

Radwaste Equipment Corrosion Associated with Exposure To Chemical Cleaning Solution

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Abstract

As chemical cleaning of nuclear plant systems has become more common, instances of loss of containment of the chemical cleaning solution have been reported. Such losses, while relatively infrequent, usually lead to waste processing difficulties.

Most losses of chemical cleaning solution have resulted in the need for special processing measures, and the generation of increased waste volumes. In cases of large-volume or high-concentration leaks, efforts are made to isolate the spilled solution and process it separately with ion exchange media. These efforts result in reduced decontamination factors (DF) and marked increases in resin waste.

This paper includes descriptions of chemical cleaning spills at several power plants. In one key incident, introduction of the cleaning solution to the liquid radwaste (LRW) stream resulted in severe corrosion to the mobile radwaste equipment used to process that stream. Discussion of this incident includes the circumstances that led to the equipment corrosion damage, as well as the special chemical and environmental conditions that precipitated it.

This information is topical and valuable to plants as they conduct project and contingency planning for chemical cleaning campaigns, and formulate response plans for processing spills or and leaks of chemical solutions.

Background

Chemical cleaning of nuclear plant systems has become a common practice for reducing dose, extending equipment life, and improving heat transfer performance of heat exchangers and steam generators. The purpose of this cleaning is to remove corrosion products and the passivated layer on piping and components.

Chemical Cleaning Processes

The vendors supplying chemical cleaning processes have developed proprietary formulations for decon of reactor coolant systems and chemical cleaning of secondary systems in PWR's, as well as specialized equipment to apply and remove the solutions. The formulations fall into two general categories: EDTA-based and citric acid-based solutions.

Despite continual tweaking of formulation and application, EDTA-based decontamination is a well-established process. EDTA is an aggressive chelate that is very effective for removing and sequestering metals. While other chemicals are used to enhance metal removal or transport, or reestablishment of the passivated layer, EDTA remains the key constituent.

Citric acid, applied in the Citrox process, is a simple, less-aggressive decontamination solution that capitalizes on the sequestering capabilities of citric acid. Various chemicals and application methods are used to enhance the process.

Process Control and Containment

While all of the vendors have proofed their products to a high degree of reliability, Chemical Cleaning remains a complex process that holds many opportunities for mechanical, electrical and human failures that can result in leaks or spills of cleaning solution.

The reasons for such losses of containment range from equipment failures to lack of procedural control and compliance. Though there is no accessible, comprehensive database of the size and frequency of losses of containment, the losses that we know about have ranged from a few liters to a few thousand gallons of liquid (tens of cubic meters), and from dilute flushing solution to concentrated chemical cleaning solution.

Chemical cleaning solution on floors or in local, isolated sumps is fairly easy to clean up. But this is not the case when the solution migrates through the plant drain and sump system to the LRW system, where it is distributed through multiple hold-up tanks and commingled with tens of thousand of gallons (25-50 cubic meters) of water from other sources.

Loss of Containment Events

In this paper, we examine four cases where loss of decontamination containment resulted in the need to clean up wastewater. Understanding the circumstances and difficulties encountered at these four sites can help other plants to formulate project and contingency plans to deal with such losses in their own decon efforts.

Plant A: Diablo Canyon

In 2004, Diablo Canyon successfully completed its Unit 1 Steam Generator Cleanup Campaign (SGCC) without incident. However, during the Unit 2 SGCC, chemical cleaning solution got past a sample isolation valve and entered a LRW collection tank.

The leak was limited to 20 gallons (75 liter), which entered into a radwaste tank that was partially filled to about 5,000 gallons (18.9 m³). It was believed that the EDTA had fully reacted in the path to the radwaste collection tank. The conductivity of the isolated solution was checked and found to be approximately 150 umhos/cc (150 uS/cc). Based on this result and the small quantity of the leak, in-plant treatment was chosen in lieu of off-site thermal processing. Nonetheless, it was acknowledged that if just two demin beds had to be discarded, the cost would be equal to off-site processing, excluding labor for sluicing out and reloading the beds.

