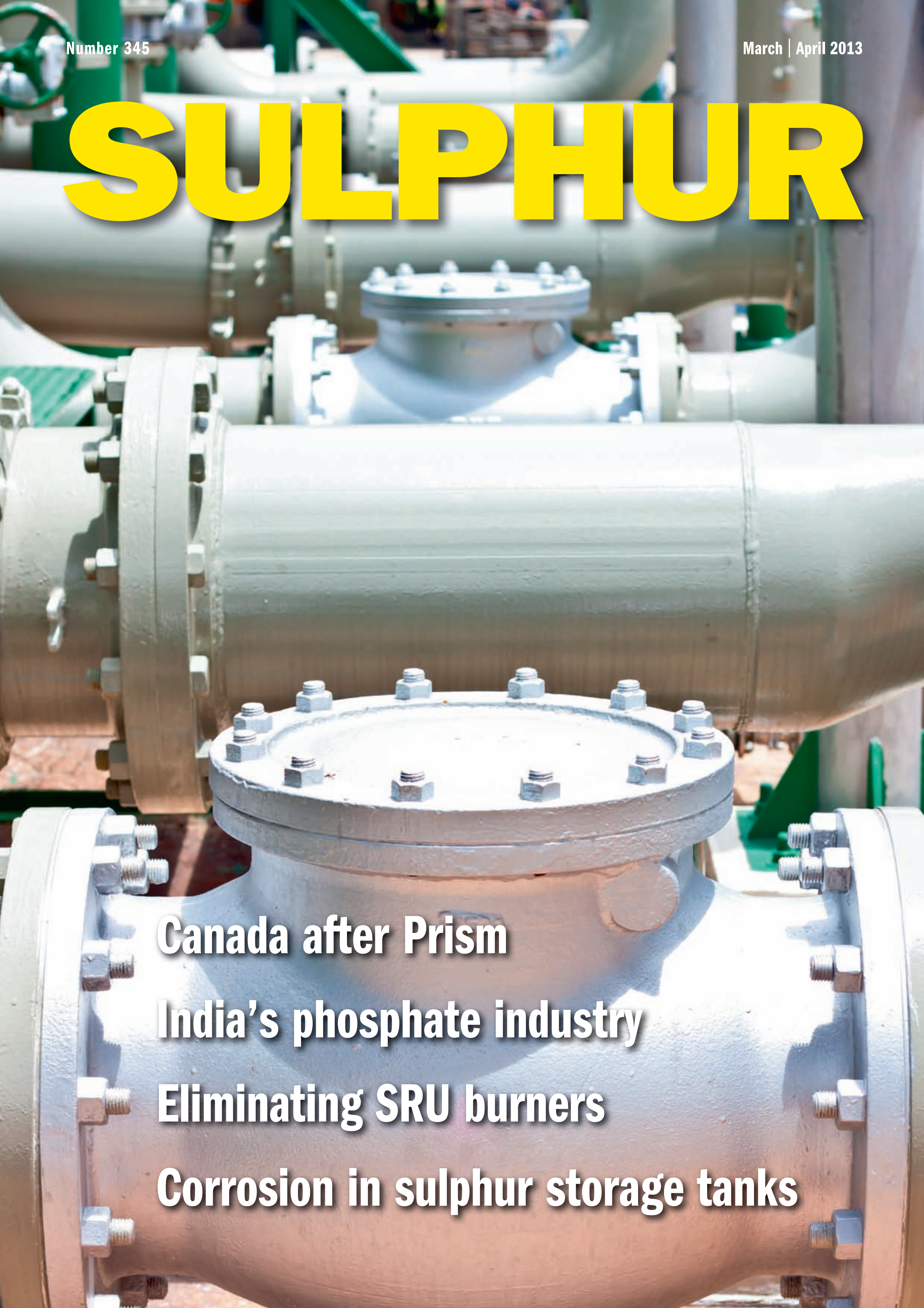
Number 345

March | April 2013

SULPHUR



Canada after Prism

India's phosphate industry

Eliminating SRU burners

Corrosion in sulphur storage tanks

Preventing corrosion in sulphur storage tanks

Corrosion is believed to be the leading root cause of safety, performance, and longevity issues associated with sulphur storage tanks. The most likely corrosion mechanism results from the combination of solid sulphur and liquid water at metal surfaces. This mechanism can be eliminated by employing a distributed external heating system such as ControTrace to maintain the temperature of all tank internal surfaces above 120°C. Other technologies for heating sulphur tanks can be effective in maintaining the sulphur in molten state, but they do not adequately heat all tank internal surfaces. In order to successfully design an external thermal maintenance system, the designer must have the capability of modelling the tank heat transfer paths and predicting the tank temperatures for the entire range of operating conditions. The success of the system is sensitive to the spacing of steam elements. The tank thermal maintenance model presented in this article by **P.D. Clark** of Alberta Sulphur Research Ltd, and **D. R. Hornbaker** and **T. C. Willingham** of Controls Southeast, Inc. has been validated with field data from multiple tanks

