

Case Study of Corrosion Rates of an Externally-Heated Sulfur Storage Tank

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Abstract

A major petroleum company's gulf coast refinery experienced rapid corrosion of their sulfur storage tanks resulting in shortened service life and additional maintenance costs. The corrosion mechanism was driven primarily by the presence of sulfur and water on the interior surface of the tank. Maintaining the entire tank wall and roof above the freezing point of sulfur was expected to prevent corrosion. In 2006, the petroleum company chose to heat a new sulfur storage tank using CSI's ControTrace™ external heating system. ControTrace was chosen due primarily to its ability to maintain a uniform tank surface temperature. After nine years of operation, The petroleum company performed an internal inspection of the same sulfur tank. Corrosion of the roof and shell was found to be negligible. The remaining life of the tank shell and roof is expected to exceed 70 years. This paper will review the design approach for heating this sulfur storage tank and the inspection results for confirming its operation.

Table of Contents

Challenges of Sulfur Storage Tanks
ControTrace Sulfur Tank Heating Solution
The Petroleum Company's Historical Experience
The Petroleum Company's Search for a Better Way
The Petroleum Company's New Sulfur Tank
Comparison Tank
Key Lessons Learned
References

Challenges of Sulfur Storage Tanks

There are several unique challenges associated with storing sulfur in field-erected tanks. The most significant challenges are those related to safety and those related to maintenance. Over the last decade, sulfur tank safety concerns have become more widely considered with more publications describing the concerns. The primary safety concerns are as follows:

Accumulation of H₂S in the tank vapor space – Explosion and Exposure

Sulfur produced via the modified Claus process will contain high levels (up to 500 ppmw) of dissolved and chemically integrated H₂S. Unless the sulfur goes through an additional degassing process, it will slowly release the H₂S into the vapor space as a gas. The lower explosion limit (LEL) of H₂S gas mixed with air is roughly 4 vol% (though it changes with temperature and other factors). Additionally, H₂S in air is lethal at concentrations as low as 500 ppm. It is therefore critical that the accumulation of H₂S gas in the tank vapor space be addressed.

Providing the tank with an inert vapor space (e.g. nitrogen blanket) is one method of addressing the LEL concern. However, this method still allows a significant build-up of H₂S gas to accumulate. This build-up could present an explosion hazard if oxygen (air) were to be inadvertently introduced; it could also present a health hazard if the vapor were to be inadvertently released. For these reasons, and other reasons described later, a continuous sweep of ambient air is the more preferred method of handling the tank vapor space.

The required rate of sweep air is calculated based on the sulfur turn-over rate in the tank, the maximum resulting H₂S release rate, and the vapor turn-over rate required to stay below the 4 vol% LEL. Excessively high sweep rates should generally be avoided as they place a significant heat load on the tank which can lead to sulfur freezing and blocking nozzles / vents, as well as corrosion – both of which can result in additional safety hazards (more on corrosion below).

This sweep air arrangement can be implemented in one of two forms: A 'forced sweep' uses an ejector or blower to move air through the tank and deliver it to a safe location for release or processing. A 'free convection sweep' uses strategically-located vents to induce a draft that pulls air through the tank and releases it from a vent in the roof. Free convection sweep is typically preferred where the sulfur is expected to have minimal H₂S content. Forced sweep is typically used where the sulfur is expected to have high H₂S content and the exhaust vapor must be treated for health, safety, and environmental reasons.

A final point regarding H₂S accumulation is the need to avoid ignition sources. Sulfur has a relatively low electrical conductivity and can therefore build up a static charge – especially if it is allowed to free-fall. The use of a dip-tube is recommended where sulfur is supplied from a roof nozzle. A second common ignition source is various forms of pyrophoric iron sulfides (more on these below).

Accumulation of pyrophoric material – Fire and Explosion

When combined, sulfur, steel, and water react together to form various iron sulfides. These sulfides are pyrophoric – when exposed to oxygen, a rapid exothermic oxidization reaction occurs. With a sufficient mass of accumulated sulfides, the temperature resulting from the oxidation reaction can be high enough to ignite H₂S in the vapor space or ignite the sulfur itself. To avoid this scenario, either the accumulation of sulfides or the oxidation of sulfides must be prevented.

