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ANALYSIS OF THERMAL STRESS AND OPTIMIZATION OF ALCOHOL WASH PROCEDURES FOR REMOVAL OF NOX GUMS/SALTS IN BAHX (COLD BOXES)

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Abstract: NO_x gums/salts are potentially unstable compounds that ethylene production facilities should include in their safety program. These compounds can form at cryogenic temperatures and high pressures, and can form deposits in equipment. NO_x gums/salts are unstable at elevated temperatures, with certain species being unstable at ambient temperatures and colder. Experimental analysis has shown that NO_x gums/salts can decompose with an energy density similar to TNT. Operators can conduct precautionary procedures to remove NO_x gums/salts from production equipment and minimize the risk of explosion. This is often achieved by flushing internal passages of equipment where NO_x gums/salts are suspected of accumulating with alcohol. This serves a dual purpose to dissolve the compounds and provide a heat-sink before the equipment temperature rises above the temperature where NOx compounds can become unstable.

Brazed aluminum plate-fin heat exchangers (BAHX, commonly installed in 'cold boxes') are susceptible to NO_x gum/salt accumulation due to equipment operating at cold temperatures and high pressures that favor their formation. Flushing cryogenic temperature equipment with ambient temperature alcohol raises concern about potentially thermally shocking and damaging the BAHX. To address this issue, Chart Energy and Chemicals (a manufacturer of cold boxes) and a close industry partner investigated an in-field BAHX undergoing an alcohol wash event. This paper details methods used including a dynamic 3-D analysis for thermal and structural simulation. Tips are provided on practices to avoid. Finally, a set of general guidelines applicable to general alcohol wash procedures is offered that mitigates NO_x gums/salts hazards and does not damage a BAHX.

Background

With respect to ethylene plants, NO_x gums/salts are undesirable compounds that can form at cryogenic temperatures and accumulate in cryogenic equipment, especially in demethanizing cold boxes. NO_x gums formation begins with N_2O_3 being formed at cryogenic temperatures, precipitating out of solution, and forming deposits. These deposits react readily with olefins or diolefins also at cryogenic temperatures to form NO_x gum deposits, or react with NH_3 to form NO_x salt deposits. They can form in ethylene plants under normal operating conditions, sometimes even when there are no obvious identifiable reactant sources. When these compounds are encountered, it is often in streams colder than -150° F, especially below -200° F (where conditions favor their formation), and where hydrocarbons undergo evaporation, which encourages precipitation and deposition. Typical locations can be seen in Figure 1.

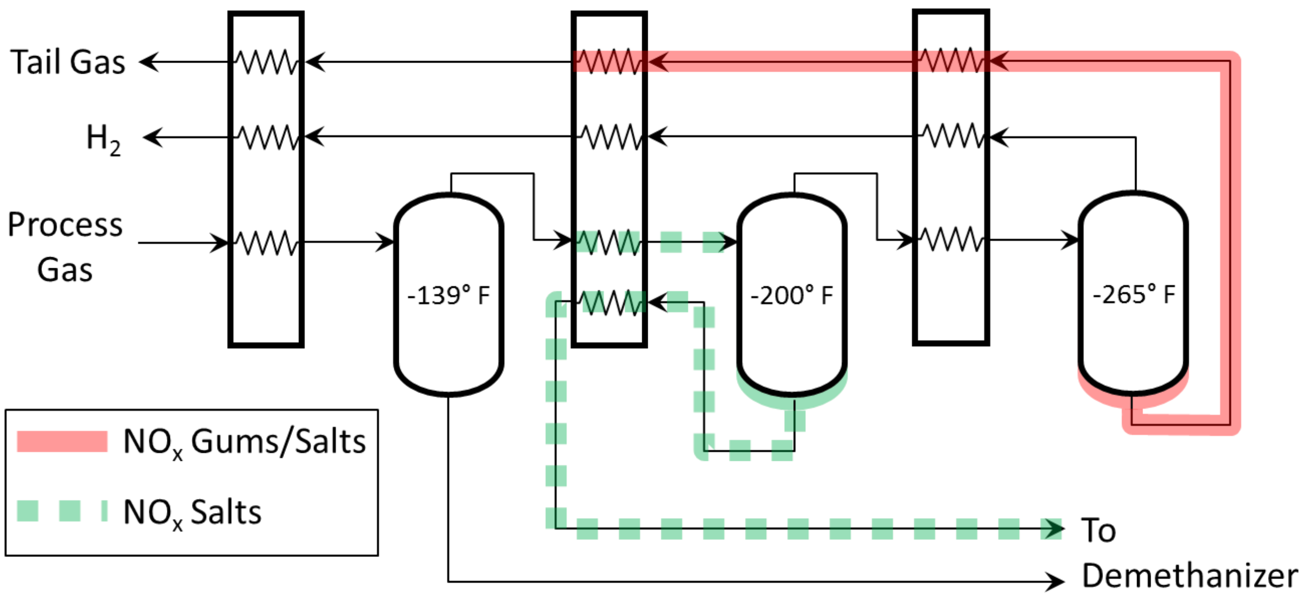

Figure 1: Typical locations of NO_x gums/salts deposits (1)

