Failure and Replacement of Ammonia Converter Baskets and Application of AmoMax Catalyst

Pressure drop across Incitec Pivot's ammonia converter baskets significantly increased over a 5-month period in 2006. This pressure drop resulted in a significant loss in ammonia production. In addition, the 35-year-old pressure vessels had developed cracks around the nozzles. Because of these two problems, Incitec Pivot Ltd (IPL) decided to replace the converter baskets, the catalyst and the pressure shells during their 2007 turnaround. After considering the options that were available, IPL decided to replace the old baskets with Casale's new slotted plate design. To maximize production from the new baskets and internals, AmoMax ammonia synthesis catalyst was chosen.

This project highlights the need to have plans in place to mitigate any potential risks that could impact plant reliability with some pro-active approaches taken during replacement of the pressure vessels and axial-radial baskets. The paper also describes in detail the systematic root cause analysis of the failure, safety and design reviews of the new baskets, hazop studies, safety measures taken while unloading the old catalyst and dense loading the new catalyst, catalyst reduction, performance tests etc.

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Introduction

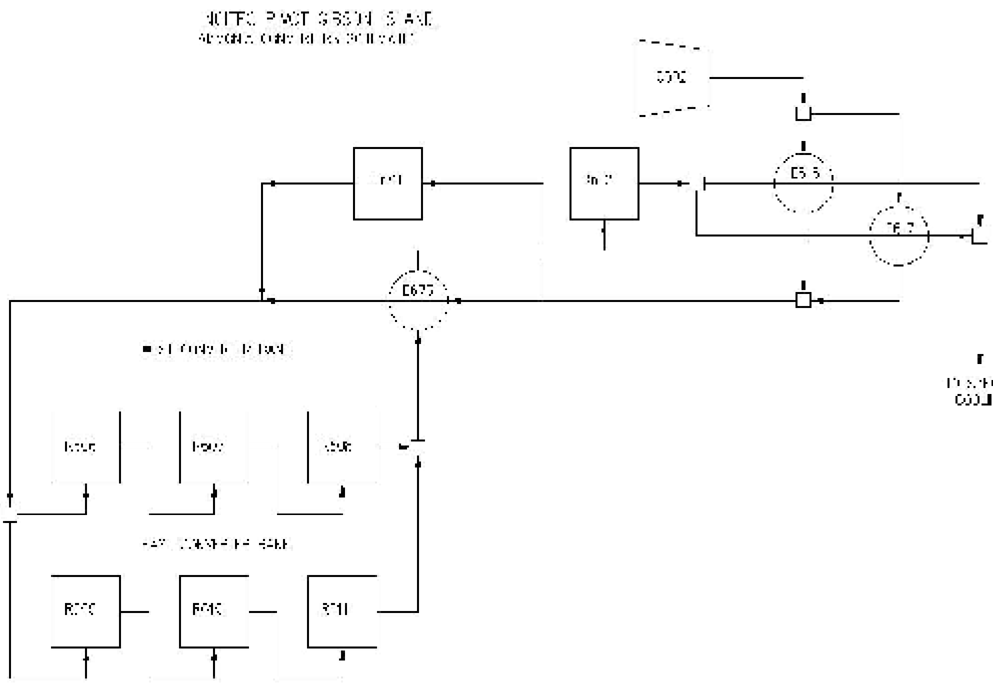
Incited Pivot operates an ammonia plant designed by J.F. Pritchard that originally produced 600 mtpd. Many upgrades have been made since the original commissioning in the late 1960's, which have increased the operating rate to more than 800 mtpd. Ammonia Casale revamped the second and third ammonia converter bottles of each bank in 1989, while a new add-on converter downstream of the original converter bottles was installed in a 1997 upgrade. Unique features of this plant are a low pressure front-end operating at 450 psig (32 bar), a high pressure synthesis loop operating at 2600 psig (182 bar), a medium pressure steam system operating at 400 psig (38 bar) and 750°F (400°C), a closed loop refrigeration system and a Jet engine that drives a reaction turbine which in turn drives the synthesis gas compressor.

The site has also a urea plant designed by Vulcan Cincinnati, USA. The urea plant has been upgraded over the years to about 850 mtpd. The plant is located at Gibson Island (GI) in the Eastern suburbs of Brisbane on the East Coast of Australia.

Synthesis loop configuration

As shown in Figure 1 the Gibson Island ammonia plant synthesis loop has two banks of ammonia converters in parallel with three bottles in series in each bank. The syngas compressor (C602) discharge is sent to these two banks after heat exchange in the converter feed/effluent exchangers (E616/617). Outlet gas from the two banks is then fed to a single booster converter (R612). The first bottles in each bank (R606 and R609) operate with an axial flow path. The second (R607 and R-610) and third bottles (R608 and R611) of each bank operate with an axial-radial flow path utilizing Ammonia Casale baskets. The booster reactor (R612) also operates with an axial-radial flow path utilizing an Ammonia Casale basket.

