

Catalyst Passivation for Safer Reactor Entry

2008 AIChE Midwest Regional Conference
September 22, 2008

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Refinery Hydrotreating Reactors

- Refinery hydrotreating reactors typically contain catalysts composed of the following elements: Molybdenum (Mo), Nickel (Ni), Cobalt (Co).
- Catalysts can either be supplied in an oxide state or a pre-sulfided state.
- Catalyst are removed from reactors in a highly reactive sulfided state.



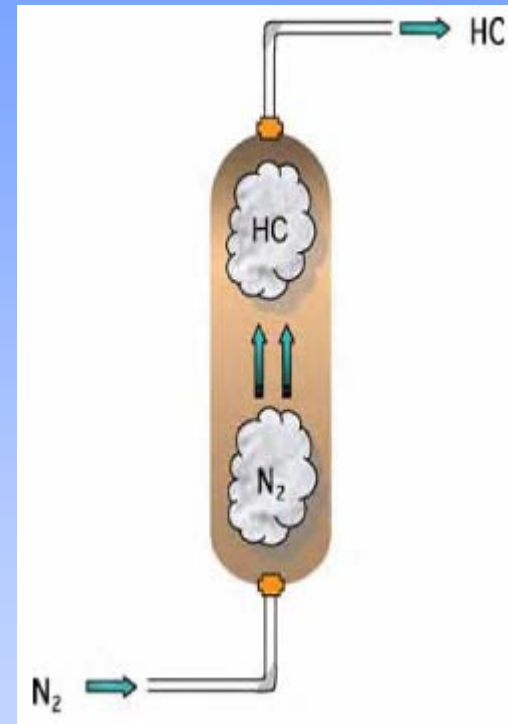
Catalyst Properties

- Catalysts are used to increase the rate of reaction in reactive processes.
- Active catalysts have both pyrophoric and self-heating characteristics which require them to be handled under a nitrogen atmosphere.



Nitrogen Usage in a Refinery

- Nitrogen has numerous safety applications within a refinery:
 - Inerting equipment to prevent flammable atmospheres
 - Welding Operations
 - Purging equipment for maintenance
 - Removing air from equipment prior to start-ups
- Although nitrogen is not toxic, it can be very harmful when localized in higher concentration than normally found in air.



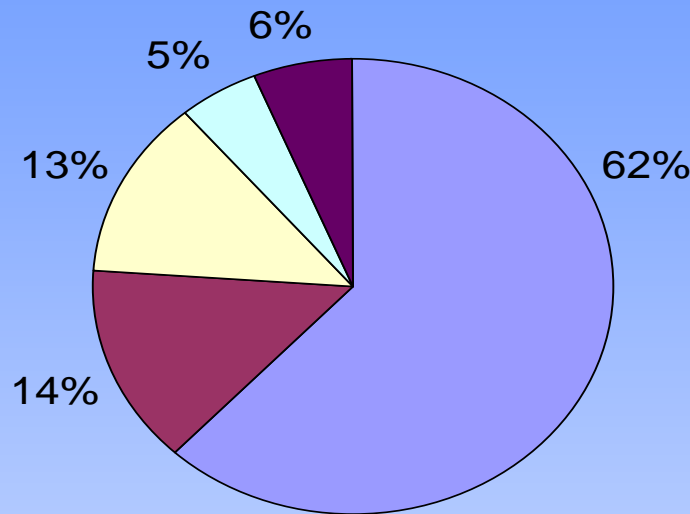
Hazards of Nitrogen

- Nitrogen is an asphyxiant in its gas/vapor phase.
- Asphyxiants can cause death or unconsciousness by suffocation.
- Asphyxiants are especially dangerous in confined or enclosed spaces.



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Areas Where Incidents Occurred



- Manufacturing/industry
- Trenches, manhole covers (not identified)
- Maintenance activities (not necessarily at manufacturing sites)
- Laboratories
- Miscellaneous (including medical facilities and transportation)

➤ A case study conducted by the CSB revealed that 85 incidents of N₂ asphyxiation during the period of 1992-2002 resulted in 80 deaths and 50 injuries.



