The mechanisms that usually limit the life of tubes in oil refining heaters are excessive wall thinning from corrosion, erosion, or creep. Tube selection for this service is usually based on material that will withstand these factors. It is not uncommon, however, to experience tube failures from operational factors. This article describes cases where flow restrictions within tubes led to melting from the inside out.

The appropriate material selection for tubes in oil refining heaters is critical to withstand the problems of erosion, corrosion, and creep in these hostile environments. The following case histories show that internal melting can occur from operational situations that if not rectified, lead to premature failures of the tubes.

Case Histories

In one case, coke formation within carbon steel (CS) tubes restricted the flow to a point of causing overheating and several tubes failures. The failures occurred in the convection section of a heater that handles light hydrocarbons.

In the second case, the failure occurred in 9Cr-1Mo steel tubes of the convection section of a naphtha reboiler in a hydrotreater unit. The flow to the heater was accidentally stopped because of an operational upset; overheating and internal fire followed, which austenitized the tubes and caused tube failure. These tubes hardened considerably when the internal fire was extinguished and the tubes cooled down to room temperature.

The third case was in a catalytic reformer heater equipped with 2 1/4Cr-1Mo steel tubes. Failure occurred during start-up while naphtha and hydrogen were circulating, and the flow of hydrogen was accidentally interrupted because of compressor problems.

The failure of all these tubes occurred by overheating, and hydrocarbon leakage caused an internal fire that further damaged the tubes.

At first, finding one or more tubes that melted locally on the inside, with solidified pieces of metal found inside some of the tubes, was very confusing. The melted material observed in the tubes was first identified as extraneous metal.
The Mechanism

The investigations revealed that the common denominator in these three cases was partially or totally interrupted flow within the tubes. In one of the cases, information was found to indicate that the affected section of the heater was internally fouled with coke prior to the incident, to the extent that the flow was severely constrained. In the other two cases, there was no evidence of prior coke formation inside the tubes, but total or partial interruption of the flow led to excessive overheating while the hydrocarbon fluid inside the overheated tubes converted to coke. The presence of coke inside the tubes constituted a source of carbon that diffused into the steel and thus caused excessive carburization while the steel was overheated.

CS, 2 1/4Cr-1Mo, and 9Cr-1Mo steels are referred to as ferritic steels because their microstructure consists of ferrite and carbides. Under normal operating conditions, heat transfer from the heater through the tubes and to the fluid occurs continuously. The flow of fluid removes heat, thus keeping the tubes cooler than the inside of the heater. As soon as the flow is interrupted or diminished, however, the heat coming from the heater raises the tube metal temperature. This heat comes not only from the flames of the burners but also from the surrounding refractory or insulating ceramic wool blankets that are much hotter than the tubes. When one or more tubes rupture, hydrocarbon leakage to the interior of the heater catches fire, even if the burners are switched off. The tubes tend to remain overheated unless the steam is quickly circulated within the tubes and also used in the fire box to suffocate the fire.

Upon overheating, these steels stay ferritic until reaching the lower critical temperature of ~727, 805, and 825 °C, for CS, 2 1/4Cr-1Mo, and 9Cr-1Mo steel, respectively. Austenite begins to
form at this lower critical temperature until reaching the upper critical temperature, at which point the transformation to austenite is complete. The upper critical temperature also depends on composition of the steel, starting at ~910 °C for pure iron and gradually decreasing down to ~727 °C for 0.83 wt% C in CS.

Ferrite is a solid solution of carbon in α-iron that has a body-centered cubic (BCC) crystal structure and rather low solubility of carbon, up to only 0.025 wt% at 727 °C. This implies that the amount of carbon the steel can take into solid solution is limited when still in the ferritic state. As carbon diffuses into the ferritic steel, it forms carbides mainly at grain boundaries and also within the ferrite grains, with the low solubility of carbon acting as the limiting factor. Carburization can thus proceed, leading to a significant increase in the amount of carbide in the steel over time. Austenite is an interstitial solid solution of carbon in γ-iron that has a face-centered cubic (FCC) crystal structure, permitting higher solubility of carbon than ferrite. Austenite does not exist below 727 °C in CS; the maximum concentration of carbon in austenite at this temperature is 0.83 wt%. This means that as soon as austenite forms in CS, it can take up to 0.83 wt% C into solid solution, with amounts of carbon increasing with further increases in temperature—up to ~2.06 wt% at 1,147 °C.

CS that has overheated to austenite and been enriched with carbon from 0.51 wt% to 2.06 wt% would, if cooling occurred, start precipitating primary cementite when reaching the upper critical temperature. If heating continues after the CS has fully austenitized, however, the steel could reach the eutectic transformation at 1,147 °C, at which point austenite could coexist with molten steel and could achieve the eutectic concentration of 4.3 wt% C.