Figure 1 – Schematic Flow Diagram



Ammonia production constraints

Magnetite catalyst was installed in all six-converter bottles during a 1997 plant turnaround. Unfortunately, performance declined over the years. The converter bottles developed a high differential pressure problem with an increase to 110 psi (7 bar) in May/June 2006, which resulted in a loss of about 100 tonnes of production each day.

IPL conducted a thorough root cause analysis of the problem in June 2006 in which Sud-Chemie and Ammonia Casale participated. As a result Incitec Pivot decided to replace the 17-year 4 old

baskets in R607, 608, 610 & 611. It was also decided to replace the entire magnetite catalyst with new catalyst in all 6-converter bottles (excluding the booster reactor).
A presentation was made by Sud-Chemie South East Asia to the Incitec Pivot team in early 2006 on the potential application of AmoMax catalyst in all 6-converter bottles. Sud-Chemie cited a number of references including that of Agrolinz in Austria and Koch N_2, Fort Dodge Iowa, USA. Incitec Pivot contacted these two plants and requested information on the catalyst performance. Both plants provided very positive feedback about the success of AmoMax catalyst in their plants.

Incitec Pivot had also observed cracks on the nozzles of the original carbon steel pressure shells, which were repaired in a backend outage in 2005. Hence, IPL decided to replace all 6-pressure shells in 2007 plant turnaround. Unfortunately, the high-pressure drop across converter banks was experienced after placing the order for the new pressure shells. If the pressure drop had occurred before the order was placed, IPL would have considered a single ammonia converter with indirect cooling of the catalyst beds.

Study by the University of Queensland (Uniquest)

Incitec Pivot awarded a project to The University of Queensland to test AmoMax catalyst. Sud-Chemie provided a sample of AmoMax 10H (pre-reduced), and IPL collected two other commercially available magnetite catalyst samples for testing. The objective of the Uniquest project was to investigate and compare the structure, deactivation, and strength of the Sud-Chemie AmoMax-10 wustite catalyst sample with the two-magnetite catalyst samples. The study was expected to yield insight into the differences between the catalysts related to reactivity, deactivation and catalyst life. The following studies were done to investigate these variables:

(i) Testing of the strength of the original and pre-reduced wustite and magnetite catalyst
(ii) Investigations of the pore structure for the pre-reduced catalyst
(iii) Microscopic examinations using scanning and transmission electron microscopy
(iv) Carbon dioxide and moisture adsorption isotherms for the pre-reduced catalyst

In addition to the above studies, Uniquest also conducted x-ray diffraction studies to confirm the structural properties and state of the iron in the different materials.

The following differences between wustite and magnetite based catalysts were observed:

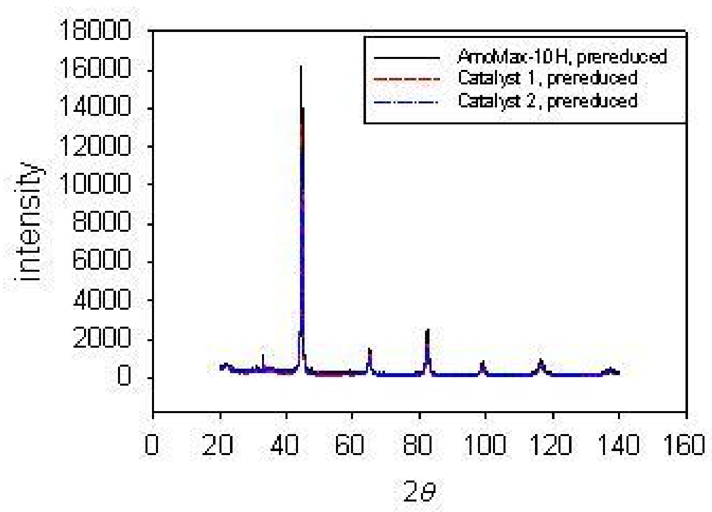
1. AmoMax-10H sample has a higher crush strength compared to the two-magnetite catalyst samples (refer Table 1).

2. X-ray diffraction patterns reveal that the bulk state of the iron is the same in the AmoMax-10H and the magnetite catalyst samples as shown in Figure 2. X-ray diffraction is NOT a surface analysis method, but gives the bulk state of the iron in the sample. The x-rays go through the sample.

