APPLICATION OF THE BEST CATALYST IN THE BEST REACTORS FOR AMMONIA SYNTHESIS

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OUTLINE

Some real and possible applications of Sud Chemie AmoMax-10 catalyst in Casale ammonia reactors have been investigated and their results are here after described.

The paper covers the results obtained by using AmoMax-10 catalyst in revamped adiabatic reactors in which the Casale axial-radial technology is used, an introduction to the new Casale Isothermal Ammonia Converter (IAC) design and the expected performances that can be reached using AmoMax-10 catalyst in this very advanced type of reactor.

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1. Ammonia Casale Adiabatic Converters

AMMONIA CASALE S.A. has a very long tradition as designer of synthesis converters, particularly for ammonia production having started, its activity in 1921.

The modern CASALE designs, based on axial-radial flow for ammonia converters, have a wide and successful acceptance so that more than 160 converters using CASALE designs are in operation and several are presently under construction.

Many different solutions have been adopted, tailor-made for each specific case, all using the so-called "axial-radial" design of the catalytic beds, which achieves maximum catalyst utilization with the simplest cartridge configuration.

Casale Adiabatic Reactor: the Axial-Radial Converter concept

The axial-radial flow (see Fig. 1) is characterized by a gas flow thru the catalytic bed that is, at the same time, axial and radial: most of the gas passes through the catalyst bed in a radial direction, while the balance passes through the top layer in an axial direction, thus eliminating the need for a top cover on the catalyst beds, necessary in the pure axial flow. In this way, the complete catalyst volume is completed utilized (see Fig. 2).

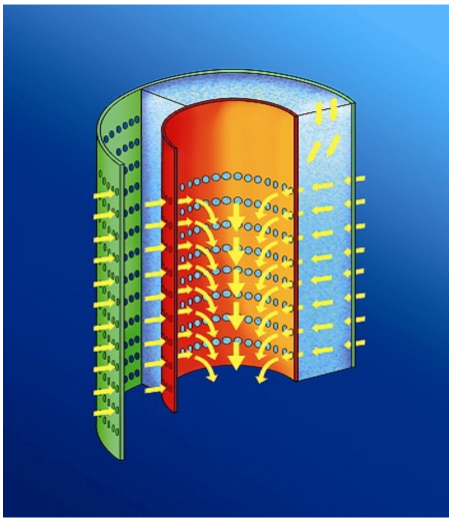


Fig 1 – Casale Axial-Radial Flow

The catalyst is contained and supported between two perforated cylindrical walls. Their function is to contain the catalyst and to guarantee an even gas distribution inside the catalytic bed.

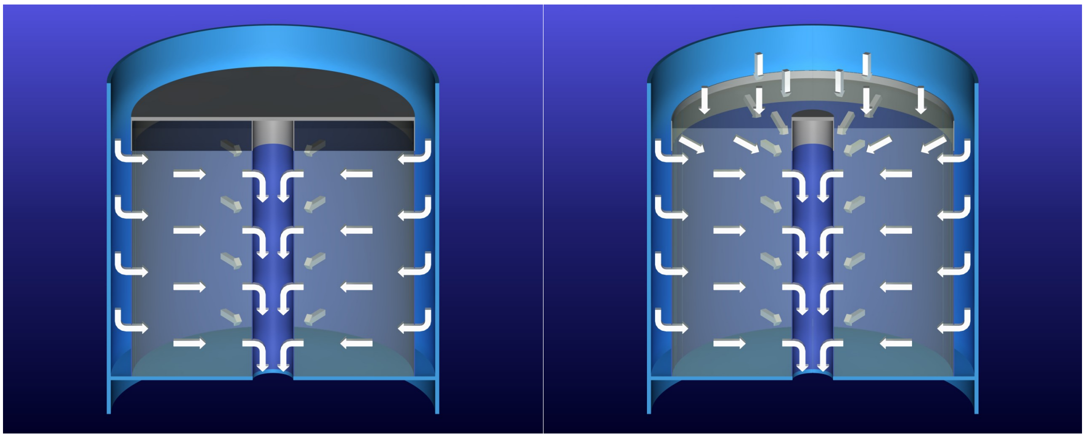


Fig. 2

Pure Radial Flow **CASALE Axial-Radial Flow**

There is a protection screen installed on the top of the catalytic bed allowing gas to flow axially through the top part of the bed.

