Tube alloy degradation in a steam cracking furnace

Understanding catalytic coke growth mechanisms to better predict and optimise furnace service times with tube alloy degradation

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In order to optimise service run length for a steam cracking furnace it is essential to understand the conditions surrounding and including the tube coil for that run. These running conditions, such as temperatures, pressures and steam dilution, allow coke growth trends to be predicted and minimised to ensure the most favourable plant operational economics. In order to understand and optimise trending of multiple service runs throughout the life span of the tube coils, different considerations must be taken into account. This article reviews a simulated case study using the software package VMGSim[1] to explain the mechanisms causing reduced run times over the lifespan of a tube coil at a Mitsubishi Chemical plant site in Kashima, Japan.

Coke formation mechanisms

Coke formation in an ethylene cracker reduces the tube cross section, the heat flux to the reacting gas mixture and yield; it increases pressure drop and consequently reduces service time. Coke growth can happen through pyrolytic and catalytic mechanisms. Both mechanisms play an important part in the formation of coke within tube coils in a cracking furnace. At the early stages, coke formation mainly occurs through the catalytic mechanism. This type of coke growth is driven by the tube alloy itself when metal sites such as iron or nickel are contacted by process material and filamentous coke is produced. Detailed kinetic models of this can be developed by including surface reactions, segregation processes, and the diffusion of carbon through specific metal particles such as nickel.[2] Chromium content in the tubes can be used to inhibit the catalysing effects of tube metals and is often found in higher service temperature tube coil materials such as Inconel or HK40.[3] One must be careful regarding less obvious effects of trace components in the tube alloys such as silicon and aluminum and the interactions between iron, nickel and chromium content that make any direct correlations cumulatively incorrect (see **Table 1**).

Alloy composition inputs for a simulated coke growth model

Metal content, %			
Alloy	**Ni wt%**	**Cr wt%**	**Fe wt%**
15Mo3	0	0	100
13CrMo4.4	0	2	98
X8CrNi18.10	10	18	72
X50CrNi30.30	30	30	40
X5CrNi20.80	80	20	0
Inconel 600	77	16	7
Inconel 800	32	21	47

Table 1

Over time, pyrolytic coke growth soon becomes the dominant mechanism within the remaining service time of the furnace tube coils. This mechanism is directly related to the concentration of components within the process material and the running pressure and temperature. The simulation model developed and used for the analysis within VMGSim applied a molecular structure-type model for prediction of the coke growth rate profiles throughout the tube coil using the PIONA oil characterisation environment.[5,6] Coke formation from each type of molecular group is predicted and general kinetic rates could be derived from open literature using this generalised structure.[7,8,9] The classifications and groupings for kinetic rates in many of the papers available showed types of molecular structures from olefin to more dehydrogenated and ringed components were already recognised as different influences towards overall pyrolytic coke growth rates.

A combined equation to determine coke growth is shown (see Equation 1) where the first term consists solely of pyrolytic coke formation and provides an asymptotic growth rate:

$$r_{Coke} = r_{Asym} * (1 + r_{Cat} * l_{Thick}) \quad (1)$$

where rAsym is asymptotic coke growth due to pyrolytic coke formation, which is a function of the local temperature, pressure, and composition; r_{Cat} is catalytic rate of coke formation, which is a function of the tube alloy material; and l_{Thick} is thickness effect related to coke thickness, that is a function of the local coke thickness.