Table 1 - Compression test results for different pre-reduced catalyst

Reduced catalyst	Mean compressive load (N)	Standard deviation for load (N)	Compressive extension (mm)	Standard deviation for extension (mm)
AmoMax-10H	154.1	50.3	0.096	0.013
Magnetite Catalyst -1	36.7	12.1	0.180	0.100
Magnetite Catalyst -2	20.2	7.4	0.124	0.057

Figure 2 - X-ray diffraction patterns for pre-reduced catalysts.



3. The pore structure of wustite and magnetite catalysts, based on argon adsorption, is similar. However, the porosity of AmoMax-10H is slightly less than magnetite, which is consistent with the lower oxygen content of wustite compared to magnetite. The results of pore structure analysis are depicted in Figure 3.

4. The pore structure of the pre-reduced AmoMax-10H shows lower accessibility during mercury intrusion, suggesting a greater level of disorder in this catalyst, compared to the pre-reduced magnetite based catalyst.

5. Microscopic examinations show that individual particles of magnetite-based catalyst are more heterogeneous than those of AmoMax-10H, with macropores consistent with the adsorption analysis. More importantly, however, the internal surface of the AmoMax-10H particles is more defective, which may contribute to its higher activity. Micrographs of AmoMax-10H are depicted in Figure 4.

Figure 3 - Pore size distribution of the various pre-reduced catalysts.

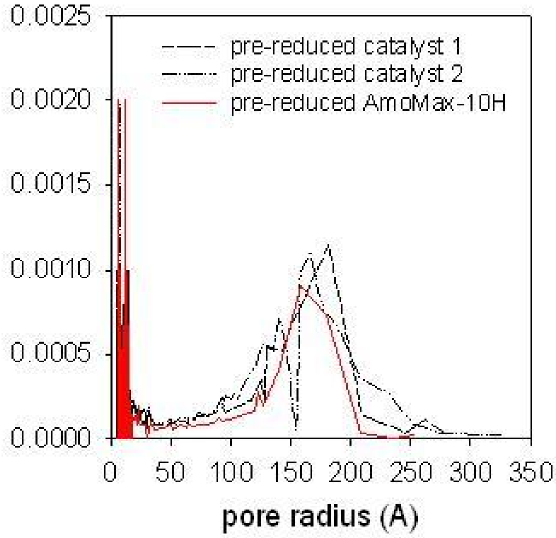
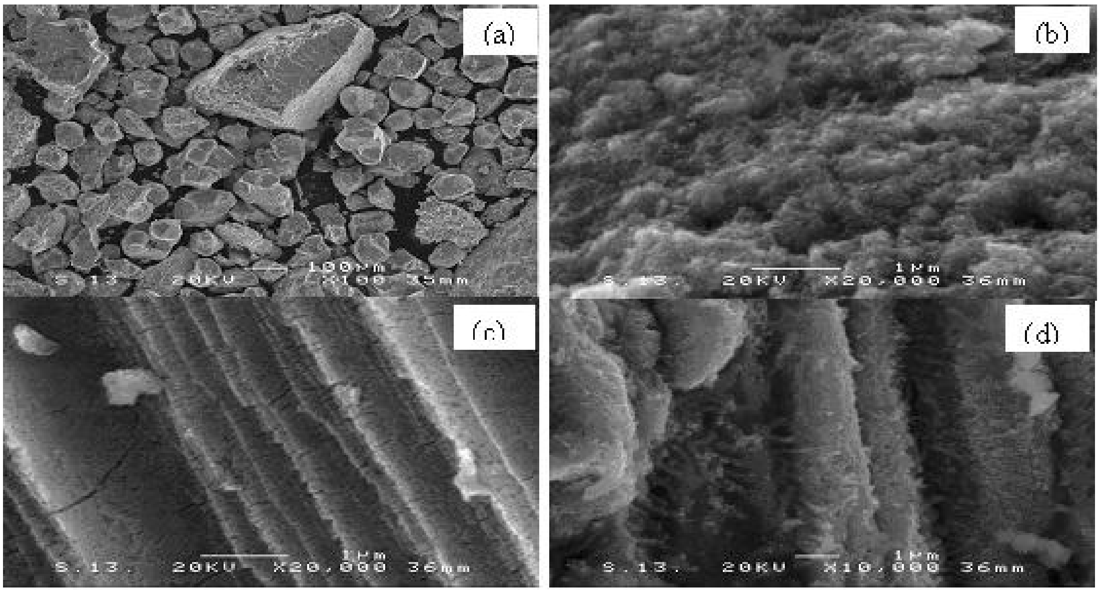