Limited information is available concerning NO_x gum/salt decomposition, except that it is very temperature dependent. Some NO_x salts have been known to decompose at temperatures around 140° F (1), while some NO_x gums are highly unstable even at cryogenic temperatures. Both NO_x gums and salts release NO and NO_2 upon decomposition, which can be fatal to humans at concentrations as low as 100 ppm.

NO_x gums/salts related incidents are rare, but they have been implicated in explosions at ethylene plants involving property damage and personnel injury. An explosion at a Berre, France ethylene plate in 1990 was attributed to NO_x gum deposits. The incident occurred 4 hours after an upset event caused the temperature in the cold box to increase to -13° F (-25° C). The explosion, estimated to be equivalent to approximately 40 lbs of TNT, destroyed the cold box and resulted in a plant shut down lasting 5 months (1).

As a safety measure, ethylene producers have developed methods for mitigating the danger of NO_x gums/salts, one of which is to dissolve the compounds with alcohol. This requires maintenance procedures to flood equipment suspected of NO_x gum/salt accumulation with alcohol to dissolve and remove the gums/salts. The primary objectives of these procedures are:

1. Dissolve NO_x gums/salts before they reach a critical temperature
2. Minimize time
3. Prevent thermal stress damage to equipment

An alcohol wash begins with the target sections of the plant being isolated, de-inventoried, and depressurized. Alcohol is introduced to the target sections via several injection points at ambient temperature and pressure, and is allowed to slowly fill the equipment and piping (similar to a bathtub filling). After all the passages are flooded with alcohol and allowed ample time to dissolve NOx compounds, it is drained and sequestered for safe disposal.

Given the time and temperature sensitive nature of NO_x mitigation, adhering to ALPEMA guidelines during an alcohol wash may not be the highest priority. Furthermore, there is no public data on the potential adverse effects of an alcohol wash on equipment e.g. thermal stress failure. Within recent history, advances in computing have allowed full 3-D transient simulations of alcohol wash procedures to evaluate these events in great detail. Chart Energy and Chemicals has conducted such simulations on an in-field BAHX undergoing various alcohol wash scenarios to ascertain their effect on cold box structural integrity. The results from these simulations have resulted in the suggestions detailed later.

ALPEMA Guidelines

Section 8.2.1 of the 2010 Third Edition ALPEMA Standards relate to fouling in BAHX (2). It explicitly warns against the dangers of NO_x accumulation and the difficulty in removing them. Flushing with a solvent cleaning solution is offered as a remedy, but no other specific advice is given.

ALPEMA and Chart recommend that when introducing a new flow, the temperature difference between the fluid and metal should not exceed 54° F (30° C). If this temperature difference must be exceeded, then the Chart OEM manual recommends slowly increasing the stream flow rate from zero to full flow according to Eq. 1.

$$Flow\ Introduction\ Duration\ [min] = \frac{Initial\ Temperature\ Difference\ [°\mathrm{F}]}{1.8\ \left[{}^{°\mathrm{F}}/_{min}\right]} \qquad \text{Eq. 1}$$

In order to adhere to the above rules, cryogenic equipment would have to be warmed up by 250° F or more before flushing with ambient temperature alcohol, a process which could take many days. Alternatively, the wash flow rate would be increased over the course of several hours. These guidelines were intended for conditions based on start-up to operating flow-rates as opposed to start-up to a slow-fill flow condition. The current study considers the effects of conducting an alcohol wash on a BAHX without adhering to the 54° F ALPEMA or 1.8° F/min Chart E&C guidelines.

Simulation Setup / Considerations / Assumptions

A simplified diagram of the hydrogen product BAHX experiencing the alcohol wash can be seen in Figure 2. This BAHX contained three streams: Process Gas, H_2, and Tail Gas, as is typical in an ethylene plant. For the purpose of this study each stream had independent alcohol injection points allowing for control of each stream.

