# Reducing Reactor Turnaround Time

How one German refinery is using CATnap catalyst passivation technology for safer, more efficient Turnarounds

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## Introduction

Bayernoil is an oil refining complex situated near Ingolstadt Germany, an asset of 4 major shareholders, BP, Varo Energy, ROG and Eni. It consists of two sites located at Vohburg and Neustadt with a combined crude processing capacity of approx. 10 million tonnes per annum. Producing a range of products which includes mogas, diesel, jet fuel, LPG and heating fuels it predominantly supplies the home Bavarian market. The Neustadt site includes a mild hydrocracker (MHC) and a diesel Hydrotreater (CHD) unit. The CHD shown in Fig.1 is a 67,000 BPD treater, contains round 321,000kgs of fresh basis catalyst and consists of two reactors in series flow processing a combination of light gas oils. Hydrotreaters are responsible for removing sulphur from gasoline and diesel to produce cleaner fuels and as in the case of the CHD are often on the 'critical path' of a larger refinery turnaround. Historically the unit has experienced unloading problems during its catalyst changeout including high concentrations of flammable vapours or LEL and agglomerated catalyst.

Fig 1- CHD Bayernoil

The lower explosive limit or LEL is the lowest concentration of a vapour in air capable of producing a flash fire in the

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presence of an ignition source. Controlling vapour concentrations to well below the explosive limit, typically <10-20% LEL is a major consideration for refiners. Shutdown of the CHD unit has always followed a conventional reactor shutdown procedure incorporating a hot hydrogen strip, however on opening the reactor manway, concentration of flammable vapors typically exceeded those deemed safe for confined space entry. Possible remedial options to reduce LEL include water flooding and hot nitrogen purging. Hot Nitrogen Purging was costly and typically required several additional days of purging to accomplish satisfactory LEL's. Water flooding involves flooding the reactor with an aqueous solution of soda ash and whilst effective at reducing LEL has several disadvantages. Valuable, reusable catalyst is lost or greatly reduced in value after flooding. The aqueous residue has an environmental impact and requires treating and catalyst handling and vessel cleanup can be difficult. Water flooding was therefore only a standby option with preference always given to hot nitrogen purging.

Bayernoil were looking for other more cost effective solutions to improve the reliability of the turnaround and mitigate against the wider economic impact from unscheduled delays on this critical path unit. Cat Tech is a specialist catalyst handling and tower services company and started talking to Bayernoil in 2010 about its CATnap passivation technology as a way to shorten the reactor turnaround time and improve the reliability of the catalyst change out. In Jan 2011 Bayernoil elected to use CATnap in a trial application on their MHC, hydrocracker unit and following its validation then applied the technology to their CHD later in the same year. Following these two previous successful applications Bayernoil once again chose CATnap for the 2014 turnaround of the CHD unit.

**History of CATnap**

The CATnap technology has successfully been used to treat almost two hundred million kilograms of catalyst to date with 23 applications last year alone. It has been widely embraced in the Far East and is becoming established in the Western World. Its development history started in the mid 80's in Japan where Kashima Engineering Company (KEC) and Softard Industries developed the technology for passivating self-heating catalysts so they could be safely removed under air. This has the obvious advantage of eliminating what is commonly

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referred to as the most dangerous operation in refineries today – inert entry operations. The technology was applied primarily to resid desulphurisation units because of the challenges they afforded with multi-bed reactors and agglomerated catalyst. The chemical treatment process involves the application of a proprietary mixture of high molecular weight aromatic compounds to a reactor system while under oil recirculation during the cooling and shutdown process. These compounds have the ability to coat all surfaces with which they come into contact. This includes reactor internals but most importantly the catalyst itself. This organic film retards oxygen penetration to the reactive metal sulfide surfaces and severely retards the dangerous and exothermic oxidative reactions. This is somewhat different to the conventional shutdown procedure which involves a hot hydrogen strip. The process oil is usually flushed from the unit and replaced with a lighter oil known as the carrier oil which is a very important part of designing the CATnap treatment. Once the unit is flushed and the process oil replaced it is put on oil recirculation followed by application of the chemical.
KEC and Softard optimised this technology through application to their native refinery and have now expanded throughout the Far East. Cat Tech International Ltd licensed the technology for application in Europe and the Middle East.

**Advantages of CATnap**
Although the opportunity to eliminate inert entry was central to developing the technology there are many other significant advantages of CATnap. For Bayernoil mitigating LEL was a prime objective and validation point for using the technology.

The advantages can be categorised as follows;

**Safety**
***Opportunity to eliminate inert entry***
The self-heating or pyrophoric nature of the catalyst and dust is suppressed or eliminated by the CATnap treatment. This allows the safe handling of catalyst in air.