As a result of processing this water for release, all four 30-cubic foot beds (0.85 m³) (carbon, zeolite, cation and anion) in the LRW system had to be disposed of. A second anion bed was also fouled. The liner containing media from all five beds was shipped to Envirocare in December 2005.

Because the four beds had already been in service, some of their useful life was probably expended before they were used for chemical solution cleanup. But even taking this into consideration, Diablo Canyon estimates that cleanup of the 20 gallons (75 liter) of chemical cleaning solution resulted in a net increase of 135 cubic feet (3.8 m³) of media waste volume.

The lesson learned was that isolation and off-site treatment of the initial 5,000 gallons (18.9 m³) of cleaning solution and contaminated wastewater would have cost less than in-plant processing of the water. Significantly more media was consumed to clean up the 20 gallons (75 liters) of cleaning solution than calculations indicated would be necessary.

Plant B: Wolf Creek

In April 2005, during Refuel 14, Wolf Creek Generating Station took action to mitigate the impact of the entrance of approximately 2,800 gallons (10.6 m³) of Steam Generator Cleaning Solution into liquid waste, after failure of an aluminum bulkhead weld associated with the chemical handling equipment. The chemical cleaning solution, which was collected in the containment area drains, contained 1% ethylene diamine tetra-acetic acid (EDTA) concentration. The local sump automatically transferred this solution to the on-line Floor Drain Tank (FDT) B. The containment sump was later flushed to reduce the concentration of any residual chemicals within the system.

In assessing the potential consequences on downstream components and processes in the LRW system, two expert evaluations were requested. The first evaluation looked at the impact/effect of the chemical solution on downstream piping, valve packing and gasket materials. The second provided information about the possible formation of ferric chloride and the potential impact/effect on materials exposed to this solution. It also provided insight to the potential impact on the radioisotope removal efficiency of the LRW process system, when processing these waters.

The two evaluations differed in their assessment of potential for harm to process equipment, as well as impact on LRW processing. Wolf Creek elected to base its remedial action on the second, and more conservative, evaluation, which painted a picture of greater potential harm and impact.

The plant's original contingency plan for a potential leak involved collecting an estimated 300-gallon (1.14 m³) volume from the local sump and placing it into 55-gallon (208 liter) drums for additional processing. When the volume and location of this leak rendered that plan impractical, several options for removing the solution from the FDT's were considered. Key to these mitigation steps were actions to reduce EDTA concentrations to a less detrimental level of <50 ppm, and reducing the Fe concentrations to low ppm ranges, to minimize potential corrosion of these components.

Waste Stream Analysis. Analysis of Both FDT's indicated greater than 2000us/cm conductivity and a pH average of 5.5. The initial solution entered the system with 160 ppm Fe and 10,000 ppm EDTA, or 1%. A total volume of 12,000 gallons (45.4 m³), including the chemical cleaning solution, was contained in the FDT's. This volume was isolated, and efforts were undertaken to minimize additional influents to maintain volumes that would require special processing as ALARA.

Process Method. The method selected was considered the quickest and most effective for removing the EDTA and Fe from the collected liquids. A polyethylene High Integrity Container (HIC), typically used for shipping radioactive materials, was loaded with 75 cubic feet (2.1 m³) of new mixed bed resin, and placed into the process shield near the High Level Waste Storage Area. A temporary procedure provided instructions for recirculating the selected FDT through the resin, while decanting to a local sump, and a Temporary Modification was implemented for configuration control of the selected flow-path and sampling connections at the vessel outlet. To complete a recirculation flow path, the sump was aligned to the process tank.

During recirc of each FDT through the resin bed, interval sampling was conducted to monitor the performance and condition of the bed. After three tank volumes were recirculated through the bed, the FDT A Fe concentrations in the 2,800 gallons (10.6 m³) were reduced to <6.5ppm from the initial 160ppm. The tank was allowed to rest for 4-hours and again at 8-hours between samplings to ensure that the EDTA did not transport additional iron from the tank sediment. Iron concentrations remained stable through the rest period.