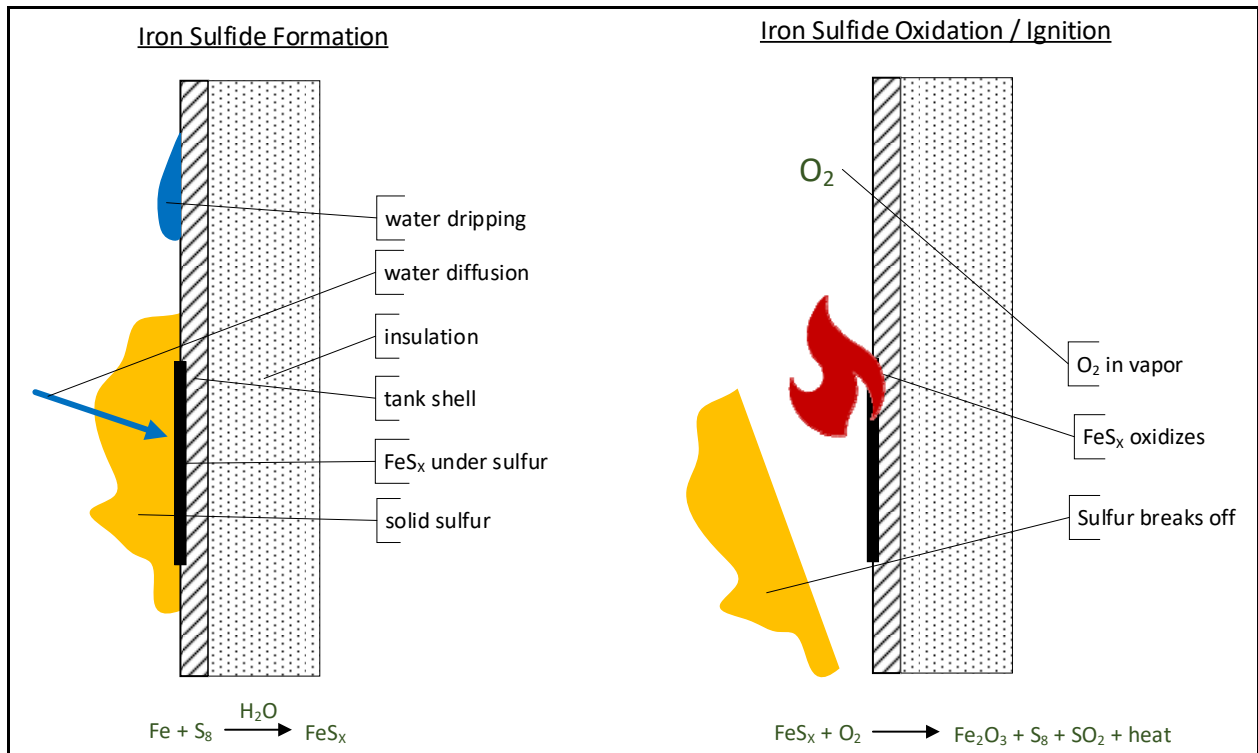


Figure 1: Iron sulfide ignition mechanism

One method of preventing the formation of iron sulfides is to maintain all carbon steel surfaces above 100°C (212°F) to prevent the accumulation of liquid water. The presence of sulfur can frustrate efforts to this end as solid sulfur that builds up on the interior surface insulates the wall and drives down the temperature. Water vapor can penetrate the porous sulfur, condense at the wall, and form iron sulfide. Worse yet, iron sulfide formed in this manner can accumulate in large masses that are only exposed to oxygen when chunks of sulfur fall away from the wall. These large masses of sulfides reach very high temperatures when they suddenly oxidize together.

A better approach is to maintain all carbon steel surfaces above 120°C (247°F) to prevent sulfur from freezing. This prevents the formation of iron sulfides. Even if some small cold spots exist, without large sections of solid sulfur accumulation, it is unlikely that large masses of iron sulfide will form. Small masses of iron sulfide not buried under frozen sulfur are typically not a problem; they tend to oxidize as they form and never reach the critical mass needed to achieve dangerously high temperatures.

One might attempt to stop the iron sulfide formation by removing water from the system. Unfortunately, this approach is not likely to succeed as there are numerous potential water sources, including:

- Leaking internal steam coils
- Inadequate vent caps
- Damaged tank roof or nozzles
- Humidity in ambient air
- Oxidation of H₂S where: $\text{H}_2\text{S} + \text{O}_2 \rightarrow \text{H}_2\text{O} + \text{SO}_2$
- Rust-catalyzed break-down of H₂S where: $\text{H}_2\text{S} + \text{O}_2 \rightarrow \text{S}_8 + \text{H}_2\text{O} + \text{SO}_2$ (note this is highly simplified as there are several reaction steps with several intermediate FeO_x and FeS_x molecules)
- Use of snuffing steam

Use of an inert vapor space (nitrogen blanket) will prevent the ignition of iron sulfides. However, this is generally considered to carry significant risk as without oxygen, any sulfides that do form will accumulate over time. When the nitrogen blanket is removed (intentionally or unintentionally) and oxygen enters the tank vapor space, there may be a very large mass of accumulated sulfides available; these will likely burn at a very high temperature, increasing the risk of a tank fire. Using an ambient air sweep will tend to oxidize the sulfides as they form via the mechanism described above and is generally considered the safer approach.

Safety summary

While each sulfur tank application should receive a specific review, the following high-level recommendations should be considered for any sulfur tank application:

- Sweeping the vapor space with ambient air is generally preferred over an inert blanket.
- The sweep rate must be high enough to prevent the H₂S concentration from reaching the LEL.
- The sweep vapor must be handled in a way that does not present an HSE concern.
- The tank should be heated in such a way that the formation of iron sulfides is prevented or severely limited.
- The sweep air system (including tank nozzles) should be heated in such a way that prevents plugging.

Tank corrosion

The primary challenges to sulfur tank maintenance are corrosion and plugging. Problems with plugging are immediately evident and can be addressed with adequate heating. Problems with corrosion can progress undetected and result in extensive damage as well as potentially hazardous material release events. There are several different corrosion mechanisms that can contribute:

Internal corrosion can occur due to the iron sulfide reaction described above. This generally occurs in the vapor space and can occur rapidly.

Internal corrosion can also occur in the more conventional manner due to the presence of water. Common sources of water are as discussed above.

External corrosion can occur due to ambient water exposure. This mechanism is not unique to sulfur storage. Water that penetrates the insulation may sit against the external tank surface for an extended period as evaporation from under the insulation will be slow. Field-erected storage tanks are also subject to water intrusion to the space between the tank bottom and the concrete pad (or ring-wall). Again, evaporation from this area will be slow and significant corrosion can result.

External corrosion can occur due to spilled sulfur. There are several mechanisms by which spilled sulfur can accelerate the corrosion of steel surfaces. Mixing sulfur and water can generate small amounts of sulfuric acid that eat through the steel. Together, sulfur, water and steel can react to decompose the steel and form iron sulfides as described above. Finally, thiobacilli bacteria can also produce sulfuric acid as they digest the sulfur. Sulfur tends to accumulate around the tank vents and on the ground at the base of the tank, these are the areas that tend to be most susceptible to this form of corrosion.