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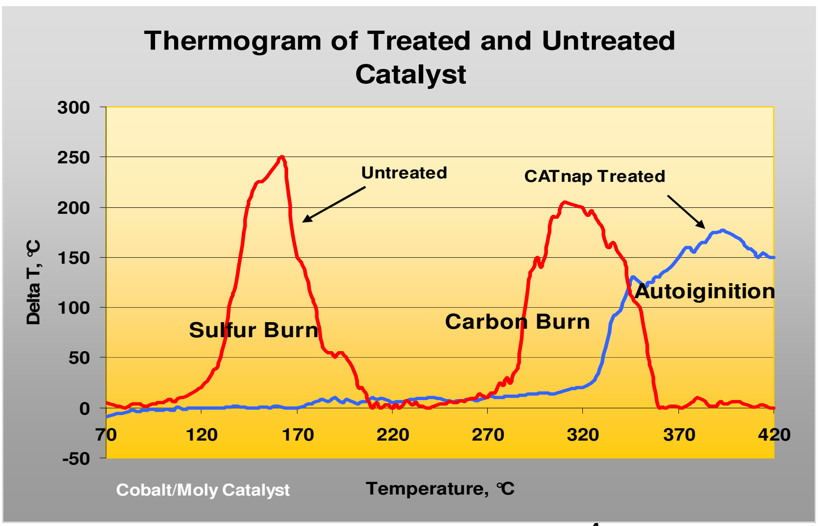
Figure 2 illustrates the passivating effect of CATnap treated catalyst. This thermogram shows the heat released by catalysts as they are heated. The red line represents an untreated catalyst whereas the blue line is the same catalyst treated by the CATnap process. As can be seen, when the untreated sample reaches about 120°C an exotherm is observed. This is the reaction of the metal sulphides reacting with air. As the temperature is further increased, a second exotherm occurs around 250°C. This is the carbon and coke on the catalyst burning. The CATnap treated sample does not demonstrate a significant exotherm until 300° C. This demonstrates the dramatic stabilisation provided by the CATnap treatment. If catalyst is removed under air it is noted that many reactors are made of austenitic stainless which may become sensitised and prone to the phenomena of polythionic acid stress corrosion cracking, (PSCC). Formation of polythionic acid requires three things to be present, sulphide corrosion products, oxygen and moisture. In the case of unloading in air, NACE international standards[1] provides guidelines for protection of the surfaces of austenitic stainless steel through the exclusion of water using dehumidified air.

Fig 2 – *Thermogram of CATnap treated and untreated catalyst*




**Dust free operation**

Dust from catalyst handling operations typically contains iron and catalyst metal sulphides which are both toxic and pyrophoric in nature. These types of dust are a risk to both people and the environment and present a challenge to both organisations and employers. With CATnap, dust and fines adhere to the treated catalyst surfaces resulting in a dust free handling operation. Employers have specific duties under a raft of environmental, occupational and other safety regulations. The technology can therefore be applied as an effective risk control measure in contributing to a safe system of work.

**Time Savings**

**Reactor shutdown time reduced**

Elimination of the hot hydrogen strip and the ability to cool under liquid oil circulation with its superior heat transfer capabilities can typically reduce conventional shutdown time by some 12 to 36 hours. This can have a positive impact on the time value of the unit particularly if it is on the critical path of a turnaround.

**Mitigation of high LEL's**

Many units using a conventional shutdown method have difficulty in achieving acceptable flammable vapour concentrations suitable for confined space entry. Controlling vapour concentrations to well below the LEL is a major consideration for refiners. The traditional hot strip method has the potential to produce volatile hydrocarbons through cracking reactions of residual oil left on the catalyst. Naphtha range material can be produced as a consequence and result in LEL in excess of those deemed safe for reactor entry. The CATnap treatment is very effective at mitigating against LEL through careful selection of a suitable carrier oil and its modified shutdown procedure.

**Catalyst Removal**

The technology tends to favour towards more free flowing characteristics of the catalyst. The hot hydrogen strip method can dry out and make compacted areas of catalyst cake worse. Unlike a hot hydrogen strip the CATnap treatment does not dry out the catalyst and provides some lubricity which can assist removal of the catalyst.

**Cost reduction**

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If the catalyst unloading is on the critical path then the reduction in downtime can have an overwhelming impact on the economics. The time value of the unit and reduced turnaround will have a positive impact on reducing third party costs including waiting time.

A major cost for inert unloading is the cost of Nitrogen, particularly during vacuum unloading. The passivated catalyst can be unloaded under air and so this cost is reduced or eliminated. Costs associated with hot hydrogen strip are eliminated

**Intangibles**
There are several advantages that cannot be quantified such as productivity increases and improved morale through avoiding working in an inert environment.

**CATnap Application procedure - Bayernoil, CHD**
The passivation process employs the injection of a proprietary organic chemical to a reactor system while under oil recirculation during the cooling and modified shutdown process. The details of the CATnap shutdown must be tailored for each application depending on such considerations as unit configuration, catalyst type, and local practices. The following modified shutdown procedure was agreed between Cat Tech and Bayernoil for both the 2011 and 2014 applications;