Catalyst Handling

- In the 1970's, catalyst handling companies developed technology for entering reactors under nitrogen with life support equipment to remove catalyst.
- Catalyst removal is typically done by vacuuming or dumping through nozzles at the bottom of the reactor.



Catalyst Passivation

- Cat Tech licenses a novel technology for passivating hydroprocessing catalysts allowing removal under breathable air.
- This technology is known as CATnap™
- BP decided to evaluate the CATnap™ technology to minimize hazardous operations associated with inert reactor entry.



BP Test Case - Blending Oil Unit (BOU)



- BOU is a gas oil hydrotreater located at the BP Whiting Refinery
- Design Specifications:
 - 19,000 B/D capacity
 - 254,000 lbs of Ni/Mo catalysts
 - One Reactor (3 beds of catalysts)



Why the BOU?

- Ideal for test case with single reactor and simple oil/gas flow.
- The unit operated on gas oil which was suitable as a carrier oil for chemical injection.
- Size is large enough to offer a real test of the technology.
- Requires people inside the reactor vacuuming catalyst for four days or more during catalyst changeouts.
- Previous shutdown procedure already had oil wash and cold hydrogen sweep which is ideal for CATnap application.
- Offered sufficient lead time to work out issues, write job notes, perform all safety reviews and handle internal Management of Change procedures.