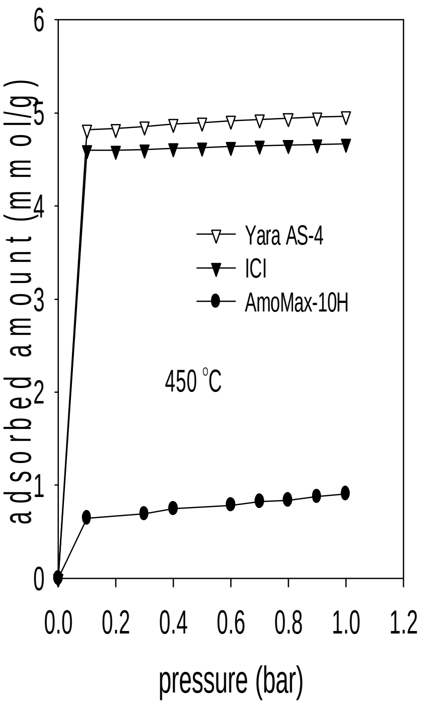
Figure 4 - Micrographs of AmoMax-10H at various magnifications



6. Pre-reduced AmoMax-10H catalyst shows considerably smaller carbon dioxide adsorption compared to magnetite based catalyst, suggesting it is less affected by this species. Figure 5 compares absorption isotherms of CO_2 on the pre-reduced catalysts at 450^{o}C. The moisture adsorption is, however, comparable on a unit surface area basis suggesting that it may not be any more resistant to moisture effects.

These results are, however, based on adsorption on the passivated (or oxidized) catalyst, and are not definitive. Conclusive studies require activity testing of the reduced catalyst in the presence of the ammonia synthesis reaction, which was not in the scope of the Uniquest study.

Figure 5 - Adsorption isotherms of carbon dioxide on pre-reduced catalysts.



Converter Project details

Following the study conducted by Uniquest, Incitec Pivot made a decision to install AmoMax-10 catalyst in 6 converter bottles. Before this was done, however, a risk assessment was carried out on the application of AmoMax-10/10H catalyst.

A purchase order was placed for new design Casale baskets and AmoMax-10/10H catalysts in July 2006. Pre-reduced 8-12 mm AmoMax-10H catalyst was ordered for the first bottle of each bank (R606 &R609) since they have only axial bed configuration. Oxidized 1.5-3.0 mm AmoMax-10 catalyst was ordered for the axial-radial baskets. The new catalyst was received in November 2006.

New design (slotted plate) Casale baskets were received in January 2007 and they were installed in the new pressure shells prior to plant turnaround.

Design of Baskets

The design of the baskets was developed by Ammonia Casale based on their previous experience and on the latest innovations developed from former revamping projects. Some characteristics of the IPL converters are peculiar, which make them unique:

- the mixing of the quench and the main inlet gas is done in the pipe feeding the gas to the converters
- the quench gas flushes the cartridge before mixing with the main inlet gas
- the flow path is outward, from the bottom to the top part of converters.

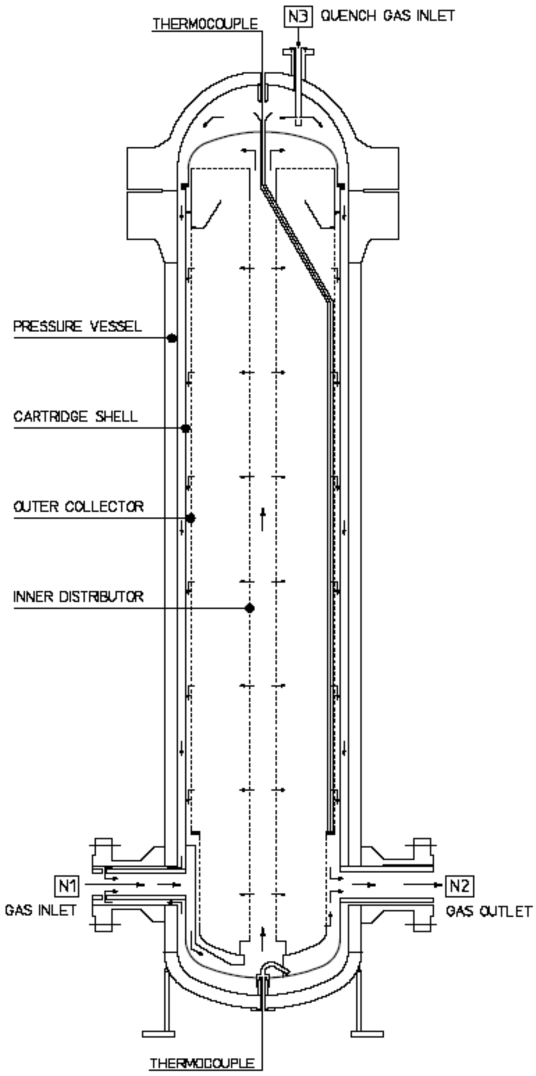
Figure 6 shows the flow path of the reacting gas through the converters, which is described as follows:

The main inlet gas from the upstream converter is fed to the reactor through the connecting pipe where it is mixed with quench gas coming from the nozzle N3 located in the top of vessel.

