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# 2024 AIChE Ammonia Safety Symposium

Venkat Pattabathula, a member of the AIChE Ammonia Safety Committee, reports on the American Institute of Chemical Engineers' (AIChE) Safety in Ammonia Plants and Related Facilities Symposium held in San Diego on 8-12 September 2024.

*San Diego, venue for this year's symposium.*

The Ammonia Safety Committee is dedicated to improving the safety of plants that manufacture ammonia and related chemicals, such as urea, nitric acid, ammonium nitrate, and methanol. The conference's objective is to improve the safety performance of the ammonia industry. This is achieved by sharing information on incidents, safety practices, and technology improvements in presentations and open discussions.

From 9th–12th September 2024, 340 engineers from more than 30 countries and 100 companies attended the AIChE's 68th Annual Ammonia Safety Symposium at the Manchester Grand Hyatt in San Diego, CA, USA. Attendees who participated in the symposium included plant managers, production managers, safety managers, process/reliability engineers, and everyone responsible for the safety and performance of ammonia plants or handling facilities. Worldwide experts discuss the latest advances in the safe production and use of ammonia, as well as case studies and lessons learned at these symposiums.

## Ammonia as an energy carrier

This year's keynote speech: 'Ammonia as an energy carrier :scaling risk' was presented by Rob Stevens, Sector Lead for Green Fuels at Topsoe Power to X. Rob looked towards a future where ammonia's use in energy applications, including as a marine fuel, as a power plant co-fuel,

and as a hydrogen carrier could total up to 10-30 million t/a by 2030, and 100-300 million t/a by 2050, the latter more than doubling the size of the ammonia market by that time. Methanol could also see similar growth if it were widely adopted as a bunker fuel. In both cases, grey production will continue to predominate by 2030, but blue and green production is expected to produce the bulk of both chemicals by 2050.

Rob discussed the makeup of ammonia safety incidents in the US and EU by industry and root cause, and whether a new use case (maritime fuel handling and use) at large volume could also

lead to an upwards scaling in ammonia safety incidents. The ARISE (Ammonia Response in Sea Emergencies) programme is looking at ammonia releases in a marine environment, to improve risk assessment and assist the maritime sector and regulators towards a safe deployment of ammonia as an alternative fuel. Other studies are looking at ammonia pipelines. But he stressed the importance of industry involvement in helping the maritime industry to develop procedures and safety documentation, via the AIChE Ammonia Safety committee, Ammonia Europe, TFI, and the Ammonia Energy Association.

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2024 AIChE Ammonia Safety Committee

Front: Ahmed Esmael Rahimi (Qatar Fertiliser Company), Venkat Pattabathula (SVP Chemical Plant Services), Kristina Balch (Dyna Nobel), Seshu Dharmavaram (Air Products), Mohamad Noueiri (Yara), Marc Gilberston (East Dubuque Nitrogen Fertilizer)  
Back: Federico Zardi (Casale SA), Ashutosh Shukla (FFI), Samuel Okulaja (Nutrien), Lari Bjerg Knudsen (Topsoe), Klaus Noelker (thyssenkrupp Industrial Solutions AG), John Brightling (Johnson Matthey), Mark Schroeder (Koch), Taylor Archer (Clariant), Umesh Jain (KBR), Eugene Britton (CF Industries).

## Safety incidents

The key safety-related papers were:

### 1. Primary reformer riser transitional assembly failure

In 2023, Nutrien's Trinidad number 4 ammonia plant had an abnormal temperature profile in the primary reformer, along the number 3 riser. Shortly after, a fire was seen emanating from the primary reformer penthouse and the plant was shut down. Subsequent analysis revealed flaws in welds from a 2009 turnaround, where modifications also left a gap in the refractory which was filled with compressed ceramic (Si/Al) fibre with a higher silicon content than that recommended. It is suspected that process gas, H<sub>2</sub> and CO bypassed through the slip joint compromised the insulation and exposed the flawed weld to the process. The suspected bypass of the process gas exposed the transition cone to carburisation temperatures above 480 °C (900 °F), which manifested in shallow pitting, reduced ductility and toughness and subsequent cracking. Elevated temperatures and the riser's subsequent bowing added more stresses on the already compromised weld, contributing to thermally induced fatigue cracking and subsequent loss of containment. It was determined that insufficient quality assurance and control (QA/QC) during the installation of the 2009 transition cone were the primary causes of the failure. Temporary repairs were conducted to return the plant to service during the 2023 outage to replace all rise transitional assemblies (RTAs) during the next scheduled turnaround. Improvements in RTA design, including eliminating the Inconel 800HT liner slip joint and dissimilar metal joints when designing future replacements, will prevent such failures in future.

### 2. Fire beneath a reforming furnace

An unexpected fire occurred two weeks after the startup of a hydrogen plant following a major plant turnaround. The fire occurred beneath the furnace box due to the loss of containment from a radiant section process gas tube. Damage was limited to instrumentation at the bottom of the furnace, including the actuator on the waste heat boiler temperature control (internal bypass) valve, refractory, and the furnace structure. Fortunately, no one was injured as no one was in the area when the fire occurred, and actions were immediately taken to shut down the plant and extinguish the fire safely.