In case of revamping, such beds can be arranged in different ways inside the ammonia converter, depending on the original design of the pressure vessel, while, for new reactors, Casale has always used the standard configuration with 3 Beds and 2 interchangers. Some examples are reported in the following figure 3.

Fig. 3A
Casale
3-Beds-2 Interchangers

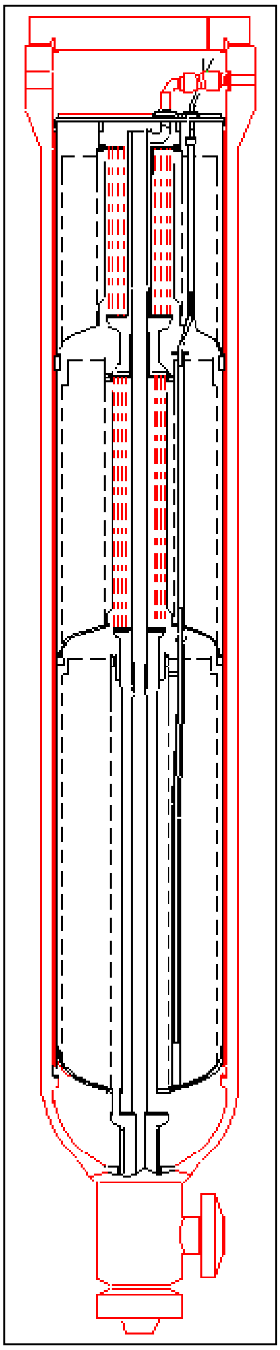


Fig. 3B
Revamped
3-beds-Quench-Interchanger

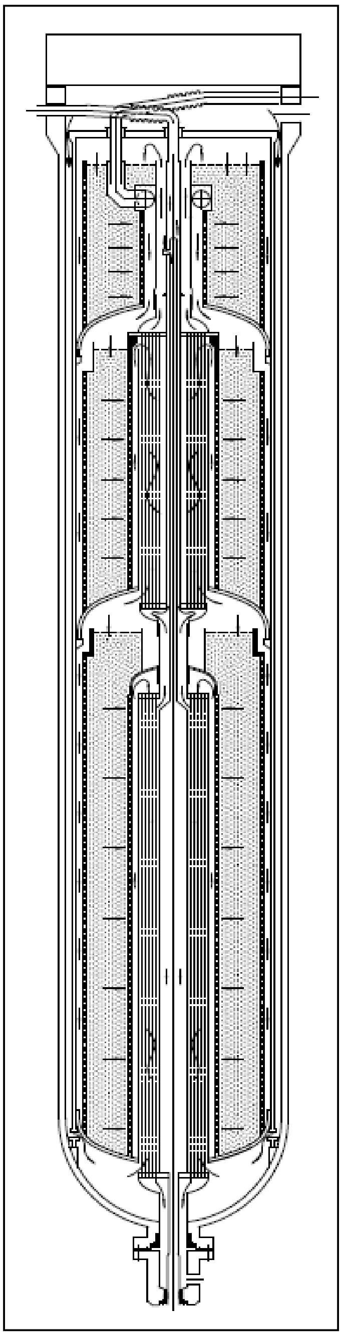
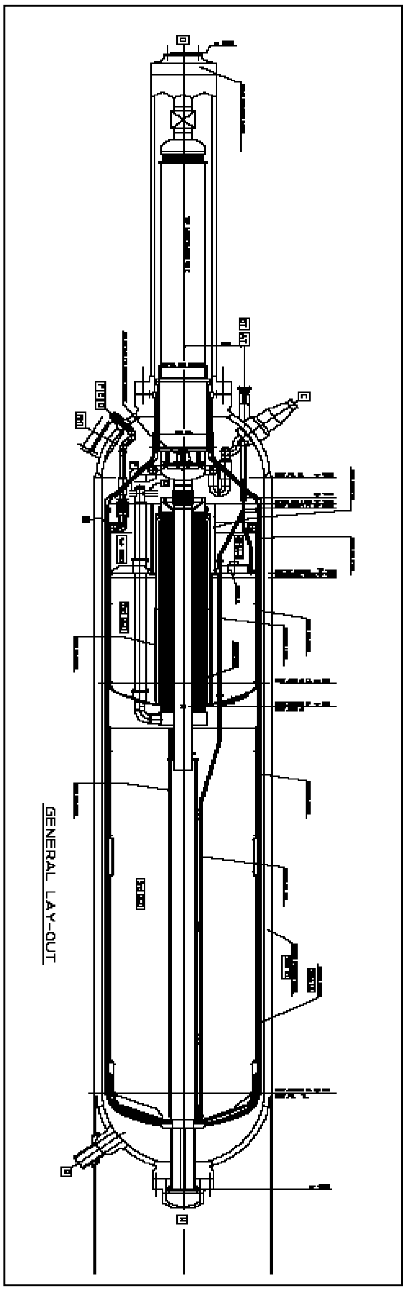


