

**Contract No:**

This document was prepared in conjunction with work accomplished under Contract No. 89303321CEM000080 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

**Disclaimer:**

This work was prepared under an agreement with and funded by the U.S. Government. Neither the U.S. Government or its employees, nor any of its contractors, subcontractors or their employees, makes any express or implied:

- 1 ) warranty or assumes any legal liability for the accuracy, completeness, or for the use or results of such use of any information, product, or process disclosed; or
- 2 ) representation that such use or results of such use would not infringe privately owned rights; or
- 3) endorsement or recommendation of any specifically identified commercial product, process, or service.

Any views and opinions of authors expressed in this work do not necessarily state or reflect those of the United States Government, or its contractors, or subcontractors.

**A Model to Predict Steel Liner Performance in Cementitious Environments for Geologic Timeframes – 22073**

Bruce J. Wiersma\*, Xian-kui Zhu\*, Mark H. Layton\*\* and Gregory P. Flach\*\*

\* Savannah River National Laboratory, Aiken, SC

\*\* Savannah River Remediation, Aiken, SC

**ABSTRACT**

For nearly seventy years, the Savannah River Site (SRS) has stored by-product liquid waste from the production of nuclear materials. Large, underground carbon steel tanks, which are surrounded by a concrete vault, have provided interim storage of the liquid waste until it can be either processed and vitrified within the Defense Waste Process Facility (DWPF) or stabilized in a grout mixture and disposed of in concrete disposal units within the Saltstone Facility. SRS is proceeding with closure of the waste tanks within the tank farm facilities. Closure consists of removing the bulk waste, heel removal, and filling the tank with tailored grout formulations. Despite best efforts, a residual heel of radioactive waste will likely reside near the tank bottom and be grouted in place. The site is required to provide a performance assessment (PA) that evaluates the fate of critical radionuclides and chemicals in this residual waste and their future impact.

A degradation model was developed for use within the tank farm PA Conceptual Models (CMs) to estimate the time to failure for the steel liners and cementitious barriers. Initially, the cementitious and steel tank materials provide a barrier to the migration of the contaminants into the surrounding soil. Over timeframes of hundreds, thousands, to tens of thousands of years, the chemical and physical properties of the cementitious and steel materials will slowly degrade due to environmental exposure. Steel liner degradation is principally by either general or pitting corrosion. Corrosion of the steel occurs under conditions characterized by 1) contact with non-degraded cementitious materials, 2) contact with cementitious materials that have been degraded by carbonation or decalcification, 3) penetration of chlorine and oxygen into the cementitious materials, 4) humid, indoor air intrusion, or 5) groundwater intrusion. Corrosion rates for steel in each environment were utilized in the model. Likewise, corrosion of the steel may result in cracking of the concrete due to internal pressure created by the steel corrosion products. The degradation model that was developed included a feedback loop such that the influence of the degradation of each material on the other was considered.

Modeling cases were postulated to assess the range on the time to failure for the cementitious and steel components. Chemical, physical and dimensional tank configuration parameters were investigated to understand their effects on the predicted time to release of the contaminants. The cases considered various degrees of conservatism and were evaluated with both saturated soil conditions (the tanks were located beneath the water table) and vadose soil conditions (the tanks were situated above the water table). Different locations within the tanks (e.g., roof, sidewall, bottom) were assessed with the consideration that the environment on either side of the steel wall may be different. In addition, the presence of steel cooling coils on the interior of the tank was considered. Finally, the possibility of an air gap forming between the grout and the steel due to grout shrinkage was included in some of the cases.

The steel degradation model provides a more comprehensive approach than was utilized for the previous closure PA analyses. The principal improvement is that the new model is more consistent with the cementitious degradation models. The model predicts failure times for the tank steel, that is the time for single through-wall penetration at specific locations in the waste tank. For the most representative case, the model predicted that the failure time for the various locations in the tank within the vadose zone ranged from 1,000 to 8,700 years, while in the saturated zone the time to failure of the steel ranged

between 2,500 to 11,000 years. For the most conservative case, the time to failure for the vadose and saturated zones ranged from 250 to 700 years and 600 to 6,300 years, respectively. The shorter failure times were typically associated with the assumption of a gap forming between the grout and the steel due to grout shrinkage.

The steel degradation model makes simplifying and generally conservative assumptions regarding the corrosion response to a change in the environment and the effects of cracks in the cementitious on the corrosion rate. These assumptions could be refined further to reduce uncertainty in the predicted failure times.

## INTRODUCTION

Liquid radioactive and chemical waste has been stored in approximately one-million gallon underground tanks at the Savannah River Site (SRS) for nearly 70 years. The tanks were constructed of carbon steel and encased in concrete vaults to provide structural stability for the below-grade tanks. SRS is proceeding with closure of waste tanks within the H-area Tank Farm (HTF) and F-area Tank Farm (FTF). The closure consists of bulk waste and heel removal, and filling the tank with tailored grout formulations.

The long-term performance of the concrete, steel, and the closure grout is an important consideration for Performance Assessment (PA) of closed tanks in FTF and HTF. Over PA timeframes of hundreds, thousands, to tens of thousands of years, the chemical and physical properties of the concrete and steel will slowly degrade due to environmental exposure and material aging. In the interim these materials will provide a barrier to the leaching of radionuclides into the soil. The current FTF and HTF PAs [1], [2] are based on multiple studies that consider the chemical and/or physical degradation of cementitious materials, either directly or indirectly [3-7]. Savannah River Remediation (SRR) is updating relevant portions of these studies to support an imminent revision to the HTF PA and a future update to the FTF PA.