Storage tanks for liquid sulphur are utilised in many refineries and sour gas processing facilities for temporary storage of liquid sulphur produced in the sulphur recovery plant. They are usually constructed from carbon steel and insulated and heated to maintain the liquid at a temperature >125°C. Depending on the facility, the tank may receive liquid sulphur which has been treated to remove H_2S dissolved in the sulphur or it may be filled with undegassed product. These two cases present significantly different conditions in the tank as undegassed sulphur will slowly release H_2S causing that gas, along with sulphur vapour, to build up in the headspace of the tank. Usually, the tank will be drafted with air at a rate so as to limit the concentration of H_2S in the headspace. This sweep air, contaminated with small amounts of sulphur and H_2S, is then vented from the tank.

A typical sulphur storage tank does not store sulphur for long periods. In a refinery, such a tank is used to store liquid sulphur only as a holding point before shipping, forming or blocking. Thus, the tank is rarely full or empty. It is normally receiving sulphur and may be pumped down from several times a day to once every two or three days. Tanks in a sulphuric acid plant are more likely to hold liquid for a longer period, but that is still usually a matter of days. Of course, all tanks are susceptible to unusual conditions that can cause them to remain in most any condition for extended periods, and they must be heated to withstand these conditions.

Different heating methods are employed to maintain the sulphur in molten state. These methods range from internal submerged coils to external heating panels. Saturated steam is most always the heating medium utilised. Historically, heating methods have not considered the temperature of internal tank surfaces. The relationship between these surface temperatures and tank performance will be explored in this article along with the effectiveness of various heating methods to maintain these internal temperatures.

Common causes of failure

The primary cause of external corrosion of a sulphur tank is ambient water which invades the insulation and becomes trapped between the tank surface and the insulation. If the tank wall temperature is below 100°C, it will not vaporise the water; consequently, the water will be able to stagnate and continually corrode the surface. This type of corrosion is commonly experienced on the tank roof and walls when inadequate heating is supplied.

Other, less frequent causes of external corrosion of a sulphur tank result from interaction with either elemental sulphur or sulphuric acid that accumulates in the ground and base area surrounding the tank. Inevitably, some sulphur is spilled around a tank facility and, if not removed fastidiously, it can work its way into the surrounding base and soils. Contact of the sulphur with the steel will result in iron-sulphur contact corrosion at a rate, depending on temperature and other factors, of 50-300 mpy. The products, FeS and related sulphides, are readily oxidised by oxygen from the air so red iron oxide may be seen building up at the steel surface around ground level, although in most cases, it will not be visible because of the tank insulation. The chemistry of the sulphide oxidation is quite complex and

Fig 1: **Destruction of the tank wall**

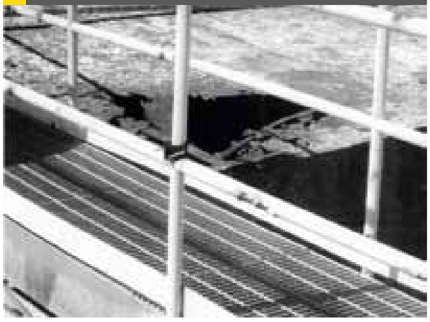
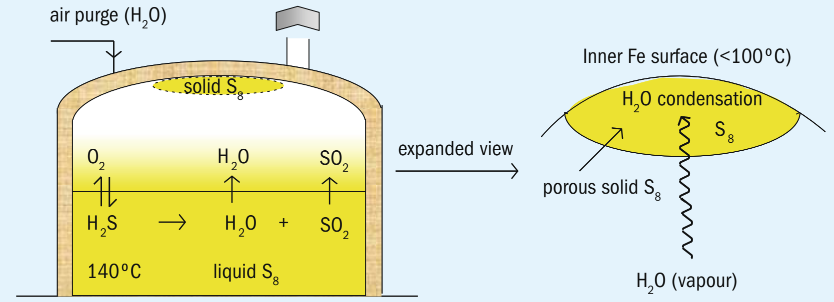