The cold quench gas, before entering the inlet pipe and getting mixed with main inlet, flows through the annulus between the vessel and the cartridge, keeping the pressure shell temperature safely below the design.

At the converter entrance (nozzle N1), the gas is diverted to the bottom part of the cartridge and into the center perforated distributor. The gas flowing through the center distributor then enters the catalytic bed. Most of the gas enters radially with the rest axially from the upper part of the bed.

Figure 6 - Converter Layout



After leaving the catalytic bed, the gas flows through the outer collector to the bottom part of the cartridge and exits the converter through nozzle N2.

To measure the reacting gas temperature, two thermowells are inserted into the cartridge, one inside the catalytic bed and the other in the bottom part of cartridge. Particularly, the second one is specifically designed with a "U" shape: this design is resulting in a high reliability of temperature measurement because the measurement point is located in a zone of the cartridge where the gas is completely mixed.

Basket Design Features

The design specifically developed for the above-described converters was studied to achieve the following goals:

- Full exploitation of catalyst.
- High reliability.
- Easy access to internal baskets for maintenance or catalyst replacement.

As described in the previous paragraph, the reacting gas flowing through the catalytic bed has an axial-radial path, which utilizes all of the catalyst loaded into the baskets. Due to the particular design of the converter (outward flow, from bottom to top, so the axial portion is opposite to the inlet opening), a thorough analysis of gas flow has been undertaken with computational fluid dynamic (CFD) simulation tools. The particular design developed for the distribution devices ensures equalized distribution between axial and radial flow.

The catalyst is contained and supported between two cylindrical walls, made by slotted plate. These plates, constructed of AISI 321 stainless steel, have the double function of containing the catalyst (the slot dimensions are designed for this purpose) and supporting the catalyst (the wall thickness is calculated based on the catalyst properties). The construction procedure used to make these slotted plates is such that it does not affect the metallurgical structure of the metal (no crack formation) resulting in high strength of the cylindrical walls.

Using the slotted plates for the catalyst bed walls made possible not to use the wire mesh to contain the catalyst used in the former design, simplifying so the mechanical construction of internals.
In the top of catalytic bed, a protection screen is installed to prevent migration of the catalyst out-

side the baskets. This also enables the gas to flow axially through the top part of the bed.
Figure 7 shows the inner & outer collector of slotted plates whereas Figure 8 shows CFD simulation results for the top part of the catalyst bed.