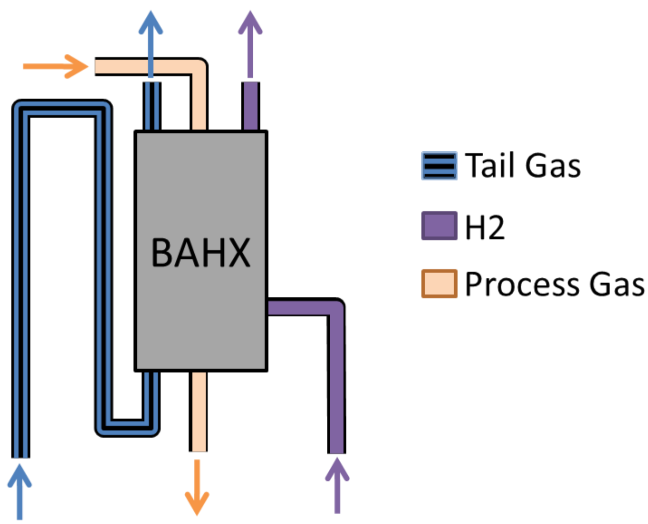

Figure 2: Simplified BAHX installation

Using structural drawings, frictional, and thermal performance data of the BAHX in question, Chart created structural, thermal, and flow models of the BAHX. A simulation was run to establish the steady state operating conditions of the BAHX prior to the alcohol wash. The thermal performance of the model at design conditions was verified against AspenTech Exchanger Design and Rating results, and agreement within 2% (3.2 F) was found in the outlet temperatures. A simulation of a shutdown and isolation procedure was performed and verified against available field data. Subsequently the metal temperature of the BAHX was approximately uniform at -110° F, and all streams were de-pressurized and de-inventoried.

Various dynamic alcohol wash scenarios were simulated, all assuming an initial alcohol temperature of 80° F. The time-dependent thermal profile results were input into finite element structural analyses to calculate the time-dependent stress values inside the BAHX. The fatigue effects of the changing stress values were subsequently calculated to estimate the number of alcohol wash cycles the unit could endure until failure

The thermal simulations assumed an adiabatic BAHX, no fluid mixing during the wash event, and incoming alcohol was introduced at the bottom of the BAHX. The structural simulations assumed no pipe or mounting related loads, and perfectly elastic materials. The fatigue analyses assumed each simulation comprised a single stress cycle.

Demonstration of a Successful Wash

A wash event was simulated where the flow rate through each stream was controlled so that the alcohol level in each stream was uniform. A representation of the alcohol level in the BAHX at various times during this scenario is shown in Figure 3. Figure 4 shows the metal cross-section temperatures of the BAHX, with the bottom of the core at the left of each graph, and the top of the core at the right. Each graph shows the minimum, average, and maximum cross-section metal temperature profiles at the same time steps as in Figure 3. At 3, 10, 17, and 20 minutes, the dashed vertical line represents the fluid height in the BAHX. At 23 minutes, the entire BAHX has been filled with alcohol, and any NO_x hazards are mitigated.