Fig. 3C
Revamped
3-beds-Quench-Interchanger



2. Süd-Chemie's AmoMax-10 Catalyst

Ammonia synthesis catalysts have been based on iron oxide since their first commercial production in the early 1910s. Conventional ammonia synthesis catalysts are made of magnetite (Fe_3O_4) with a number of structural and electronic promoters.

In the middle of the 1980's, in the Zhejiang University of Technology, China, a new catalyst was invented. Nowadays this catalyst is commercialized by Süd-Chemie under the trade name of AmoMax-10.

AmoMax-10 is based on non-stiochiometric ferrous oxide, Wustite (FeO). Wustite has a different crystal structure compared to the spinel-like structure of magnetite: this provides the catalyst with an improved pore structure, higher surface area and better mechanical strength.

This catalyst is, therefore, more active at lower temperature and lower pressure (compared with a standard magnetite catalyst, AmoMax is about 15% to 20% more active). Its use allows a more efficient ammonia production providing a very significant contribution to ammonia plant efficiency and economy, a contribution that can significantly increase when used in advanced reactors.

There are already several industrial applications in China and the catalyst has been used for the very first time outside China as well.

Among the use of AmoMax-10 in Casale internals, we have to mention:

- Terra Woodward, a 1250 MTD, Casale revamping of an original Topsoe S-200 started up in 2009;
- Dorogobuzh, Russia, 1600 MTD, started up in 2008;
- Incitec Pivot, Australia, started up in March 2007;
- Koch Nitrogen, Fort Dodge, Iowa, USA,2* 450 MTD ammonia reactors, started up in 2005;
- Achema, Lithuania, a 1360 MTD plant started up 2006 and Perm, Russia another 1360 MTD plant started up 2004.

3. Ammonia Casale Experience with AmoMax 10

As mentioned above, Ammonia Casale has already a significant experience with AmoMax 10, as there are several of its adiabatic converters already in operation with this catalyst. Some case histories are reported herebelow:

Incitec Pivot Ltd (IPL), Bribane, Australia

IPL operates an ammonia plant, designed by J.F. Pritchard, with a nameplate capacity of 600 MTD. Many upgrades have been made since the original commissioning in the late 1960's, which have increased the operating rate to more than 800 MTD.

As shown in Figure 4 the Gibson Island ammonia plant synthesis loop has two banks of ammonia converters in parallel, with three reactors in series in each bank.