FDT B was then recirculated through the same bed used to treat FDT A with effluent samples drawn each hour. After 4-hours of recirculation of FDT B, containing 9,000 gallons (34.1 m³), the bed was removed from service on the criteria of increasing effluent conductivity and Fe concentrations. The initial HIC was transferred to storage and a new liner and 70 cubic feet (2.0 m³) of mixed bed resin was placed in service. Recirc of FDT B was restarted and the tank volume turned over approximately three times. The FDT B analysis indicated that Fe was reduced to 1.1 ppm, and the EDTA was reduced to <7 ppm from the initial 10,000 ppm.

To flush the plant systems, several hundred gallons (1-2 m³) from the cleaned up FDT A were directed to the DRW Sump that had received the original batch of chemical cleaning solution.

This water was sent back to FDT A, and then 400-500 gallons (1.5-1.9 m³) from the WHUT was routed to the DRW sump for additional dilution and flushing back to FDT A. Finally, FDT was recircled through the temporary HIC demineralizer to removal the final EDTA vestiges, in preparation for processing through the LRW process system.

Diversified Technologies' evaluation suggested reduction the EDTA concentration to 10 to 50 ppm prior to processing through the ZERO™ Liquid Waste Processing System. Each tank was well below those values, and was successfully processed, with the permeate subsequently released. The FDT's were later recircled through the temporary demin to make efficient use of the remaining unexhausted resin capacity in the temporary demin.

Summary. This cleanup effort was successful, but the reduction of EDTA and Fe from Wolf Creek's liquid waste stream required extensive resources to support the procedure development, resin handling, Temporary Modification, chemical analysis, liner and fill head installation, and process oversight. This effort competed with other crucial outage evolutions for plant manpower and resources. During the following year, no indication of any corrosive damage to plant or vendor LRW process equipment has been observed. It is impossible to know whether damage would have occurred had these steps not been taken, but this conservative course proved effective and prudent.

Plant C

In the early 1990's, Plant C undertook an SGCC. The project plan called for the chemical cleaning solution to be accumulated, processed and solidified in a new on-site radwaste facility.

When treatment of the cleaning solution was plagued by operating and chemistry problems, the solution was sent to an isolable waste tank to be stored until a new treatment plan could be developed. Two to three years later, when the solution was removed from the tank, it was discovered that there was widespread corrosion in the tank, piping and components associated with storage of the solution. Ultimately, the tank and much of the piping had to be replaced.

No investigation was made to determine the exact corrosion mechanism. Because no pH or other analytical samples were taken, it is impossible to establish whether a low pH condition existed that would support ferric chloride formation (since iron would certainly be present). A source of chlorides is less certain, but since this is a brackish water plant, and the SGCC solution was treated in the LRW system, it is reasonable to expect chloride contamination.

Plant D

Plant D undertook an SGCC for dose rate reduction of system piping and components, to extend steam generator life until a change-out could be conducted. The decon vendor mobilized equipment, including a process system to concentrate the cleaning solution in preparation for off-site processing.

Processing Difficulties. Routine plant LRW processing proceeded normally until late in the campaign, when DFs for isotopic removal fell from 20-100 to 1-2, and throughputs fell from 25,000 to 50,000 gallons per cubic foot (25 to 50 m³ per liter) of ion exchange media to <500 gallons (1.9 m³). In one instance, throughput dropped to <100 gallons (0.38 m³) per cubic foot of media, as measured by isotopic breakthrough. Previously, the process train of ultrafiltration

(UF), carbon, selective exchangers and organic resins, which had a history of effective cobalt removal; became ineffective within a few days.

Many methods of addressing the problem were tested, including pH adjustment (high and low), precipitation, flocculation, various media (both common and uncommon to LRW processing), as well as oxidation with hypochlorite. Ultimately, the decision was made to mobilize a Reverse Osmosis (RO) unit in an attempt to make releasable water in the $1.0E-5$ uCi/ml range -- a full decade and half better than could be achieved with any other configuration or combination.

