Improving reformer tube reliability through effective insulation management

The objective of this paper is to share the result of the root cause analysis of the reformer tube failure at an ammonia-producing facility in Malaysia. The root cause analysis was conducted by employing a Kepner-Tregoe approach. The hypothesis of the preliminary root cause was supported by computational fluid dynamics (CFD) simulation and laboratory analytical analyses. The result of the detailed study shows that the root cause of the reformer tube failure is metal dusting. The metal dusting occurred due to outside ambient air flow into the reformer box from the insulation gaps at the bottom of the reformer tube, causing the tube temperature to drop to 700°C–800°C (1292°F – 1472°F).

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Introduction

This paper will highlight the reformer tube damage that occurred in an ammonia-producing facility in East Peninsular Malaysia due to metal dusting. The failure mechanism is rare due to the nature of the ammonia producing facility; however, there could be a potential risk of a similar occurrence in other similar plant setups.

Site introduction

PETRONAS Chemicals Ammonia Sdn. Bhd. or PCASB is a company integrated within PETRONAS Petroleum Industry Complex (PPIC), located in Kerteh, Terengganu, which lies to the east of Peninsular Malaysia. The company is a wholly-owned subsidiary of PETRONAS Chemicals Group (PCG) and was incorporated in July 1997. The company is a certified ISO 9001 and ISO 14001 company. The technology licensor is Haldor Topsoe A/S.

The PCASB plant is a syngas plant where the excess hydrogen is utilized for ammonia production. The main product, aside from syngas and ammonia, is carbon monoxide, with the following capacities:
- Synthesis gas – 258 MTPD (284 STPD)
- Carbon monoxide – 740 MTPD (815 STPD)
- Ammonia – 1,380 MTPD (1521 STPD)
The process for producing synthesis gas includes steam methane reforming using a pre-reformer and reformer configuration with a S/C ratio of 1.5 to yield a desired H₂/CO of more than 3.0/1.0. The carbon dioxide recycle is maximized based on the CO product demand specified by the customer. The CO concentration in the synthesis gas ranges from 19% to 23.5% by volume, depending on the S/C ratio.

The reformer consists of two parallel furnace chambers (chamber A & B), each containing 144 catalyst tubes loaded with Haldor Topsoe nickel oxide catalyst type R-67-7H, 7-hole cylinder shape. There are 432 burners in the two reformer chambers providing uniform heating across six levels of burners by side firing. The fuel used for the reformer consists of off-gases from the downstream units such as a pressure swing absorption unit and natural gas containing approx. 92% methane.

PCASB is not a typical ammonia plant which operates at S/C of 1.5 compared to conventional operating at 3.0. The reformed gas outlet temperature for a classical ammonia plant is below 800°C (1472°F) compared to +900°C (1652°F) for PCASB plant. The design limit for PCASB reformer tube temperature is 1020°C (1868°F).

**Description of incident**

On November 16, 2015 at 09:00 pm, the shift operator observed that the reformer bottom plate for chamber A was glowing, indicating a severe hot spot. A few tubes near the hot spot location also showed signs of improper insulation, as glowing was seen at the tube outer ring. The surface temperature was taken at the bottom plate hot spot and showed a high temperature of 820°C (1508°F) which exceeded the design temperature of 370°C (698°F). The inspection from the reformer side peephole showed that the glowing was localized to the fire brick floor insulation near the hot spot area, suggesting a tube leak from within the fire brick floor insulation. The tube surface temperatures were also analyzed; however, there was no excursion beyond the safe operating limit (SOL) of 990°C (1814°F).

A steam sparger was put in place however, the bottom plate temperature remained higher than the design temperature. The plant was immediately shut down to identify the root cause and plan for equipment repair. The repair scope included removal of the affected firebrick floor insulation within the hot spot area to replace all identified problematic reformer tubes, reload catalyst, and perform fire-brick floor insulation installation.

**Findings and observation**

During the first entry into the reformer box area, it was detected that most of the fire brick floor insulation had been damaged by the heat. The
remaining fire brick debris was physically removed to identify the location of the tube leak. The physical tube damage at tube #6 exhibited a horizontal ‘fish-mouth’ rupture, which was approximately 4 cm (1.57 in) in length and 1 cm (0.40 in) in height. The tube was located in the south side of chamber A. The location of the leak was within the fire brick floor insulation approx. 10 cm (3.94 in) below the surface. The leaking tube was installed in 2011 and manufactured by Kubota Corporation. All the reformer tubes are made of 5Cr/35Ni steel material. Based on a previous inspection report conducted by Quest Integrity using Mantis, the remaining tube life time was calculated to last until 2023.