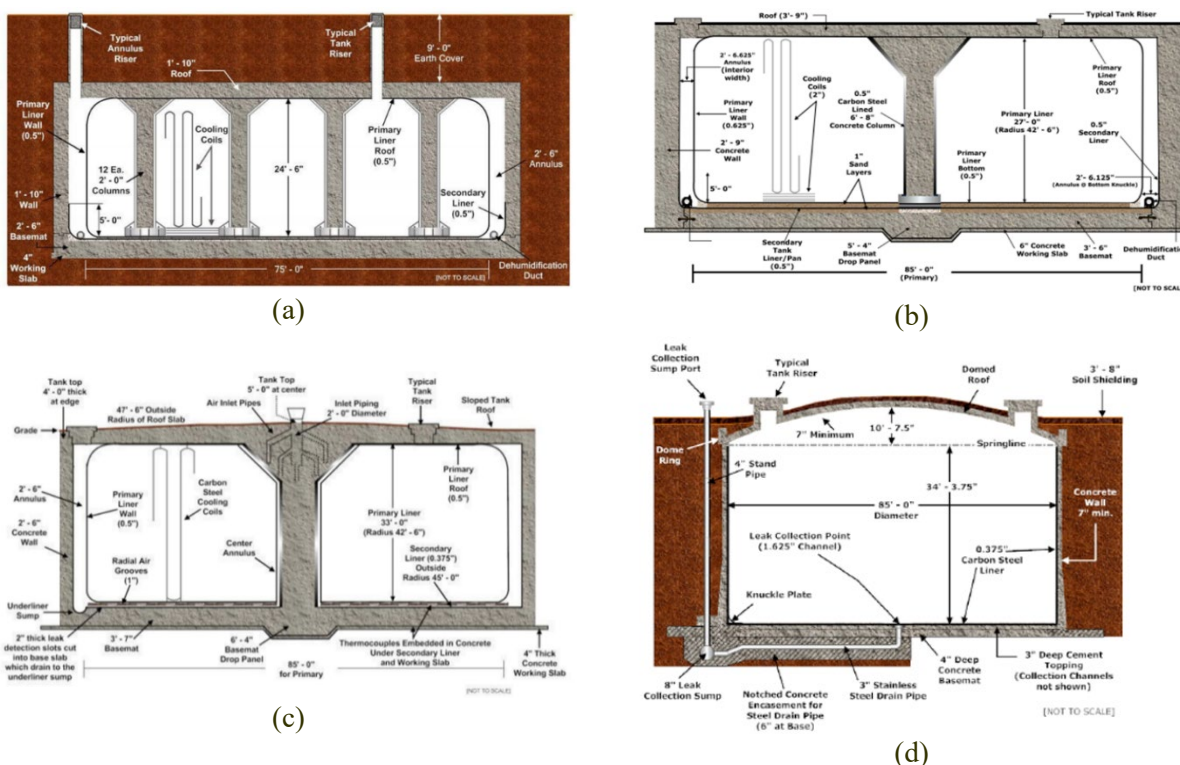
This investigation focuses on the degradation of steel due to corrosion. Corrosion initiation and propagation are coupled to the quality of the cementitious material that contacts the steel. For concrete and grout, the high pH environment creates a passivated surface oxide on the steel that minimizes corrosion of steel. Unless this passive oxide is disrupted, the steel will corrode at a very low, general rate. However, if the concrete degrades due to chemical or physical changes, aggressive species such as chloride, oxygen, or carbon dioxide will migrate to the steel and initiate and propagate corrosion. SRR has updated the analysis for cementitious material degradation in coordination with this study [8]. Savannah River National Laboratory (SRNL) was requested to concurrently assess how the changes to the analysis will influence corrosion of the steel components. This analysis updates the previous PA inputs for steel corrosion [6], [7].

The Central Scenario for the PA analysis includes three postulated modeling cases: 1) Realistic Case, 2) Compliance Case, and 3) Pessimistic Case. The present analysis also includes a Fast Flow Path Case. This latter case considers the circumstance where concrete is completely degraded initially, and grout shrinkage exposes steel to the soil environment immediately. In effect, the steel is unprotected by the concrete and grout. The cases have various degrees of conservatism. Chemical, physical and tank configuration parameters were investigated to understand their effects on the predicted time to release of the contaminants. The assessment reviewed the initial tank and steel configuration, service life of the steel, and potential corrosion mechanisms associated with degradation of concrete and grout.

Limiting life calculations consider the corrosion of the steel under the influence of concrete degradation. The results illustrate how steel degradation progresses with time (e.g., which mechanisms are significant) and which configuration and chemical properties are significant.

## WASTE TANK DESIGN

The dimensions of the concrete and steel for the tanks are critical for estimating time to failure. Four general waste tank designs define the relevant dimensions. Type I tanks, as shown in Figure 1 (a), have a nominal capacity of 750,000 gallons, with a diameter of 75 feet and a height of 24.5 feet. The Type I tanks are completely buried, approximately 9 feet below grade. The primary tanks are a closed cylindrical tank with flat top and bottom constructed from 0.5-inch thick carbon steel plate. The top and bottom are joined to the cylindrical sidewall by curved knuckle plates. The 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. A 5-foot high steel pan provides partial secondary containment for the tanks and a concrete vault encompassing the primary tank and the steel pan provides additional containment. The thickness of the steel pan wall is 0.5 inches. The tank and pan are set on a 30-inch thick concrete base slab and are enclosed by a cylindrical 22-inch thick reinforced concrete wall and a flat 22-inch thick concrete roof. There are twelve 2-foot diameter concrete columns within the primary tank to support the roof. Each column has a flared capital and is encased in 0.5-inch thick plate of A285 carbon steel.



**Figure 1. Waste Tank Designs: (a) Type I Tanks, (b) Type II Tanks, (c) Type III/IIIA Tanks, and (d) Type IV Tanks**

Type II tanks have a diameter of 85 feet and a height of 27 feet with a capacity of 1,030,000 gallons, as shown in Figure 1 (b). The concrete vault for the Type II tanks is surrounded on three sides by soil, while the roof is at grade-level. The primary carbon steel tank is annular in shape with a central concrete roof support that rests on the bottom slab of the tank. The outer cylinder of the tank is joined to the top and bottom plates by curved knuckle plates. The nominal thicknesses of the cylinder walls are listed in Table 1.

A five-foot high carbon steel pan provides secondary containment for the Type II tanks and forms an annular space where leaking waste may collect. The thickness of the steel pan wall is 0.5 inches.

The tank and secondary pan assembly are set on a concrete foundation slab that is 42 inches thick. The primary is enclosed by a cylindrical reinforced concrete wall that is 33 inches thick and a flat concrete roof that is 45 inches thick. The roof is supported by the walls and a central concrete column nestled within the inner cylinder of the vessel.

**Table 1. Type II Tank Wall Thickness**

Plate	Thickness (in.)
Top and Bottom	1/2
Upper Knuckle	9/16
Wall	5/8
Lower Knuckle	7/8

The most recently constructed double shell tanks are designated as Type III/IIIA tanks. Twenty-seven Type III/IIIA tanks were constructed between 1967-1981 in both F and H areas. Figure 1 (c) shows a cross-sectional drawing of a Type III/IIIA tank. Each tank is 85 feet in diameter and 33 feet high with a capacity of 1,300,000 gallons. Type III tanks have a toroidal shape that is 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 were of varying thicknesses, as summarized in Table 2. The secondary vessel is 90 feet in diameter and 33 feet high (i.e., the full height of the primary tank) and is made of 0.375-inch thick steel.

**Table 2. Steel Plate Thickness in Type III/IIIA Waste Tanks**

Plate	Thickness, in.
Top and Bottom	1/2
Upper Knuckle	1/2
Outer cylinder wall	
Upper band	1/2
Middle band	5/8
Lower band	3/4
Inner cylinder wall	
Upper band	1/2
Lower band	5/8
Lower knuckle	
Outer cylinder	7/8 (Tanks 25-28 and 33-51)
	1 (Tanks 29-32)
Inner cylinder	5/8

The primary tank rests on a 6-inch bed of refractory concrete. Beneath the refractory is a minimum 42-inch thick concrete foundation slab. The cylindrical walls of the secondary are enclosed by a 30-inch thick reinforced concrete wall and a 48-inch thick flat reinforced concrete roof. Typically, there is three inches of cover above the reinforcement steel. A central concrete column fits within the inner cylinder of the vessel.

Single-walled, uncooled tanks are designated as Type IV tanks, including Tanks 17F-20F and 21H-24H. Tanks 17F-20F were constructed in 1958, while Tanks 21H-24H were constructed between 1959-61. Each tank is 85 feet in diameter and 34 feet high with a capacity of 1,300,000 gallons. The tanks are essentially a steel lined, pre-stressed concrete vertical cylinder with a domed roof (Figure 1 (d)). The carbon steel plates used to line the cylindrical walls and the tank bottom were 3/8 inch thick. The knuckle plates at the junction of the bottom and side wall are 7/16 inch thick.