Fig 2: **Sulphur corrosion resulting from solid sulphur deposition**



Cooling of roof may result from removing liquid S_8 from the tank; most likely when only a steam coil is used to heat the sulphur

Solid sulphur insulates Fe surface allowing it to cool <100°C

H_2O diffuses through porous solid sulphur

Fe / S_8 contact corrosion

$Fe + S_8 \xrightarrow{H_2O} Fe + S_x$

further hydrolysis of ferric sulphates will cause the acidity of the surrounding area to increase very significantly. Thus the original FeS corrosion product may lead to tank corrosion by sulphuric acid.

One major mechanism for internal corrosion of a sulphur tank is attack of the steel by solid elemental sulphur that builds up on the interior tank walls (including the roof, side walls, and vent nozzles) in the vapour space above the liquid level. This can contribute to the destruction of the tank wall as shown in Fig. 1. How can solid sulphur accumulate inside a tank designed to store liquid sulphur? Overall, either the heating system and/or the tank insulation are inadequate to maintain the inner steel surfaces >115°C. In particular, such a situation may arise at the interior walls in the vapour space in a tank that has a steam coil immersed in the bottom of the tank. In this case, there are many heat transfer paths by which the heat from the submerged coil can be lost before it reaches the inner surfaces.

As is depicted in Fig. 2, a layer of solid sulphur may form at the cooler wall surface in the vapour space and, because of its excellent insulating properties, further prevent internal heat transfer to the metal surface from the hot components inside the tank. If the steel surface temperature continues to fall, water may condense at the steel/sulphur interface creating an ideal condition for iron/sulphur contact corrosion and formation of FeS. At first glance, it may seem that water condensation would be very difficult, but there are several sources of water and mechanisms for formation of conducting films that enhance iron/sulphur corrosion. Water may enter the system with the air purge, but it may also be formed by oxidation of H_2S either in the liquid sulphur or in the headspace. Thus, the amount of water in a tank will be related to the amount of residual H_2S in the liquid sulphur with undegassed sulphur leading to the highest quantities. A leaking internal steam coil can be a very large source of water. Water, as with the other gaseous components in the headspace, can diffuse through the solid sulphur and condense at the cooled steel surface thus creating the ideal conditions for iron/sulphur corrosion. In cases where SO_2 is present in the headspace of the tank, it too may diffuse through the solid sulphur combining with the water at the cooler steel surface creating a conducting microfilm of polythionic acids. Once iron/sulphur contact corrosion has commenced, the corrosion product, FeS_X, enhances the corrosion since it is able to conduct electrons between the iron and sulphur. Here, the subscript x denotes that the iron sulphide is a non-stoichiometric substance being able to function as a semi-conductor.

FeS formed by iron/sulphur contact corrosion is very pyrophoric such that a "quarter-size" lump will become red-hot when exposed to air. At least two scenarios can be imagined in which FeS that has built up inside a tank becomes exposed to air. Refilling of a tank with hot liquid sulphur may melt the solid sulphur at the roof or at another location exposing the FeS to oxygen. In this case, as the FeS oxidises it may ignite sulphur vapour or H_2S in the headspace of the tank leading to an "uncontrolled" combustion. Remelting, in combination with mechanical vibration, could dislodge the red-hot corrosion product such that it falls into the liquid sulphur starting a fire in the tank. This type of ignition has been noted by numerous field workers whenever FeS and liquid sulphur come into contact in the presence of air.

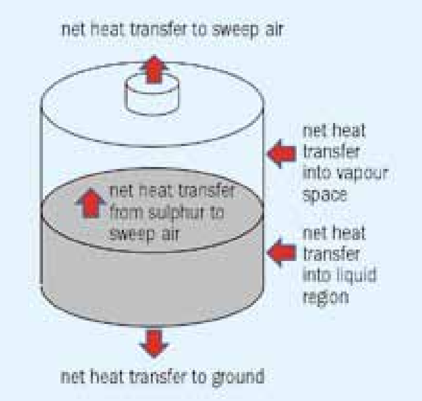
In one case at a refinery, it is believed that removal of liquid sulphur from the tank caused air to be sucked back into the tank through the vent cap, dislodging FeS at that location; the rapid heating of the FeS, caused a detonation within the tank that damaged it beyond repair. Clearly, build up of FeS in a sulphur tank is to be avoided.