The RO unit positioned downstream of the UF unit consistently produced MDA or near-MDA water in a single pass, which permitted the backlog of water to be reduced to a manageable level. The reject was accumulated in an isolated tank; since return of this reject to the plant would be recontaminate the water inventory with the cleaning solution agents.

During this processing campaign, hypochlorite was used aggressively in an attempt to destroy the high level of TOC present. The LRW was also noted to be higher in conductivity than usual, though this was thought to stem from incursions of brackish water.

Equipment Damage. After two to three weeks of successful LRW processing, a pinhole leak was noted in one of the UF pressure vessels. This was unusual, in that no such leak had been observed in the previous two and half years of UF operation. While the first pinhole leak was being repaired, a second was noted, then a third and a fourth over the next two to three weeks. All these pinhole areas were temporarily repaired, as it was important to maintain process capability for plant water management.

In the fifth week of processing, a pinhole leak was observed in the pressure vessel in the RO unit. This was highly unusual, because this unit was new, and the membrane pressure vessels were heavy-walled stainless vessels rated for 900 psi. These leaks too were patched, but more developed over the next few weeks on both the UF and RO systems.

The pinholes observed were in both the heat-affected zone (HAZ) and the field metal. It is fairly common for pinhole corrosion to occur in LRW systems over many years (sometimes decades), but highly unusual for it to develop in a few weeks in new stainless steel piping and pressure vessels.

Investigation. During investigation of the cause of the leaks, technicians operating the LRW system noted a distinctive odor coming from the concentrate. One of technicians, who had smelled the same odor while performing supervisory duties at Plant C in 1992, identified it as EDTA-containing chemical cleaning solution. Further, the LRW had a TOC concentration and conductivity higher than a brackish water intrusion, seeming to rule out such an intrusion as a source of the problem LRW water.

Independently, a plant operator informed the vendor technician that water from a flushing or drain-down of the SG had been directed to the drain system, instead of being drummed and processed off-site. The chemical cleaning plan had called for 1,000 to 1,500 gallons (3.8 to 5.7 m³) of cleaning solution to be drained from system low points, drummed and moved to the

vendor's equipment for processing. However, this sequence of events could not be independently confirmed and it was not determined with certainty if this activity occurred, or what quantity or concentration of the solution might have gone to the drain instead.

It is important to note that representatives of Plant C and its parent Utility firmly maintain that no chemical cleaning solution or flush water was directed to the drain, as this would be against operating procedure, and contrary to project plan. Nonetheless, given: 1) the abrupt change in water chemistry, 2) the degradation of processing capability for water cleanup, 3) the odor and color of the LRW water, 4) the acute corrosion damage to new stainless equipment, and 5) the unsolicited comment by a plant operator regarding introduction of chemical cleaning solution to the floor drains, it seems likely that SGC solution may well have been the source of the corrosive water.

Theory Development. Though EDTA seems a credible cause of the problem water from a processing perspective, the question remained as to how this substance could have initiated such aggressive corrosion. EDTA itself would not be expected to be particularly aggressive, and brackish water (if an incursion did occur) had been processed before without impact. The vendor equipment used for SGC solution processing is partially constructed of stainless steel yet has processed tens of thousands of gallons of decon solution without apparent damage.

Based on extensive literature search and consultation with a corrosion expert, ferric chloride appears to be a prime candidate. This substance is known to be very aggressive to stainless steel, and its two key components -- iron and chlorides -- were present in abundance. Small concentrations of iron are likely always present in LRW, but the SGC process mobilizes hundreds of pounds of iron. Brackish water intrusion or hypochlorite used for TOC destruction was a ready source of chlorides.

The missing factor is low pH. A pH of 2.0 or lower is ideal for formation of ferric chloride, and sample logs from the waste hold-up tanks indicated the LRW was typically in the 6.0 - 6.5 pH range. At this higher pH, little or no ferric chloride formation would be expected. Though acidic pH adjustment had been bench-tested to see if it would aid in processing with UF and demineralization, it was not used during full-scale processing.