The concrete vault is buried in the soil with the roof rising above the surrounding grade level. The concrete was built-up around the steel vessel by the "shotcrete" technique, a pneumatic application

method in which a thick, semi-fluid mixture is blown through a nozzle. The concrete dome roof, sidewall, and floor are all approximately 7 inches thick.

## TANK ENVIRONMENT

The soil environment adjacent to the tanks was categorized as either saturated or vadose. The soil is saturated if the pores of the soil are filled with groundwater. Saturated soils are at or below the water table and promote flow of ground water into a degraded tank vault. A few of the Type I tanks are in saturated soils. The soil is vadose if there are pockets of air present with water. The soil resists the flow of water and therefore humid air would flow into the tank vault. Most of the SRS waste tanks are in a vadose zone.

Seven different local environments within the tank concrete vault were identified based on the descriptions given by the central scenario PA model. How the steel is exposed to each of these environments are described briefly.

*Concrete/Grout* - The steel is in intimate contact with either the original concrete vault or the grout that has been added to stabilize the waste.

*Contamination Zone* – The steel is in intimate contact with residual waste that has been mixed with the stabilizing grout. The waste contains corrosive species such as nitrate, chloride, and sulfate. However, the grout and residual nitrite and hydroxide serve to inhibit significant corrosion.

*Indoor Air* – Due to postulated grout shrinkage an air gap forms between the steel and grout on the interior of the primary tank or in the annulus. Initially, the concrete vault is still intact and provides a barrier to the soil environment. Thus, relatively dry indoor air may be in contact with certain sections of the tank.

*Humid Air* – Due to postulated grout shrinkage an air gap forms between the steel and grout on the interior of the primary tank or in the annulus. Over time, the concrete vault degrades and allows moisture from the soil environment to penetrate the gap. If the tank is in the vadose zone, humid air may contact certain sections of the tank.

*Groundwater* - Due to postulated grout shrinkage a gap forms between the steel and grout on the interior of the primary tank or in the annulus. Over time, the concrete vault degrades and allows moisture from the soil environment to penetrate the gap. If the tank is in the saturated zone, groundwater may be in contact with certain sections of the tank.

*Carbonated Concrete* – Carbon dioxide can penetrate through the pores of the concrete and react with the cementitious material. The result is that the pH of the pore water decreases along a migrating front through the concrete. Once the lower pH front reaches the concrete steel interface, the steel corrosion rate will increase.

*Chloride Contaminated Concrete* – Chloride and oxygen can also penetrate through the pores of the concrete. Once the chloride and oxygen penetrate to the concrete steel interface, corrosion is initiated once the chloride concentration exceeds a critical concentration necessary to breakdown the passive oxide film. The rate of corrosion is controlled by the concentration of the oxygen at the surface of the steel. The corrosion products from this reaction are voluminous and create stresses on the concrete that result in the formation of cracks in the concrete.

## DEGRADATION OF CONCRETE AND STEEL

Modeling of the chemical and physical degradation of the concrete materials of the tank vault was coupled to the progressive degradation models for the tank steel and rebar in this investigation. The chemical evolution analysis was performed with equilibrium chemistry simulation software, namely The

Geochemist's Workbench® (GWB) and PHREEQC® [9]. Custom thermodynamic databases formatted for these codes were developed from Denham [3], CEMDATA18.1 [10], and ThermoChimie [11]. Initial simulations defined the equilibrium chemical state of SRS rainwater, soil moisture, groundwater, and hydrated grouts and concrete. Subsequent simulations predict the chemical evolution of the initially cured cementitious materials when subjected to long-term 1) successive pore volume flushes (advective transport) and 2) leaching to adjoining soil/sediment (diffusive transport).

The physical evolution analysis is based on simplified conceptual models (abstractions) that facilitate analytic mathematical solutions. A feedback mechanism is provided whereby physical damage to concrete predicted by reactive transport in turn affects species transport rates. Results for penetration depth in concrete as a function of time are generated for 1) carbonation and physical damage fronts, 2) decalcification and damage fronts, and 3) combined carbonation + decalcification and damage fronts. Methods for estimating 1) oxygen flux and cumulative mass transported and 2) chloride concentration were also developed. The results from the physical evolution analyses were used for the steel degradation analysis.

Methods, input values, and assumptions in the study generally represent a varying blend of best-estimate and pessimistic settings. Sensitivity case studies were performed in the chemical evolution analysis to provide a sense of model biases and uncertainties. For physical evolution, three cases representing varying conservatism are considered. The three cases reflect the same general conceptual model, but apply different biases with respect to developing initial assumptions: a "*Realistic Case*" that assumes best estimate assumptions; a "*Pessimistic Case*" that relies on assumptions that are intentionally biased to generate faster degradation to maximize defensibility; and finally, a "*Compliance Case*" that assumes a combination of the most probable and defensible assumptions and is used for demonstrating compliance to performance objectives. The key parameters that were varied for the physical evolution calculations were: liquid saturation, gas-phase intrinsic diffusion coefficient, liquid-phase effective diffusion coefficient, apparent diffusion coefficient in the liquid, carbonation + dissolution rate constant, and damage front lag.

The physical evolution model generally did not assume the presence of initial structural cracks in the concrete vault, the exception being the concrete floor for the Pessimistic Case. Concrete exhibits excellent strength properties in compression, but cracks form when the monolith is in tension, flexure, or shear. To ensure that large beams can sustain these stresses rebar is added to the concrete monolith [12]. The presence of cracks shortens the corrosion initiation time for the steel and accelerates the corrosion rate during service life. The degree to which cracks influence corrosion is dependent upon the orientation of the crack, the crack width, crack frequency or spacing, crack depth, and concrete composition characteristics (e.g., admixtures such as fly ash). The most common cracks due to structural loads are referred to as transverse cracks as they run perpendicular to the rebar. Longitudinal cracks, which run parallel to the rebar, form after the corrosion of the rebar. These cracks are considered more dangerous than transverse crack because more of the steel area is exposed to the aggressive environment. However, for the initiation of corrosion, the transverse cracks are likely to play a larger role for the concrete vaults.

There have been many studies on the influence of crack geometry and spacing on corrosion of rebar [12] - [14]. Although general principles regarding the effects are understood (e.g., corrosion increases with crack width and frequency), results from experiments show inconsistencies in the relationship between the propagation of the carbonation front in a cracked versus an uncracked concrete due to the variation in the experimental approaches. The ratio of the rate of penetration of the carbonation front for cracked versus uncracked concrete ranges between 2 to 10. Given that carbonation is one of the mechanisms of concern, data from a source relative to that mechanism was considered [15]. The experimental data was input into a service life model. The model predicted that the carbonation depth for the cracked concrete would be three times greater than that for an uncracked sample. This value, although it is perhaps on the low end, is within the range observed by other authors and was performed for the carbonation mechanism.

Thus, for this assessment, structural cracks will be assumed to increase the diffusion rate of the aggressive species by a factor of three.