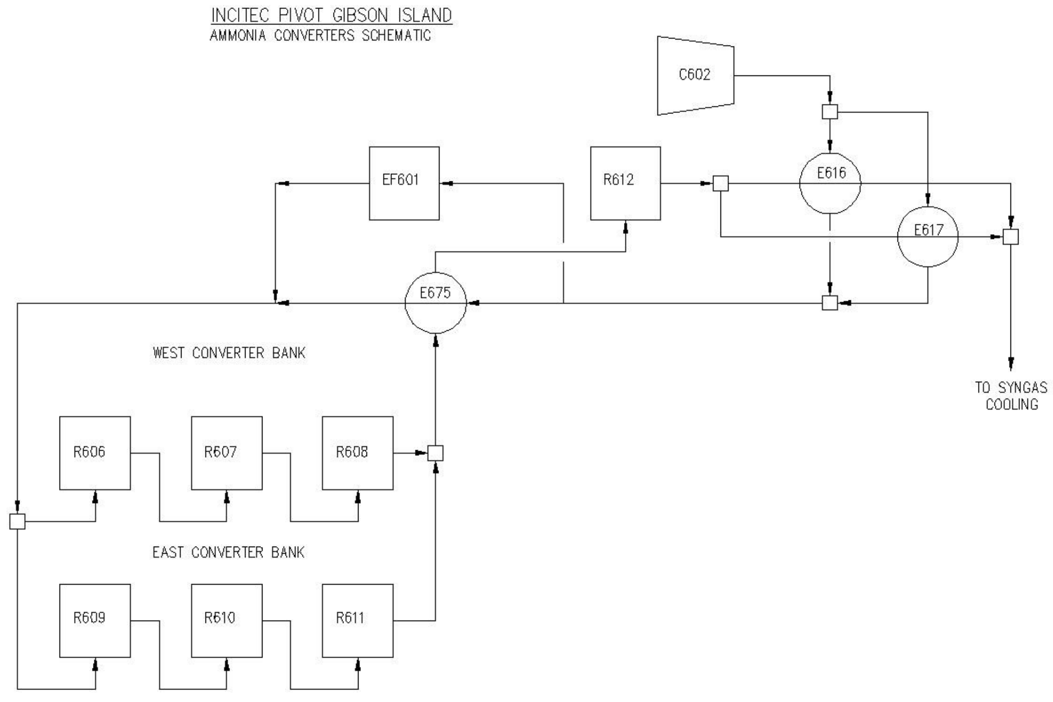
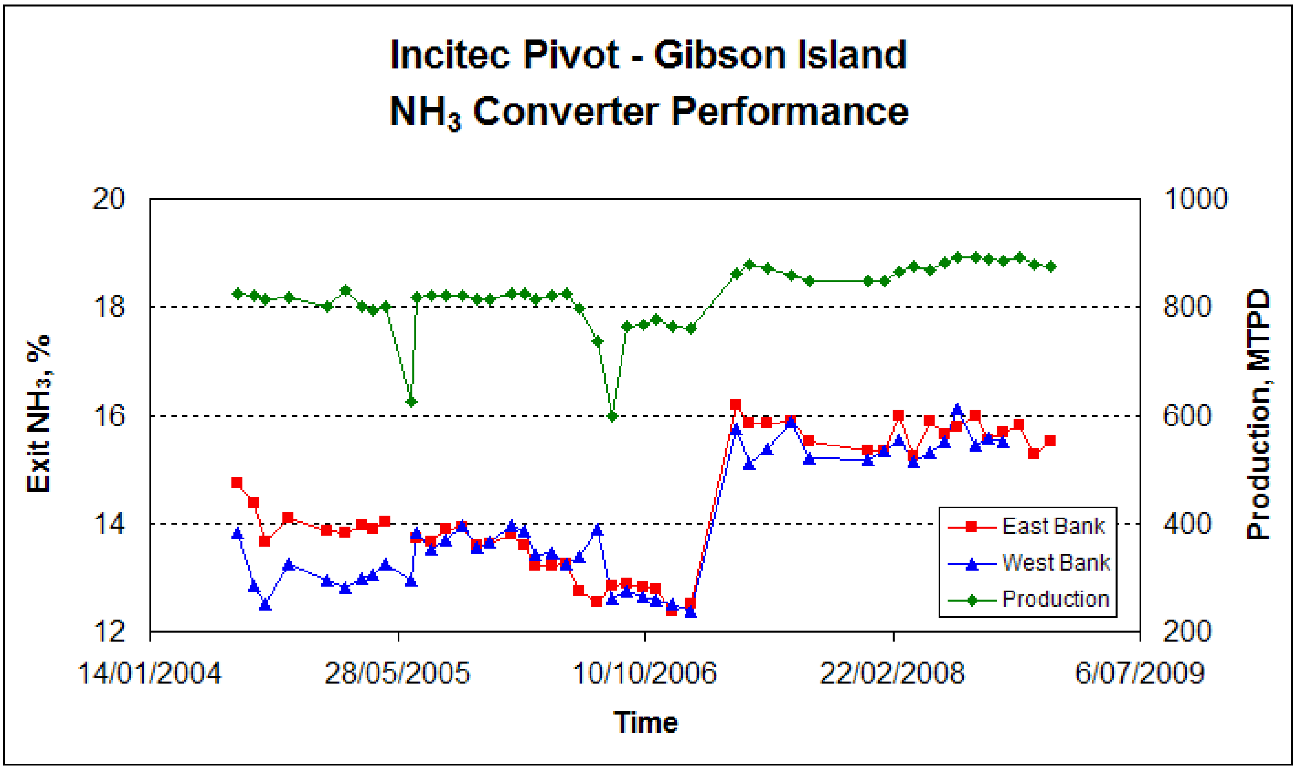