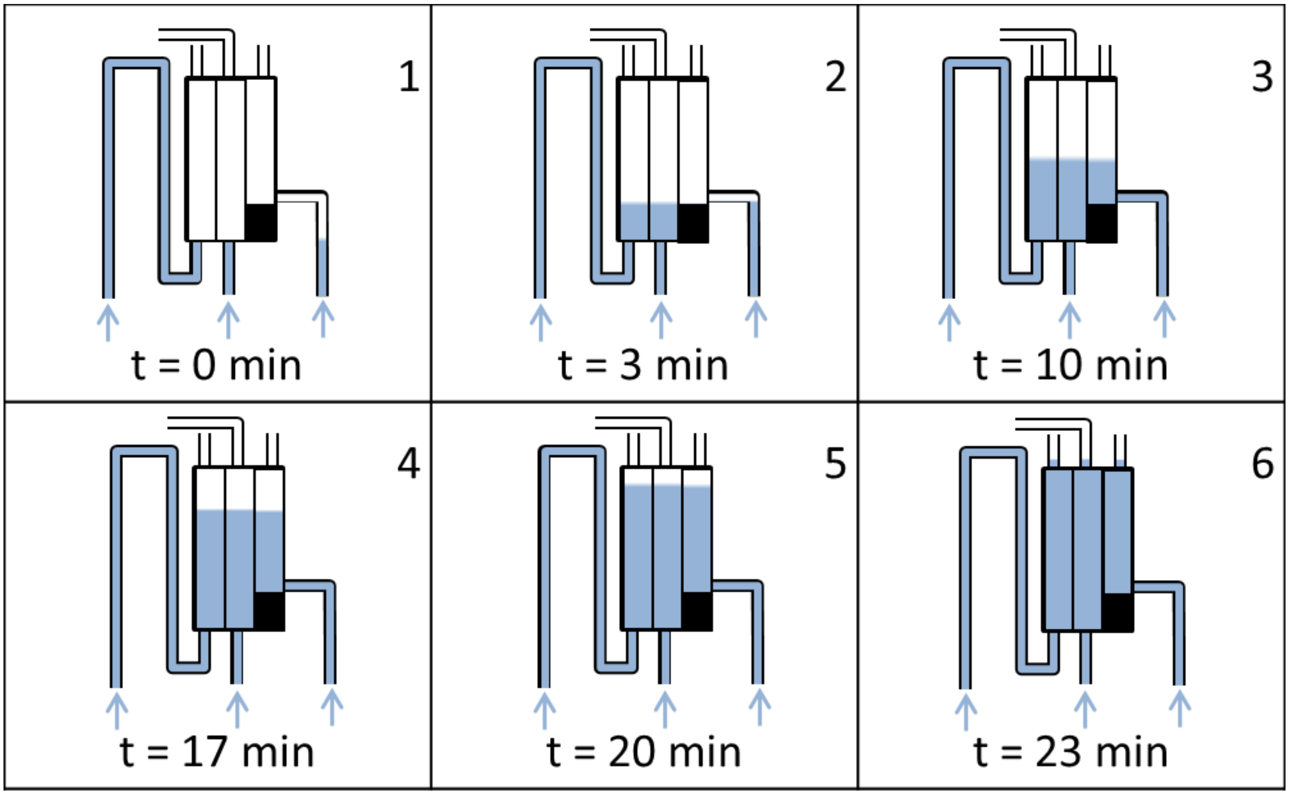

Figure 3

The alcohol flow rate in each stream was controlled so the fluid level rose at a uniform 3.6 in/min in each stream. This velocity was chosen so that the thermal conduction wave through the heat exchanger metal did not advance far beyond the alcohol level. This can be seen in Figure 4, where the unwashed areas are not significantly warmed.