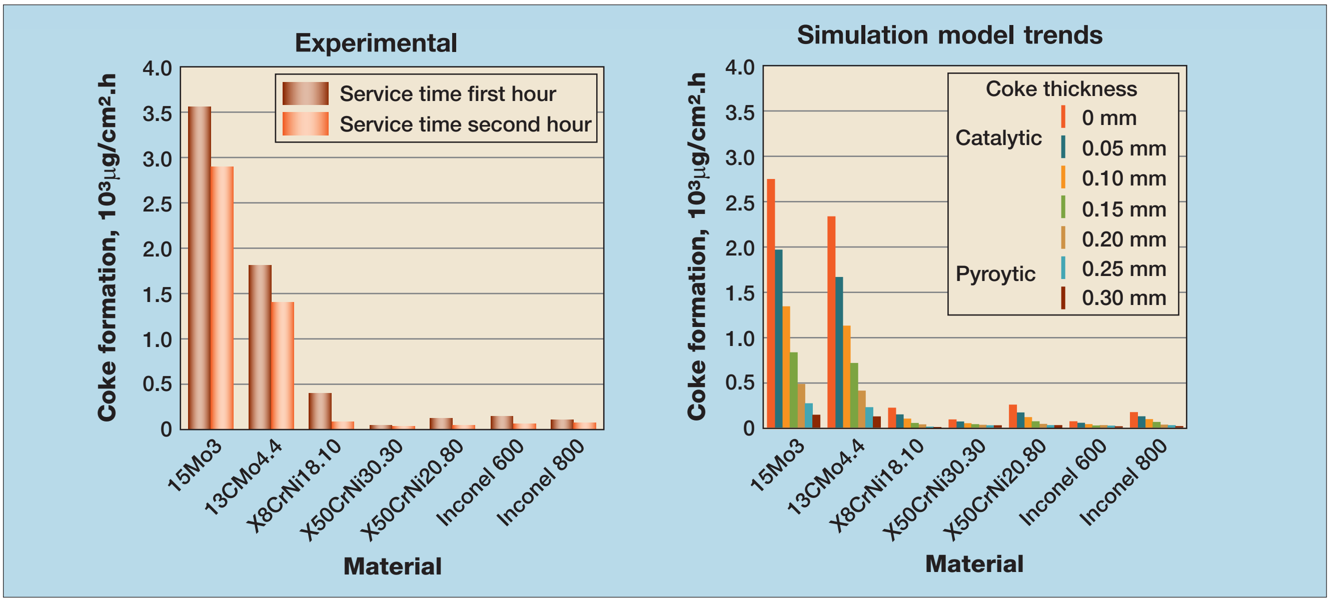

Figure 1 Pyrolytic versus catalytic coke growth model comparisons

Alloy degradation effects on service run times

As coke builds on the inside of the tube coils, the added roughness, reduced internal diameter and heat flux resistance cause the inlet coil pressure and furnace box temperatures to increase to keep outlet product specifications constant. Once a maximum tube coil temperature or pressure drop is reached, the inner tube coil must be cleaned. In this process of decoking, the tube coil metallurgy is affected and the metal content of the surface of the tube coil changes. Regular operation of the cracking furnace also alters the composition of the tube surface as iron, nickel, chromium and other elements can be found in coke formed within the coil during service time.[7]

Possibilities of tube coating and feed inhibitors

Tube coatings come in the form of aluminum, magnesium, zinc, and other metals and their associated oxides. These coatings are specifically good at reducing catalytic coke growth since they hide the iron and nickel sites that would typically catalyse the coke formation surface reactions.[10] Inhibitors used are commonly sulphur, phosphorous, aluminum, or silicon based and also focus on reducing the catalytic coke growth by passivating the metal surface.[11,12]

In order to bring the effect of tube coatings or feed inhibitors into the simulation model, the overall coke growth rate is calculated using Equation 2:

$$r_{Coke} = r_{Asym} * r_{AsymInhib} * (1 + r_{Cat} * l_{Thick} * r_{CatInhib}) \quad (2)$$

where $r_{AsymInhib}$ is a reduction in asymptotic coke formation due to using inhibitors or coatings; and $r_{CatInhib}$ is a reduction in catalytic coke formation due to using inhibitors or coatings, which is a function of tube coating or feed inhibitor effects on the catalysed coke growth mechanism.

Although this study focused mostly on the changing content of tube alloy, the roughness of the tubes is also suspected of playing a role in the reduced service time seen in older tube coils. In addition, the metals deposit as oxide films and their effect is not as simple as direct weight percentages, as described here, and carburised layers are created where carbon can more easily intrude. These are two details of the service time performance over tube aging that could potentially be further refined if more performance data and analysis were available.