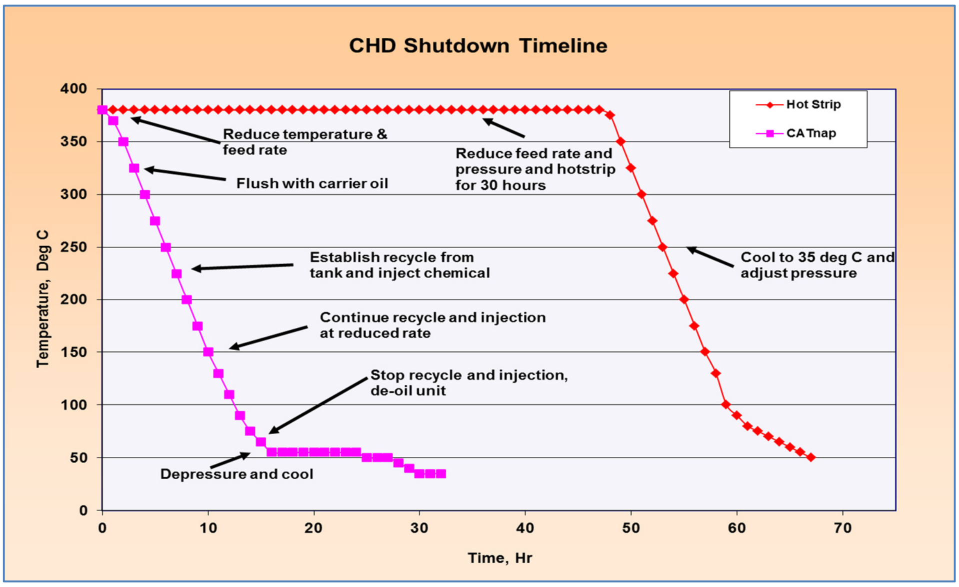
CHD feed rate and unit temperature were simultaneously reduced. The reduction in feed rate is necessary to avoid excessive unit pressure drop whilst the unit is cooling down. At the same time the flow must be high enough to maintain good liquid distribution in the reactor for treatment of the catalyst. The reactor temperature is reduced to avoid unwanted cracking and desulphurisation reactions during the chemical application. When target conditions were met with regard to temperature and flow rate, in this case 230ºC and $240 m^3 hr^{-1}$, the identified carrier oil was introduced to flush the unit of the normal feedstock. The carrier oil selected was a light atmospheric gas oil with a flash point >90ºC, IBP > 200ºC and a viscosity of 4-5 cSt. Samples were periodically taken at the stripper bottom and the feed tank and analysed for viscosity and

flash point to monitor progress of the flushing operation. After approximately 5 hours the unit was flushed out and put on internal oil recycle.
The CATnap passivating chemical was injected over a 2 hour period at the suction side of the feed pump and this was followed by 5 hours of circulation whilst continuing to cool the reactors.
Bayernoil wanted to take advantage of cooling under oil circulation as far as possible due to its superior heat transfer capabilities. A target temperature of 60ºC was achieved which was 10 deg C above the minimum depressurisation temperature of the unit. Target temperature is dependent on many variables including oil viscosity, unit pressure drop, minimum depressurisation temperature, compressor characteristics and other variables.
Once target temperature was achieved the unit was de-oiled using maximum hydrogen gas flow. The unit was then depressurised and degassed according to normal procedures whilst cooling to entry temperatures.
The manway was removed and the vapour space analysed for hydrocarbon vapor (LEL), CO, H2S and SO2

**Results**
In March 2011 and 2014, the CHD unit was successfully shut down with the CATnap technology. Fig 3 compares and outlines the steps involved in the CATnap and prior shutdown procedures. As can be seen elimination of the hot hydrogen strip and the ability to cool under liquid oil circulation allowed the unit to be shutdown some 36 hours earlier then the traditional shutdown method. On opening the reactor manways, gas samples were taken and found to be LEL free. This was a key objective and a validation point of the technology as historically levels of flammable hydrocarbons typically exceeded confined space limits. Start of catalyst unloading operations was expedited as the need for remedial hot nitrogen purging typically requiring an additional 3-5 days was eliminated. Catalyst was removed by a combination of gravity flow through dump nozzles and vacuum extraction. Catalyst handling operations were essentially dust free as fines adhered to the CATnap treated catalyst surfaces. Although the

catalyst was well passivated and showed no self- heating tendencies, Bayernoil elected to unload under Nitrogen.

Fig 3– *CHD CATnap shutdown Timeline, 2011 & 2014*



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**Conclusion**
Cat Tech's patented CATnap technology provided new possibilities for Bayernoil to reduce the risk for the financial penalty associated with turnaround delays. A reduced reactor shutdown time, mitigation of LEL and elimination of toxic and pyrophoric dust all contributing to the safety, reliability and reduced turnaround time of the catalyst changeout. In the case of further improvements, the catalyst is well passivated and the option to unload under air would eliminate the hazards and additional costs associated with working in an inert environment.

*Note: The foregoing is not intended to be an endorsement of the CATnap Technology by Bayernoil. Each reactor unit must undergo a comprehensive engineering evaluation to assess its suitability and the refiner must exercise its own independent judgment to decide whether the CATnap Technology is appropriate for use.*

**Acknowledgements**

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Special thanks to all the team at Bayernoil for the support and valuable assistance provided during all three CATnap applications. Bayernoil has a motto "*successful together*" in that's its success extends down to the commitment and co-operation of its people including its contracting personnel.

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