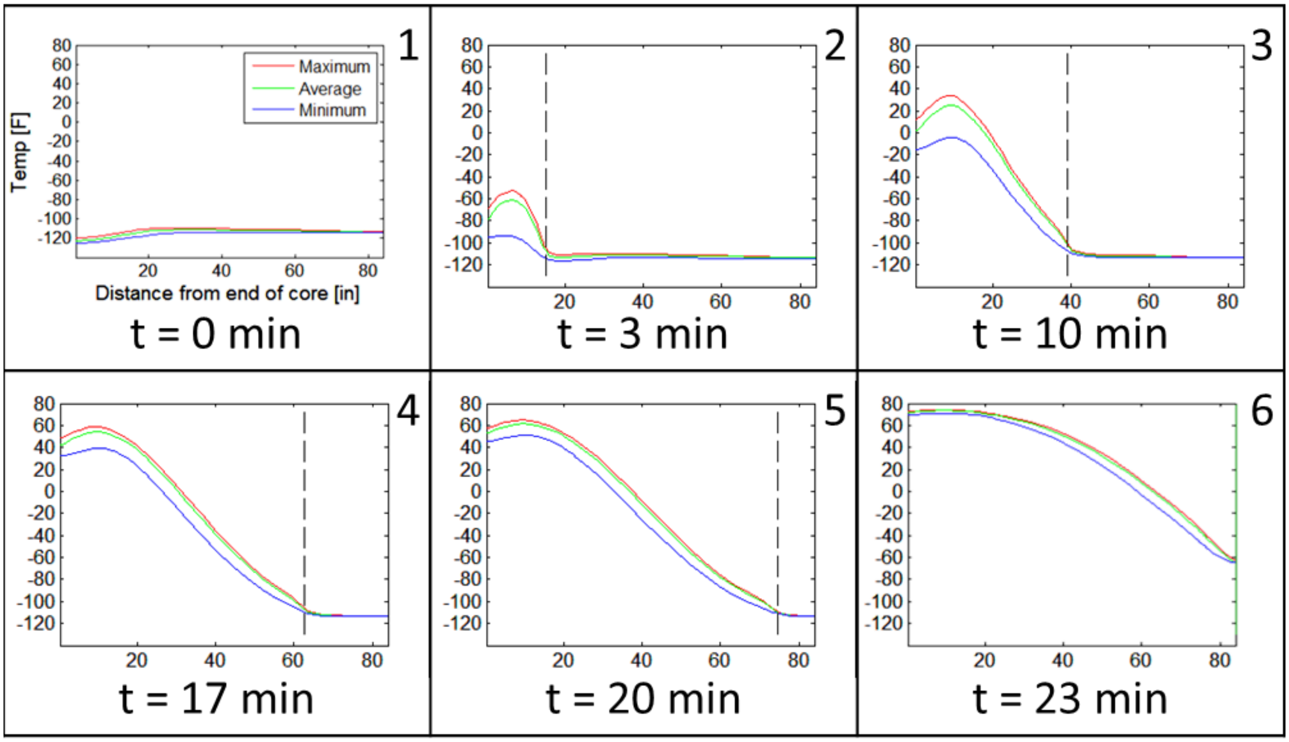

Figure 4

Demonstration of a Flawed Wash

A wash process was simulated to demonstrate characteristics of a flawed alcohol wash, where all three passes pose a NOx hazard. In this scenario, the alcohol flow through each stream was not controlled independently, but behaved as if filled by a common injection point. This filling process can be seen in the figure below. Due to the routing of the pipework, two of the streams are completely filled before the third stream even begins filling.

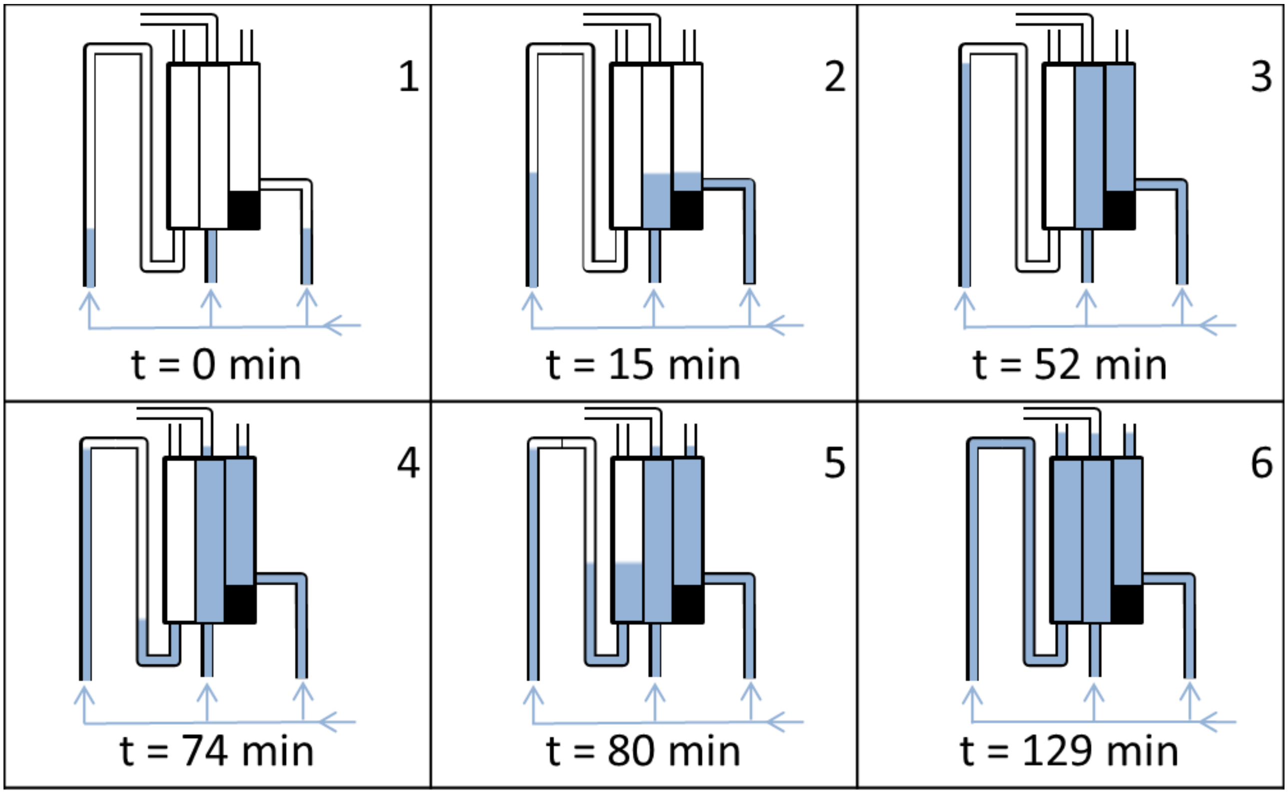

Figure 5

Figure 6 shows the metal cross-section temperatures of the BAHX, with the bottom of the core at the left of each graph, and the top of the core at the right. Each graph shows the minimum, average, and maximum cross-section temperature profiles at the same time steps as in Figure 5. At 15 and 80 minutes, the dashed vertical lines represent the fluid height in the BAHX.