The Missing Puzzle Piece. Faced with strong circumstantial evidence, the search for the last key item began. After hundreds of documents were reviewed, a single log page seemed to hold the answer. In a plant operating log, an entry was made regarding a sample of LRW processing water with a pH of 1.0. The entry gave no indication of how long this condition had existed, nor the source or cause. Though the log stated that it was to be investigated, there was no follow-up posting to indicate what, if any, action was taken. Only a step-by-step examination of the processing logic revealed the chain of events that likely created the low pH environment and permitted the formation of ferric chloride.

As mentioned previously, hypochlorite was used to destroy TOCs via oxidation. The oxidation of organics liberates carbon dioxide which reacts with water to form carbonic acid. It is well established that carbonic acid has the ability to drive the pH down to the values observed.

The radwaste processing vendor had years of experience using hypochlorite for this purpose without damage to equipment or any remarkable pH shift. The difference here was that, unlike the typical instance where the organics being destroyed are in a range of a few ppm, the TOCs were known to be very high (though the absolute number was not determined); at several hundred ppm, they would have liberated enough H⁺ ions to sharply lower pH values. When water is processed by demineralization, pH data is monitored carefully, as it is a key indicator of resin condition. However, in this case, since the LRW vendor was processing with UF and RO, pH data was not routinely logged and analyzed. Therefore, these lower pH values were not noted.

With all these circumstances considered, it seems clear that a low pH value could have, and did, exist. While this could have been confirmed through analysis of samples from the waste hold-up tanks, and while samples from several of these tanks had been taken to be sent to an off-site laboratory, unfortunately, the samples were discarded after the problem waters had been sampled and released.

An Alternate Theory. Plant C suggested that SGC solution could not have entered the LRW system, and theorizes instead that the corrosion damage was caused by use of hypochlorite, which is known to be mildly corrosive to stainless. This theory lacks basis, for several reasons.

First, vendor had an extensive history of using hypochlorite in similar applications without corrosion.

Second, both the UF and RO suffered similar corrosion damage. The UF was exposed to the hypochlorite as the hypochlorite was injected directly into the feed stream circulating through the UF. But just downstream of the UF and in front of the RO, a carbon bed was situated to destroy hypochlorite. Effluent from this bed was routinely sampled to ensure that no hypochlorite was present, as even a few ppm of it would, within hours, oxidize and destroy the RO membranes. The membranes were never damaged during this processing, and (based on sampling), it is conclusive that the RO was never exposed to hypochlorite. Nonetheless, the RO pressure vessels suffered the same corrosion damage as the UF.

Finally, the residual chloride from decomposition of the upstream hypochlorite was not a credible agent, as chlorides from brackish water incursions had been processed the preceding 12 years without notable corrosion damage.

The Moral of the Story. Both circumstantial and direct evidence fully support the theory that, in the presence of chlorides, iron, and low pH; ferric chloride formation resulted in corrosive damage to stainless steel piping and pressure vessels in the process equipment. This conclusion is further buttressed by lack of any credible alternative hypothesis.

Lessons Learned

The history and experience of these four plants suggest that in the event of a SGC solution spill, the first step for contingency planning is to aggressively isolate the spill as close to the source and in as small a volume as possible, for assessment and treatment.

If the spill has migrated to the drain, sump and general radwaste system, demineralization can be effective, but a significant volume of resin may be expended in the cleanup effort, and the expended resin will likely require incineration to meet the burial site criteria for chelates. RO has been consistently effective in producing near-MDA, or better, effluent water. However, since both iron and chlorides may be present, pH should be scrupulously monitored and controlled, both inter- and intra- system, and not be allowed to drop below a range of 4.0 – 5.0. Maintenance of a pH above this level will provide a protective buffer against ferric chloride formation, and the potential for aggressive corrosion damage to process equipment.

The general caution against allowing a chloride, iron and low pH environment to exist may be applicable to other water processing scenarios beyond those that exist during a chemical decon or chemical cleaning solution spills. Planning and prevention can effectively prevent, or mitigate these conditions and protect plant systems and components.