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**Administrative and Engineering Controls for the Operation of Ventilation Systems for  
Underground Radioactive Waste Storage Tanks – 14197**

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**ABSTRACT**

Liquid radioactive wastes from the Savannah River Site are stored in large underground carbon steel tanks. The majority of the waste is confined in double shell tanks, which have a primary shell, where the waste is stored, and a secondary shell, which creates an annular region between the two shells, that provides secondary containment and leak detection capabilities should leakage from the primary shell occur. Each of the DST is equipped with a purge ventilation system for the interior of the primary shell and annulus ventilation system for the secondary containment. Administrative flammability controls require continuous ventilation to remove hydrogen gas and other vapors from the waste tanks while preventing the release of radionuclides to the atmosphere. Should a leak from the primary to the annulus occur, the annulus ventilation would also serve this purpose. The functionality of the annulus ventilation is necessary to preserve the structural integrity of the primary shell and the secondary. An administrative corrosion control program is in place to ensure integrity of the tank.

Given the critical functions of the purge and annulus ventilation systems, engineering controls are also necessary to ensure that the systems remain robust. The system consists of components that are constructed of metal (e.g., steel, stainless steel, aluminum, copper, etc.) and/or polymeric (polypropylene, polyethylene, silicone, polyurethane, etc.) materials. The performance of these materials in anticipated service environments (e.g., normal waste storage, waste removal, etc.) was evaluated. The most aggressive vapor space environment occurs during chemical cleaning of the residual heels by utilizing oxalic acid. The presence of NO<sub>x</sub> and mercury in the vapors generated from the process could potentially accelerate the degradation of aluminum, carbon steel, and copper. Once identified, the most susceptible materials were either replaced and/or plans for discontinuing operations are executed.

**INTRODUCTION**

Liquid, radioactive wastes at the Savannah River Site (SRS) are stored in large, underground, carbon steel tanks. The majority of the waste is confined in double shell tanks (DST), which have a primary shell, where the waste is stored, and a secondary shell, which creates an annular region between the two shells, that provides secondary containment and leak detection capabilities should leakage from the primary shell occur.

The DST are credited as safety class equipment. The DST provides passive containment for the tank contents to prevent a release of liquid radiological material to the environment and provide passive confinement to mitigate an airborne radiological material release. Therefore, administrative control programs, such as the flammability and corrosion control programs, are in place to ensure the DST functionality. The flammability control program describes compensatory measures that are taken to ensure that the concentration of flammable gases (e.g.,

hydrogen) does not exceed the lower flammability limit as defined by the Technical Safety Requirements (TSR). The corrosion control program describes the compensatory measures that are necessary to mitigate degradation to the DST wall that could lead to failure of the tank wall.

The DST annulus is credited as safety significant equipment. The annulus provides passive confinement of the annulus contents to prevent a release of radiological material to the environment and provides passive confinement to mitigate an airborne radiological material release. The annulus provides a path for ventilation flow around the outside of the tank for corrosion and temperature control, and contains level detection instrumentation to measure liquid level in the annulus. The functionality of this system is also ensured through administrative control programs such as the structural integrity program and the corrosion control program.

Each of the DST is equipped with a purge ventilation system for the interior of the primary shell and an annulus ventilation system for the secondary containment. The DST purge ventilation exhaust is also designated as safety class system. Since there are multiple paths for inflow, the air inlets are not classified as safety class. The safety class designation requires that the structural integrity of the pressure boundary of the exhaust system and its components (i.e., including duct work) is demonstrated. Materials compatibility evaluations and structural integrity inspections are performed to ensure integrity of the purge ventilation system is maintained during all operations modes (e.g., normal, chemical cleaning, etc.).

For the older DST, where chemical cleaning operations are performed, the annulus ventilation system has a safety significant designation. The purpose of the system is to maintain the concentration of flammable vapors in the annulus bulk vapor space to less than or equal to 25% of the lower flammability limit. The system for the older DST also provides an active elevated release path (i.e., stack) to ensure adequate dispersion of potential chemical vapors that may occur during chemical cleaning. Materials compatibility evaluations and structural integrity inspections are performed to ensure that integrity is maintained during chemical cleaning.

From this overview of the safety functions of the DST and its annulus, it is clear that the purge and annulus ventilation systems have a key role in the administrative control of these safety class and safety significant systems. Therefore, it is equally important that the structural integrity of each of these systems can be demonstrated. This paper reviews the compensatory measures for the key administrative control programs (i.e., flammability and corrosion control) related to how the purge and annulus ventilation protect the tank and tank annulus. Secondly, the paper reviews the structural integrity inspections and material compatibility reviews that have been performed to ensure that the ventilation systems are functional such that the administrative control programs may be executed.

## **SYSTEM CONFIGURATION**

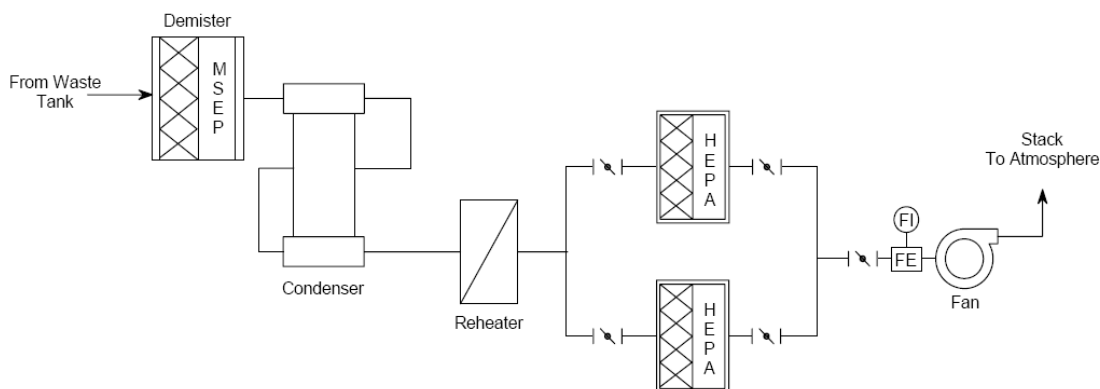
### **Purge Ventilation**

Radiolytic decomposition of water and organic materials in the waste tanks generates hydrogen and other organic vapors. These combustible vapors can accumulate in the tank vapor space and create an explosion hazard. The DST purge ventilation system is designed to continuously

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purge the tank vapor space of flammable gases and prevent the release of radioactive particulate to the environment.