Further inspection was conducted using an outside diameter (OD) check with pi-tape. The reading was found to be within tolerance of 3% OD growth. Radiography testing was conducted to determine the condition of the tube internals. The failed tube was cut and studied. It exhibited a pit-like localized corrosion.
During the removal of the failed tube, a layer of dust was observed at annulus between the catalyst support grid and reformer tube. A sample of the dust was collected and analyzed for its composition.

![Figure 7. Radiography testing of leaked tube](image)

<table>
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<th>Component</th>
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<tr>
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<tr>
<td>5</td>
<td>Ni</td>
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</tr>
<tr>
<td></td>
<td>Total</td>
<td>100</td>
</tr>
</tbody>
</table>

*Table 1: Reformer dust composition*

Initial result indicates presence of reformer tube metal wastage and oxidation products.

![Figure 8. Dust layer on catalyst support grid](image)

An abnormal operating condition was also noted for tube #6. The feedback from the operation team suggested that the bottom insulation was not intact.

**Methodology for root cause analysis**

A formal investigation team was established to identify the root cause of the incident. This team was on tight schedule to determine the root cause and ensure that a correct mitigation was put in place before plant start-up.

The incident investigation team and resource parties comprised of experts from PETRONAS, Manoir Industries and Kubota Corporation (tube manufacturer), Haldor Topsoe A/S (technology licensor), Quest Integrity (tube inspection specialist), and a few local laboratories for analytical support.

Due to time constraints the Kepner-Tregoe approach (ref. 2) was used to determine the potential root cause of the incident. Tube #6 was clustered in different sets of categories (see below) and further inspection was conducted of other reformer tubes to examine the tube internals based on this cluster.

Some of the following categories were considered by the investigation team:


2) Operating conditions (high or low tube temperature excursion, insulation gap vs. intact insulation).

3) Catalyst installation data (high DP outage vs. normal outage).

4) Location of the tube (north vs. south due to the physical arrangement of the reformer)
From the categories that were considered, an internal inspection of a total of 22 additional tubes was carried out. The catalyst was unloaded from each tube and video borescope was conducted to check for similar symptoms at the location of the defect.

**Design of tube**

The reformer consists of both Kubota Corporation and Schmidt & Clemens tubes with three separate sets of installation years. Different tubes with different manufacturer and years of installation were sampled to determine whether the failure was due to a manufacturing defect or tube installation error. No direct correlation was found between the tube design and the tubes that had failed.

**Reformer operating conditions**

The tube metal temperature (TMT) data, collected prior to the tube failure, was reviewed. The data revealed a low temperature drop below 900°C (1652°F) near tube #6 (south side). The low temperature was due to a few problematic burners near the south side that had been taken out of service for the past 1 month.

During the initial inspection of the failure, the tube outer ring was also observed to be glowing, suggesting that the bottom insulation was no longer intact. Repair data from the bottom insulation was extracted from the SAP system. In chamber B, other tubes had issues with a loose bottom insulation.

**Catalyst installation data**

The data from the catalyst loading in 2011 was reviewed (installation year for tube #6) to determine whether a high DP variance of the reformer catalyst loading caused the failure. A high DP variance in the reformer catalyst tube will promote low flow, potential channeling, and high tube metal temperature excursion. There was no abnormal DP variance for tube #6, as the outage was within the recommended tolerance of ±5%.

**Location of tube**

The reformer tubes were sampled from both sides in both chambers to check for similar symptoms of metal loss at a localized area near the catalyst support grid. The findings revealed that there was no specific correlation with a similar failure based on location within the reformer.
chamber although most of the south side had a low temperature excursion below 900°C (1652°F).

A preliminary analytical analysis of the failed tube was also conducted with a local laboratory within PETRONAS Petroleum Industry Complex. The preliminary analysis using X-ray fluorescence (XRF) indicated a high content of reformer tube metal wastage which includes nickel, chromium, and iron.