At 0 minutes, the entire BAHX is at a temperature of approximately -120° F, which is the temperature profile after depressurization. At 15 minutes, the 80° F alcohol has begun to warm up the bottom of the BAHX. The first two streams have been completely filled with alcohol at 52 minutes, and the third stream doesn't begin to fill until 74 minutes. During this time, the third stream has continued to warm up to the same temperature as the adjacent streams, despite being empty. At 80 minutes, the last stream is ~1/3 filled with alcohol, and completes filling at 129 minutes. It is clear that any NO_x gums/salts in the third stream have been warmed before being dissolved in alcohol, which is against the intentions of the procedure.

It can be seen that this wash procedure failed to achieve its main goal of submerging passages suspected of having NO_x gum/salt deposits before they exceeded 60° F. This was primarily due to the tail gas stream, which likely contained NO_x gum/salt deposits, being submerged long after adjoining passages. This allowed heat to conduct into the NO_x gum/salt passages prior to them being exposed to alcohol.

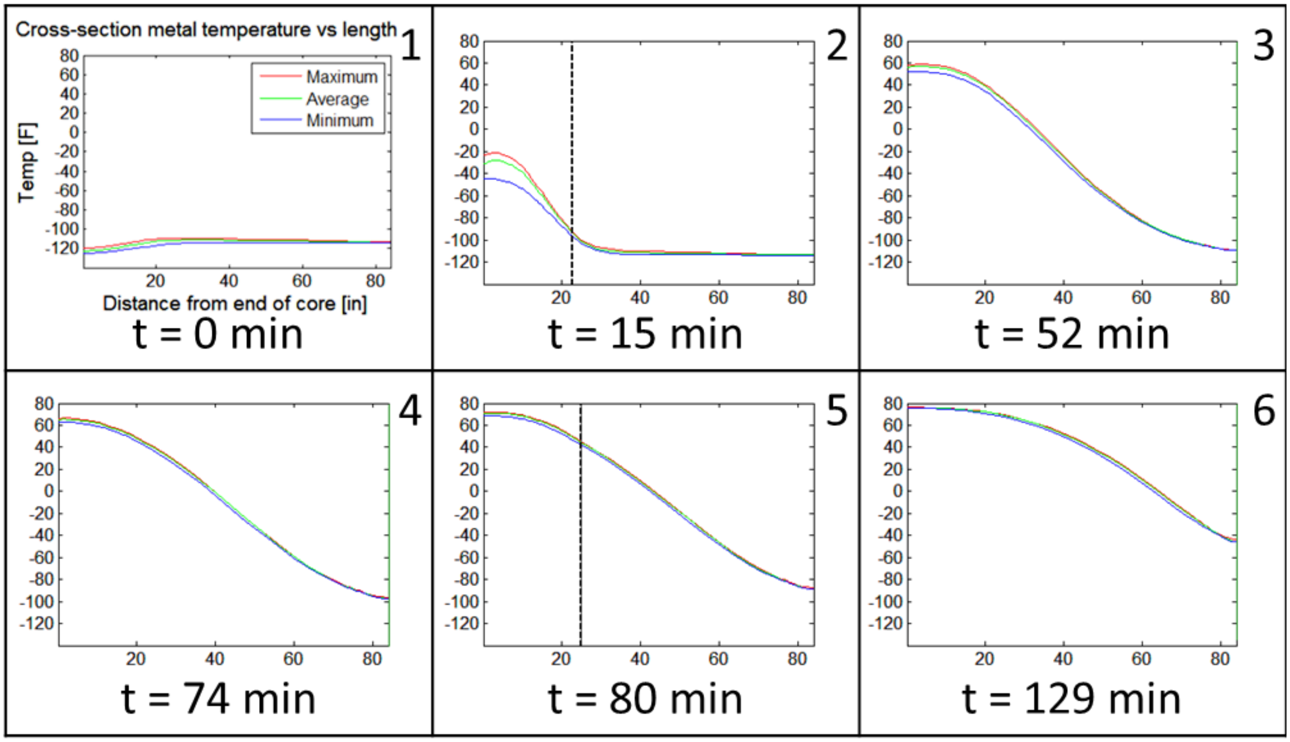

Figure 6

Stress Considerations

Stress analyses were performed on the two alcohol wash scenarios. The thermal profiles were imported into ANSYS®, which calculated and output the nodal stress levels for each time step. A stress-time history was compiled for each node, from which mean and alternating stresses were calculated. These were adjusted to an equivalent alternating stress with zero mean stress according to the Goodman relation seen in Eq. 2, and a conservative fatigue life for each node was calculated from published fatigue data.