The ventilation system is designed to purge the vapor space above the waste at a rate in excess of 100 cfm. In a typical installation, ambient air enters through a HEPA filter and is then conducted via a 4 inch pipe through the roof and into the vapor space of the primary tank. Air leaves the primary tank by way of a 12 inch riser pipe positioned 180 degrees across the tank. Figure 1 is a schematic drawing that shows the components of the purge ventilation exhaust system. The primary function of the exhaust system is to remove moisture that is damaging to the HEPA filters and radioactive particulates from the air before release to the atmosphere. The exhaust air first passes through a demister, which intercepts large droplets of liquid and returns the liquid to the tank. The air then passes through a condenser that further extracts moisture from the air. Subsequently, the air is passed through a re-heater to raise the temperature of the air above the dew point. The de-humidified air then flows through a HEPA filter to remove any solid, radioactive particulates. The air is finally discharged to the atmosphere via the exhaust fan. These components are all interconnected by a network of carbon steel or stainless steel ductwork.



**Fig. 1. Typical Purge Ventilation Exhaust System Arrangement**

### Annulus Ventilation

Should a leak occur from the primary tank, the annulus ventilation system would serve a similar purpose to the purge ventilation. The annulus ventilation also serves a vital function in the preservation of the integrity of the primary tank and the tank vault. A drawing of a typical annulus ventilation system for DST is shown in Figure 2. Depending on the design of the DST, air is either forced or drawn through the annulus space via a fan or blower. Figure 2 shows an example of the system for the newer DST, which draws air through the annulus and therefore has the fan on the exhaust of the system. The forced air system, on the other hand, has a fan positioned on the inlet side. Ambient air passes through a pre-filter bank which removes debris and large particulate. The air then passes through a pre-heater to provide warm, dry air to the annulus. The temperature of the circulated air is controlled so that either the annulus exit air

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temperature is a pre-set value (40 °C) or 10 °C greater than the ambient air temperature. Heat, provided by the steam, is utilized in the system to raise the temperature of the air, causing the relative humidity to decrease, and thus minimizes the potential for condensation.

For the newer DST, dampers direct the air into the annulus through two locations: the inner annulus between the primary tank wall and the central support column liner, and the outer annulus between the primary tank wall and the outer tank wall. The dampers adjust the flow rate of the air into the annulus, which ranges between 1500 to 6000 cfm, dependent upon the tank design and the decay heat of the waste. More flow is typically directed to the inner annulus to remove the decay heat by cooling the bottom of the tank. Air flows along the bottom of the tank through radial grooves in a concrete pad below the primary tank and then into the outer annulus from where it is removed. Finally, the air is drawn through the annulus duct work and released to the atmosphere by the exhaust fan. Although not shown in the figure, a portable exhaust HEPA filter assembly may be inserted in the system prior to the exhaust fan if the primary tank should develop a leak.