Fig. 4: IPL, Brisbane, Ammonia Converter Scheme

In 2006 Incitec Pivot made a decision to install AmoMax-10 catalyst in 6 converter bottles.
A Purchase Order was also placed for new design Casale 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.

The results of this revamping are shown here below.



It is possible to see that after the revamping in March 2007 the production rate and the conversion per pass has increased sharply.

Terra International, Woodward, Oklahoma, U.S.A.

Terra Int. operates an ammonia synthesis loop in its Ammonia Production Complex located in Woodward, Oklahoma, having a nominal capacity of 1'225 MTD of ammonia.

The original reactor design was a two adiabatic beds with one interchanger layout, and it has been revamped adopting the Casale design 3- beds with quench and interchanger (see Fig 3B). AmoMax was loaded for the catalyst charge.

This converter has been started up very recently (March 2009) and it fulfilled the performance test.

The following table summarizes the converter performances before and after the revamping:

		Before	**After**
Converter capacity	**MTD**	**1'225**	**1'257**
Ammonia content at converter inlet	% mol.	4.04	4.02
Ammonia content at converter outlet	% mol.	14.78	16.5
Converter outlet pressure	Bar g	207	170

Also in this case, the increase in conversion per pass is evident, even if at lower pressure, due to the revamping.

4. Casale Isothermal Ammonia Converter (IAC)

The Isothermal Ammonia Converter (IAC) design abandons the use of multiple adiabatic catalyst beds, commonly used in the ammonia industry for the pseudo-isothermal design, to offer a more efficient reactor. The new design is based on the use of plates immersed in the catalyst bed (see Fig. 5) to remove the reaction heat while it is formed.

This concept has already been applied and is in operation in methanol reactors (see fig. 6) and ammonia converters as well.

