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The Melamine Story

How a single company has contributed to the transformation of a small-scale business into a multi-million-dollar industry

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ON THE COVER

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OPTIMISING TUBE LIFE

Paresh Haribhakti and Ketan Upadhyaya, TCR Advanced Engineering, India, look at operational control for the enhancement of tube life and the role of automated reformer tube inspection.

Steam reforming of hydrocarbons is one of the most vital processes used for the production of hydrogen in ammonia plants for the fertilizer industry. The process involves an endothermic reaction where heat is supplied by the fuels burnt in a furnace to produce hydrogen and carbon monoxide in the presence of a catalyst at approximately 900°C and 25 – 30 barg. The operating parameters are such that every reformer tube must withstand up to the edge of its creep limit with minimum margin of error. Even minor process variations in terms of temperature, either nominal or local, increase the tube skin temperature resulting in reduced creep life. In-service failure of reformer tubes can bring enormous economic losses and affect the overall performance of a fertilizer plant. Of late, it is realised that the different damage mechanisms and life limiting factors afflicting reformer tubes are mainly dependent on the operational philosophy and control.

Reformer tubes are typically designed for 100 000 hours (11.5 years), but many fertilizer industries have been able to extend their use over 200 000 hours (23 years) with systematic operation and periodic inspection. However, in today's industry, the world is moving towards increasing the shutdown intervals to gain economic advantage and edge over competitors. The side effect of increased production above rated capacity, results in higher flow rates and requires increased furnace temperature for reaction to complete. All this has an adverse effect on the tube life. The increase in tube skin temperatures reduce the tube life with increased risk of premature tube failure. When the service life in excess of 10 years for reformer tubes is attainable for conventional high nickel, high chromium centrifugally cast alloys, there are instances of early failures, even with tubes made of high grade micro-alloyed materials.

The fitness for service assessment is based on the estimation of skin temperature of the reformer tubes and its correlation with creep parameters. TCR has developed a novel approach for the estimation of skin temperature of the reformer tubes by a non-destructive test (NDT), using a proprietary software driven crawler, known as the Automated Reformer Tube Inspection System (ARTiS). The system can accurately measure the tube diameter, detect mid-wall fissures, and the effect of aging through a combination of techniques. The data collected is used to estimate the tube life in conjunction with the other techniques, such as microstructural examinations and proprietary software-based calculations from the measured diameter.

Figure 1. Multiple reformer tubes failed in a side-fired furnace design due to thermal shock/flame impingement.

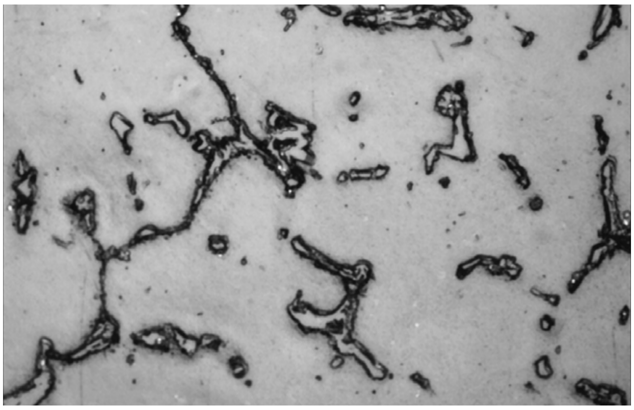

Figure 2. Microstructure of a new HP modified alloy showing primary carbides and very finely distributed secondary carbides within the matrix.

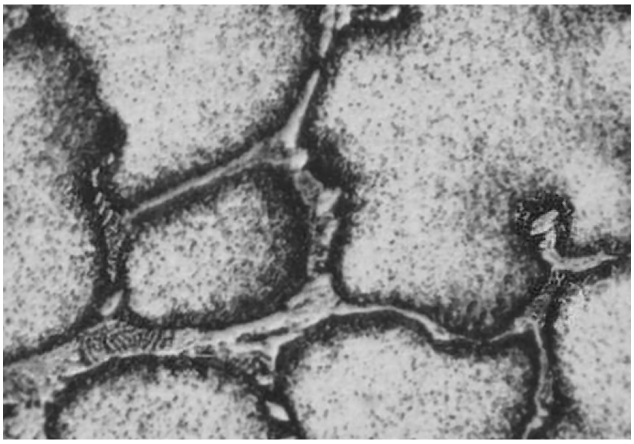

Figure 3. Microstructure of HP modified alloy after ageing, showing coagulated carbides migrated towards primary carbides.

This article is aimed at highlighting that the operational control has a major role to play in averting the failure of the reformer tubes based on different damage mechanisms including creep, oxidation, carburisation, bowing, and thermal fatigue. The knowledge of damaged mechanisms is essential for an operation manager to achieve the controlled operation, thus ensuring extended life output from the reformer tubes.