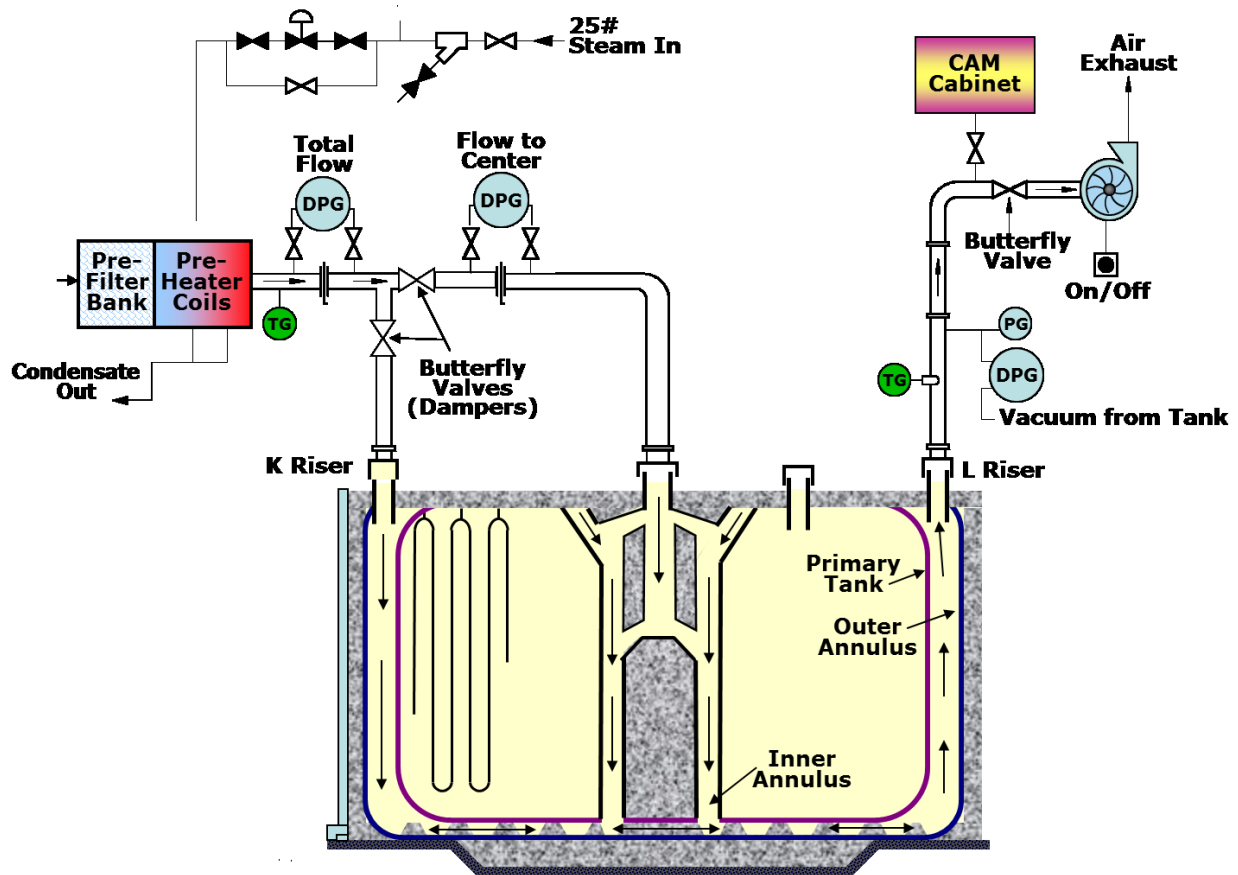


Fig. 2. Typical Annulus Ventilation System Arrangement for the New DST Design

## **ADMINISTRATIVE CONTROLS FOR FLAMMABILITY AND STRUCTURAL INTEGRITY**

### Purge Ventilation

Waste tank purge ventilation is designed to sweep tank vapor spaces of flammable vapors and to prevent the release of radiological contaminants to the environment. In addition, operation of the purge ventilation systems provides some cooling of the tank; this may provide additional margin to meet temperature requirements established for corrosion purposes, although it is not credited as part of the Corrosion Control Program. Ventilation is typically permanently installed on the tank, although portable systems may be used as necessary to provide additional airflow to the installed system, or to provide temporary ventilation while the installed system is out of service.

The Flammability Control Program (FCP) [0] at SRS establishes requirements for the purge ventilation systems on waste storage tanks based on: tank contents (volume and composition), physical tank configuration (size, installed pumps/jets, cooling capability), tank mode, and planned operations (e.g. storage of waste, sludge agitation, salt dissolution, Bulk Oxalic Acid Cleaning [BOAC]). Waste Tanks are classified based on the time in which radiolytic hydrogen generation could cause the tank to reach the lower flammability limit (LFL) for hydrogen upon loss of ventilation:

- Very Slow Generation Tanks - Waste storage tanks that have been determined to never reach 100% of the LFL, considering atmospheric breathing.
- Slow generation tanks – Waste storage tanks that have been determined to go from the SAV to 100% of the LFL in greater than or equal to 28 days following a loss of ventilation.
- Rapid generation tanks – Waste storage tanks that have been determined to go from the safety analysis value (SAV) to 100% of the LFL in less than 28 days (but not less than 7 days) following a loss of ventilation.

For Very Slow generation tanks, minimum purge flow is not required for flammability concerns [11]. The hydrogen generation rate is low enough in these tanks that atmospheric breathing is adequate to maintain the vapor space below the LFL. Periodic (typically quarterly) ventilation operation is required for tanks that are calculated to reach equilibrium with a hydrogen concentration of 60% of the LFL or higher (alternatively, vapor space hydrogen measurements can be used to show that the concentration in the vapor space remains low) [0]. Ventilation operation in Very Slow generation tanks may still be required to prevent release of radiological contaminants during certain operations, such as mixing, mechanical cleaning, or steam jet operation.

Slow generation tanks have a required minimum purge flow rate of 45 cfm. This flow has been shown to provide adequate flow to maintain the vapor space below 25% of the LFL using bounding waste tank conditions [11]. Typical flow capacity for installed purge systems is 150-900 cfm. Due to the relatively long time to LFL compared to Rapid generation tanks, and the margin between the minimum required purge flow and the system capacity, no installed flow indication is required. Fan capacity is tested every two years (typically by transversal measurement), and the system is verified to be functioning every 24 hours. If the installed ventilation system is not operating properly, forced ventilation (may be a portable system) must be employed within 28 days (minimum time to LFL for Slow generation tanks) [0].

The required minimum purge flow rate for most Rapid generation tanks is 72 cfm. However,

certain waste tanks have been designated as Extended Sludge Processing (ESP) tanks; these tanks must still meet the time to LFL requirements of Rapid generation tanks, but have a required minimum purge flow of 188 cfm due to the possibility for higher hydrogen generation rates [11]. Tanks that have been designated as ESP Sludge Slurry tanks must meet the requirements whether actively processing an ESP batch or not. As with Slow generation tanks, the purge flow requirements for Rapid generation tanks were shown to maintain the vapor space below 25% of the LFL using bounding waste tank conditions. Due to the higher hydrogen generation rates for Rapid generation tanks, a flow indicator must be installed on the purge ventilation system [11]. The flow indicator is calibrated once per year, and flow is verified to be in range every 24 hours. If the installed ventilation system is not operating properly, forced ventilation (may be a portable system) must be employed within 7 days (minimum time to LFL for Rapid generation tanks) [0].

