
Question 10: What causes metal-catalyzed coking (MCC) that obstructs catalyst circulation in CCR reformers? What actions do you take to mitigate MCC formation?

BILL KOSTKA (AXENS NORTH AMERICA)

Metal-catalyzed coke (MCC) formation typically occurs on 3d valence transition metals such as iron and nickel. Under CCR-like conditions of low hydrogen partial pressure (less than about 620 kpa), high temperature (more than about 480 °C) and low or stagnant flow, hydrocarbons can adsorb and completely dissociate on these metals. The resulting adsorbed, dissociated carbon can then dissolve into and change the metal structure. Once a nanosized portion of the metal becomes supersaturated with carbon, carbon begins to precipitate in a tubular crystalline form breaking the carburized-metal fragment away from the parent metal with the carbon nanotube continuing to grow between them. Despite their fragile appearance, these carbon nanotubes are incredibly strong and can readily damage equipment when present in sufficient numbers.

Mitigation of filamentous carbon growth is best achieved by reducing the possibility of hydrocarbon adsorption on the problematic iron surface. Two methods have been used to successfully achieve this goal in CCR reformers: 1) passivation of the metal surface with an adsorbate such as sulfur and 2) use of a more appropriate metallurgy.

Research done by HJ Grabke et al. has shown that very little sulfur, about 0.5 wppm in the naphtha feed, is required to adequately passivate the metallurgy of a CCR reformer. As a result, most CCR reformers are operated with roughly 0.5 wppm sulfur in the feed. Some refiners may rely on incomplete naphtha pretreatment to supply this sulfur, however, addition of a known amount of a sulfur-containing species to the feed ensures adequate passivation on a continuous basis.

Carbon steel is very vulnerable to MCC formation. Alloying carbon steel with increasing amounts of chromium and molybdenum reduces this vulnerability. These two metals tend to migrate to the steel's surface and greatly dilute iron's presence there. As a result, there are much fewer Fe-Fe neighbors necessary for hydrocarbon adsorption, dissociation and dissolution into the steel structure. A 9Cr-1Mo alloy steel greatly reduces MCC even at 650 °C. Utilization of this alloy with on-oil sulfur injection virtually eliminates MCC even at 650 °C.

DAVINDER MITTAL (HPCL Mittal Energy)

The catalyst circulation in CCR may be obstructed due to other reasons as well besides metal-catalyzed coking (MCC). However, the metal catalyzed coking presents a serious problem especially in low pressure CCR reforming units.

The processes of metal catalyzed coke formation will cause particles of the heater tube metal to break away from the tube surface. There is also an increased risk immediately following replacement of heater tubes. The coke formed in the furnace tubes may eventually migrate to the reactors and lodge behind

the scallops or baskets. These coke deposits can grow until the scallops or baskets are deformed, affecting catalyst circulation, unit performance or even leading to an unplanned shutdown.

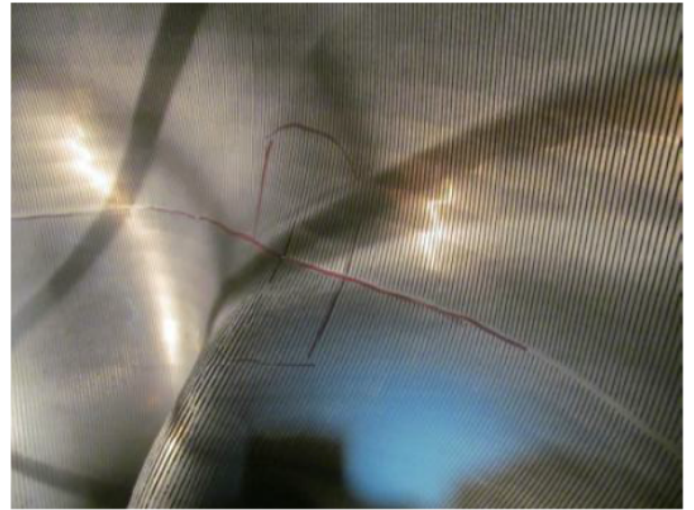
The recommended approach is to generally operate the Naphtha Hydro-treating (NHT) unit to remove essentially all of the sulfur in the feed. This will ensure that other contaminants (nitrogen, metals, oxygenates, etc.) are also removed from the feed to the extent achievable by the NHT. Organic sulfur is then added to the CCR reformer unit feed with a chemical injection system pumping in a specific and controlled amount of organic sulfur compound to achieve the target recommended by the licensor. This provides the refiner with independent control of the sulfur in the feed to the unit that can be changed as needed if feed rate or operating conditions change.