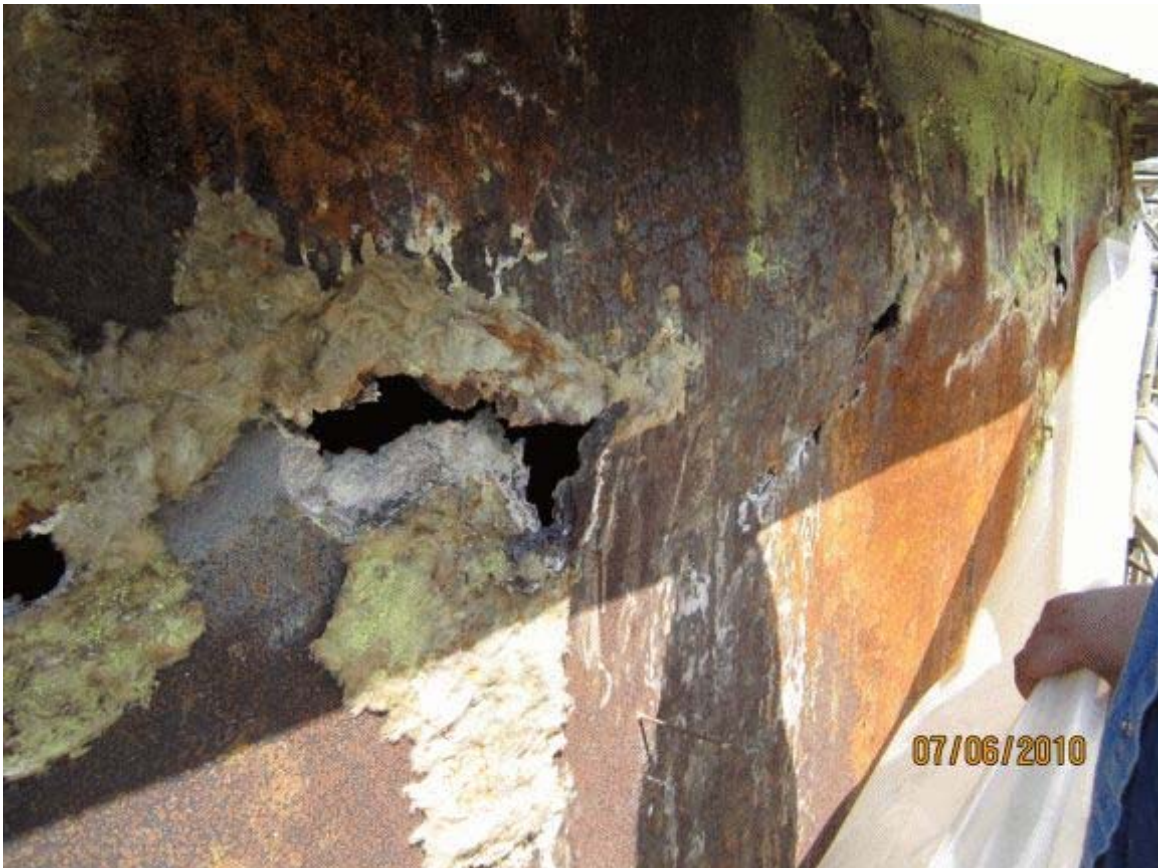


Figure 2: Example sulfur tank shell corrosion



Figure 3: Example sulfur tank structure corrosion

ControTrace Sulfur Tank Heating Solution

CSI has developed a tank heating technology utilizing ControTrace engineered bolt-on jacketing. The system uses a distributed heating arrangement that provides uniform heating to the entirety of the tank shell and roof surfaces. Nozzle and instrument heating can also be provided. The goal of the design is to address multiple safety and reliability concerns by addressing the various root causes:

- Prevent H₂S accumulation in the vapor space by heating of the vent nozzles. This prevents sulfur solidification in the nozzles that could restrict or block the vapor flow.
- Prevent iron sulfide formation by maintaining the shell and roof above 120°C (247°F) at all locations. This prevents sulfur solidification and water condensation which prevents iron sulfide formation.
- Prevent plugging of nozzles by providing direct heating.
- Prevent corrosion by maintaining the tank wall and roof temperature. Preventing water and sulfur condensation on the tank surfaces effectively blocks the corrosion mechanisms described above.

Additionally, the ControTrace external heating system provides heat directly to the liquid sulfur in the tank. This eliminates the need for internal coils, subsequently eliminating costly coil maintenance and potential water intrusion into the tank.

The ControTrace heating system is comprised of multiple heating panels, each comprised of multiple individual heating elements. The heating elements are spaced at a specified distance that maintains the tank wall temperature above the target temperature (typically 125°C) at all locations. Additionally, the panels themselves are shaped to fit closely together and to wrap closely around nozzles and other tank protrusions. In this way, all locations on the tank shell and roof are maintained above the target temperature.

Maintaining the liquid sulfur temperature typically requires additional heat input to offset the heat loss into the ground. The ControTrace heating panels located at the bottom of the tank wall typically utilize additional heating elements in order to provide the additional heat required. This is especially critical when the liquid level is low and the liquid contact area with the heated tank wall is reduced.

CSI determines the heating system design and predicts the tank temperatures utilizing a proprietary finite-difference model. The model accounts for all relevant heat paths to determine both the liquid and the vapor temperature in the tank. Also, the model calculates the tank shell and roof temperature profile based on a given ControTrace element spacing. In this way, not only is the sulfur temperature maintained, but also a uniform shell and roof surface temperature. CSI's thermal model was developed using CFD modeling to verify uniform sulfur temperature distribution within the vessel. The model has been validated with detailed field temperature measurements including infrared imaging.

With each panel custom-fabricated for the application, the ControTrace heating system has several major advantages over other external heating systems:

- The element spacing and panel locations are fixed; thus the wall temperature is assured at all locations.
- Each panel is an independent unit attached to a pre-determined location on the tank; thus removing any guesswork and minimizing the labor required to install the system.
- Panels are arranged in columns with a single steam circuit per column; thus minimizing the number of circuits and required steam infrastructure.