Based on the Kepner-Tregoe analytical analysis and the physical findings and inspection, it was hypothesized that the failure mechanism was due to metal dusting caused by affected part operated at metal dusting temperature region in a carburizing environment. The tubes which are within this category were replaced with new tubes while awaiting further detailed confirmation through computational fluid dynamics (CFD) and detailed analytics to verify the hypothesis. The plant was restarted once all the affected tubes had been replaced. A total of 10 tubes were replaced during the shutdown.

**Analysis of reformer tube**

To verify the root cause of the premature failure (the remaining life time of the tube was calculated to last until 2023) and the loss of material observed at reformer tube #6 and some other tubes, samples were sent to Haldor Topsoe for investigation.

The samples consisted of damaged as well as undamaged reformer tubes and dust collected on the inside of the failed reformer tubes.

The samples underwent a metallurgical examination to verify the cause of the crack and cause of loss of material. The samples went through a series of tests including Chemical Analysis (CA), Light Optical Microscopy (LOM), Scanning Electron Microscope (SEM) equipped with Energy Dispersive Spectroscopy (EDS) for semi-quantitative composition analysis and X-ray diffraction (XRD).

The conclusion from the metallurgical examination was that the cause of the material loss on the inside of the reformer tubes was metal dusting.

Metal dusting has been described extensively in the literature (ref. 1 & 3).

**Metal dusting phenomena**

When exposed to high temperature, stainless steel will form a Cr-rich oxide layer, which will protect the steel against further corrosion. Defects will form in this oxide layer, allowing corrosive species, like CO, to penetrate it. CO will dissociate at the metallic surface, and free carbon will diffuse into the metal matrix.

Two processes drive the formation of free carbon. The reduction reaction:

\[ \text{CO} + \text{H}_2 \leftrightarrow \text{C} + \text{H}_2\text{O} \]

and the Boudouard reaction:

\[ 2 \text{CO} \leftrightarrow \text{C} + \text{CO}_2 \]

The metallic matrix becomes oversaturated with carbon. This results in formation of graphite and release of free metallic particles.

Coke grows catalytically by the reaction of gas with free metallic particles. In order for metal dusting to take place, a carbon monoxide containing gas with a carbon activity of 1 or more is required.

At operating conditions of 905°C (1661°F) and 22 bar g (319 psig), the exit dry gas composition from the reformer tubes was calculated to be H\(_2\) 69.4%, N\(_2\) 0.2%, CO 19.1%, CO\(_2\) 3.6%, and CH\(_4\) 7.7%. The reformer tube temperature was calculated to be 945°C (1733°F). For the specific gas composition, the temperature at which the carbon activity is equal to one, has been calculated. For the reduction reaction the temperature is calculated to be 841°C (1546°F). For the Boudouard reaction the temperature is calculated to be 855°C (1571°F).
Thus for metal dusting to take place it will require that the temperature of the metal surfaces be 855°C (1571°F) or below. The speed of reaction will be relatively slow at temperatures close to 855°C (1571°F), but at a temperature from 700°C - 800°C (1292°F - 1472°F), the speed of reaction will be considerably faster.

Normally, graphite layer forming on the metal surfaces will slow down the carbon forming reactions due to diffusion limitations, but in areas with a high gas velocity, the graphite layer will be eroded away, thus adding to the speed of metal dusting.

As the calculated reformer tube metal temperature of 945°C (1733°F) was well above the critical carbon formation temperatures of 855°C (1571°F) and 841°C (1546°F), metal dusting should not be possible.

Nevertheless, the metallurgical examination clearly indicated that metal dusting was the cause of the reformer tube failure. So how can the reformer tube temperature drop to the metal dusting temperature area?

**Reformer gas outlet system**

The temperature gradient in the bottom of the reformer tube is very high.

At the bottom of reformer tube, (Figure 12), below the catalyst support grid, the reformed gas is guided into a small center tube inside the reformer tube. The annulus between the reformer tube and center tube is filled with a castable refractory which insulates the hot gas and centers the tube from the reformer tube. The reformer tube metal temperature will stay above the critical metal dusting temperature where it is exposed to the aggressive reformed gas. In the area with the refractory on the inside of the reformer tube, the temperature gradient is +800°C (+1472°F). A part of the reformer tube will therefore be in the very critical metal dusting temperature area. The casting on the inside of the reformer tube prevents metal dusting from taking place, as the refractory will act as a diffusing barrier, slowing down the metal dusting reaction to an insignificant value.