Figure 7 - Inner and outer collectors with slotted plates

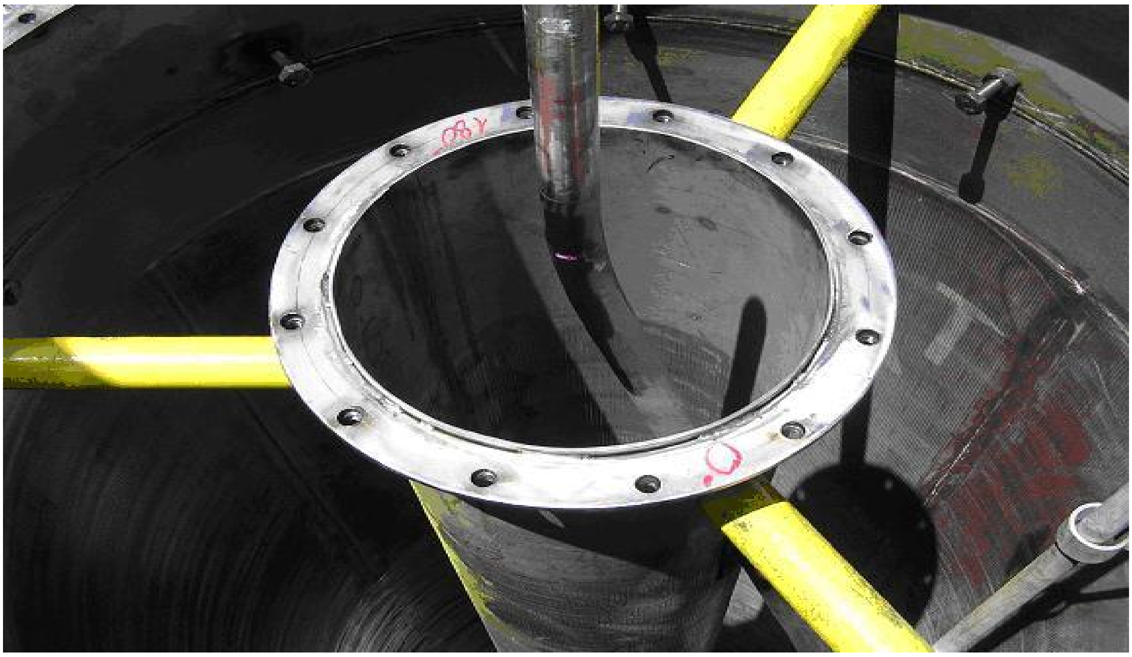
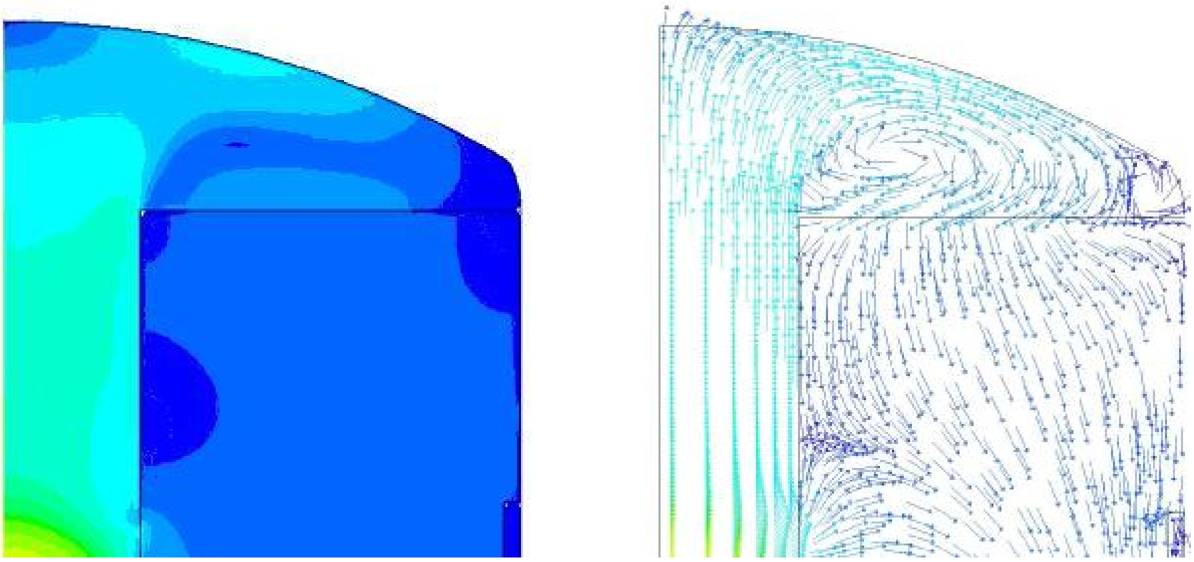


Figure 8 - Simulation results in the upper part of the catalytic bed



From an operability point of view, it is important to have the most reliable measurement of outlet temperature. Thermowells were specifically designed with a "U" shape, (shown in Figure 9) so that the measurement point is located in a zone of the cartridge where the gas is completely mixed.

Figure 9 - "U" shaped thermocouple

To feed the synthesis gas into the central part of the converter (inlet distributor)), Casale designed a cover diverting the gas to the bottom and the support point of the cartridge with a free zone to allow the gas to flow through. This feature results in high reliability of the design because it eliminates the need for an expansion joint by eliminating the need for a central pipe to feed the gas to the catalyst bed. Expansion joints have the possibility of failure.

On top of the cartridge where the quench gas is fed into the reactor, an impingement plate has been installed to avoid any possible damage due to a high velocity of gas impacting the cover. Even if this could not occur in normal operation, there could be some particular conditions where the quench flow rate is increased a lot, leading to a potential risk of damage.

The cartridge has been designed to be fully opened which allows easier access for maintenance in the future. Lifting lugs have also been installed in case it has to be removed.

Catalyst Loading

Since the AmoMax-10 catalyst for the 4 axial radial baskets was in the oxidized form, the loading was done in fresh air.

AmoMax-10 catalyst was loaded in the 4 new Ammonia Casale baskets in January 2007 using a Casale developed dense loading method. The catalyst was screened prior to loading and Contract Resources, an Australian company, performed all the catalyst activities.

After completion of the loading activities and protection screen installation, thermocouples were inserted into their thermowells. Thermocouples measure the temperature in different positions in the catalytic bed, thus allowing optimisation of the operation.