Evaluation of reformer tubes and metallurgy

The reformer tubes are conventionally made of high nickel and high chromium and iron. The history of material development indicates popular primary alloy HK40, followed by the development of alloy IN519 with the addition of niobium. Later, micro-alloyed materials having increased chromium and nickel content with addition of 1% niobium, and other proprietary micro-alloying elements, such as titanium, tungsten, zirconium, aluminium, and silicon, including rare earth elements, were developed for improving creep life. There are many proprietary alloys in the market with various claims towards the tube life improvement. The developments are towards increased tolerance of tube wall temperature and higher creep strength with reduced wall thickness. However, this evolution is chiefly purported to minimise the capital cost as well as downtime.

Damage mechanisms and their correlation with operation

Below is a brief discussion of common damage mechanisms for reformer tube failures with its correlation to operational aspect and its control.

Creep rupture

Creep is the time dependent degradation of the material under constant stress at elevated temperature that results in permanent deformation. The temperature necessary to cause creep depends on properties of the alloy and is generally >0.4xTM (melting point). Considering the operating temperature in the reformers, the life limiting damage mechanism is creep.

There are three stages of creep, namely primary, secondary, and tertiary. In the case of the reformer tubes, during early stages, the creep voids initiate in the mid-wall section of the tube. This is typical of damage in reformer tubes as the maximum stress zone occurs at mid-wall due to a combination of hoop stress and thermal stresses. Subsequently, the creep damage advances towards the inner diameter and finally towards the outer diameter of the tube. The fissures originate at mid-wall, one-third of the wall section, and can be identified by various NDT methods at different stages. Their detection is critical because their presence points towards the extinction of tube life.

The operational aspect has close relation with creep damage. The skin temperature of the tube depends on the thermal efficiency of the combustion, uniformity of temperature distribution in the furnace, emissivity of the cera-wool that affects the corner tubes, etc. The degradation and degeneration of the catalyst can also increase the skin temperature of the tube as accumulation of catalyst dust chokes the flow path of the gases, thereby increasing the tube skin temperature. A measurement of pressure difference between the tube inlet and outlet can provide a clue about catalyst condition. All of these factors affect the tube skin temperature and subsequently, the creep life. The knowledge of these parameters would help in improving the life of reformer tubes by reducing its skin temperature.

Localised overheating

Localised overheating of reformer tubes occurs mainly due to two reasons: either due to misalignment of the burners; or due to clogging within the tube banks. Over a period of time, due to reasons such as ageing, increased flow rates, and thermal cycling, the catalyst becomes friable and gets crushed to powder form. The fine particles of catalyst formed have a tendency to choke the gas path and restrict easy movement of the gas leading to tube clogging. Insufficient and irregular gas flow raises the tube metal temperature and ultimately leads to failure of the tube due to localised overheating.

The tubes are vulnerable to failure when subjected to a direct flame impingement because of mis-firing/uncontrolled firing of the burners. This can result in multiple failures of tubes that were subjected to impingement

Microstructural degradation

A virgin reformer tube has a microstructure comprising of inter-dendritic primary carbides along with nitrides or carbonitrides in the matrix of austenite. However, during service, the microstructure changes, especially by way of coarsening of primary carbides precipitates including secondary carbides. The rate of coarsening of carbides and secondary precipitations depends on operating temperature and exposure time. With the in-situ metallography, an experienced metallurgist can predict the skin temperature by correlating morphology carbides and the nature of precipitates.

Thermal fatigue flame impingement

Thermal fatigue is the result of cyclic stresses caused by variations in skin temperature of reformer tubes.

Similar to direct flame impingement, temperature fluctuations in the furnace zone, either by power dips or due to process upset condition, also give rise to multiple tube failures. The typical failures of reformer tubes are shown in Figure 1. The condition of the burners needs proper inspection during available turnaround opportunities to ensure their functionality.

Effect of catalyst damage

The catalyst changeover in the reformer tubes results in an 8 – 10°C reduction in temperature. The extended use of catalyst can result in degradation of catalyst by way of dust formation and decrease in catalyst efficiency. It also leads to a higher process temperature and an increase in tube metal temperature. The catalyst dust forms by uncontrolled crushing during thermal contraction of the tube due to cyclic operation of reformers in the form of frequent cold starts. Ultimately, the region where gas becomes relatively stagnant causes local increase in tube metal temperature and attributes to tube failure.