Figure 4: Example ControTrace tank roof heating

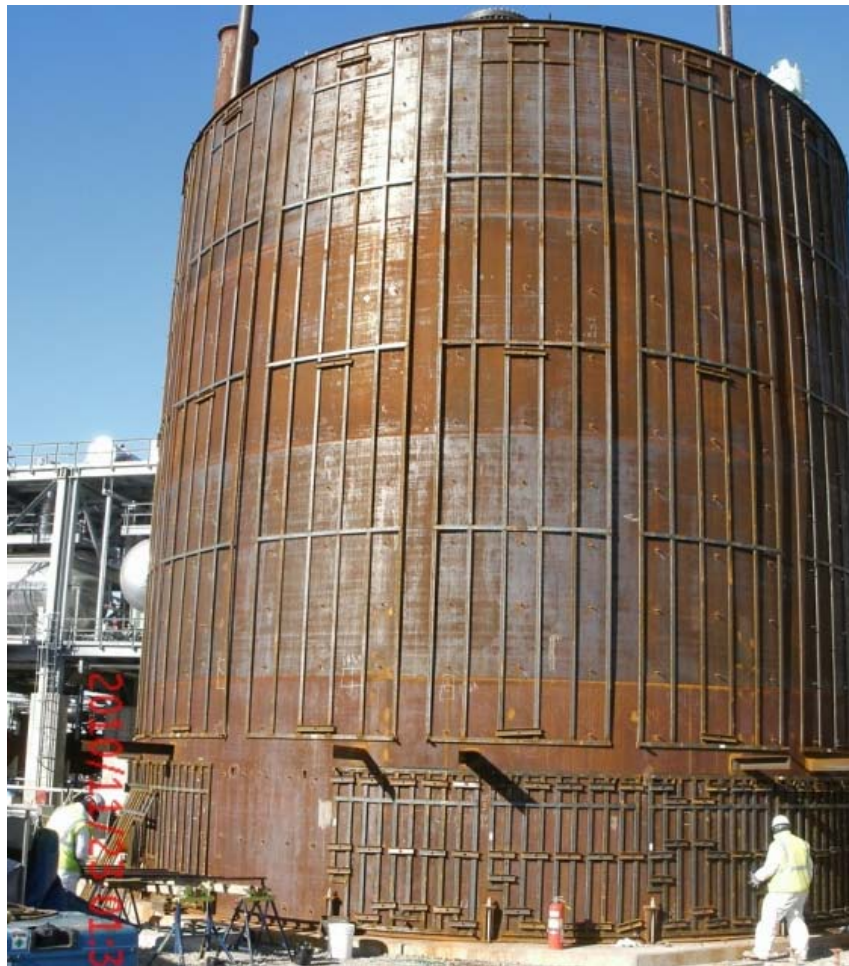


Figure 5: Example ControTrace tank shell heating

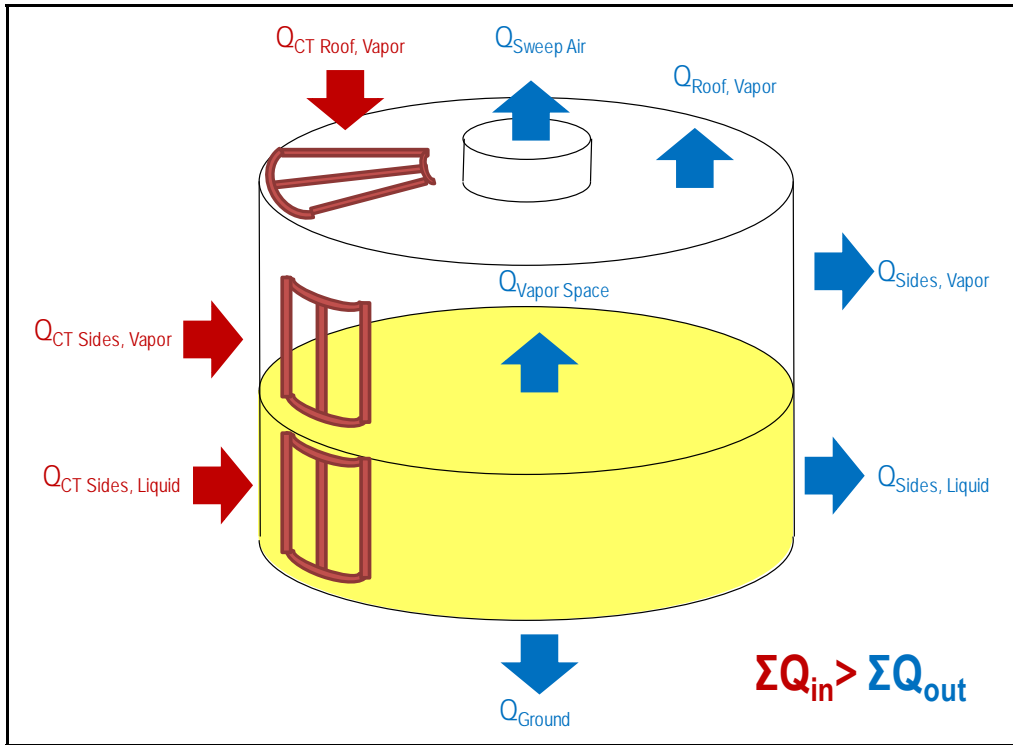


Figure 6: CSI Tank model macro-level heat transfer accounting

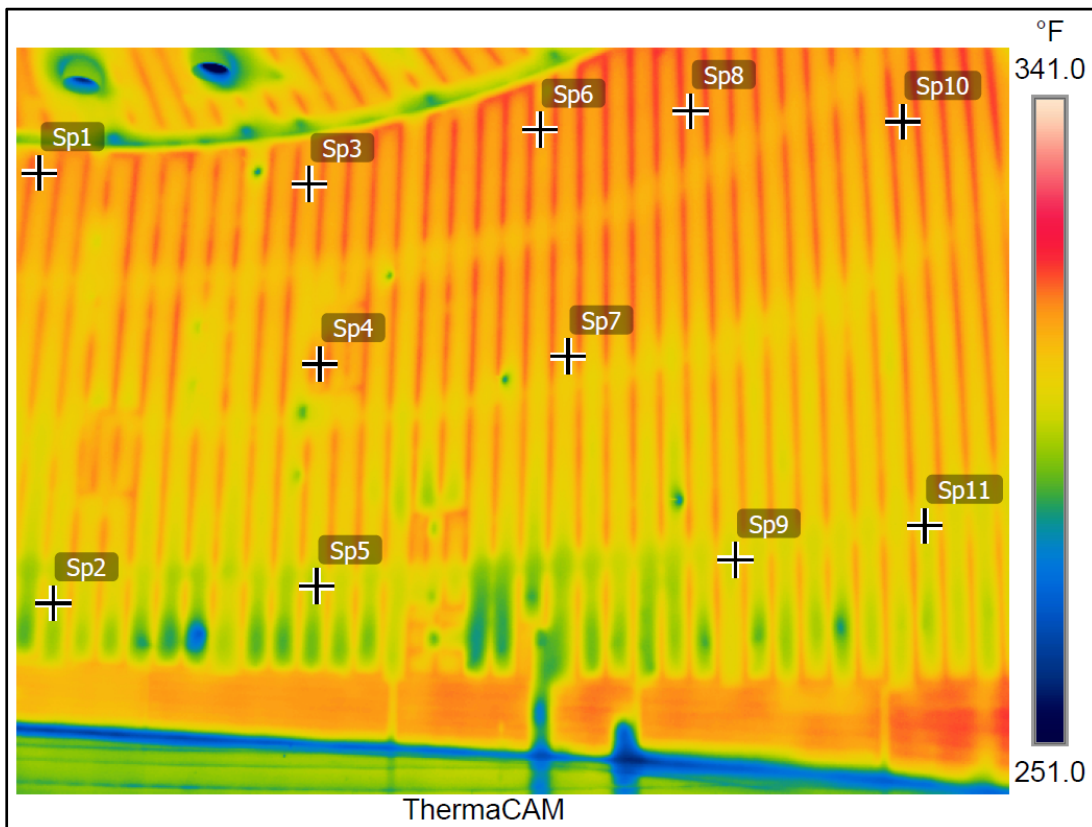


Figure 7: Thermal image of ControTrace-heated sulfur tank interior

The Petroleum Company's Historical Experience

Prior to 2006, sulfur tanks at the petroleum company's gulf coast refineries were heated primarily with internal steam coils. The tanks were fully insulated, but no additional methods were employed to maintain the wall or roof temperature. These tanks did not typically last longer than 10 years before full replacement was required due to extensive corrosion.

Corrosion would occur in several locations with the roof and upper shell being the most common. Corrosion of the roof and upper sidewall would occur both from the inside and from the outside. Corrosion from the inside was likely due to iron sulfide formation; corrosion from the outside was likely due to ambient water contact.

Additionally, the internal steam coil would occasionally fail and release steam into the tank. The increased moisture content would accelerate the formation of iron sulfide and compound the problems.

Repairs were typically required on a yearly basis to patch or replace corroded sections. Implementing repairs required that the tank be taken out of service and cleaned so that maintenance personnel could enter the tank. This process was both costly and disruptive to plant operations.

The Petroleum Company's Search for a Better Way

In 2006, a sulfur tank at one of the petroleum company's gulf coast refineries was identified as being beyond its usable service life; this sulfur tank was only 7 years old. The petroleum company started looking for an alternate tank heating method to apply to the replacement tank. This heating system needed to increase tank safety and reduce tank corrosion to extend the service life. Preventing the formation of iron sulfides was considered to be of primary importance as this would reduce the amount of flammable material in the tank as well as reduce the corrosion rate. The petroleum company established two key improvements that they wanted to see in a tank heating system:

1. The heating system should be configured in such a way that steam leaks would not introduce additional moisture to the interior of the tank.
2. The heating system should provide heat to the shell and roof.

At the time, CSI had extensive experience heating tanks and vessels using ControTrace panels; these were typically applications where the objective was process temperature maintenance. CSI also had extensive experience heating sulfur vapor and tail gas lines where the objective was to maintain a uniform pipe wall temperature. CSI's experience with sulfur tanks specifically, where the objective is both process and wall temperature maintenance, was limited to only