![Figure 12. Configuration of internal tube near the catalyst support grid](image)

The pressure in the bottom of the reformer chamber on the combustion side is approx. -20 mm WC (-0.8 in WC). Air is prevented from entering the reformer chamber by a specially designed sealing system consisting of a combination of ceramic fibers and high temperature fabric.

The insulation of the reformer tube penetration out of the reformer chamber bottom (and top) requires maintenance, especially if the reformer tube is to be replaced. Failing to do so may lead to gaps and could cause outside air to be drawn in along the reformer tube and into the reformer chamber. The outside air will affect the reformer performance and lead to an undesired cooling of the reformer tube.

**Cooling of reformer tubes by air ingress**

Computational fluid dynamics (CFD) analysis was used to determine the cooling effect of air flowing up along the hot reformer tube.

In the analysis, a gap size of 10 mm (0.4 in) covering 1/10 (36°) and 1/20 (18°) was simulated.
In case of a small gap (Figure 13), the temperature of the metal will reach 836°C (1537°F) which is judged safe from a metal dusting perspective. For the larger gap (Figure 14), however, the temperature drops to 790°C (1454°F) and in that case, metal dusting is very likely to occur.

Based on the photos taken (Figure 15), the gaps are most likely larger compared to the simulated large gaps.

Failure mechanism conclusion

Failure mechanism of the incident was metal dusting due to affected part operated within a metal dusting temperature region in a carburizing environment. The cause of the incident was the flow of cool outside ambient air into the reformer box through a gap in the loose insulation of the outlet tube. This resulted in a localized temperature drop to the metal dusting temperature region of 700°C–800°C (1292°F - 1472°F).

Lessons learnt and way forward

It is important to manage effective insulation. For reformer equipment, this not only relates to energy and loss management, as it has been proven to impact reformer reliability as well.
One way forward considered by the investigation team is to upgrade the insulation to a more airtight design.

KLAY EnerSol was approached to come up with a better design of the reformer bottom insulation. The new design consists of two pieces of insulation:

1) The top portion was a quilted sleeve, designed and fabricated by Insulcon B.V. to provide a tight seal to prevent film of air ingress that can promote metal dusting.

2) The bottom portion was a removable insulation jacket designed and fabricated by KLAY EnerSol for ease of monitoring/inspection.

3) Both portions will provide additional heat insulation to the reformer tubes.

The insulation material for the top portion consists of silica fabric and ceramic fiber while the bottom portion consists of glass cloth + aerogel insulation + ceramic fiber.

The main benefit of the two pieces of insulation is to allow monitoring and inspection by removing the bottom portion only without allowing air film ingress into the reformer box, as the top layer will remain intact.

Figure 17. Comparison between new insulation and old insulation

In addition to its main objective as an airtight insulation material, it was also proven to provide more heat insulation. During product trial, it was observed that the surface temperature dropped from an average of 70°C (158°F) to 50°C (122°F), which benefits the energy consumption in reformer.

Recommendations from the incident

Below is a summary of the recommendations from the investigation team:

1) Insulate the bottom insulation properly to avoid external air ingress.

2) Conduct round check (physical inspection) for bottom insulation as part of the Equipment Basic Care (EBC) program.

3) Establish proper monitoring (using temperature gun) and track program for bottom insulation.

4) Repair and reinstate immediately if any bottom insulation gap is observed.

Figure 18. New design of insulation materials
What does it mean for other classical ammonia plants around the world?

As mentioned in the introduction, the PCASB plant is a syngas plant, where the excess hydrogen is utilized for ammonia production. The operation of the reformer and the outlet system differs compared to a classical ammonia plant, as a classical primary reformer has an outlet hairpin system.

![Figure 19. Typical Topsoe Syngas outlet system](image)

The S/C ratio of a typical ammonia plant is approx. 3 compared to the S/C of 1.5 for the PCASB plant. The reformed gas outlet temperature for a classical ammonia plant is below 800°C (1472°F) compared to +900°C (1652°F) for the PCASB plant. The difference in S/C ratio and reforming temperature makes the reformed gas for a classical ammonia plant less aggressive. For a typical reformed gas outlet, the Boudouard temperature of the primary reformer is approx. 723°C (1333°F) whereas the reduction temperature is 706°C (1303°F), reducing the risk of metal dusting. Never the less, Haldor Topsoe always recommends maintaining the insulation material on the reformer outlet and keeping the hairpins in good condition.

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