The other aspect to consider in this evaluation is the location of the highest tensile, flexure or shear stress. Typically for the concrete tank vaults the highest stress occur in one of two places: 1) near the corner of where the floor and the sidewall intersect, and 2) on the floor beneath column supports. An increase in the density of rebar (i.e., smaller spacing and thicker diameter bars) is typically seen in these areas. For this investigation to demonstrate the effect of structural cracks on the projected service life, it was assumed that the greatest crack density was on the floor or the foundation. Thus, for the Pessimistic Case the gas diffusion coefficients for the floor were increased by a factor of three compared to the sidewall to account for postulated cracks, although none have been observed.

The two primary degradation mechanisms are general or uniform corrosion and pitting corrosion. General corrosion proceeds by removal of metal via an electrochemical reaction that occurs uniformly over an exposed surface. For uniform corrosion to occur, the corrosive environment must have access to all parts of the metal surface, and the metal itself must be metallurgically and compositionally uniform. In contrast, pitting corrosion is a localized form of attack that occurs at specific sites on an otherwise resistant surface. The surface is typically protected by an oxide film. Deleterious ions may breakdown this protective film at local sites and result in accelerated attack at a specific site. General corrosion proceeds at a relatively predictable rate, whereas pitting corrosion has random initiation times and growth rates.

The susceptibility of steel to each of these mechanisms for the seven local environments was evaluated. Table 3 shows the mechanism and the rate of corrosion for each environment that was assumed for the steel liner degradation model. The rates were determined from a literature review. The last two local environments may also result in corrosion of the rebar in the concrete vault. Corrosion of the rebar may result in cracking of the concrete and easier access of aggressive species to the tank steel. The steel liner corrosion model accounts for the degradation of the concrete coupled with the increased corrosion rate of the steel.

**Table 3. Corrosion Mechanisms and Rates for Local Environments in Tank Vault**

Local Environment	Corrosion Mechanism	Corrosion Rate ( $\mu\text{m}/\text{yr}$ )
Concrete/Grout	General	1 [6]
Contamination Zone	General	1 [6]
Indoor Air	General	10 [16]
Humid Air	General	50 [6]
Groundwater	Pitting	Model based on local groundwater and soil conditions [17]
Carbonated Concrete	General	6 [15]
Chloride Contaminated Concrete	Pitting	Model based on diffusion of oxygen through concrete [10]

## MODEL DEVELOPMENT

A progressive degradation model was developed to determine the minimum failure time for a given plate location in each tank type for each scenario. Release of contaminants to the environment is predicated on complete degradation of the concrete and steel. Complete penetration of the primary and secondary liners was utilized as the failure time for the steel. A decision logic diagram was created to illustrate the model, as shown in Figure 2, where different failure times are defined as:

$t_{if}$ : total time until the wall thickness is penetrated given the corrosion rate for the initial condition



$t_L$ :	total time to complete degradation of concrete or limiting time
$t_a$ :	time when accelerated corrosion is initiated
$t_{ar}$ :	total time until the wall thickness is penetrated given the corrosion rate for the initial condition by accelerated condition
$t_{fr}$ :	total time until the wall thickness is penetrated by fast flow path mechanism

Figure 2 (a) determines whether a plate of steel degrades completely by corrosion in the initial environment prior to degradation of the concrete or after the initiation of an accelerated corrosion mechanism (e.g., carbonation). If the concrete degrades completely prior to failure in the initial environment or the Fast Flow Path Case is being considered, the calculations were continued in Figure 2 (c)). On the other hand, if an accelerated mechanism (e.g., carbonation) is initiated prior to failure of the plate of steel, the calculations were continued in Figure 2 (b)).

Figure 2 (b) determines the time for degradation by an accelerated corrosion mechanism. If the concrete degrades completely before the steel plate is penetrated by the accelerated mechanism, the calculations were continued in Figure 2 (c). In Figure 2 (c), the time to failure of the steel by the Fast Flow Path Case was determined.

The degradation model has two key aspects. First, the model assumes an immediate transition between corrosion mechanisms (e.g., anoxic, passive corrosion transitions to carbonation induced corrosion upon the arrival of the carbonation front). While this transition is unlikely to occur immediately due to the presence of iron oxides, it may be expected that the transition occurs gradually over a period that is relatively short in comparison to the failure times. Secondly, the exterior and interior sides of a plate may experience different environments at the same time and thus different corrosion rates. Thus, the total corrosion rate for the plate is simply the sum of the two corrosion rates (e.g., anoxic, passive corrosion occurs at 0.04 mpy and indoor air corrosion occurs at 0.4 mpy, thus the total corrosion rate on a secondary wall plate would be 0.44 mpy).

## STEEL LINER TIME TO FAILURE PREDICTIONS

The progressive degradation models developed above are applied to predict time to failure for steel liners of the four type tanks for different scenarios in Saturated Zone and Vadose Zone and described here.

The range of failure times for each tank type and case study are shown in Table 4. For the Realistic Case in the saturated zone, the failure typically occurred due to uniform corrosion in the concrete/grout environment. In this situation, both the interior and exterior sides of a plate of steel corroded at 1  $\mu\text{m}/\text{yr}$ . The range of years is due to the thickness of the tank steel at various locations within the tank (e.g., the roof, sidewall, etc.). As an example, Figure 3 shows of the time to failure at each of these locations for a Type III/IIIA tank. There were three exceptions: the floor of the secondary and primary tank for the Type I tank and the floor of the Type IV tank. In these cases, the concrete degraded due to failure of the rebar, and thus did not meet the minimum diameter criteria for structural stability in year 2484. The rebar had corroded by general corrosion as well at 1  $\mu\text{m}/\text{yr}$ . Once the concrete had degraded, the exterior of the floor was exposed to a groundwater environment. This evolution is shown in Figure 4. The floor of the liner achieved 25% breach within 11 years after the concrete had degraded. This evolution illustrates how the degradation of the concrete and the corrosion of the steel are coupled in this model.