two prior applications in 2003 and 2005 (and one concurrent 2006 application). These were working well but were young enough that a detailed review of the tank condition had not yet been performed. Thus, the use of ControTrace on sulfur tanks was a relatively new technology.

The petroleum company recognized that CSI's ControTrace external heating system met and exceeded their criteria. Specifically, the ControTrace heating system not only provided heat to the tank shell and roof but did so in a way that assured a uniform surface temperature throughout. The petroleum company therefore chose this technology for their new sulfur tank at the gulf coast refinery.

The Petroleum Company's New Sulfur Tank

In 2007 the petroleum company commissioned a new sulfur tank at the gulf coast refinery. The tank is 40 ft diameter by 48 ft tall and fabricated from A36 carbon steel. Sulfur in the tank typically contains roughly 100 ppm H₂S. The tank utilizes CSI's ControTrace heating system designed to maintain the sulfur at or above 275°F (135°C) and the tank wall/roof surface at or above 255°F (124°C). The system is comprised of external, bolt-on heating panels applied to both the shell and the roof. ControTrace heating elements were also provided for various nozzles including the roof vents.

The ControTrace panels are attached with a combination of circumferential cables on the shell and studs on the roof. Overall, the installation went smoothly. A few improvements to the installation hardware were identified including: increasing the cable length, decreasing the stud length, providing extra attachment hardware near large nozzles where tank wall distortion is likely, and improving the instructional clarity of the documentation. CSI's current offering considers these and other design improvements.



Figure 8: The tank completed in 2007

In 2016 the petroleum company performed the first major inspection of this sulfur tank. No issues of concern were observed in the nine years of operation between 2007 and 2016. The inspection revealed corrosion of the tank floor, but no significant corrosion of the heated tank wall, roof, or nozzles. Highlights of the inspection by tank region are as follows:

Tank External

Insulation deterioration was noted at several locations. One quadrant of the roof had particularly poor insulation; regular water intrusion was likely occurring in this area. At the base of the tank, significant corrosion was observed on the under-side of the chime (joint between the shell and the tank bottom). Additionally, sulfur was observed seeping out from under the tank at two locations around the tank perimeter. Some cracking and chipping of the concrete tank foundation was observed, particularly in the area closest to the tank base.