Results

The built layer of coke thickness within the tubes also acts as a major parameter of how catalytic coke growth rates are determined. As the coke layer becomes thicker, diffusion rates through the coke slow the rates of material mass transfer to a point where this catalyst type coke growth becomes negligible. This transition from where catalyst growth is dominant to that where it is negligible depends on the growth rates of the coke itself, but can range from hours to days in an ethylene cracking furnace. **Figure 1** shows model predictions of coke growth rates as compared to literature from the catalytic dominated regions to the pyrolytic dominated region for different tube alloys. It is obvious how the effects of chromium content for the inhibition of coke growth – from the metal contents used as input into the model given in **Table 1** – compared to observations from specific tube alloys provided by Zimmermann *et al*[4] in **Figure 1**.

Unfortunately, the chromium content of the tube can decrease quicker than the iron and nickel contents, and the simulation model predicted higher initial catalytic coke growth from the new apparent tube coil metal content with less inhibiting make-up. Service times can be heavily over-predicted over the lifespan of the tube coils if this alloy degradation is left out of a coking simulation model for the reactor. Analysis of tube coil from the Kashima plant confirmed this type of tube alloy degradation and showed chromium content on the

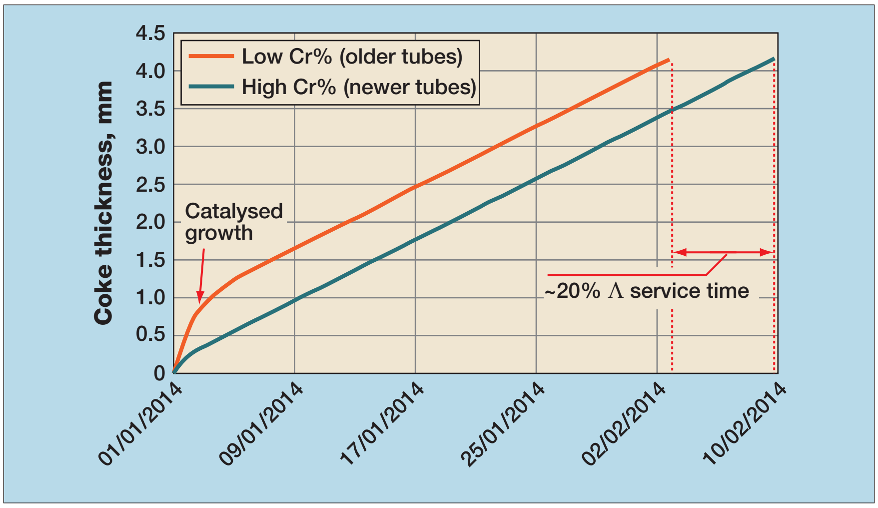

Figure 2 New vs old tube coke growth profiles

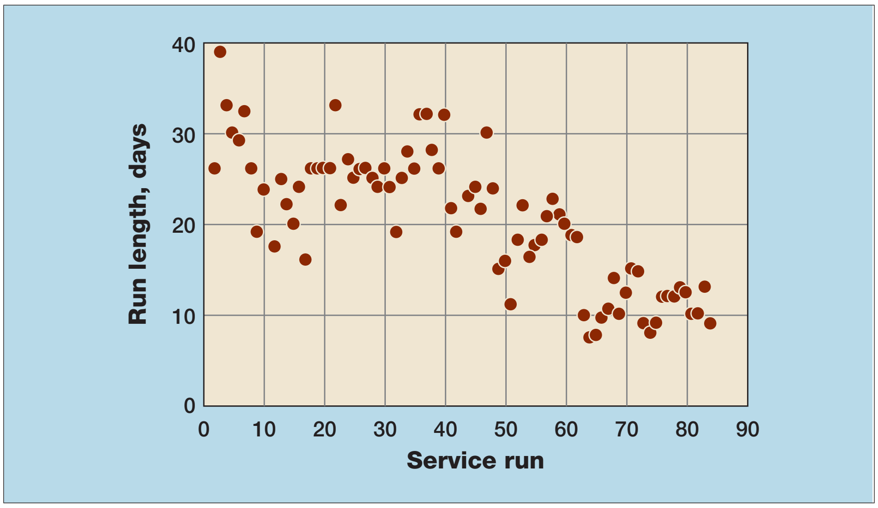

Figure 3 Run length for ethane feed unit in terms of service run (with outliers removed)