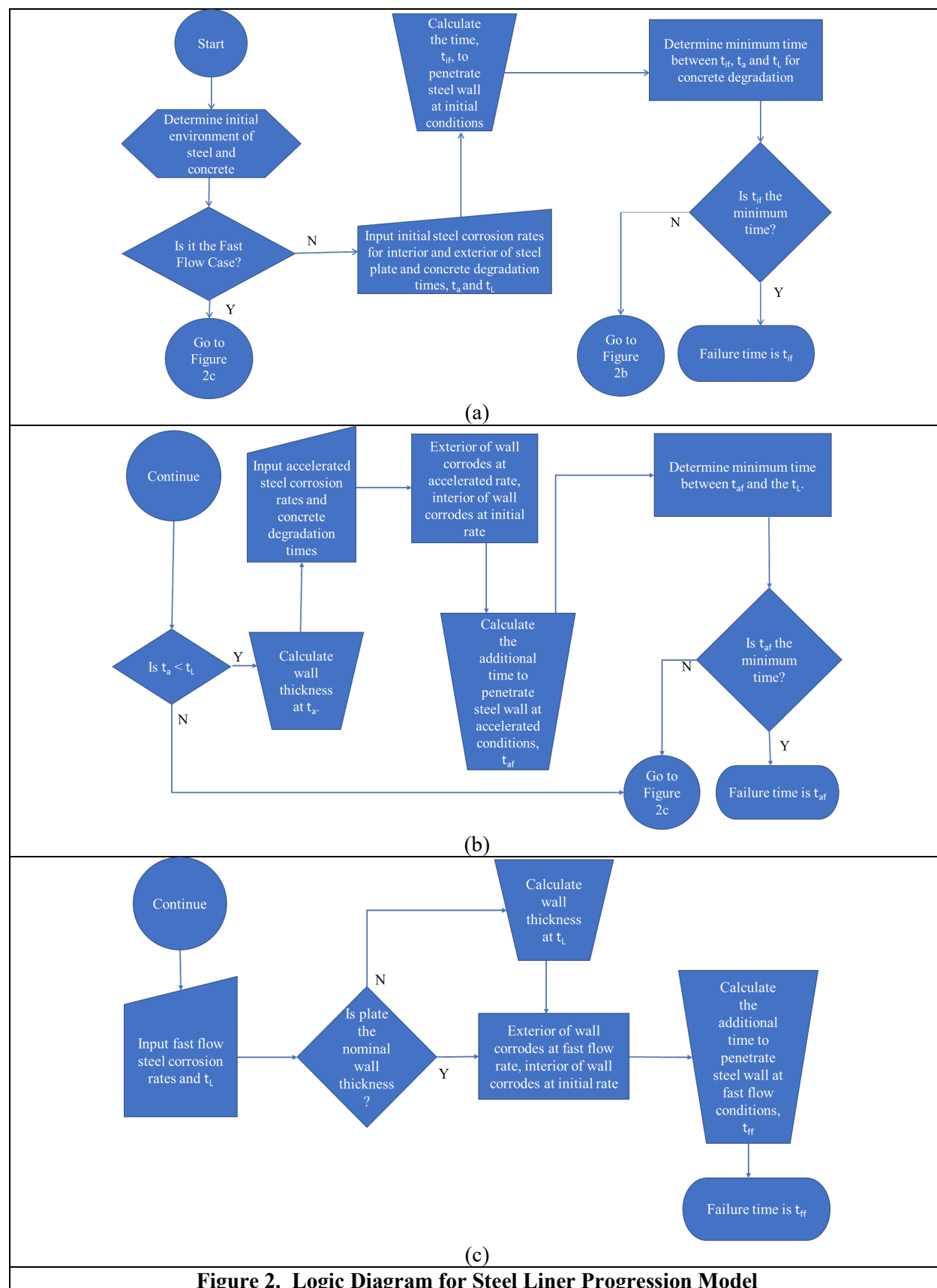


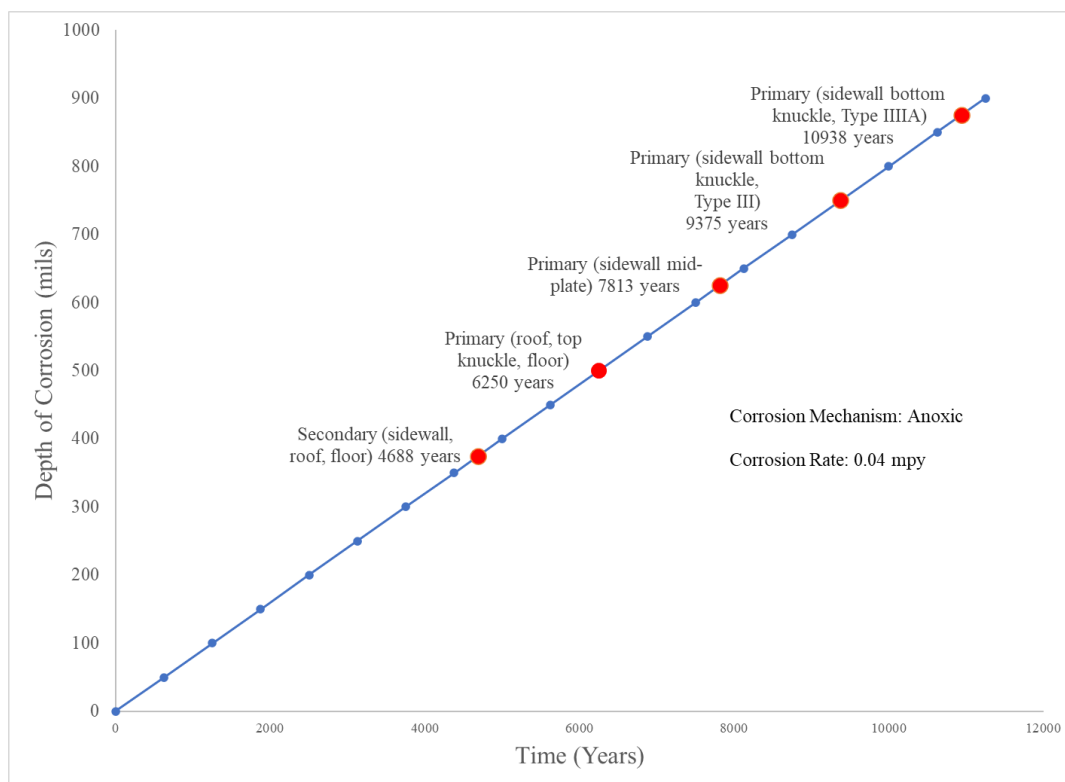
Figure 2. Logic Diagram for Steel Liner Progression Model

**Table 4. Summary of Failure Times for the Saturated Zone for the Scenario Cases by Tank Type**

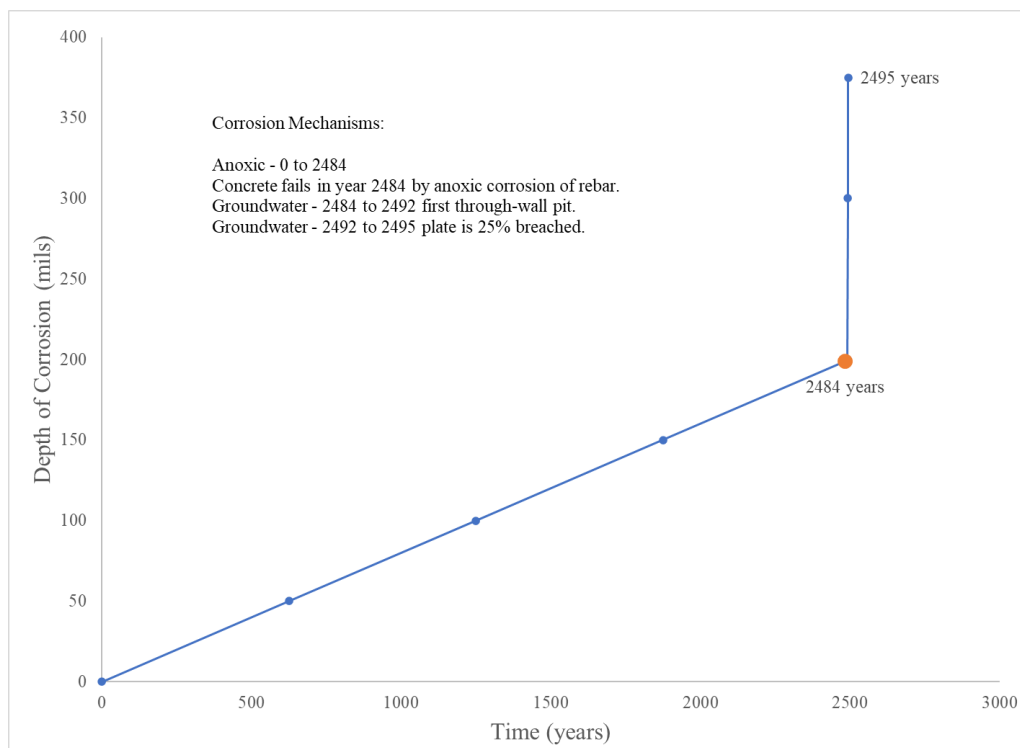
Tank Type	Saturated Zone			
	Realistic Case (years)	Compliance Case (years)	Pessimistic Case (years)	Fast Flow Path Case (years)
I	3929-6250	3929-6250	625-3941	13-65
II	6250-10938	6250-10938	704-6250	14-65
III/IIIA	4688-10938	4688-10938	625-6250	13-59
IV	2495-5469	2495-5469	852-2477	20-42