Investigation found that the bottom flanges were not tightened adequately to ensure tight closure while in operation. The evidence indicated the contractor assigned to tighten the bottom flanges did not execute their standard work practice, with quality issues on flange closure details. The investigation team also found two completely loose studs on one flange and one completely loose stud on three other flanges that were worked on during the turnaround and were all outside the fire zone. The quality control processes were inadequate in identifying the compromised enclosure tightening. The shutdown contractor appeared to have not executed their own QA process to audit whether their enclosure practice was utilised or that the bolts were insufficiently tightened. The QA process relied on the contractor's audit practice, which only involved a spot audit of the contractor's records.

Subsequently, the contracting company has developed a certified training program to familiarise all levels of workers with contractors' procedures, including a bolting training program and competency training assessment for its workers. The operator has also enhanced its own in-house Quality Assurance process with defined roles and responsibilities.

### 3. Hydrogen assisted cracking (HAC) in an ammonia synloop

Hydrogen assisted cracking (HAC) may occur in low alloy steel welded components in hydrogen service. It is normally seen in the heat-affected zones of equipment operating at high hydrogen partial pressure (>7 MPa/1015 psi) and operating wall metal temperatures (>250°C). This phenomenon can be considered a type of hydrogen embrittlement, resulting in the formation of cracks. The presence of ammonia can be a detrimental factor for crack nucleation, possibly promoted by nitriding and internal (thermal) stresses. Yara's complex at Sluiskil in the Netherlands has suffered a number of HAC incidents in recent years.

In 2019, during a scheduled turnaround of one of the ammonia plants, the second synthesis loop converter was inspected for internal corrosion, nitriding and hydrogen-assisted cracking (HAC) according to the risk based inspection (RBI) plan. Several cracks were found, mainly between the manway and the top head. Cracks were uniformly distributed along the weld seam with a depth of about 40% of the total thickness. The reactor was taken out of service and bypassed as no repair option

was possible. The converter was a hot-walled type, and the operating conditions were in the range of susceptibility for HAC.

In 2020, during a scheduled turnaround of the second ammonia unit, an unexpected crack was found during the weld inspection between the ammonia converter (R406) and the waste recovery boiler (E416). This could have potentially led to a leakage of syngas with safety risks. The configuration of the failure of the waste heat boiler object with the indication of the cracked weld. The site has multiple boilers with the same design and one spare unit, so a preventive replacement and maintenance strategy is in place. The boiler object of the failure was removed – by cutting the welded connections – in 2012 from the third ammonia unit and installed in 2014 in the second unit after some repair activities at the workshop. As a lesson learned and mitigation action for future projects and on-the-field welded connections and repair, the internal Yara post-weld heat treatment (PWHT) technical standard was updated to include specific requirements for installing thermocouples at the inner surface of thick components during the treatment.

In 2023, during normal plant operation, a hot spot in the insulation of the outlet nozzle of the E516 waste heat boiler connected to the ammonia converter of the third unit (R507) was noticed by an operator, indicating a possible leak of syngas. The plant was shut down, and the inspection confirmed the presence of a trough-wall crack in the circumferential weld between the outlet nozzle and the connecting outlet pipe. An improper PWHT procedure resulting in non-acceptable hardness levels and the detrimental impact of other degradation mechanisms, such as nitriding, considerably reduced the resistance to HAC of these pressure equipment.

A detailed analysis of the operating conditions and the definition of specific minimum pressurisation temperature curves, considering the amount of available hydrogen and the geometry of the equipment and operating loads, have been identified as the best approach to mitigate the risk of HAC in combination with a proper inspection plan involving advanced NDT techniques. However, the recent experiences within Yara proved that this degradation could be difficult to predict and prevent with proper in-service inspection. For these reasons, Yara's internal procedures have been updated to increase quality control on the manufacturing and repair action, such as strong prescription PWHT and hardness checks.

#### 4. Secondary reformer waste heat boiler tube rupture

Ammonia Kujang's 1A plant experienced significant failure events in the secondary reformer waste heat boiler, where the tube ruptured during two successive startup attempts. Both cases led to boiler feed water (BFW) flooding in the high-temperature Shift (HTS) catalyst bed. Total replacement of the HTS catalyst was required after the first event, whereas efforts to heat up more slowly following the second event restored the HTS catalyst performance. The team decided to repair and re-install the damaged tube bundle and amended the plant shutdown procedure to include a leak test of the WHB, steam superheater and HTS effluent BFW pre-heater to make they are in good condition and to prevent catalyst being submerged by boiler feed water. Startup has emphasises the importance of controlling the temperature rate increase at the inlet of the WHB, with a new temperature rate indicator at the inlet installed to prevent similar failures from taking place in the future.