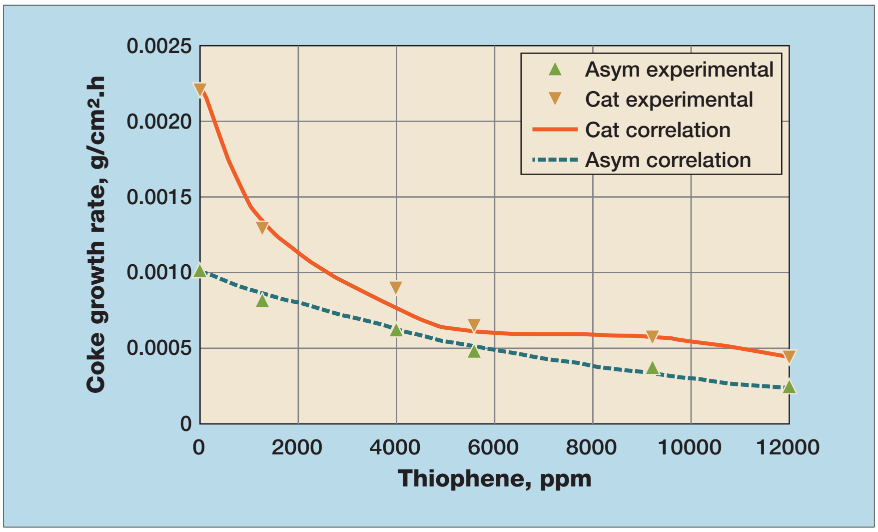

Figure 4 Coke formation rate as a function of thiophene inhibitor for two types of asymptotic and catalytic coke formation (experimental data[11] and correlation given in Eq.2)

tube's inner surface falling from 30-35 wt% in a new tube coil to 4-6 wt% at the end of the tube's life. **Figure 2** shows the results from two separate simulation model runs where initial and older tube content was entered for the service time runs. If the resulting furnace temperature and pressure drop are dependent on a set coke maximum thickness, 20% differences in service time can easily be encountered. The constant coke growth rate after initial catalyst coke growth is due to equivalent operational inputs being used and therefore equal pyrolytic growth rates were determined.

The speed at which the chromium content decreased, therefore reducing the length of each service run, could be trended when looking at the plant's operational data. **Figure 3** shows the operational service runs versus the run number for one of the ethane cracking furnaces. The severity of service runs being reduced by more than half is shown and points to the importance of understanding and planning for these trends. A similar trend could be observed in the simulation model when the tube alloy content used as input was updated per run. This was mainly due to a sharp increase in the coke thickness at the start of the run times as seen in the older tube profile in **Figure 2**.

In **Figure 4**, the coke formation rate as a function of dimethyl disulphide (DMDS) inhibitor is shown for asymptotic and catalytic coke types from experimental data and correlated using equation 2. **Figure 4** shows that the correlation used in VMGSim agrees well with experimental data and illustrates the reducing effects of DMDS on coke growth rate for either asymptotic or catalytic conditions.[11]

Even though the tube's metal content changes during the life of tube coils there are still inhibiting solutions available to keep longer run times. These solutions include tube coating and feed inhibitors since they do not directly relate to the operational conditions. Solutions such as increased steam dilution work to a limited degree, but keeping constant outlet yields with the resulting reduced residence times requires increased coil temperatures and decreases any significant advantages gained.

Conclusions

In this study the inevitable degradation of tube coil alloy over time was reviewed alongside measured alloy compositions and recorded service run lengths. Chromium depletion in the inner tube coil surface and resulting increased catalytic coke growth rates caused the service run length times to decrease over time. Plant data showed chromium content falling from 30-35 wt% down to 4-6 wt% over the tube's life. During this time, run lengths were found to decrease to less than half the possible days when the tubes were new. The use of different tube coatings and feed inhibitors was then suggested as a potential application to mitigate this problem and prolong tube coil lifespan without altering operational conditions. Addition of dilution steam as a solution to prolong service times was seen as less affective due to increased coil temperatures and therefore faster coke growth rates in order to match product yields. Further improvements to the simulation model of coke growth over tube coils would potentially come from the addition of roughness and metal oxide formation details, although more data would be required for confirmation of these effects to coke growth and their quantification.

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