Effect of startup and shutdown

In large steam reforming furnaces, risk of over firing prevails during start-up.[1] This can also happen during transient conditions. Factors such as increased production rates and higher ramp rates can result in increased transient stresses on the tubes and thus the accumulated creep damage is expected to be at its peak during such events. The shutdown has the opposite behaviour with respect to cooling rate. An undesirably high rate of cooldown would result in an inducement of thermal shock or uneven thermal contraction of the tube, which can cause bowing.

Tube wall temperature measurement inaccuracy

Normal practice in an operating philosophy is to measure the tube metal temperature by optical pyrometers twice a day. The pyrometers work on the principle of emissivity. For a new tube, having a good rough surface can have emissivity as high as 0.9. The tubes tend to lose the roughness by oxidation during the service and hence the emissivity reduces to a level up to 0.6. This can result in inaccurate measurement of tube wall temperature, although the reformer operation is based on the active feedback of the tube metal temperatures.

Reduction in effective wall thickness

Reformer tubes are prone to oxidation and scale formation on their outer surface on account of exposure to elevated temperature conditions within the reformer furnace. The oxide scale not only retards the diffusion of oxygen and carbon from the gas phase into the metal matrix, but also blocks the catalytically active alloying elements, such as Fe, from reaching the surface. Reformer tubes are also subjected to carburisation on their inner surfaces. Both oxidation and carburisation processes reduce the effective thickness of the tubes, which can withstand the stresses acting on them.

The balanced combustion with air and fuel is very important to avoid oxidation damage to the tube surface. Periodic audit by a process and combustion design expert would help in reducing oxidation damage. Though internal carburisation is difficult to control, it depends on the conversion efficiency of the catalyst. The presence of unconverted hydrocarbons will promote the carburisation at the high temperature zone that is towards bottom side.

Bowing of tubes

The bowing of tubes can be attributed to restriction in expansion due to hanger issues. However, from an operational point of view, severe thermal stresses and uneven temperature zones in the furnace can also lead to bowing. The bowed tubes are not of great concern unless one of the tubes wedges to an adjacent one or until it comes in direct path of flame; with generally acceptable bowing of up to 1.5X tube outer diameter.[2]

The fitness for service assessment approach by multi NDT methods

Table 1 summarises the different NDT techniques along with damage mechanisms that should be employed for effective assessment of the condition of the reformer tubes.

Conclusion

The refomer tubes can have a much higher life than the design life if the operational aspects are monitored and controlled. The perodic assessment of tubes with a combination of NDT techinques, such as 'automated crawler' to measure tube diameter, internal fissures, carburisation and oxidation, along with microstrucure examination, can proivde reasonable confidence in predicting the remaining life of the reformer tubes. An attempt has been made here to bring out a very important correlation of extracting maximum life from reformer tubes with good operational practices. WF

Reference

1. Reformer Performance and Tube Life Management', Journal of Nitrogen Syngas 339, (2016).
2. Oil Industries Safety Directorate, Ministry of Petroleum, Government of India, (2015).

Table 1. Different damage mechanisms and NDT methods for detection

Damage mechanism	NDT method for detection	Assessment results
Creep damage	Diametric measurements	Calculation of accumulated creep damage
	Ultrasonic scanning for attenuation measurements	Detection of early stage of creep in terms of aligned voids and microfissures
	Eddy current testing	Detection of very advanced stage of creep damage
	Metallography	Early stage of reduction of creep strength is reflected from microstructural changes relating to carbide coarsening (sizing) and distribution pattern of secondary carbides. It also aids in the estimation of surface temperature based on microstructure degradation
	Radiography	Direct film imaging – complimentary NDT for confirmation of advanced stage of creep fissures
Localised overheating	Pyrometers/thermography in operation	Detection of hotspots – either by flame/flue gas impingement or damage of catalysts leading to disturbed internal gas path
	Metallography	Overheated structures around 1000˚C for short duration would dissolve the secondary carbide precipitates
Degradation of catalysts	Pyrometers/thermography in operation	Increased skin temperature and trend monitoring provides information on hotspots/channelising
	Pressure gauges and online readings	Pressure difference between inlet and outlet gases indirectly reflects disturbance of flow and damage to catalysts
External tube oxidation	Visual inspection	By touch and feel, loss of surface roughness reflects external oxidation
	Thickness measurements	Reduced wall thickness due to oxidation
	Permeability measurements	Reflects to higher depth of layer formations on OD/ID surfaces resulting in change of magnetic permeability
Thermal fatigue	Visual inspection	Typical bowing of tubes reflect disturbance in thermo-mechanical stress distribution, which may result in thermal fatigue over the period
	Dye penetration test	DPT, essentially at the points of fixity, such as weld joints between top and bottom pigtails as well as between tube to tube, can detect thermal fatigue cracks, which are generally found circumferential in direction
	Spring tension/counter weight balance readings at penthouse area	Indicates disturbance in thermo-mechanical stress distribution