#### 5. Catalyst overheating due to feed pre-heat coil failure.

On 18 March 2023, Ammonia Kujang 1A faced operational disruptions due to a vacuum system issue, causing speed fluctuation in all compressors and subsequent shutdown of the back-end section. Control measures stabilised the air and natural gas compressors, but overheating in the HTS and LTS catalyst bed increased the temperature up to 1010 °C and 515 °C respectively, prompting a total plant shutdown while no interlock was triggered. Inspection revealed damages, including coil fracture and catalyst breakdown due to overheating caused by air exposure and water submersion.

Considering the extreme increase in catalyst bed temperature, the decision was taken to initiate a total shutdown of the facility for a thorough analysis. During the shutdown process, a high-level alarm was triggered in the HTS effluent knockout drum, necessitating the implementation of manual drainage in the field. The condensate exhibited a dark brown colour, with analysis confirming that it had a PO4 content of 16 ppm. The existing interlock system had not adequately mitigated the risk of feed preheater coil failure, the risk of which is substantial, especially in aging plants. The failure of the feed preheater coil unit led to extreme overheating of the HTS-LTS catalysts and resulted in an 18-day shutdown of Ammonia Kujang 1A.

To prevent similar incidents in the future, several programs have been implemented, including the addition of a low flow feed gas sensor downstream of the feed preheat coil, feed preheater coil replacement; ensuring that all pressure gauge indications in the vacuum system can be read correctly and regularly maintained; routine checks of piping in the vacuum system; and a review of the existing interlock system for potential unmitigated risk.

#### 6. Failure of primary reformer tubes

PT Pupuk Kujang also suffered a fire in the primary reformer of their ammonia 1B plant in 2018. Pupuk Kujang suspected a rupture in a primary reformer tube and, based on this condition, decided to shut down the ammonia 1B plant. Upon inspection, it was discovered that there was a rupture between the catalytic tube and the bottom reducer. Out of the 192 tubes, one tube was ruptured, three tubes had more than 4% creep, and the rest showed no visual indications. These tubes have been in service since October 2004, approximately 14 year. Pupuk Kujang's root cause analysis indicated that the rupture of the primary reformer tube was caused by creep initiated by a hot spot in the primary reformer tube. Field measurement results indicated a significant increase in tube wall temperature, which reached a peak of more than 922 °C. High temperatures on the tube catalyst induced carbon formation on the catalyst's active sites, causing metal sintering. This led to further catalyst deactivation, which worsened the tube wall temperature.

The most effective method to prevent primary reformer tube failure is by thoroughly examining the composition of natural gas entering the primary reformer and adjusting operating parameters based on the data. Tube wall temperature of the primary reformer tube need to be checked to verify the burner adjustment. Good teamwork between the operations, process engineers, and maintenance teams was key to achieving optimum operating parameters and smooth operation. Since primary reformers in the Ammonia 1B plant primarily run at full loads and above design production rates, it is important to still operate within the design envelope without exceeding the design parameters.

#### 7. Syngas compressor oil-seal failure with fire

On 6 March 2023, at 7 pm, an electrical blackout occurred at the Cubatão 2 production complex, causing the shutdown of all

production plants simultaneously. Subsequently a fire was observed in the ammonia plant at the atmospheric vent of the synthesis gas compressor oil reservoir. Firefighting actions were initiated and eventually succeeded after the compressor's gas intake valve could be closed. After evaluating the operational conditions, it was decided to initiate a cold production shutdown to maintain the ammonia plant, correct the damage caused by the lack of electricity, and assess the potential damage caused by the fire.

A failure analysis study was carried out using the fault tree method. The results indicated no damage to the compressor and seals, and it became clear how the fire had occurred by comparing the operational data under normal conditions versus upset conditions and linking the main events from the blackout until the end of the emergency. With the loss of the barrier fluid and the pressurisation of the oil system with synthesis gas coming from the compressor's internal pressure, gas escapes together with oil through the atmospheric vents, creating conditions conducive to the start of a fire. The high concentration of hydrogen in the synthesis gas coming into contact with the various heat sources and hot surfaces close to the vent of the oil reservoir (turbines and pipes with damaged insulation) likely caused the leaking gas to ignite, allowing the fire to start.

Short term remedial actions included rerouting atmospheric vents that may contain synthesis gas to suitable locations, i.e. from oil reservoirs and coupling covers and degassing the entire oil inventory with thermo-vacuum equipment. Longer-term actions included installation of a water mist firefighting system connected to a fire detection system, a hydrogen detection sensor and a nitrogen smothering system in the oil tank, installation of an automatic surge control system, and re-evaluation of steam and power supply during different upset and emergency scenarios.

#### Round table

On Day 4, a round table Session was held, which provided open exchange and discussion through brief presentations from panellists, followed by a question-and-answer session on topics of interest such as ammonia converter catalyst issues; the future of AI in ammonia plant operations; and improving CO<sub>2</sub> removal system operational efficiency with AI.

Next year's Symposium will be in Atlanta, Georgia, USA, on 7-11 September 2025. ■