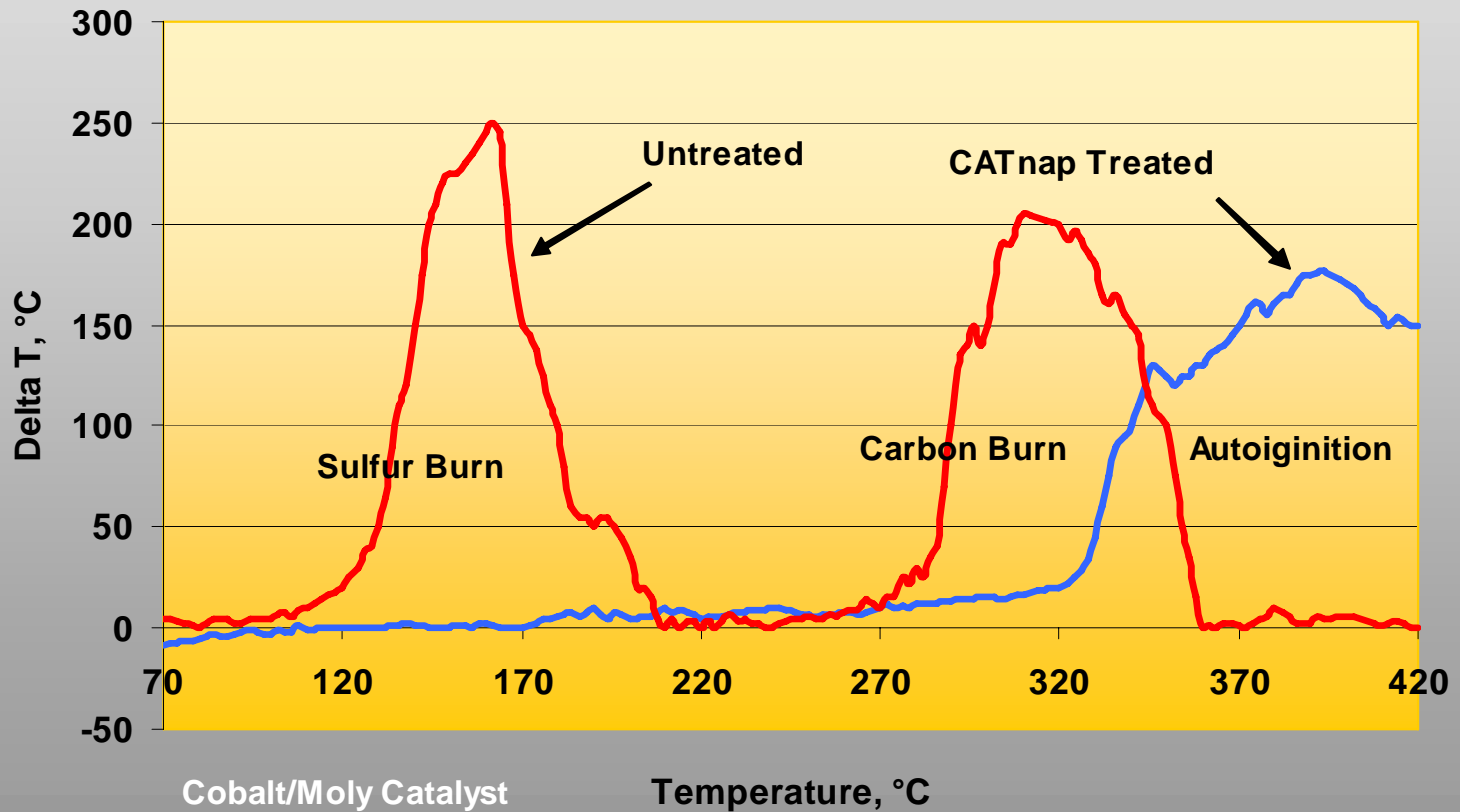


What is CATnap™?

- A proprietary process for treating catalyst during shutdown to render it safe to handle and unload in air
- Passivating chemical is injected into a recycle oil steam while the unit is cooling down
- The chemical coats the catalyst surface
 - Catalyst can be safely handled and unloaded from the reactor under air avoiding hazardous inert entry procedures
 - The coating retards oxygen penetration to the catalyst surface thereby inhibiting any pyrophoric or self-heating characteristics



Thermogram of Treated and Untreated Catalyst



History of CATnap

- **1984 – CATnap™ introduced in Japan**
 - Met with rapid success, especially with resid units
- **1991 – Cat Tech licensed CATnap™ technology**
- **1998 – Changes in spent catalyst classification**
 - Led to de-emphasis of CATnap™
- **2005 – Re-introduction of CATnap™**
 - ◆ Driven by new emphasis on safety and unit economics



Commercial Experience

- Over 200 million pounds of catalyst in over 200 applications
- 31 applications in North America
- All catalyst unloaded (dump and/or vacuum) under air
- No incidents of catalyst pyrophorics