Iron with carbon content from 2.06 to 4.3 wt% is no longer CS but cast iron. When the temperature of steel with this range of compositions reaches 1,147 °C, it contains primary austenite crystals and some amount of the liquid phase. Upon cooling, the liquid metal decomposes by the eutectic mechanism to a mixture of austenite with either cementite or graphite. The presence of various alloying elements and the cooling rate during solidification control whether the metal undergoes the stable iron-graphite or the metastable iron-carbide (cementite) transformation during cooling. The eutectic graphite is arranged in rosettes consisting of graphite flakes, as in gray cast irons. The austenite and cementite eutectic is a fine mixture called ledeburite. If there is excess carbon, the final microstructure would be primary cementite in a matrix of ledeburite.

The coke inside the tubes may form prior to or during the incident. The coke represents the source of carbon that causes the transformation of steel into cast iron. This transformation occurs when overheating austenitizes the steel and the steel becomes significantly enriched with carbon through the carburization process. The transformation also reduces the melting point to 1,147 °C. This explains why the tubes start melting from inside out—the carbon-enriched metal at the inside surface can start melting at ~1,147 °C while the uncarburized steel at the outside surface still has to reach ~1,493 to 1,539 °C to melt, depending on the carbon content and other alloying elements.

The above explanation is derived from the iron-carbon equilibrium phase diagram. The situation is similar in the case...
of 2 1/4Cr-1Mo and 9Cr-1Mo steels but more complex to describe because they are alloys that require making reference to at least three-phase C-Fe-Cr equilibrium diagrams.

**Gray Cast Iron**

Figure 1 shows a former pool of molten metal that solidified on the interior wall of a finned tube. At first it was mistaken as a deposit formed on the tube inside surface; but when attempting to chisel it out, it was found to be metallic. Figure 2 shows a metallographic section through the rupture of this tube. The presence of gray cast iron is evident by the graphite flakes. There were other failed finned tubes in this section of the heater, one with a split several feet long. Wall thinning occurred because of superficial melting of the inside surface of the tube. The tube was installed horizontally and the liquid metal collected in the bottom half of the affected tube. Here the remaining wall thickness was thin enough to fail by plastic deformation, which left a knife-edge rupture. The fins were severely embrittled and were easily removed with a hammer to uncover the rupture.

**White Cast Iron**

Figure 3 also shows a former pool of molten metal that solidified on the wall at the bottom of this horizontal 9Cr-1Mo steel. The 11% Cr steel fins had not melted. Wall thinning occurred to perforation at the top because of superficial melting of the inside surface of the tube. These perforations occurred in the absence of internal pressure, which is why there was no bulging in the tube. The liquid metal collected in the bottom half. Figure 4 shows a cross section through the bottom of a similar tube. The microstructure of the solidified metal deposited on the bottom of this tube is white cast iron while the remaining wall is fully martensitic 9Cr-1Mo steel. The white needles in the frozen metal are primary carbides in a matrix of ledeburite; the
Bottom view of one metal piece found inside the tubes with flow lines resembling lava. The scale is 1/16 in (1.6 mm).

Microstructure found in the loose pieces inside 2 1/4Cr-1Mo tubes indicates white cast iron etched in Vilella’s reagent, original magnification 100X.

remaining austenite within the carbide network transformed to pearlite, bainite, or martensite that etched almost black. Because this matrix offered a black background, the white needles appear as if they were loose, isolated extraneous material. Higher magnification, however, revealed the true nature of this microstructure—typical interdendritic network of carbide (white) in the black etching constituent.

Figure 5 shows the underside of one of the solidified molten pieces of metal found inside the 2 1/4Cr-1Mo steel tubes. It has a lava-like appearance. Figure 6 demonstrates that these pieces were white cast iron, originating from molten steel that was enriched with carbon from the coke to the point that it converted to cast iron, and melted at lower temperatures than the parent 2 1/4Cr-1Mo steel, which did not melt because the overheating temperature did not reach a sufficiently high level.

Conclusions

Different explanations may be put forward to account for steel tubes melting from the inside out, but explanations assuming that melting could occur while the heater is in service will be difficult to sustain. Even assuming that these were indeed extraneous metal pieces accidentally left inside the heater coils or tubes, it would be necessary to assume that they were cast iron pieces that melted at lower temperatures than the tube.

Melting that started from the inside of the tube led to perforations or ruptures of the tubes. During overheating, the steel was fully austenitized first and then carburized to an extent that the layer of metal inside the tube turned into cast iron, which has a lower melting point than the steel from which it originated. In the case of CS, the molten metal solidified as gray cast iron; in the case of 2 1/4Cr-1Mo and 9Cr-1Mo steel, it solidified as white iron.

This seems to be the natural process by which steel tubes would fail in a fired heater when partially or totally obstructed. The interrupted flow and resulting overheating first leads to coke formation, then continues to increase the temperature to levels reaching 1,147 °C and higher. Such tube failures would not have anything to do with the incident, but the failure could create a great deal of confusion if it is not properly interpreted. Improper interpretation would lead to wrong conclusions.

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