Both external and internal sulphur tank corrosion can be complex processes with a variety of mechanisms in play. External corrosion may be prevented by ensuring that exterior wall surfaces are maintained >100°C and that elemental sulphur does not accumulate around the base of the tank. Design of the tank base should be not just for structural integrity but also to prevent accumulation of water around its base. Internal corrosion is the most likely cause of destructive tank corrosion. It can largely be avoided by ensuring that sufficient heat is delivered to system to prevent build up of solid sulphur inside the tank and at the vent points. The rest of this article is devoted to describing the best way of achieving this objective.

Evolution of heating systems

Thermal maintenance technology for sulphur tanks has evolved in response to a growing understanding of potential safety and performance issues. The first generation of tank thermal maintenance consisted of an internal submerged steam coil and external insulation. The steam coil was designed to replace the heat loss from a full tank. This method focused solely on maintaining the liquid sulphur temperature

Fig 3: **Model control volume and heat transfer paths**



and ignored the temperature of the tank wall, tank roof, internal support structure, and vapour space. Submerged coils were effective in maintaining the liquid sulphur temperature, but were prone to steam leaks over time. Furthermore, since the roof temperatures were not maintained above the freezing point of sulphur, tank roofs were known to cave in due to sulphur vapours condensing, freezing, and building up on the roof interior to a point which overstressed the roof's structural integrity.

In response to roof collapse, the second generation featured exterior steam coils on the roof to keep the roof interior wall temperature above the sulphur freezing point. However, the interior wall temperatures in the vapour space above the liquid level were not completely addressed. Cool temperatures continued to allow the build-up of solid sulphur on the interior walls as well as the failure to vaporise any ambient water which had invaded the insulation. Additionally, more sour oil and gas led to excess buildup of H_2S in tanks which, in turn, led to the requirement for sweep air. The low interior wall temperatures were exacerbated by cold sweep air swirling through the tank. Consequently, the risk of internal corrosion, fire, and explosion remained (as previously discussed).

The third (and current) generation of sulphur tank thermal maintenance features the design of external jacketing to heat the tank shell and roof. An external steam jacket is simply an external chamber that is attached to the tank. A heating medium (typically steam) is circulated through the jacket to transfer heat to the tank wall. Heat transfer mastic is commonly applied between the jacket and tank wall to improve heat transfer. External jacketing offers the flexibility of supplying heat to the specific parts of the vessel that require it. Additionally, if the external jackets are sized correctly, they can completely eliminate the need for an internal coil and any chance of cross contamination (steam leaks). External steam jackets are typically sized to cover a calculated percentage of the surface area to make up for heat lost to the ambient. After determining the amount of surface area required, the heated area is commonly distributed somewhat uniformly around the tank surface. There are currently two types of external jackets. One features a large, flat, bendable, steel sheet which contains steam passages. The other features a lattice work of rectangular tubing (trade name ControTrace) formed to fit a tank.

Tank thermal maintenance model

A sulphur storage tank presents a complicated heat transfer problem. Heat is lost from the sulphur through the tank bottom and into the ground, through the tank walls to the ambient, and to the internal vapour. Significantly more heat is lost to the internal vapour when the vapour space is swept to prevent a build-up of H_2S in the tank. The sweep air dynamics have a large influence on the vapour space temperature, and the vapour space temperature has a significant influence upon the internal wall temperatures. In order to evaluate the thermal maintenance effectiveness of various heating systems, a finite-difference computer model was developed to account for all of these heat transfer paths. In addition to modelling the various heat transfer paths, the model accounts for variables such as tank diameter, tank height, tank wall material, tank wall thickness, insulation type, insulation thickness, sulphur level, ambient air temperature, sweep air entering temperature, sweep air flow rate, internal heat transfer coefficient, external wind conditions, heating medium, and length of time tank has been in service (since this affects the heat loss into the ground). The model allows for heating via internal submerged steam coils and/or external steam jackets. In the model, each method of heat input can be applied separately or in combination. The model performs an energy balance on the molten sulphur section and the internal vapour section of the vessel simultaneously. The result of the calculation is the steady-state equilibrium temperature of the molten sulphur, vapour space, and minimum local tank wall temperature. Figure 3 shows the model control volume and heat transfer paths considered.