For the Compliance Case, the time to failure was dictated by general corrosion in the concrete/grout environment as well. There were three exceptions: the floor of the secondary and primary tank for the Type I tank and the floor of the Type IV tank. In these locations, the concrete degraded due to failure of the rebar, and thus did not meet the minimum diameter criteria for structural stability. The rebar had corroded by general corrosion. Once the concrete had degraded, the exterior of the floor was exposed to a groundwater environment. The floor of the liner achieved 25% breach, the criterion of failure for pitting corrosion, within 11 years after the concrete had degraded.

The Pessimistic Case and the Fast Flow Path Case both assume that gaps exist between the poured grout and the steel at various location in the tank (e.g., exterior of the primary tank wall). The Fast Flow Path additionally assumes that the concrete vault has degraded to the point that the tank steel is immediately exposed to groundwater in the soil. For the Pessimistic Case failure times ranged between 625 to 1136 years for all but the floor locations, which is approximately a factor of 5 reduction compared to previous scenarios. The failure times for the Fast Case decreased by 1-2 orders of magnitude, which demonstrates the significance of assuming that the concrete vault is protecting the steel from exposure to groundwater.

**Figure 3. Failure of Type III/IIIA Tank for Realistic Case**

The range of failure times in the vadose zone for each tank type and case study are shown in Table 5. For the Realistic Case, the failure occurred due to general corrosion in the concrete/grout environment similar to the saturated zone case. In this situation, both the interior and exterior sides of a plate of steel corroded at  $1 \mu\text{m}/\text{yr}$ . There are three exceptions noted: the floor of the secondary and primary tank for the Type I tank and the floor of the Type IV tank. As with the saturated zone case, the concrete degraded due to failure of the rebar, and thus did not meet the minimum diameter criteria for structural stability. The rebar had corroded by general corrosion as well. Once the concrete had degraded, the exterior of the secondary floor was exposed to a humid environment. The corrosion rate of the exterior secondary floor accelerated to the value for humid air, while the interior floor corroded at the low general corrosion rate. The general corrosion rate was taken to be the sum of these two corrosion rates or  $51 \mu\text{m}/\text{yr}$ . The floor of the primary wall continued to corrode at the low general corrosion rate until the floor of the secondary was penetrated at year 4008, for the Type I tank. At this stage the exterior floor of the primary was assumed to be under humid air conditions, and the rate of corrosion for the whole plate accelerated to  $51 \mu\text{m}/\text{yr}$ . This evolution is shown in Figure 5. The primary floor was penetrated by year 4095, which is about 90 years after exposure to the humid air. Clearly the groundwater is a more corrosive condition than humid air once the environment contacts the steel.

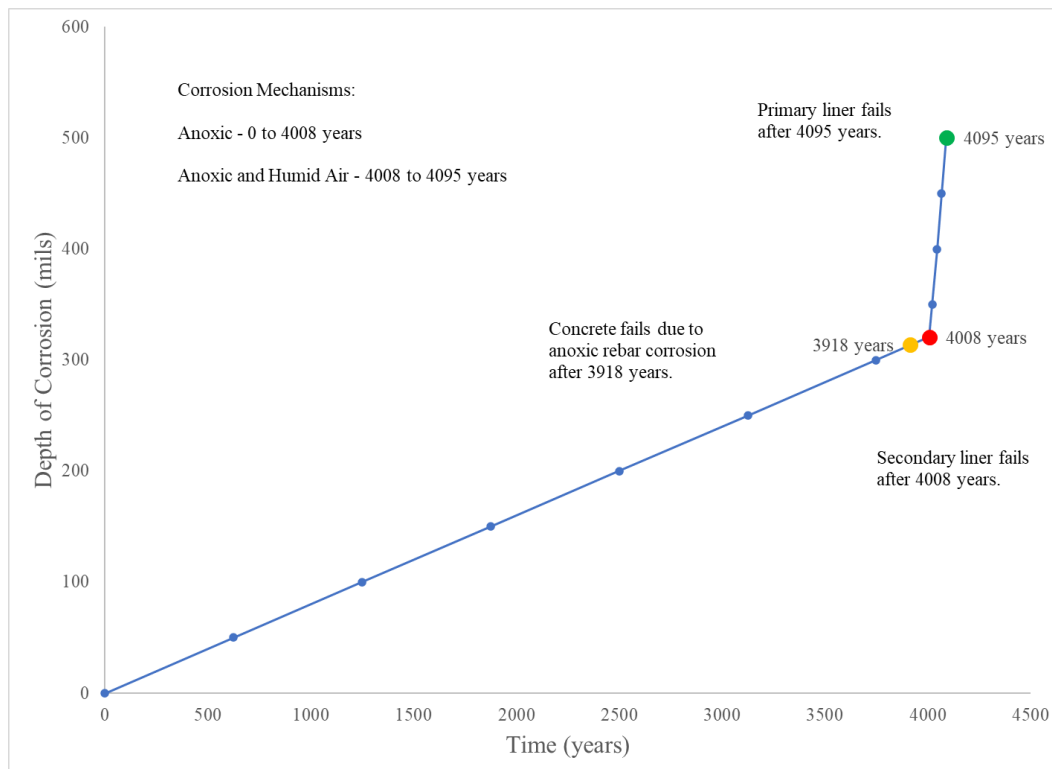


**Figure 4. Failure of Type IV Tank for the Saturated Zone, Realistic Case**

For the Compliance Case, the failure occurred due to a sequence of corrosion mechanisms. The most common sequence was 1) anoxic, passive corrosion, 2) carbonation, and 3) humid air. This sequence occurred on all but the primary tank sidewall. Figure 6 illustrates this progression for the sidewall secondary location of a Type III/IIIA tank. In this situation, both the interior and exterior sides of a plate of steel initially corroded at  $1 \mu\text{m}/\text{yr}$ . The carbonation front arrived at the exterior of the secondary wall in year 3657 and the corrosion rate accelerated to  $11 \mu\text{m}/\text{yr}$ . Before the secondary wall is penetrated, the concrete sidewall fails due to general corrosion of the rebar in year 3844. The plate was now exposed to humid air on the exterior side and the corrosion rate accelerated to  $51 \mu\text{m}/\text{yr}$ . Thus, failure occurred due to humid air on the exterior and anoxic, passive corrosion the interior in year 3860.