In addition to the flammability classifications, planned activities which could result in a rapid release of dissolved or trapped gas are evaluated and controlled so as not to exceed the SAV, thus protecting the assumptions used in determining the flammability classification [0]. Dissolved hydrogen can be released in the event of a temperature increase of the waste or a decrease in pressure in the tank head space. Dissolved hydrogen is not typically a concern in the waste tanks; a sufficiently rapid change in temperature or pressure cannot occur during most operations. Operations that can cause the release of significant dissolved hydrogen (i.e. steam jet operation) are prohibited for tanks where the additional release of hydrogen is not acceptable or has not been analyzed (e.g. tanks that are designated for ESP Sludge Slurry or BOAC). Trapped gases are released primarily due to dissolution of saltcake or agitation of sludge. The performed evaluation may lead to entry into Gas Release Mode (GRM) during activities that could result in the rapid release of significant volumes of hydrogen.

Waste tanks that require entry into GRM are subject to additional control requirements, but are also allowed additional flexibility. All waste tanks in GRM must meet the flow requirements for RAPID tanks, regardless of flammability classification. Flow indication is required with a control room alarm with audible and visual indication and low flow interlocks for equipment that could cause the release of trapped hydrogen (mixing devices, transfer devices, liquid addition valves) [11]. No allowance is made in GRM for purge system breaches as with Operations Mode; the ventilation system must be intact throughout.

Once most of the waste has been removed from a waste tank, the BOAC process may be utilized to remove as much of the solids heel as possible. This process introduces oxalic acid (up to 8 wt% for brief periods without mixing, up to 4 wt% for longer durations with mixing) to the waste tank, shifting the waste from a typical pH of 12 to 14 to less than 1. For these waste tanks, a minimum purge flow of 110 scfm is required (with flow indication) due to the potential for corrosion-induced hydrogen. This maintains the vapor space below 25% of the LFL while ventilation is operating; however, tanks undergoing BOAC have the potential to reach the LFL in as little as 3 days upon loss of ventilation [11]. No allowance is made in BOAC for purge system breaches in the treatment tank or in a tank that may receive spent acid from the treatment tank; the ventilation systems must be intact throughout. This process is limited to a maximum duration of one year for any waste tank, but in practice is typically complete in less than two months.

Closure mode is entered once the waste has been removed to the maximum extent practical. In this mode, the tank has a minimum amount of residual waste (and therefore a slow hydrogen generation rate) and is isolated from the transfer system. Installed systems (e.g. ventilation,

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instrumentation) may be removed, and the tank is prepared to be filled with grout. Prior to grouting, these tanks are treated as a Very Slow tank; any required ventilation operation may be performed by an installed system or a portable system. Once grouting begins, ventilation is operated continuously while actively pouring grout, and periodically when grouting is paused [0].

### Annulus Ventilation

The annulus ventilation system is designed to be operated continuously. The administrative corrosion control program also assumes that the annulus ventilation is operated continuously with steam to the re-heater. The purpose of this requirement is to prevent corrosion degradation of the exterior primary wall, the secondary pan, and the secondary wall of the double wall tanks. Additionally, operation of the ventilation system minimizes the risk of a brittle fracture event for the older DST.

Operation of the annulus ventilation in high heat tanks lowers the temperature of the primary steel and thus minimizes the potential for corrosion degradation of the steel or thermal degradation of the concrete. A field test was performed to demonstrate the impact of the ventilation system on the tank and waste temperature [1]. During one test sequence, the annulus ventilation was turned off for approximately 60 hours. The temperature of the tank bottom was monitored during this time period (See Fig. 3). Without the benefit of air passing through the radial grooves, the temperature of the tank bottom increased approximately 15 °C during this time. Although the temperatures, did not approach the maximum temperature limit for corrosion control due to the relatively short outage time, prolonged outage of the airflow beneath the tank, could result in an increased risk of tank bottom corrosion.

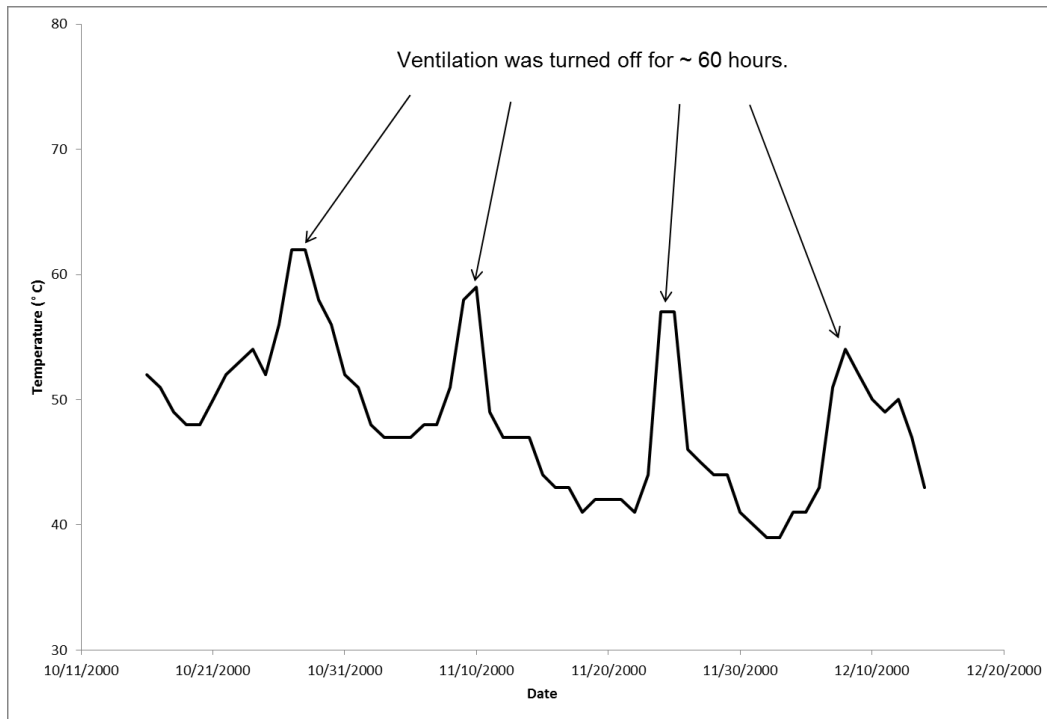


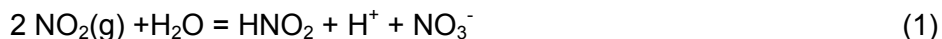
Fig. 3. Tank bottom temperature as a function of annulus ventilation operation.