Our Continuous Catalytic Regeneration Reformer Unit was commissioned in May'2012. However, within one year of operation, the unit started experiencing several performance issues including restriction of catalyst flow in some of the spider legs of all 04 reactors , higher pressure drop and lower endotherm in reactors (more severe in 2nd Reactor, 60-70% of design value) and lower RON than design.

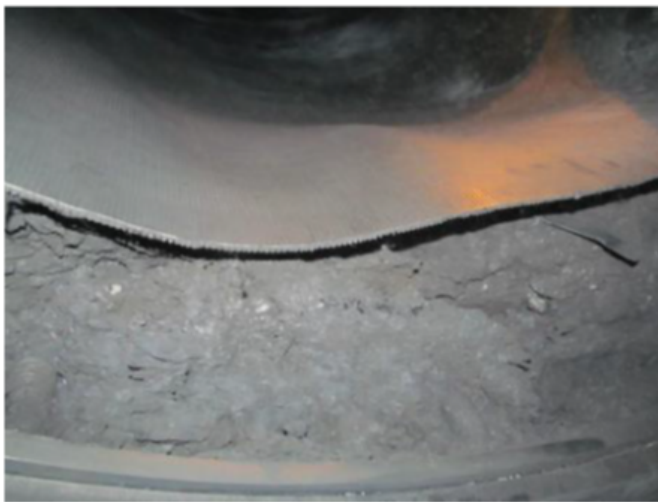
In view of the above issues, it was decided to shut down CCR during March-April'2014 and inspect reactors. Significant unexpected damage of reactor internals was found.



Picture-1: Huge quantity of coke in annular space between reactor grid and shell



Picture-2(a): Last panel of outside reactor grid found fully bulged with huge coke build up



Picture-2(b): Last panel of outside reactor grid found fully bulged with huge coke build up



Picture-3(a): Shiny coke between and inside scallops leading to bulging and fish mouth cracks



Picture-3(b): Shiny coke between and inside scallops leading to bulging and fish mouth cracks
A joint root cause analysis with Licensor confirmed presence of Fe and carbon graphite (high carbon content) in the coke samples. During cleaning of the scallops, presence of lot of hard shining coke (metallic coke) was observed along with soft coke. It was concluded that coke build up in reactors/scallops/grids may have taken place due to metal catalyzed coking considering problem with DMDS dosing pump during initial year of commissioning as well as due to other reliability issues like frequent trip of recycle gas compressor. The presence of metallic coke in reactors may have acted as nuclei and further catalyzed the coke growth during recycle gas failure.

The heater tube thickness measurements also indicated some loss of thickness indicating metal catalyzed coking in addition to other forms of coke. The level of thickness loss was fortunately not alarming to inhibit future operation.

Based on root cause analysis certain recommendations were made to minimize metallic coking and damage to reactor internals.

Metallic Coke:

Maintain sulfur level 0.3 to 0.5 ppmw on CCR feed to be substantiated by presence of detectable amount of H₂S in recycles gas and 100-150 ppmw of 'S' on catalyst sample.

Operate Naphtha Hydro-treating (NHT) unit to remove essentially all of the sulfur and other contaminants in the feed. Inject DMDS in CCR feed through dedicated facility to maintain recommended range of sulfur.

No flame sweeping/scattering on the furnace coils.

Maximum Tube Metal Temperature (TMT) to be restricted below 620oC.

Operation of heater burners within the design regime (maximum allowable process absorbed duty per burner: 1.0 Gcal/h).

Perform positive material identification of tube metal to confirm P9 (confirmed).

Other Coke/ catalyst agglomeration due to coke:

Improvement in reliability of recycle gas compressor.

Check for cold spider legs and try to restore catalyst circulation

Check for quality and temperature of net gas from CCR to avoid condensation in reactor spider legs

Maintain recommended coke (4 -5 wt%) on spent catalyst

Stress build up in Reactor internals:

Carry out emergency catalyst circulation in case of unplanned trip of the Recycle Gas compressor to relieve the mechanical stress built up due to difference in the thermal expansion coefficient between catalyst and reactors internals.

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