a response to the undeclared nuclear capability of Israel.

Another chapter of interest (all are worthy of mention) is that by Bruno Tertrais on the future of security assurances. He nicely reviews the history of these little-known legal entities and analyzes their effectiveness. It's an interesting tour that explains why France took an independent road to nuclear technology and why North Korea has chosen the path it has. The role these assurances now play and how they can both help and hinder nonproliferation policy is discussed. Tertrais illustrates how positive and negative assurances can work at cross purposes potentially negating their original intended results.

Etel Solingen provides an insightful essay stressing that analyses of proliferation based solely on regional "balance-of-power" considerations are not as helpful as one might imagine. Instead, one must consider the viewpoint of the nation in question to the global economy. Does it embrace it or eschew involvement in it? Another consideration is the "political survival" mode of the ruling government. Is it democratically or autocratically based? Using Argentina, Brazil, and Venezuela as examples, Solingen suggests that democracies involved in the world economy are less likely to develop nuclear weapons programs. They build regime-legitimacy through sustained economic growth rather than by appealing to inward looking constituencies that value military build-up.

The last chapter of the book is a synopsis of the entire work. Though somewhat pedestrian in its approach (it's not easy to write an exciting summation), it was a welcome addition for its restatement of salient points that may have been overlooked by the reader — especially one who has never encountered this material before. Admittedly, the content of this book can be considered complicated subject material. But it cannot be stressed enough that each contributor performed an excellent service by keeping the chapters understandable. There are few if any sections in this work that, from a clarity perspective could stand to be improved. If the editors had a hand in this result, they are to be commended.

There is a certain understated value to treatments such as this book, which survey the broad landscape of nonproliferation issues, albeit in this case with a particular focus. Not only do such books provide the reader with a clear mountain-top view from which he or she can become conversant in the subject matter, but it also provides other information that broadens the perspective of those working in nonproliferation who are interested not only in measurements, accountability, forensics and interdiction but in the associated policy-making issues that drive the science. In this one volume for instance, one finds perspectives from the counter-intelligence, political science, and international arenas. The authors have, intentionally or not, provided nonproliferation scientists and their colleagues with a healthy dose of motivation to continue their efforts. This book teaches us that nonproliferation remains a dynamic arena that relies on many perspectives to explain. It is highly recommended for its forward thinking, its well-edited format, its highly comprehensible expert contributions, and for the incentive it gives practitioners of nuclear-accountability and policy-making. The uncertain future is a bit more certain because of it.

Mark L. Maiello, Ph.D., is a contributing editor at Health Physics News. *His publications include papers and editorials about the security of Cs-137 irradiators and pre-catastrophe planning for sheltering-in-place. He also serves as a peer reviewer for the journal* Radiation Protection Dosimetry. *He currently is employed as a health physicist.*

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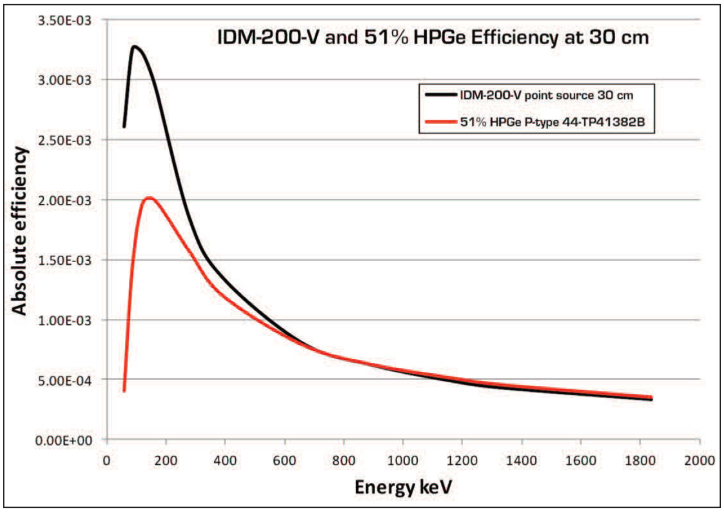

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