Tank Roof and Vent Nozzles

Ultrasonic wall thickness measurements were taken at 24 different location on the tank roof and 4 location on each vent nozzle. A light coating of rust was noted on both the internal and external surfaces, but there was no scale/pitting and UT measurements showed that no wall thinning had occurred. The vents were all clear with no significant sulfur build-up.

Tank Shell

Ultrasonic wall thickness measurements were taken at 156 different location on the tank shell. Again, a light coating of rust was observed on both the internal and external surfaces. Wall thinning of the shell was observed only on the bottom 1 inch near the chime. Wall thinning in this region was calculated to be occurring at a rate of 0.0034 in/yr. At this rate, the tank wall thickness is projected to drop below the design thickness in the year 2082.

Tank Floor

Ultrasonic wall thickness measurements were taken at 209 different locations on the tank floor. Measurements at 32 of those locations showed that the floor thickness was at or below the design thickness. All 32 of these locations were within 1 inch of the chime. A single through-hole was found - also at the tank perimeter. The corrosion of the tank bottom occurred primarily on the bottom-side of the plates (from the ground-up); the top surface of the plates was observed to be relatively corrosion-free.

Epoxy Coating

The tank utilizes an internal epoxy coating applied only to the tank floor and bottom 10 ft of the shell. The epoxy coating was mostly intact, but had failed around weld seams and a few other locations. No additional corrosion was observed in the areas where the coating had failed, leading to the conclusion that the coating is likely not providing much benefit.



Figure 9: Tank chime overview (bottom corner)



Figure 10: Corrosion and scale under tank chime



Figure 11: Typical interior shell/roof surface with light coating of rust

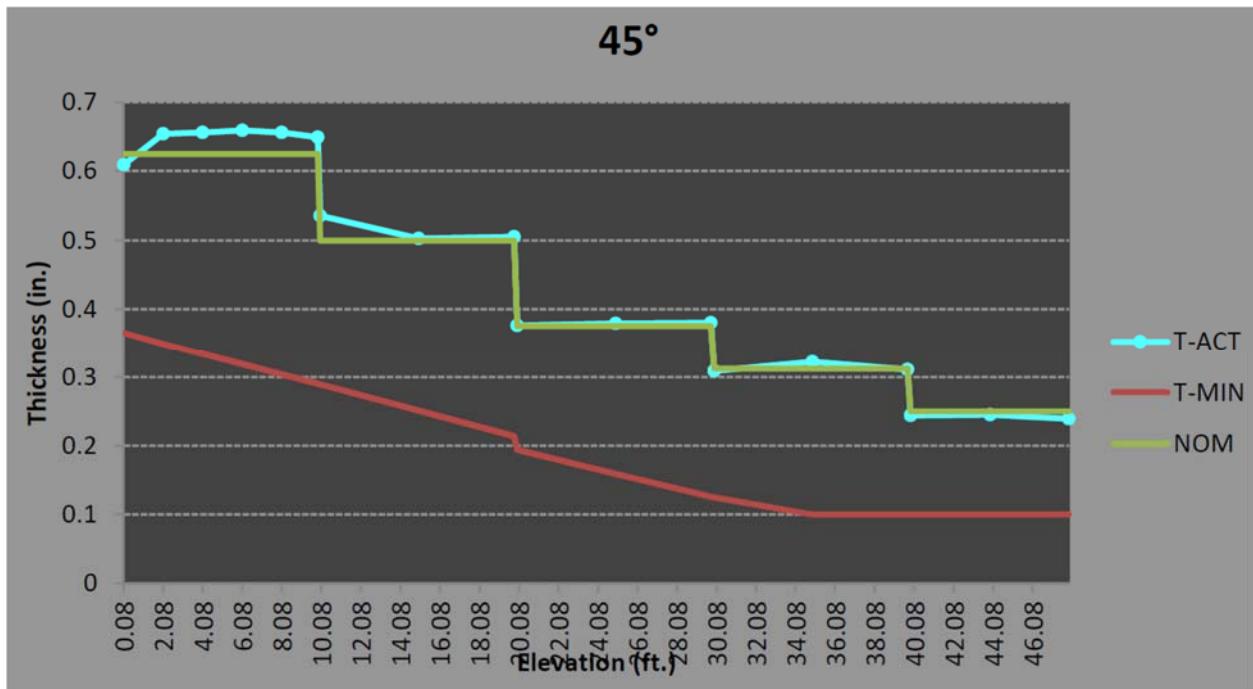


Figure 12: Tank shell measured thickness compared to nominal and minimum thickness; note single point of wall thinning at 0.08 ft elevation



Figure 13: Typical tank floor surface with bottom-up corrosion near perimeter; boxes mark UT measurement locations

Corrosion Mechanism

As can be deduced from the above observations, the only significant concern revealed by the inspection was the corrosion of the tank floor occurring from the outside-in. The mechanism for this corrosion is thought to be water and sulfur making their way under the tank from the outside. The concrete pad on which the tank sits is a significantly larger diameter than the tank and does not slope away from the tank. Rain water that falls on the pad sits up against the chime and seeps under the tank. The water by itself is likely to cause some corrosion of the tank floor. But if sulfur were to mix with the water, the corrosion rate would be accelerated. The hot tank bottom would likely drive off some portion of the water, leaving a more concentrated water/sulfur mixture. This mixture is likely to form sulfuric acid and/or iron sulfide. In either case, accelerated corrosion would be expected. Sulfur is observed to condense around the tank vents and occasionally spill as a result of maintenance activities. Thus, some quantity of sulfur is typically observed on the concrete pad. There is high confidence that the corrosion mechanism described above is accurate.