**Table 5. Summary of Failure Times for the Vadose Zone for the Scenario Cases by Tank Type**

Tank Type	Vadose Zone			
	Realistic Case (years)	Compliance Case (years)	Pessimistic Case (years)	Fast Flow Path Case (years)
I	4008-6250	2960-6250	625-850	123-502
II	6250-10938	4280-8719	704-1136	123-502
III/IIIA	4688-10938	3860-7751	625-1078	92-441
IV	2569-5469	1082-1127	263-367	181-226

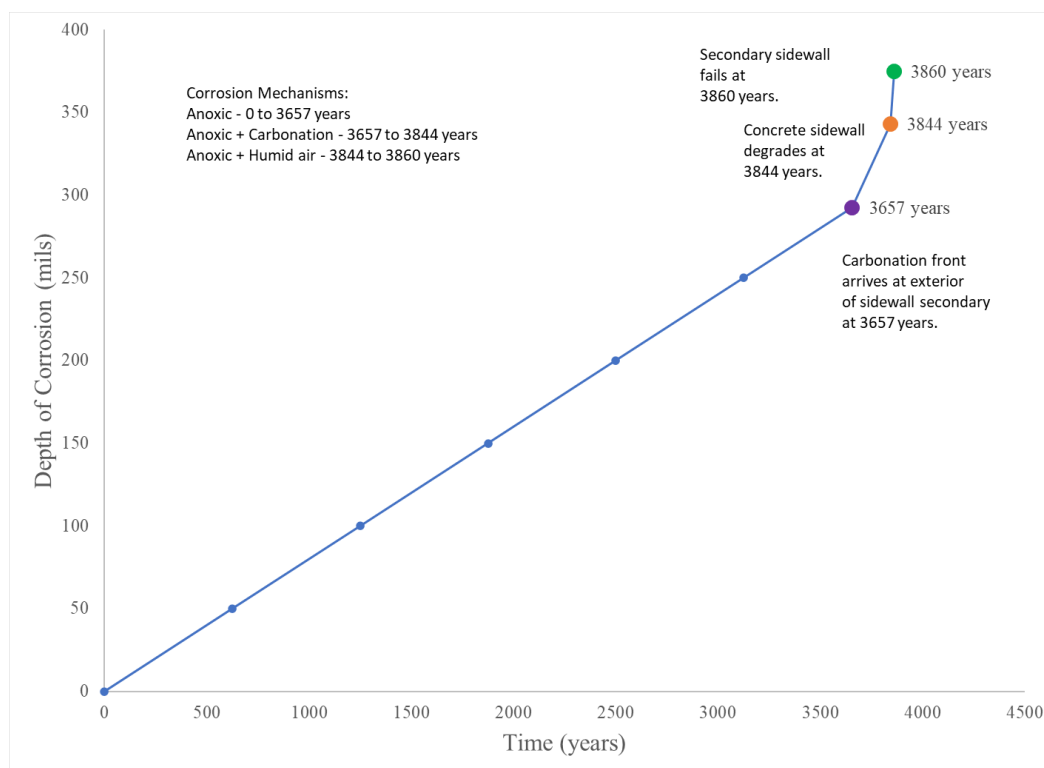
**Figure 5. Failure of Type IV Tank for the Vadose Zone, Realistic Case**

The primary sidewall was afforded more protection because of a 30-inch layer of grout that exists in the annulus between the secondary and primary wall. In this case the carbonation layer does not reach the exterior of the top plate of the primary wall before it is penetrated by anoxic, passive corrosion. The remaining plates of the primary wall are thick enough such that the carbonation front reaches the exterior wall before it is penetrated.

The final variant is seen in how the roof and floor are penetrated. In both situations, the secondary steel is penetrated by anoxic, passive corrosion. However, afterwards before the primary can corrode in the same manner, the rebar corrodes such that the minimum diameter requirement is not met and thus the concrete degrades. Thus, the exterior of the primary is exposed to humid air just before the wall is penetrated. These examples again show how the degradation of the steel and concrete are coupled together.

For the Pessimistic Case, indoor air is the predominant mechanism prior to complete degradation of the concrete. In fact, it is the only failure mechanism for the primary sidewall for the Type I, II and III/IIIA tanks. Because the concrete vault wall is thinner for the Type IV tanks, carbonation initiates corrosion on

the exterior secondary wall and causes complete degradation of the concrete, which allows humid air corrosion to fully penetrate the sidewall.

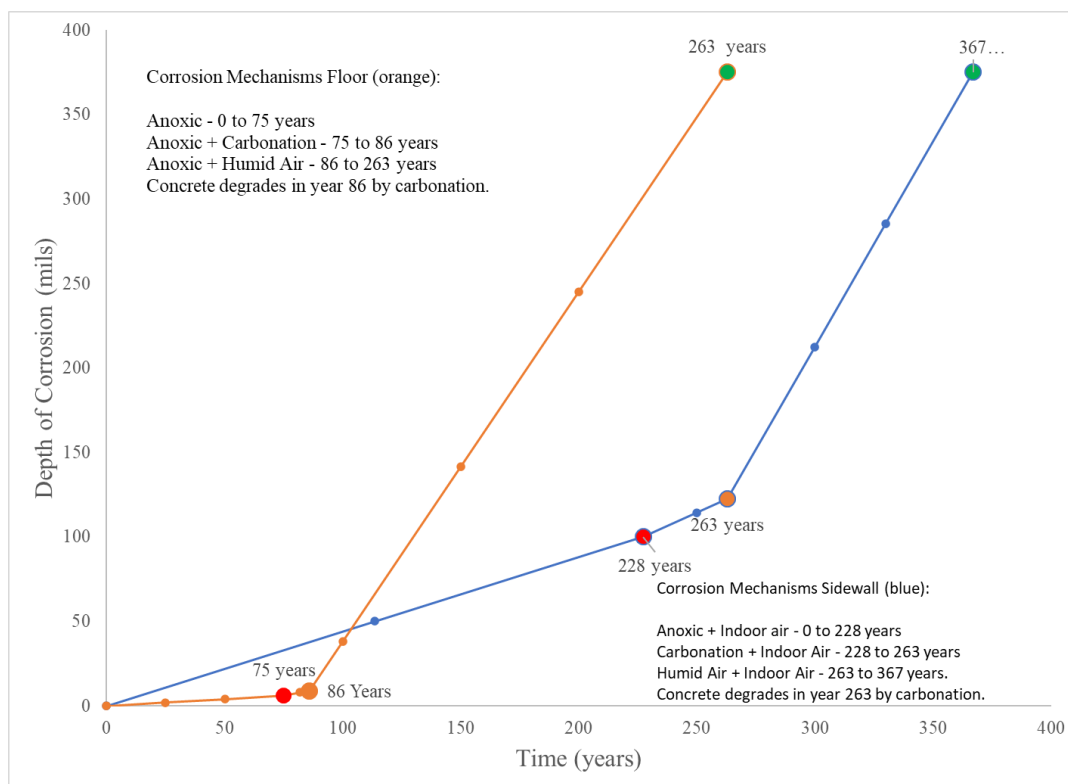


**Figure 6. Failure of Type III/IIIA Tank for the Vadose Zone, Compliance Case**

The secondary roof and sidewall may fail by a combination of anoxic, passive corrosion and indoor air provided the wall is thick enough (e.g., see Type II and III/IIIA tanks). For thinner concrete walls, such as the roof of the Type I tanks, the carbonation front reaches the exterior of the roof and results in degradation of the concrete prior to penetration. Thus, humid air corrosion also occurs for the roof of the Type I tanks.