Pre-reduced catalyst, AmoMax 10-H catalyst was loaded under N_2 using a dense loading method in the first bottle of each train. The loaded bulk densities of AmoMax 10-H and AmoMax 10 were 2.7 and 3.1 kg/l respectively.

After final cleaning, the special Casale gas distributor was placed in position at the reactor inlet nozzle and the reactor boxed up and made ready for start-up.

Figures 10-12 below show the catalyst-loading equipment used at the Gibson Island ammonia plant:

Figure 10 – Catalyst Loading Hopper

Figure 11 – Catalyst loading hoses

Figure 12 – Catalyst loading

Catalyst Reduction

On 14 March 2007, reduction of the ammonia synthesis catalyst was started. Details are shown on the following graphs:

Figure 13 - Catalyst reduction chart / Exit water v/s Time

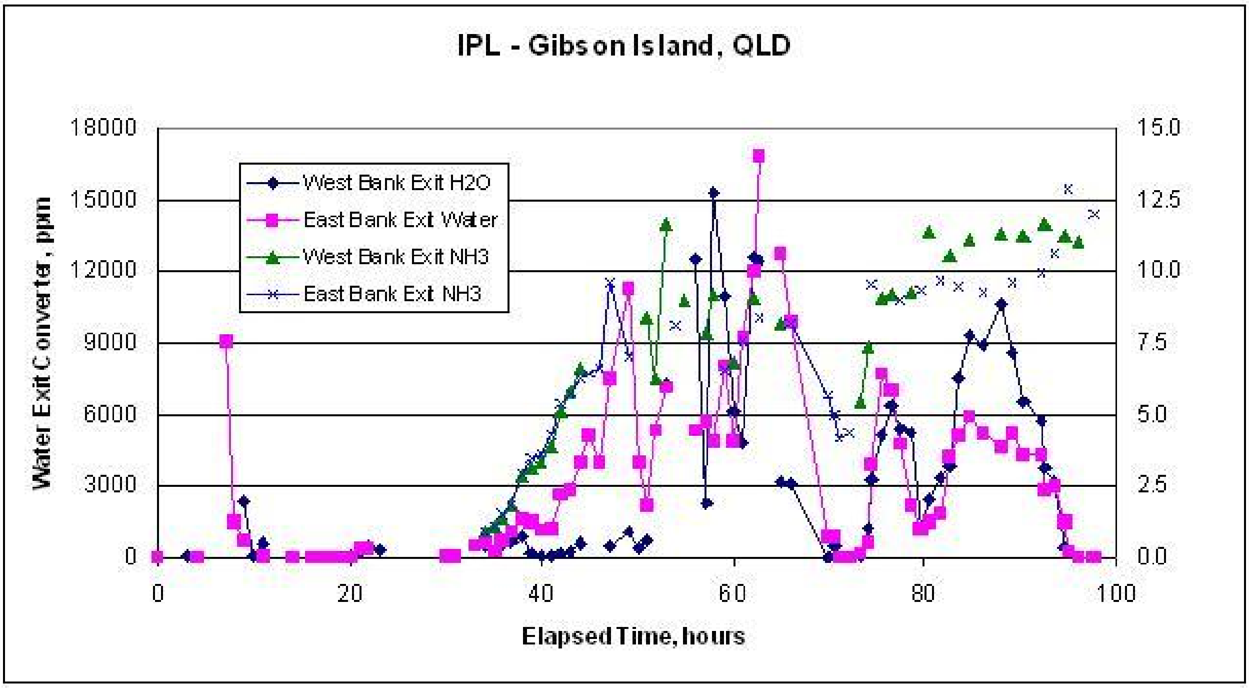
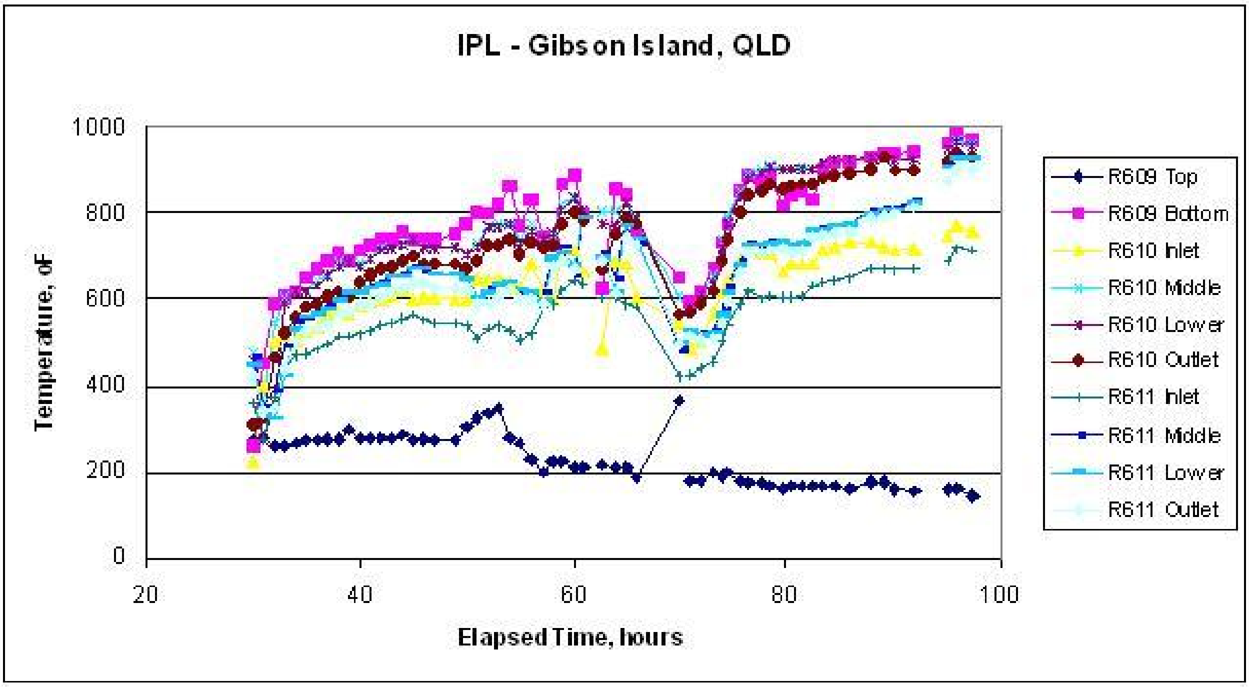