ControTrace Heating System Performance

The ControTrace heating system provides heat to the tank shell, roof, and vent nozzles. Of these surfaces, the only area that experienced corrosion was the bottom 1 inch of the tank shell. This result shows that the ControTrace heating system was effective at keeping the tank surfaces hot and preventing the corrosion mechanisms that had been experienced with previous sulfur tanks.

The corrosion on the bottom 1 inch of the shell is likely the result of three factors:

1. The diameter of the tank bottom is roughly 12 inches larger than the tank shell. Thus the floor plates extend out beyond the tank shell and insulation forming a thermal 'fin' that draws heat away from the bottom corner of the tank.
2. Water intrusion under the tank creates a significant heat load that also draws heat away from the bottom corner of the tank.
3. The tank insulation does not extend all the way down to the floor of the tank. A small section of the tank shell is left exposed further lowering the shell temperature at the bottom corner of the tank.

Tank Repairs

To address the tank floor corrosion, the petroleum company replaced the old 3/8" floor with a new 1/2" floor. The new floor is expected to provide a service life of roughly 10 years at which time it is likely to need replaced again. Other minor findings were addressed including replacing the insulation, applying a new internal epoxy coating, and sealing the cracks observed in the concrete pad. It is expected that sloping the pad away from the tank and changing the design of the bottom corner of the tank would significantly reduce the rate of floor corrosion. But it was decided that the cost of such changes could not be justified on an existing tank.

Comparison Tank

A separate (second) sulfur tank was also commissioned in 2007, this one located at a separate gulf coast refinery owned by the same petroleum company. Similar to the (first) tank discussed above, the petroleum company wanted to use an external heating system that would eliminate the internal coils and maintain the temperature of the shell and roof. To reduce cost, the petroleum company chose to use panel coils (or plate coils) to heat the second tank.

Panel coils are constructed from two plates that are stitched together to form a panel. Steam is applied to the space between the plates, and the assembly is attached to the exterior surface of the tank. Panel coils are practically limited to a rectangular profile; thus, they must be placed on the tank with considerable space between them to accommodate the tank roof geometry and to avoid nozzles. These gaps between the panels are large enough that the resulting tank surface temperature is non-uniform.

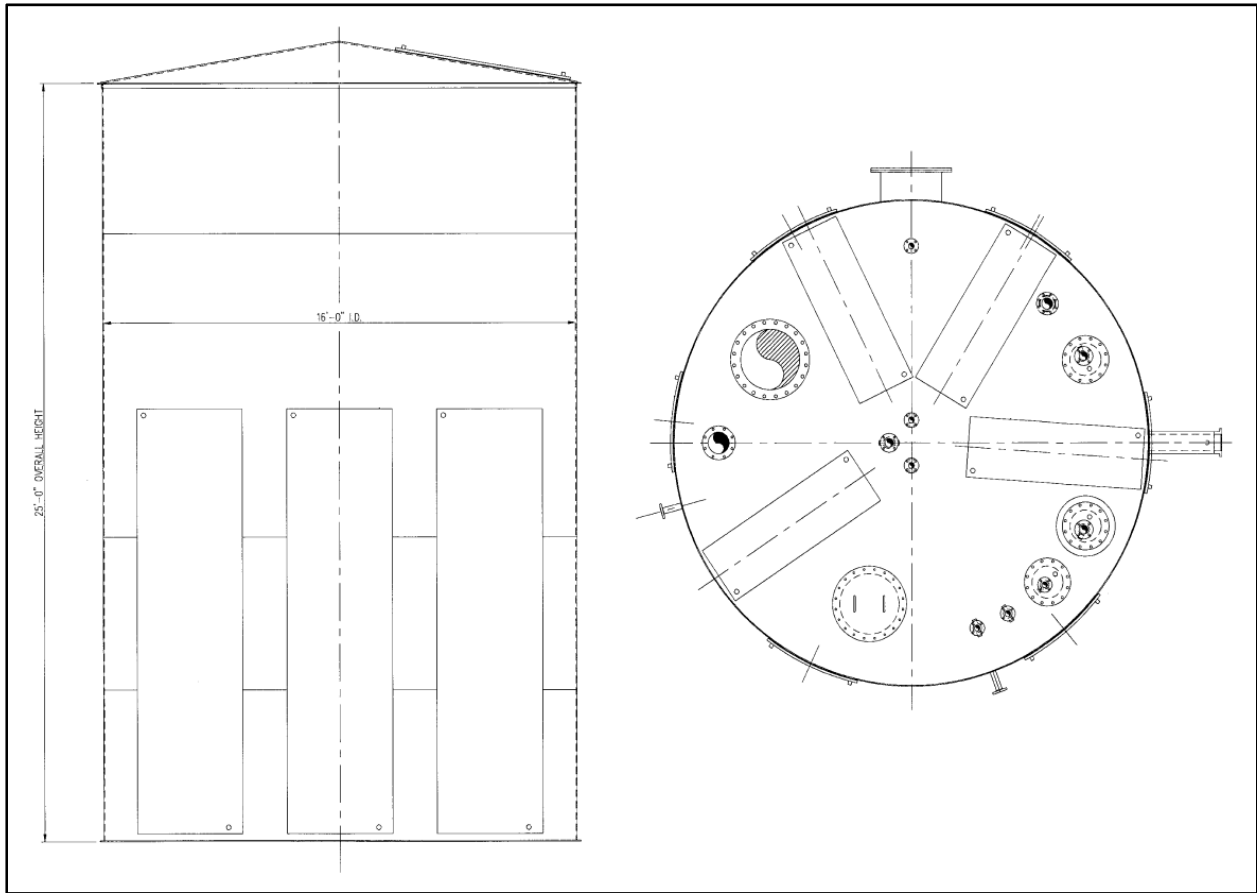


Figure 14: The second sulfur tank panel coil arrangement

In 2017, the second sulfur tank was inspected in the same manner as the first. The detailed report was not made available for review, but the following repairs were necessitated due to extensive corrosion:

- The complete tank roof was replaced; roof corrosion was most prominent around the nozzles.
- Two patches were required on the shell due to wall thinning.
- Two patches were required on the floor due to wall thinning.
- An annular ring was installed on the floor to address wall thinning at the perimeter.