For tanks with a low heat generation rate, continuous operation of the annulus ventilation system with steam on prevents condensation from forming on the exterior of the primary tank wall and the secondary pan or wall of double-walled tanks as well as evaporating any standing liquid from the annulus pan. Moisture in the annulus causes four concerns for DST integrity, (i) for DST with cracks, the moisture will dissolve salt deposits covering the leaksites and allows for intrusion of waste into the tank annulus, (ii) for all DST, condensation can result in excessive corrosion of the primary and or secondary walls, (iii) for all DST, loss of the annulus ventilation could allow the accumulation of stagnant water in the annulus, thereby increasing the risk of initiating microbiologically induced corrosion (MIC), and (iv) for all tanks, corrosion products may hide defects and therefore prevent the detection of changes in the tank wall surface by tank inspection. In addition, the materials for the older DST have a low ductile to brittle transition temperature [2]. As a result, if warm air to the annulus is lost for a significant period of time (i.e., there is a loss of steam to the re-heater), particularly during the colder winter months, the tank may be at risk for a brittle fracture event [3].

Several of the older DST have leaked waste through cracks into the annulus. The warm air circulating through the annulus evaporated the water from the waste and formed salt deposits that plugged the cracks and prevented further leakage. Inspections have shown that when the annulus ventilation is turned off, these deposits begin to dissolve and leakage of waste into the annulus resumes [2]. The dissolution of the salt deposits is likely due to the formation of condensation on the tank walls as the air cools. Although the waste should be inhibited when it enters the annulus, dilution due to rainwater intrusion or reaction with carbon dioxide may change the chemistry of the leaked waste significantly from that of the waste inside the tank. Thus a new corrosive condition may be created.

Moisture by itself will cause general corrosion. Accelerated general corrosion may occur due to air radiolysis. This mechanism is initiated by gamma rays that irradiate the annulus air to produce NO<sub>2</sub> gas [4]. A nitric acid solution will form wherever air containing NO<sub>2</sub> is in contact with moisture. The reaction producing the nitric acid is:



If it is assumed that the dose rate is 1000 R/hr (a representative value for the annulus air [5]), and the volume of air in the annulus is approximately 23,000 ft<sup>3</sup>, the production of NO<sub>2</sub> gas is 1.9 x 10<sup>-8</sup> atm/hr. Assuming that equilibrium is instantaneously established, the pH of the standing water may reach 2.9 within 1 hour. At this pH, carbon steel corrodes at a rate of approximately 40-50 mils per year [6]. If these conditions were allowed to persist, significant wall thinning may occur. This mechanism was observed to occur in the reactor process room at SRS [7].

Inspections of the annular space to date have not revealed indications of excessive general corrosion even with occasional steam and blower outages. There are several possible explanations for the lack of observed general corrosion. First, the rate at which the nitric acid production reaction occurs in cold dilute solutions may be slow, and therefore, the reaction may not attain equilibrium rapidly. Second, the contents of the tank may have contributed sufficient heat to maintain the temperature of the annulus air above the ambient temperature. Condensate would not form under these conditions. Third, the above calculations assume that the air in the annulus is stagnant. A small air flow in the annulus may dilute the NO<sub>2</sub> concentration sufficiently. Fourth, in tanks that have salt deposits, the condensate or standing water may contain other

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dissolved salts. The presence of these dissolved salts would likely decrease the absorption of the NO<sub>2</sub> gas into the water and the formation of nitric acid.

Continuous operation of the system also reduces the risk for MIC. MIC was observed in the annulus pan during construction of the Type III tanks [8]. Wet, stagnant conditions are ideal for initiating pits beneath the microbes. The solution to the problem was to run warm annulus air to remove the moisture that sustains the microbes and the corrosion reaction. Maintaining warm air in the annulus minimizes the potential that this mechanism will initiate new pits or reinitiate pits that are present.

In addition to moisture due to condensation, rainwater leaks into the annulus through risers and other penetrations such as transfer lines. Conductivity probes are set near the floor of the waste tank annulus to detect the presence of liquids. Two benefits are realized by minimizing the accumulation of liquid: 1) the potential for deflagration or the accumulation of flammable gases is reduced, and 2) long-term corrosion degradation of the pan, annulus floor, annulus wall or primary tank is mitigated or prevented. The first benefit reduces the risk of releasing a radioactive dose to the public. Given that this is the more immediate concern of the two, the level that the probe is set above the annulus floor (in the presence of debris or accumulated waste) will be based on this consideration. The second benefit maintains the structural integrity of safety class structures over an extended period of time.

Circulation of warm air will evaporate rainwater and prevent the possibility of corrosion. A field test was performed that showed that operating the annulus ventilation at 2200 CFM, with an inlet temperature of 96°C, would evaporate approximately 10 gallons of liquid per hour [9].