Finally, time to failure calculations for the floor illustrate the effect of assuming the presence of structural cracks in the horizontal beam. It was assumed that the floor had structural cracks present on the exterior of the concrete vault, and thus the diffusion coefficient for carbonation was three times greater than a beam with no cracks (e.g., the sidewall). The effect can be demonstrated by comparing the time to failure for the Type IV tank sidewall and the Type IV tank floor (see Figure 7). Initially the sidewall corrodes at a faster rate because the interior is exposed to indoor air, while the floor corrodes at the low general corrosion rate. However, the carbonation front reaches the exterior of the floor much sooner than the sidewall (75 years vs. 228 years). The concrete floor completely degrades within 11 years and exposes the floor to the humid air condition, which accelerates corrosion significantly. Thus, the floor is predicted to fail in 263 years, while the sidewall fails in 367 years. This same effect is also seen when comparing the sidewall secondary and the floor secondary for the Type I, II, and III/IIIA tanks.

The concrete and grout provide essentially no protection, except that initially it was assumed that there was no grout shrinkage next to the floors. Thus, general corrosion could occur in these areas. Humid air results in a general corrosion mechanism and is not as aggressive as the groundwater. Once humid air corrosion commenced, the failure times were typically within 100-200 years.



**Figure 7. Failure of Type IV Tank for the Vadose Zone, Pessimistic Case**

This Fast Flow Case illustrated the effect of direct exposure of the steel plates to a corrosive humid air environment. The concrete and grout provide essentially no protection, except that initially it was assumed that there was no grout shrinkage next to the floors. Humid air results in a general corrosion at a rate of 51  $\mu\text{m}/\text{yr}$  and is not as aggressive as the groundwater. Once humid air corrosion commenced, the failure times were typically within 100-200 years.

## CONCLUSIONS

This analysis provided the following updates to the previous PA inputs for steel corrosion. The Central Scenario for the PA analysis includes three postulated cases: 1) Realistic Case, 2) Compliance Case, and 3) Pessimistic Case. This work also included a Fast Flow Path Case. The latter case considered the circumstance where the initial condition of the concrete was in a completely degraded state and that grout shrinkage exposed the steel to the soil environment. In effect, the steel was unprotected by the concrete and grout. The cases have various degrees of conservatism considered. Chemical, physical and tank configuration parameters were investigated to understand their effects on the predicted time to release of the contaminants. The assessment reviewed the initial tank and steel configuration, service life degradation of the steel, and potential corrosion mechanisms associated with degradation of the concrete materials.

There is a strong link between the degradation of the concrete and steel corrosion rate. Likewise, there is a link between the steel corrosion and the degradation of the concrete. This steel liner progression model coupled two degradation models to provide SRR with an estimate of barrier failure times important in controlling the release of radioactive contaminants. The models make simple assumptions regarding the corrosion response to a change in the environment and the effects of cracks on the corrosion rate. These assumptions could be refined further to reduce uncertainty in the predicted times.

## REFERENCES

1. Savannah River Remediation, LLC, "Performance Assessment for the F-Tank Farm at the Savannah River Site," SRS-REG-2007-00002, Savannah River Remediation, Aiken, SC, March 2010.
2. Savannah River Remediation, LLC, "Performance Assessment for the H-Area Tank Farm at the Savannah River Site," SRR-CWDA-2010-00128, Rev. 1, Savannah River Remediation, Aiken, SC, November 2012.
3. M. E. Denham, "Evolution of Chemical Conditions and Estimated Solubility Controls on Radionuclides in the Residual Waste Layer During Post-Closure Aging of High-Level Waste Tanks," SRNL-STI-2012-00404, Savannah River National Laboratory, Aiken, SC, August 2012.
4. C. A. Langton, "Chemical Degradation Assessment of Cementitious Materials for the HLW Tank Closure Project," WSRC-STI-2007-00607, Savannah River National Laboratory, Aiken, SC, September 2007.
5. C. A. Langton, "Chemical Degradation Assessment for the H-Area Tank Farm Concrete Tanks and Fill Grouts," SRNL-STI-2010-00035, Savannah River National Laboratory, Aiken, SC, January 2010.
6. K. H. Subramanian, "Life Estimation of High Level Waste Tank Steel for F-Tank Farm Closure Performance Assessment," WSRC-STI-2007-00061, Rev. 2, Savannah River National Laboratory, Aiken, SC, June 2008.
7. B. L. Garcia-Diaz, "Life Estimation of High Level Waste Tank Steel for H-Tank Farm Closure Performance Assessment," SRNL-STI-2010-00047, Savannah River National Laboratory, Aiken, SC, March 2010.
8. G. Flach, "Chemical and Physical Evolution of Tank Closure Cementitious Materials," SRR-CWDA-2021-00034, Savannah River Remediation, Aiken, SC, 2021.
9. D. L. Parkhurst, and C. A. Appelo, Description of input and examples for PHREEQC version 3—A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: U.S. Geological Survey Techniques and Methods, book 6, chap. A43, 497.
10. B. Lothenbach, "Cemdata18: A chemical thermodynamic database for hydrated Portland cements and alkali-activated materials," *Cement and Concrete Research*, vol. 115, pp. 472-506, 2019.
11. E. Giffaut, "Andra thermodynamic database for performance assessment: ThermoChimie," *Applied Geochemistry*, pp. 225-236, 2014.
12. F. Uddin, "Effect of Cracking on Corrosion of Steel in Concrete," *International Journal of Concrete Structures and Materials*, 2018.
13. B. Gerard, "Influence of cracking on the diffusional properties of cement based materials. Part I: Influence of continuous cracks on the steady state regime," *Cement and Concrete Research*, vol. 30, pp. 37-43, 2000.
14. H. Cho, "Estimation of Concrete Carbonation Depth Considering Multiple Influencing Factors on the Deterioration of Durability for Reinforced Concrete Structures," *Advances in Materials Science and Engineering*, vol. 2016, p. 18, 2016.
15. V. Carevic, "Influence of loading cracks on the carbonation resistance of RC elements," *Construction and Building Materials*, vol. 227, pp. 1-12, 2019.
16. J. Gonzalez-Sanchez, "Indoor atmospheric corrosion of carbon steel and copper in tropical humid climate," in *Environmental Degradation of Infrastructure and Cultural Heritage in Coastal Tropical Climate*, 2009, pp. 35-51.
17. T. M. Sullivan, "Assessment of Release Rates for Radionuclides in Activated Concrete," BNL-71537, Brookhaven National Laboratory, Upton, NY, 2003.