Comparison of heating systems

In order to demonstrate the wide range of internal tank temperatures which can exist, the tank thermal maintenance model previously described was run for four heating scenarios on a representative tank. The representative tank has a diameter of 10.8 m and height of 8.5 m. The tank is insulated with 100 mm of calcium silicate insulation, heated with 3.5 barg saturated steam, and subjected to a minimum ambient temperature of -18°C. The four heating scenarios evaluated are shown in Table 1.

Each scenario was analysed to determine the molten sulphur temperature, bulk vapour temperature, and tank wall temperature. In order to be considered successful, the thermal maintenance system must maintain all temperatures above 120°C to keep the sulphur molten and prevent solid sulphur build-up on internal surfaces which can lead to tank corrosion.

Table 1: **Heat scenarios evaluated**

	Scenario 1	Scenario 2	Scenario 3	Scenario 4
Heating system	**submerged coils**	**submerged coils**	**sheet panels with submerged coils**	**ControTrace panels**
Sweep air flow rate, cfm	0	145	145	145
Sweep air inlet temperature, °C	N/A	145	145	-18

Table 2: **Scenario 1: Modelled temperatures for various sulphur levels**

Sulphur level	$T_{Sulphur}$	T_{Vapour}	$T_{Min\ Wall}$
75%	141°C	118°C	100°C
50%	141°C	111°C	93°C
25%	141°C	101°C	85°C

Fig 4: **Exterior sheet panels applied to the tank shell**

Fig 5: **Exterior sheet panels applied to the tank roof**

Scenario 1

Scenario 1 is the simplest case, featuring no sweep air and heating via an internal submerged coil. Table 2 shows the modelled temperatures for various sulphur levels.

The results of Scenario 1 show that the internal vapour temperature of the sulphur tank is 101-118°C depending on the sulphur level. This translates to an interior tank wall temperature of 85-100°C, which is significantly below the freezing point of sulphur. Furthermore, condensation of water vapour on the tank exterior will be possible when the tank is less than 75% capacity because the wall temperature will be less than 100°C. Therefore, based on the success criteria of maintaining all temperatures above 120°C, the use of internal submerged coils alone fails to address the corrosion mechanisms previously discussed.

Scenario 2

In Scenario 2, the same tank is heated via an internal submerged coil, and the vapour space of the tank is swept with air. The sweep air in this scenario is pre-heated to 145°C as a best-case operating condition; in actuality, sweep air is not typically preheated, especially to such a high temperature. Table 3 shows the modelled temperatures for various sulphur levels.

Table 3: **Scenario 2: Modelled temperatures for various sulphur levels**

Sulphur Level	$T_{Sulphur}$	T_{Vapour}	$T_{Min\ Wall}$
75%	141°C	120°C	101°C
50%	142°C	113°C	95°C
25%	142°C	103°C	87°C

Table 4: **Scenario 3: Modelled temperatures for various sulphur levels**

Sulphur Level	$T_{Sulphur}$	T_{Vapour}	$T_{Min\ Wall}$
75%	138°C	122°C	101°C
50%	138°C	119°C	98°C
25%	137°C	117°C	96°C

Prior to modelling, it was assumed that the 145°C sweep air would be able to maintain the vapour and tank wall temperatures above 120°C. However, the results show that the walls in the vapour space lose heat faster than the sweep air can resupply it. Below 75% capacity, the vapour temperature is below 120°C, and at all levels the wall temperature is below 120°C. The results of Scenarios 1 and 2 show that even with significantly preheated sweep air (preheated 25°C above the freezing point of sulphur), an internal submerged coil fails to address the corrosion mechanisms previously discussed. To maintain the tank wall and internal components above 120°C, heat must be added to the vessel (and not just to the sulphur).

Scenario 3

In Scenario 3, the tank is heated via large sheet panels applied to the exterior tank shell and roof along with an internal submerged coil. The panels cover 22% of the shell wall surface area and 13% of the roof surface area. Figures 4 and 5 show an example of exterior sheet panels applied to the shell and roof of a tank, respectively.

In Scenario 3, the sweep air is again pre-heated to 145°C as a best-case operating condition. Table 4 shows the modelled temperatures for various sulphur levels.

