FIORDA Case Study

Corrosion Attack on Primary Reformer Tubes

Case Study Report

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AmmoniaKnowHow

NH3 HNO3 CH3OH NPK (NH4)(NO3)

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Summary Incident Database, No: 7

No:	7
Date	08/15/2018
Plant Code	AMOXY
Incident Code	AMOXY07
Technology	Ammonia
Plant section	Primary Reforming
Main Equipment	Primary Reformer
Sub-Main Equipment	Primary Reformer Catalyst Tubes
Operation phase (during event)	Normal Operation
Operating parameters (during event)	Unknown
Medium	NG Fuel
Risk category	Operational
Hazard type	Corrosion
Failure Cause	Poor control procedures
Failure Mode	Contamination

Hours of operation	17520
No of failures last 6 months	65
No of failures last 12 months	>1
No of failures last 24 months	>1
Warning signs	Unusual spots
Event description	Ammonia plant primary reformer was retubed by replacing HK-40 tubes with Nb-modified HP alloy having the same outer diameter but reduced wall thickness. After about twenty four months of the plant startup, during routine visual inspection plant operator observed unusual spots on some of the reformer tubes. During turnaround, severe degradation and loss of material was observed at isolated locations on several tubes. Out of 300 tubes, 65 tubes were replaced as their wall thickness was reduced significantly.
Immediate response action	Routine observation
Findings	A combination of burner geometry anomalies, over firing and insufficient or poor combustion air flow distribution created conditions for poor combustion, irregular flame patterns and high levels of CO. The corrosion products formed are consistent with sulphurdising with hydrogen sulphide in the fuel gas of 0.6% and high partial pressures of S2 of 10-8 atm at high temperature. Increasing temperatures leads to a higher rate of sulphidation. The mixed oxides and sulphides present in the corrosion products indicate that the flue gas around the affected tubes was not constant and was alternating between oxidizing and sulphurdising. Microscopic examination, chemical analysis, combustion survey and the high sulfur content in the corrosion products reveals that the reformer tubes failure occurred due to Sulfidation.
Consequence Primary	Primary reformer tubes replaced
Consequence Primary cost	Unknown
Consequence Secondary	Extensive TAR

Consequence Secondary cost	Unknown
Consequence Details	
Comments	Many of the burners flame were observed to be unstable rather long straight and narrow and were moving towards the reformer tubes. A number of burners were observed to have the flame slowly moving away from the burner because of irregular air supply probably due to partial blockage of nozzles. Some haziness was also observed at the lower level indicating after burning due to insufficient combustion air in some parts of the primary reformer. Prior to reformer re-tubing client was not cautioned about the HP micro alloy tubes susceptibility under reducing environment to sulfidation attack due to the presence of sulfur in the fuel gas.
C	Catastrophic
L	Unlikely
R	10
Prevention Safeguards	Implement a MOC procedure Implement a MOC procedure that require a HAZOP study for any significant change in plant design. Use keywords and COMPOSITION during the HAZOP workshop. Invite a material specialist from the supplier to respond to the technical queries related with equipment specifications. Develop internal guideline and company standards Develop internal guideline and company standards that require a BOD (Basis of Design) to be developed for any major design change. in BOD include all stream parameters and composition that may influence the affected equipment. (e.g high content of Sulphur from NG fuel gas shall be given to tubes manufactures as BOD document, so the manufacturer can perform a material analysis and consequence modelling for their tube materials. Plant monitoring and reformer tubes inspection Plant monitoring and reformer tubes visual inspection during shifts.

	Plant survey Perform plant survey and inspection conducted by the contractor or equipment supplier with purpose to collect and validate data presented by the Client in the Basis for Design document.
Mitigation Safeguards	Unknown Unknown
Corrective Recommendation	Reduce Hydrogen Sulfide Reduce Hydrogen Sulfide contents in the fuel gas to reformer. Modification was conducted to pass the fuels gas A modification was conducted to pass the fuels gas through sweetening plant before mixing with purge gas. It reduced the Hydrogen Sulfide contents from 0.6% up to 0.02% in the fuel gas. Improve the air distribution To improve the air distribution the burners combustion air dampers and fuel valve were fully opened. Burners wind box pressure survey Burners wind box pressure survey was conducted to ensure equal distribution of combustion airflow to the individual burner. Reformer tubes temperature mapping Frequent reformer tubes temperature mapping and visual inspection is being conducted to detect any abnormality with in the fire box. Excess O2 in the furnace discharge Excess O2 in the furnace discharge has been increased from 0.8% to ~1.8 to 2.0 % in both ammonia plants. Air ingress check Air ingress check through convection zone was conducted by smoke test to eliminate the air ingress to get the representative sample of the flue gas.

Lesson Learned	With change in fuel gas quality and increasing the combustion air, after six months of service no corrosion attack has been observed on reformer tubes. And the appearance of new corrosion spots on second reformer tubes are on the decreasing trend.

Risk Matrix used for assessing FIORDA incident cases

Consequence	Category	Ref No.	Safety	Environment	Financial (EUR)	Reputation	Schedule Delay	Likelihood: Rare	Unlikely	Moderate	Likely	Almost Certain
								<1% Chance	1-20% Chance	21-50% Chance	51-80% Chance	>80% Chance
								$<10^{-5}$ Freq	10^{-5}-10^{-4} Freq	10^{-4}-10^{-2} Freq	10^{-2}-10^{-1} Freq	$>10^{-1}$ Freq
								Never heard of in the industry	Heard of in the industry	Happened in the organisation or more than once in the industry	Happened at the facility or more than once in the organisation	Happened more than once at the facility
	Catastrophic	1	≥1 fatalities / 6 serious injuries requiring hospitalization for ≥24hr	Major permanent / long term effect	≥2m	Widespread serious adverse impact	>12 months	7	10	12	14	15
	Major	2	<6 serious injuries requiring hospitalization for ≥24hr	Serious medium to long term effect	2m to 1m	Widespread moderate impact	6-12 months	5	8	11	13	14
	Moderate	3	Single serious injury requiring hospitalization for ≥24hr	Moderate short to medium term effect	1m to 500,000	Localised moderate impact	3-6 months	3	6	9	11	12
	Minor	4	Injury requiring hospitalization for <24hr	Minor short term effect	500,000 to 50,000	Localised minor impact	1-3 months	2	4	6	8	10
	Insignificant	5	First Aid / minor injury	Low short effect	≤50,000	No impact	<1 month	1	2	3	5	7

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