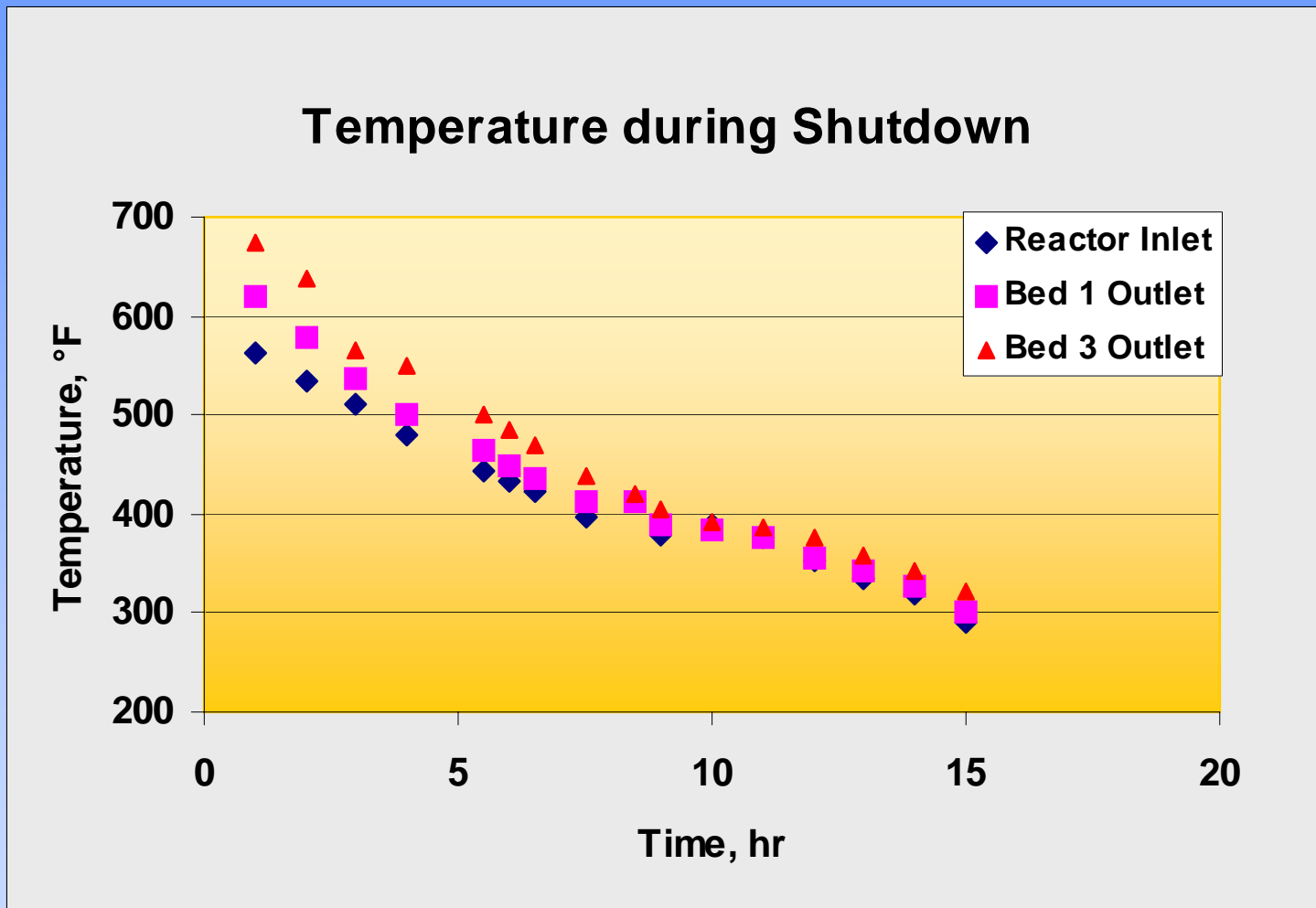


Shutdown Procedure

- Reduce feed rate and unit temperatures
- Introduce carrier oil, flush out process oil and establish oil recycle
- Inject CATnap™ passivating chemical at feed pump
- Circulate chemical and continue cooling to 280° F
- Discontinue circulation and de-oil unit
- Cool and purge with nitrogen to remove hydrogen and hydrocarbon vapor
- Introduce dry air flow to remove catalyst by dumping or vacuuming