The results of Scenario 3 show that the large sheet panels are unable to maintain the preheated sweep air at its entering temperature. Due to large spacing between the external steam jackets (Fig. 4), the heat loss to the ambient exceeds the heat input capabilities of the steam jackets. The resulting equilibrium vapour temperature is significantly less than the entering sweep air temperature. The minimum tank wall temperature occurs at the midpoint location between panels. All minimum wall temperatures are well below the freezing point of sulphur; furthermore, below 75% capacity, the wall will not be hot enough in these locations to vaporise any liquid water which reaches the wall (inside or outside). So, while the sheet panels provide localised sections of heat to maintain sections of the tank wall above 120°C, they do not maintain all sections of the tank above 120°C. The large spacing between panels allows cold spots to exist and the potential for sulphur to solidify on these sections of tank wall. Therefore, the distance between external steam elements is critical to maintaining the tank wall at elevated temperatures.

Fig 6: **ControTrace panels applied to the tank shell**

Fig 7: **ControTrace panels applied to the tank roof**

Scenario 4

In Scenario 4, the tank is heated via ControTrace panels applied to the exterior tank shell and roof. There is no internal submerged coil. The ControTrace panels cover 20% of the shell wall surface area in the bottom 4 feet (1.22 m) of the tank; for the remainder of the tank, the ControTrace panels cover 10% of the shell and roof surface area. Figures 6 and 7 show an example of ControTrace panels applied to the shell and roof of a tank, respectively.

In Scenario 4, the sweep air is not preheated but enters at ambient temperature (-18°C). In contrast with the other three scenarios analysed, this cold sweep air represents a worst-case operating condition for the tank heating system. Table 5 shows the modelled temperatures for various sulphur levels.

The results show that the ControTrace maintains the internal vapour and tank wall temperatures above 120°C for all sulphur levels. Internal support members surrounded by the vapour will be maintained very close to these temperatures. Therefore, all internal tank surfaces will be maintained above the freezing point of sulphur, and will not allow sulphur to solidify. Furthermore, any potential water trapped externally between the tank surface and insulation will be vaporised.

Together, all four analyses show that external jacketing is required to maintain all tank surfaces above 120°C to prevent the mechanisms previously discussed which can lead to external corrosion, internal corrosion, fire, and explosion. The external heating strategy must consider not just the heat required to offset heat loss to ambient but also the distribution of that heat to maintain the wall temperatures. Spacing of the external heating elements is critical. The ability to model the tank heat loss and predict tank temperatures for a given scenario is essential to a successful application.

Table 5: **Scenario 4: Modelled temperatures for various sulphur levels**

Sulphur level	$T_{Sulphur}$	T_{Vapour}	$T_{Min\ Wall}$
75%	139°C	125°C	128°C
50%	139°C	127°C	129°C
25%	138°C	129°C	130°C

Model validation

Having established that the ability to predict sulphur tank temperatures is essential to successfully design a tank thermal maintenance system, it seemed appropriate to validate the tank thermal maintenance model. Actual temperature data were collected from two tanks located in the US. The first tank (9 m diameter x 5 m height) was located in the Northeast, and the second tank (14 m diameter x 12 m height) was located in the Gulf Coast region. Both tanks are heated via ControTrace steam panels applied to the shell and roof exterior and had been in service for a year at the time of temperature measurement.

External tank wall temperatures were measured on each tank in several vertical locations using Type-K thermocouples attached to the tank wall via high-temperature adhesive tape. The tank wall was accessed by cutting holes in the insulation. After attaching the thermocouples, the holes were reinsulated, and the thermocouples were allowed to reach equilibrium over the next three hours before recording the temperatures. All temperature locations were positioned midway between vertical ControTrace elements in order to provide the minimum wall temperature on each tank. Both tanks were equipped with internal thermocouples for measuring the molten sulphur temperature and a level sensor for determining the sulphur level in the tank. The refinery data logs were used to collect these data points in order to include them in the model. All wall temperature locations were taken above the sulphur level at time of measurement. The actual steam pressure in the header feeding the tank jacketing was recorded for the model. Other data collected and included in the model were ambient temperature, wind conditions, insulation type and thickness, sweep air flow rate, and the length of time the tank had been in service. All of these conditions were input to the tank thermal maintenance model, and model predictions of minimum wall temperature were compared to actual temperatures measured midway between ControTrace elements. Average offset between the measured and modelled wall temperature was -0.6°C across all measurements.

These results confirm the validity of the tank thermal maintenance model presented in this article and lend significant confidence to its use in the design of future thermal maintenance systems for sulphur storage tanks.