Both ControTrace and panel coils effectively maintain the liquid sulfur temperature. But only the ControTrace system maintains a uniform wall temperature distribution. Contrasting the first and second tank highlights the benefit of keeping the tank surface above the freezing point of sulfur at all locations.

Lessons Learned

The petroleum company's tank experience leads to several key take-aways that can be applied to other sulfur tank applications:

1. Maintaining the tank shell, roof, and vent nozzles above the freezing point of sulfur should be a high priority. Without adequate heat, plugging of the nozzles can result in hazardous H₂S build-up in the vapor space, and sulfur on the wall/roof surface can result in the formation of pyrophoric iron sulfides and rapid tank corrosion.
2. The ControTrace tank heating system by CSI maintains a uniform temperature for the tank shell, roof, and vent nozzles. This approach can reliably prevent costly corrosion and the hazardous situations mentioned above.
3. The ControTrace tank heating system also effectively maintains the temperature of the liquid sulfur. While it was not discussed in detail in this report, this sulfur tank included internal steam coils as a back-up heating system, but they were never used.
4. The bottom corner of the tank is susceptible to corrosion due to a combination of heat loss and water/sulfur intrusion under the tank. Adopting some minor design changes to this area should reduce the corrosion rate significantly:
 - Slope the concrete foundation away from the tank; this will help prevent water/sulfur from seeping under the floor.
 - Design the tank chime area so that it does not protrude beyond the tank insulation; this will help maintain the temperature of the bottom corner.
 - Extend the tank shell insulation all the way down to the foundation; this will help maintain the temperature of the bottom corner. Foamglass or other water-proof insulation should be used where the insulation meets the ground.
 - Configure the tank vents and other equipment to minimize the amount of sulfur that drips on the concrete pad; this will help prevent sulfur from seeping under the floor. Minimizing the diameter of the concrete foundation is one method of achieving this.

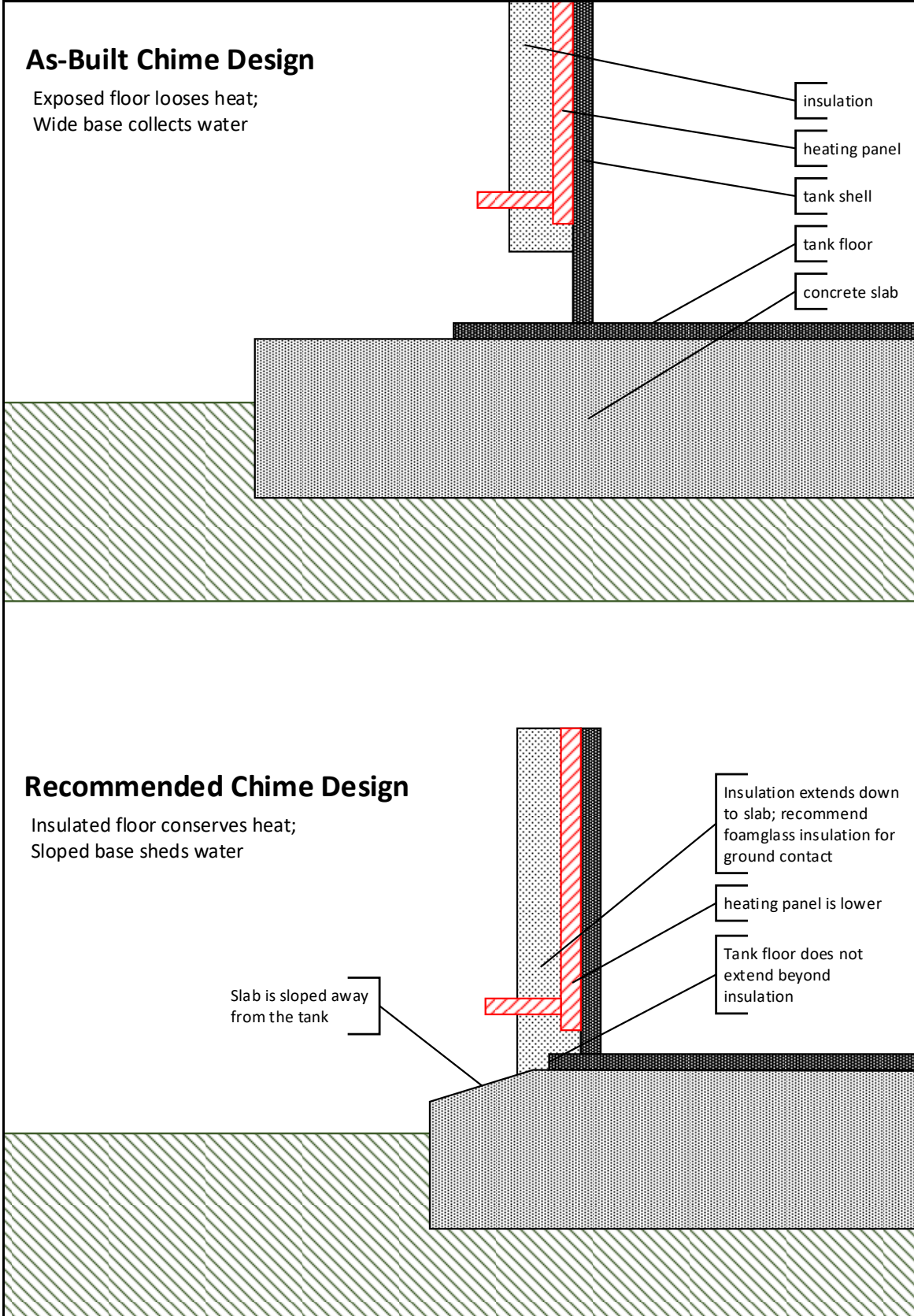


Figure 15: Summary of recommended changes to tank design to reduce floor corrosion

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