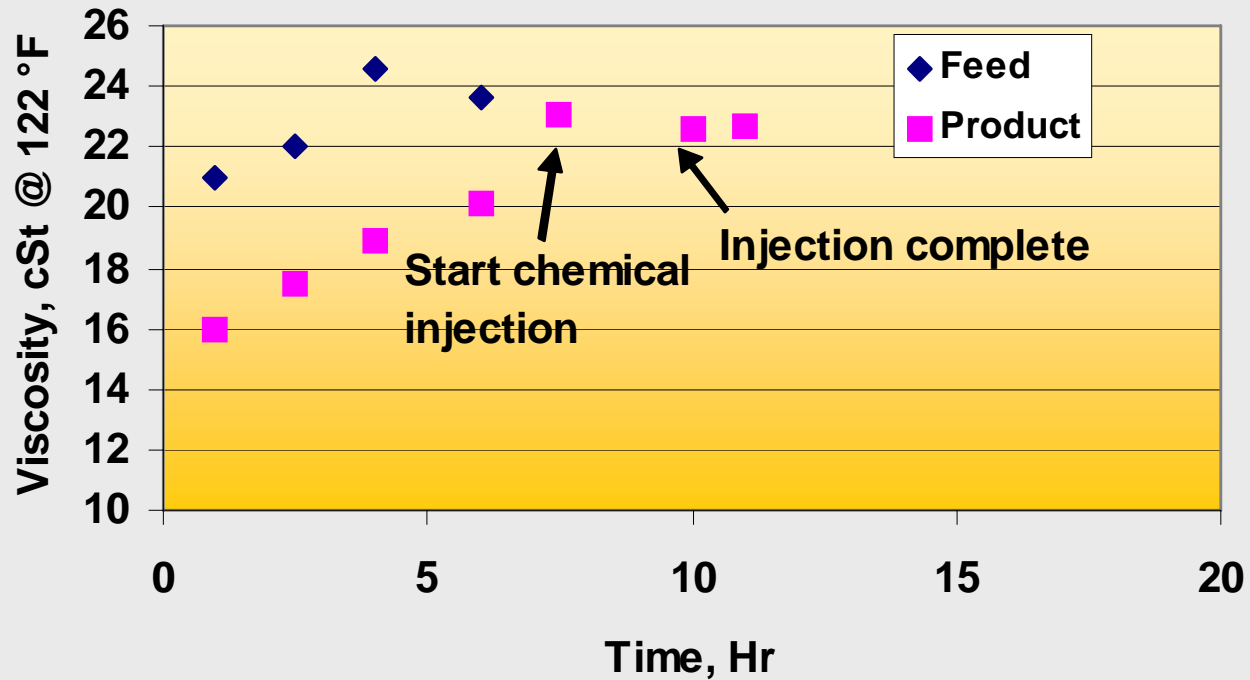


Unit Shutdown



Unit Shutdown

Viscosity during Shutdown



Results

➤ Safety

- All catalyst was unloaded under air
- Eliminated catalyst self-heating and pyrophorics characteristics
 - Slight heating in bottom of bottom bed due to air leaking
- Eliminated dust emissions

➤ Time savings

- Faster shutdown procedure – no hot H₂ strip
- No delays for dust or pyrophorics
- Permitting procedure was simplified
- Unloaded catalyst faster than previous changeout utilizing inert entry



Results

➤ Cost savings

- Reduced time to shut down unit and unload catalyst
- No nitrogen required for inert entry operations

➤ Intangibles

- Reduced concern of entry operations by technicians and refinery personnel
- Improved quality and productivity



Concerns

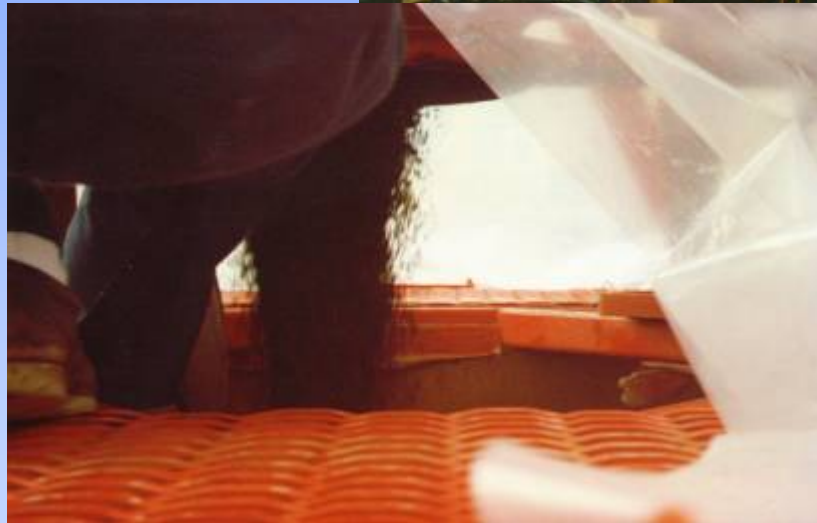
- **Reactor reached embrittlement temperature**
 - May be due to faulty thermocouples
- **Unit was de-oiled at low pressure**
- **Catalyst had some “oily” areas**
 - May be improved with better de-oiling procedure
- **Heating of catalyst in bottom bed**
 - Likely due to valve not fully closed
- **Oil in reactor**
 - Residual oil film removed by hydro blasting



Conclusions

- **CATnap™ application was a success**
- **Passivation offers a viable alternative to inert entry operations**
- **Offers possibility to largely eliminate what is commonly believed to be the most dangerous activity in petroleum refineries**
- **CATnap™ technology is being evaluated for other BP operating units**





Questions and Answers