Rapid, unstable flaw growth may occur if the combination of a large flaw, high stresses, and a low temperature embrittled material co-exist in a local region. Several of the older DST have pre-existing flaws due to stress corrosion cracking during service [3]. Literature data indicates that for the carbon steel material that these tanks are constructed from maintaining the wall temperature greater than 21 °C mitigates the risk of brittle fracture in these tanks. A field test was performed to determine the impact of steam and blower outages on the annulus air and steel wall temperature for the older DST. Figure 4 shows the annulus air and steel wall temperature during a 30 hour steam outage in January vs. normal operation of the system. Air continued to blow into the annulus at a rate of 1500 cfm. During normal operation, the steel wall temperature was at 55 °C. Once the steam was turned off, the annulus air and steel wall temperatures decayed rapidly. The coolest region of the tank was near the tank bottom where there was a 15 °C decrease in the tank steel temperature. Although the temperature remained greater than the minimum 21 °C, the benefit of the heated annulus air is evident.

Occasionally the annulus ventilation system needs to be shut-down for repairs to supporting systems such as low pressure steam. SRS has placed limits on the time which the annulus ventilation system may be shutdown to minimize the risk of degradation of the primary and annulus. The administrative corrosion control program requires that the facility monitor the ventilation system by:

1. Every week (7 days) a check shall be made to ensure that each annulus ventilation system is receiving steam and that each annulus ventilation system is operating.

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2. If the steel wall temperature of the tank is above 40°C (lowest steel wall temperature reading), there is no requirement for the operation of steam, unless liquid is detected in the annulus. In the event liquid is detected, steam shall be used until the annulus is dried.

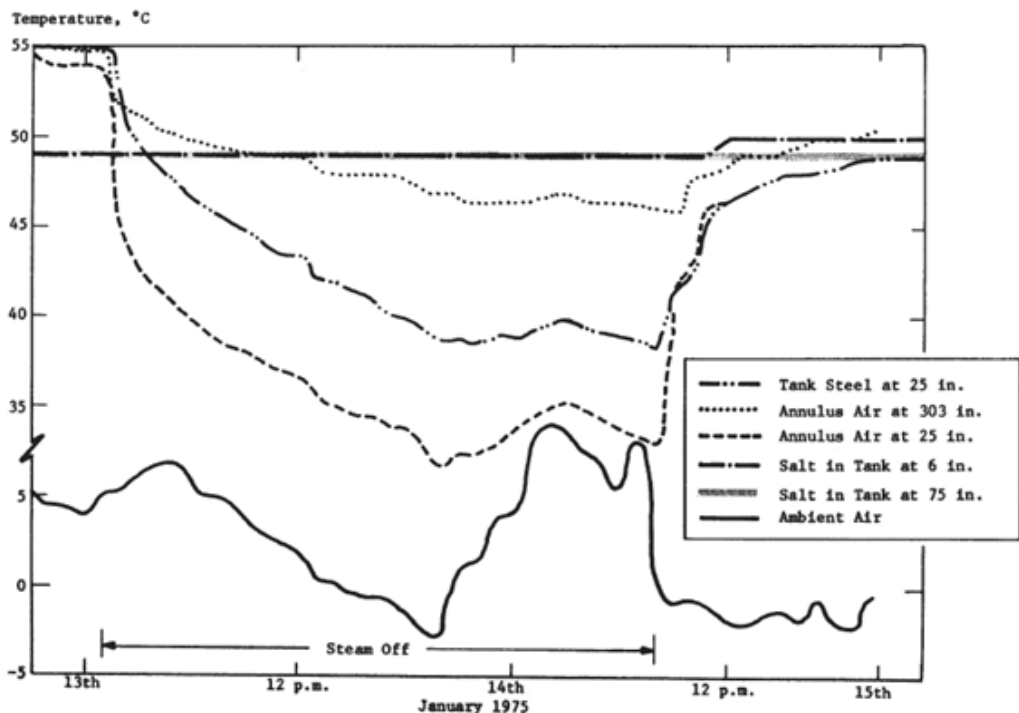


Fig. 4. Tank steel wall temperature as a function of annulus ventilation operation.

If the annulus ventilation is not in operation or steam is not supplied to the annulus pre-heater and the tank steel-wall temperature is below 40°C the following compensator activities are required:

1. For the older DST these conditions shall be corrected within 30 days.
2. For the newer DST these conditions shall be corrected within 90 days.
3. If no steam is available, the ventilation shall be operated continuously (as long as the tank wall temperature is above the lower operating limit (i.e., ~5 °C greater than the DBTT).
4. If liquid is verified to be in the annulus, the ventilation system shall be operated; also, ensure that steam is supplied to the annulus pre-heater. This action shall be completed within 24 hours.