Figure 14 - Catalyst reduction chart – Bed temperatures v/s Time



As can be seen from these graphs, the total reduction time was approximately 4 days. However, the first day was not productive since troubles with the Startup Heater (SUH) resulted in most of the day lost. So, assuming no compressor or SUH problems, reduction could have been completed in 3 days. It must be pointed out that water evolution during the reduction was faster than targeted due to the large SUH in the loop.

The sequence of catalyst reduction was the same as when reducing conventional magnetite catalyst. No special requirements or procedures were needed.

Table 2 describes the performance of the ammonia with AmoMax and Table 3 shows the plant performance results.

Table 2 - Loop Performance Summary With AmoMax-10

Date	12-Apr-07	6-Mar-08
Days On-stream	28	330
Production, TPD	867	865
Makeup Gas Rate, lb MPH	10,319	10,382
Composition, %		
H_2	73.87	73.82
N_2	25.17	25.02
CH_4	0.61	0.84
Ar	0.34	0.32
Reactor Inlet Composition, %		
H_2	67.63	67.70
N_2	23.75	22.76
CH_4	4.28	5.48
Ar	2.50	2.31
NH_3	1.84	1.75
NH_3 Concentration Exit, %		
Six Bottles	15.95	15.99
Loop	19.27	19.49

Table 3 - Plant performance results

	Design Basis	**Actual**
Capacity	850 tpd	866 tpd
First bed (R606/609) inlet temperature	680°F	767°F
Quench gas temperature	111°F	118°F
Converter inlet H/N ratio	3.0	2.85
Pressure at R612 outlet	2484 psig	2450 psig
Inerts at first bed inlet (CH_4+Ar)	7.1%	6.78%
Ammonia content at first bed inlet	1.58%	1.84%
Total flow including quench gas at converter banks	14,000 kmol/hr	15,720 kmol/hr
Maximum content of oxides of carbon	3 ppm	<4 ppm

Project Milestones

- Commenced study by The University of Queensland (Uniquest) in February 2006.
- Uniquest study was completed in May 2006.
- A request for quotation was sent to catalyst vendors in January 2006.
- Made a decision to purchase new Casale baskets and AmoMax-10 catalyst in July 2006.
- Catalyst received at plant site in November 2006.
- New baskets were received in January 2007.
- AmoMax catalyst was loaded in February 2007.
- Catalysts were reduced and activated in March 2007.
- Plant performance tests of catalyst completed in April 2007.

Conclusions

The success of the project has been justified by the performance of AmoMax catalyst and new design Casale baskets in the synthesis loop and by the stable and smooth operability of the plant during the last 12 months. There is no doubt that the exceptional performance of AmoMax catalyst has helped us to produce more tonnes (870 mtpd) than the design rate of 850 mtpd. There is still room in the synthesis loop pressure, which used to be a constraint prior to the 2007 shutdown to make at least another 30 mtpd. A production rate of 890 mtpd is expected at this time as one of the process compressors was overhauled recently.