$$\sigma_{equ.alt.} = \frac{\sigma_{alt.}}{1 - \frac{\sigma_{mean}}{\sigma_{ultimate}}} \qquad \text{Eq. 2}$$

The maximum stress level achieved during the uniform alcohol wash was 33 MPa, with a peak equivalent alternating stress of 20 MPa. For comparison, the yield and ultimate strength of the BAHX base material is 41 and 110 MPa, respectively. Figure 7 shows the equivalent alternating stress map overlaid on the BAHX schematic for the uniform wash scenario. The maximum stress during the flawed wash was 28 MPa, with a peak equivalent alternating stress of 21 MPa. For both the successful and the flawed wash scenarios, the fatigue life was beyond 500e6 cycles.

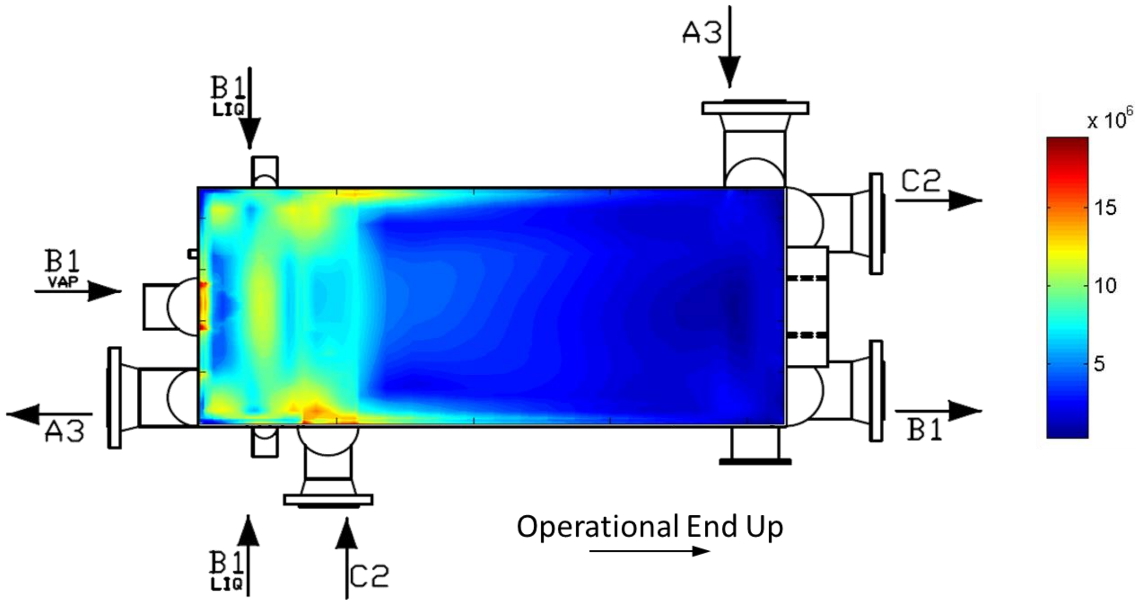

Figure 7: Projected maximum equivalent alternating stress [Pa] for uniform wash (3.6 in/min vertical fill rate)

A parametric study was conducted where a uniform vertical fill rate was varied from 0.15 to 48 in/min, and the number and location of stream passages being washed were varied. Higher vertical fill rates (faster filling) correlated with higher stress levels and lower fatigue lives. The number and location of stream passages being washed had little effect on the stress levels in the BAHX. The depressurization of the BAHX allowed for all available mechanical strength to resist the thermal stress, which resulted in the low stress levels.

Figure 8 shows a schematic of a different BAHX overlaid with an equivalent alternating stress map from a uniform alcohol wash. For this scenario, only the B3, C, and D passages were filled, at a vertical velocity of 48 in/min. The highest stress levels occurred at the bottom of the exchanger near the inlet headers and bar columns. This further validates the simulations, as experience has shown that these areas are more vulnerable to fatigue failure. For this analysis, the maximum stress level was 56 MPa, the maximum equivalent alternating stress was 36 MPa, and the predicted fatigue life was 300,000 cycles. A BAHX typically experiences fewer than 50 alcohol washes during its service life.