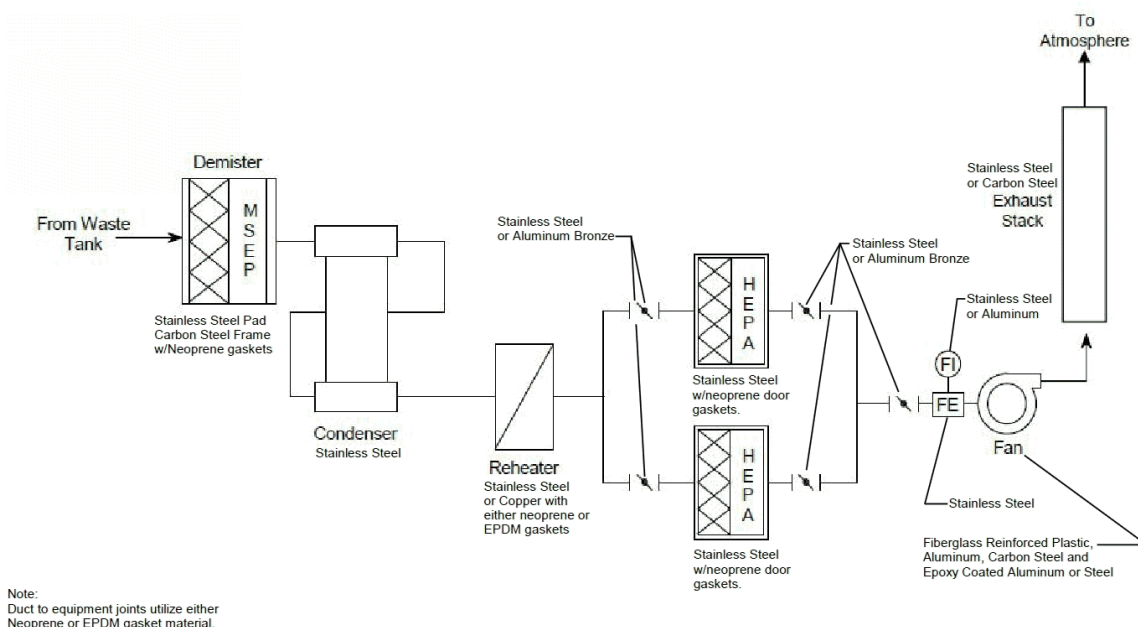
## ENGINEERING CONTROLS TO ENHANCE MATERIALS PERFORMANCE

### Purge Ventilation

There are multiple materials of construction throughout the ventilation system. The ventilation system is primarily constructed of stainless steel and low-carbon steel and has been successfully operated for many decades. However, there are many components within the system constructed

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of aluminum/aluminum alloys, copper, bronze, brass, and various polymers. A map of the nominal materials of construction of a typical ventilation system is shown in Figure . An intact flow path from the waste tank through the ventilation system is important for meeting the purge flow requirements and control of contaminants present in the vapor stream. For tanks in Operations Mode with a breach of the ductwork of up to 0.55 in.<sup>2</sup> (cumulative in the case of multiple breaches), the purge system may be operated with extra margin on the flow rate and increased surveillances for up to 90 days [0].



TYPICAL WASTE TANK PURGE EXHAUST SYSTEM

**Figure 5: Nominal Materials of Construction of a Typical Tank Purge Exhaust System**

Several instances of cracking of the ventilation ductwork have been observed in the SRS tank farm facility. The ventilation duct consists of a fabricated galvanized steel duct, two fabricated reducers, a fabricated elbow and flanges at either end. An example of the cracks is shown in Figure 6. The cracks were beneath thermal insulation and were found during planning for upgrading of the exhaust flow monitoring system. Cracks occur from the inside, are in the heat affected zones of both seam and girth welds, and have a circumferential orientation.

The stress corrosion cracks initiated on the interior of the duct work were associated with nitrate-rich deposits. Therefore, it is clear that the tank vapors played a significant role in the degradation mechanism. It has been hypothesized that the generation of NO<sub>x</sub> vapors from the tank waste potentially create a corrosive environment for the duct work. This hypothesis was

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assessed based on previous duct work failures. If the hypothesis is reasonable, the tank waste that produces the highest NO<sub>x</sub> generation rate will be recommended for the inspection.

A review of the affects that different environmental variables have on NO<sub>x</sub> generation within waste tanks was performed. These variables include:

- 1) A high dose rate, as determined by gross gamma measurements, results in higher generation rates.
- 2) A high concentration of nitrate and nitrite results in a high generation rate.
- 3) A high supernate temperature results in thermal degradation of NO<sub>x</sub>, and therefore depresses the generation rate. Conversely, a low supernate temperature does not depress the generation rate as much.
- 4) Dissolved oxygen in the supernate reacts with NO<sub>x</sub> and therefore depresses the NO<sub>x</sub> generation rate. Dissolved oxygen concentration decreases as the sodium salt concentration increases.
- 5) Organics present in the waste serve as reducing agents, and therefore increase the production of NO<sub>x</sub>.
- 6) Above pH 11, NO<sub>x</sub> generation is facilitated.



**Figure 6. Section of ventilation ductwork removed from the exhaust of the purge ventilation system. Two cracks are evident. A third crack, located on the opposite side of the weld, occurred on the inside surface but did not penetrate to the exterior. Magnification is 1.25 X.**

Chemistry and thermal histories of the tanks were examined for information on these variables. It was observed that all tanks have a pH > 13, therefore factor 6 does not discriminate.

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Additionally, data for the concentration of organic compounds in the wastes was incomplete, and therefore were also not considered. Thus, the first 4 variables were considered for this assessment. Variables 1) and 2) accelerate the NO<sub>x</sub> generation rate, while variables 3) and 4) depress the generation rate. Each of the variables was rated on a scale of 1 to 4, with 1 representing the conditions for higher NO<sub>x</sub> generation rates.

The assessment was performed assuming that each of the variables had an equal influence on the NO<sub>x</sub> generation rate. The assessment also assumed that the purge ventilation rate for each tank is the same.

The results of the analysis showed that six of the eight systems that have experienced cracking were exposed to vapors from wastes with higher NO<sub>x</sub> generation rates. Thus as a general predictor of the most vulnerable purge ventilation system, this approach appears to be reasonable.

The tank with the lowest average ranking was selected for system monitoring. The inspection included wall thickness measurement of all galvanized carbon steel confining duct and components. Visual inspection was also conducted on the surface for cracks. A magnetic particle test or equivalent will be performed at each weld and at least 3 inches adjacent to the weld. This inspection will be used as a commodity group that is representative of all the tank exhaust ventilation systems in the facility. If the inspection fails the acceptance criteria then all carbon steel duct sections must be inspected or replaced. The replacement material of construction for the duct is stainless steel.

During BOAC, the vapors that pass through the purge ventilation system may contain higher concentrations of NO<sub>x</sub> and may also contain mercury [10]. Aluminum and brass materials found in the in the re-heater and fan components of the system are susceptible to accelerated mercury induced corrosion under certain conditions. If the ventilation system is functional, the demister, condenser, and reheater ensure that mercury is primarily condensed prior to the reheater, with any remaining mercury traveling in the vapor phase through the stack, in addition to any corrosive anionic species (e.g. NO<sub>x</sub>) vapors generated from the waste. However, if the ventilation system malfunctions during BOAC, nitric acid could form due to the condensation of NO<sub>x</sub> and lead to the breach of the aluminum oxide films. Due to the low pH condensates, this may lead to mercury induced corrosion of the aluminum and brass components.

During BOAC controls have been instituted to ensure functionality of the ventilation system components (i.e., demister, condenser, and reheater) to prevent any mercury induced and other corrosion mechanisms from condensation of corrosive species. If exposure conditions are such that this cannot be justified the vulnerable components are replaced or an operational response is planned. An operational response to mitigate the impact of mercury induced corrosion in the event of malfunctioning ventilation equipment may include stoppage of mixing and cooling the tank.

#### Annulus Ventilation

During normal operations, annulus ventilation systems are not typically exposed to the same atmospheres as the purge systems. Leaks into the annuli of old-style tanks have occurred, but the waste typically has dried to salt nodules in relatively short time [11]. Exposure concerns for the annulus systems are limited to those of any system that is exposed to the elements.

Annulus ventilation systems are typically constructed of carbon steel. Exposed surfaces are painted, but due to wear (e.g. manipulation of dampers) and weather the carbon steel surfaces may become exposed. Over time, these surfaces may become corroded due to contact with rain water. These systems are inspected periodically and monitored for performance. Components are repaired or replaced as necessary.

Accumulation of water from rain or condensation can lead to relatively rapid corrosion of ventilation system components. This led to the failure of a fan on an annulus ventilation system several years ago. The systems are equipped with drain lines in low spots to minimize liquid holdup, but in this case the drain line in the fan housing was plugged. Lack of adequate drainage, coupled with absence of a rain cover, allowed for accumulation of a significant amount of water in the housing. This led to extensive corrosion that eventually breached the housing (see figure 7). As a corrective action, rain covers have been installed on ventilation system stacks where applicable.



**Figure 7. Breach of annulus fan housing due to accumulation of water.**

As described above, during normal operations at SRS, waste tank annulus ventilation systems are not significantly exposed to vapors associated with tank waste; the primary exposure concern is rain and humidity. During the BOAC process, however, the tank wall is assumed to leak in the safety analysis. Because of this assumption, active negative pressure ventilation is required on the annulus, and ventilation system components must be acceptable for use in contact with the expected vapors from the process.

To ensure that the annulus ventilation system remains operable throughout the BOAC process,

system components must be selected that are compatible with species that may be present in the annulus vapor space. Mercury, carbon dioxides and nitrogen oxides are evolved into the vapor space during the BOAC process; these species are evaluated for contact with ventilation system components [10]. Oxalic acid has a low vapor pressure, but droplets may be present in the vapor if there is splashing or spraying (this is a reasonable scenario inside the tank primary due to the presence of mixing devices, but is not likely in the annulus); oxalic acid is evaluated for material compatibility as well. Components that are incompatible with chemical cleaning atmospheres (e.g., aluminum, brass, TPO, polycarbonates) are replaced with compatible materials (e.g. 304L stainless steel, PTFE, EPDM) if they will be directly exposed to the vapor stream. Components that have some limited resistance may be replaced, or may be approved for use during the short duration of the process.

## **CONCLUSIONS**

The purge and annulus ventilation systems have a key role in the administrative control of safety class and safety significant systems such as the primary tank and annulus of the DST. A review of the compensatory measures for the key administrative control programs (i.e., flammability and corrosion control) related to how the purge and annulus ventilation protect the DST was performed. Secondly, it was shown that structural integrity inspections and material compatibility reviews that have been performed to ensure that the ventilation systems are functional such that the administrative control programs may be executed.

## **REFERENCES**

1. B. J. Wiersma and K. M. Marshall, "Analysis of Annulus Relative Humidity for HLW Tanks 12, 15, 39", WSRC-TR-2003-00147, Rev. 0, April, 9, 2003.
2. B. J. Wiersma and R. L. Sindelar, "Limits on Annulus Air Outages in Type I, II, and III Waste Tanks", WSRC-TR-95-0178, April 12, 1995.
3. J. A. Donovan, "Materials Aspects of SRP Waste Storage – Corrosion and Mechanical Failure", DP-1476, November, 1977.
4. M. Steinberg, "Chemonuclear and Radiation Chemical Process Research and Development", *Isotopes and Radiation Technology*, Vol. 4, No. 2, Winter 1966-1967, pp. 143-155.
5. T. L. Davis, et. al., "History of Waste Tank 16: 1959-1974", DPSPU-77-11-17, July 1977.
6. H. H. Uhlig, Corrosion and Corrosion Control, John Wiley and Sons Inc., New York, 1971, pp. 129-134.
7. F. B. Longtin, "Air Radiolysis", DPSP-69-1403, September 19, 1969.
8. D. A. Mezzanotte, "Preventing Re-initiation of Pitting in Waste Tank Annuli", DPST-81-590, July 21, 1981.
9. T. L. Davis, et. al., "History of Waste Tank 13: 1956-1974", DPSPU-78-11-2, June 1978.
10. T. E. Britt, et. al., "Materials Compatibility Evaluation of Waste Tank Ventilation System Materials of Construction with Mercury", SRR-STI-2012-00627, October 2012.
11. "Concentration, Storage, and Transfer Facilities Documented Safety Analysis", WSRC-SA-2002-00007, Rev. 14, July 2012.
12. A. Hansen, "CSTF Flammability Control Program Program Description Document", WSRC-TR-2003-00087, Rev. 21, July 23, 2013.  
"Concentration, Storage, and Transfer Facilities Technical Safety Requirements", S-TSR-G-00001, Rev. 40, April 2013.