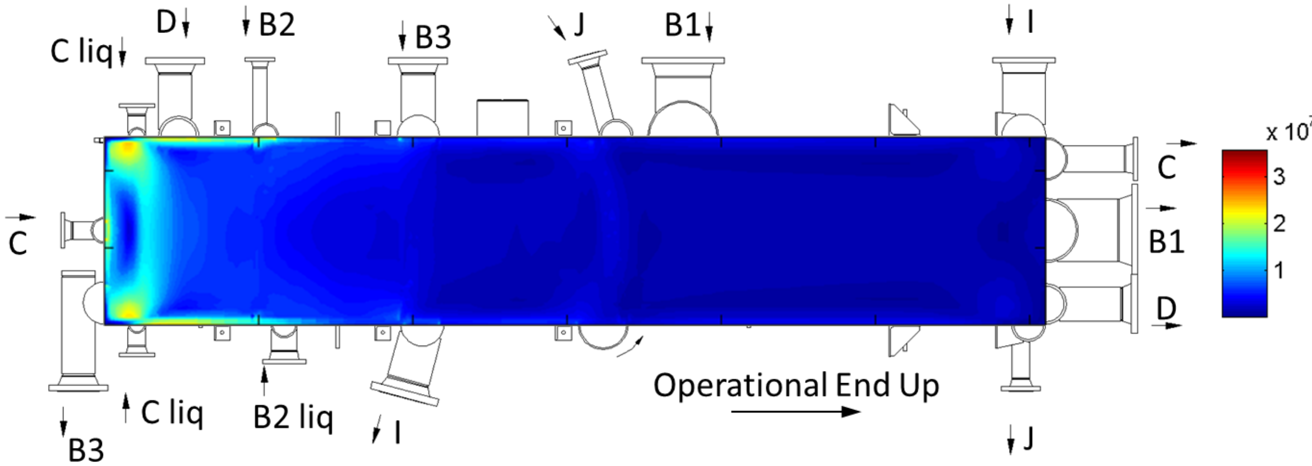

Figure 8: Projected maximum equivalent alternating stress [Pa] for uniform wash (48 in/min vertical fill rate)

Guidelines

1. Wash all passages simultaneously with uniform fluid height

This accomplishes two goals. Most importantly, it prevents submerged passages from transferring heat to adjacent unsubmerged passages, which creates the opportunity for NO_x gums/salts to heat up and become unstable before being neutralized by alcohol. Simultaneous washing also minimizes temperature gradients between adjacent passages, minimizing the stress levels in the BAHX.

2. Maintain a vertical velocity between 0.15 and 48 in/min inside the BAHX

A fill rate below the minimum vertical velocity allows a thermal wave of conduction to advance in front of the alcohol fluid level, which could heat up NO_x gums/salts prior to their submergence. A fill rate above the maximum vertical velocity would cause unnecessarily high stress levels in the BAHX. A fill rate defined in vertical in/min is insensitive to dimensions such as core width, height, and free area.

In order to maintain a proper vertical velocity, it is recommended to block all pipework not suspected of containing NO_x gums/salts that would interrupt the alcohol from filling the BAHX passages first. Block the pipework as near to the core as possible to minimize extraneous volumes.

3. Begin the wash process from a cold, de-inventoried, and unpressurized state

It is important to maintain any passages suspected of containing NO_x gums/salts at cryogenic temperatures before being exposed to alcohol. Depressurizing the BAHX allows for maximum material strength in resisting thermal shock effects (distortion due to high thermal gradients).

4. Follow ALPEMA standards in isolating and returning the BAHX to operation.

Conclusions

Chart has developed guidelines for successful thermal stress reduction during alcohol wash procedures and insights into NOx salt/gum hazard mitigation. These guidelines are supported by 3-D transient thermal simulations that were conducted using in-field data. The thermal results were carried forward to predict the mechanical and thermal stress and fatigue life of the BAHX. Analysis of various wash scenarios reveal that a successful wash procedure is very dependent on the vertical fill velocity of the alcohol, and filling all passages uniformly is highly recommended. Stress levels in all the simulations were acceptably low, and had an insignificant impact on the life expectancy of the BAHX.

Procedures that contradict these guidelines may also effectively mitigate NO_x gums/salts hazards while maintaining the structural integrity of the BAHX, but situation-specific analyses must be done to qualify these procedures.

References

1. *NOx Safety in Ethylene Plants.* Grenoble, Dane, et al., et al. s.l. : AIChE, 2007. Ethylene Producers Conference.
2. *The Standards of the Brazed Aluminium Plate-Fin Heat Exchanger Manufacturers' Association.* s.l. : Brazed Aluminium Plate-Fin Heat Exchanger Manufacturers' Association (ALPEMA), 2010.