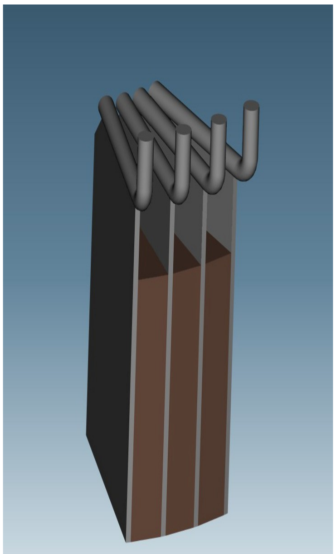


Fig. 5

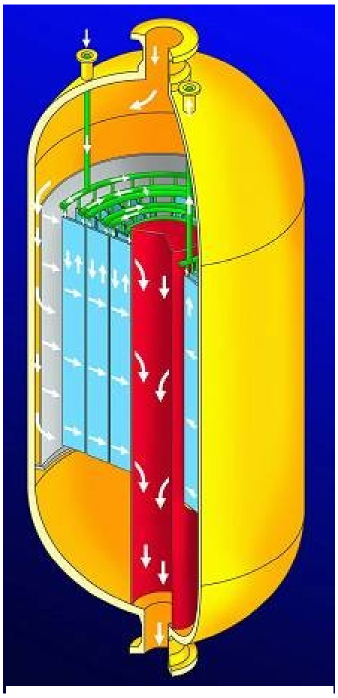


Fig. 6
Isothermal Methanol ReactorConverter

Temperature Profile of the IAC

The improved efficiency of IAC is due to the direct removal of the reaction heat from the catalyst bed. This allows to obtain an optimized temperature profile in the bed. As indicated in the diagram below (Fig 7), the temperature profile achieved in the catalyst bed of an IAC follows the line of maximum reaction rate, so obtaining the highest possible conversion per pass from a given catalyst volume.

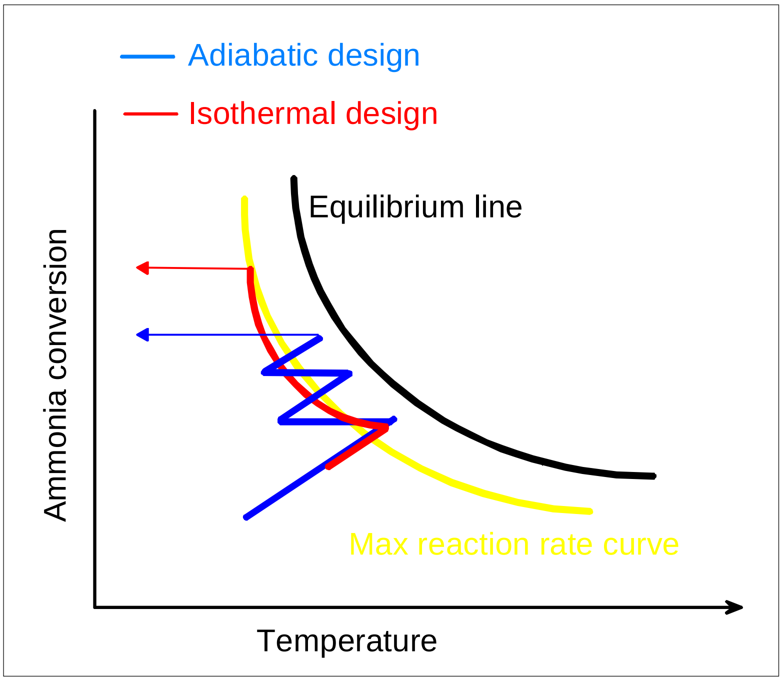


Fig. 7 – Catalyst Temperature Profiles
Adiabatic Multibeds vs Isothermal

The construction of pseudo-isothermal converters is nothing new, as it was practiced since the early years of the ammonia industry by Casale and others. In the old design efficiency and maximum capacity was limited though, because the catalyst bed was axial and the cooling elements were tubes fixed to a tube-sheet.

Use of plates for cooling, allows the design of a pseudo--isothermal converter without tube-sheets, eliminating the size restriction, simplifying the construction of the internals and the operation of catalyst loading and unloading. In addition, the non-adiabatic beds are axial-radial, featuring a low pressure drop and allowing the use of small-size, highly activity catalyst.

Cooling Plates

The cooling elements immersed in the catalyst beds are hollow plates.

These elements are disposed along the beds radius, allowing the axial-radial flow to take place easily in the catalyst beds (see Fig. 8).

The plates are made by two adjacent sheets of metals, which are continuously welded along the perimeter and spot-welded in between. The plates then undergo then a forming process, essentially consisting in their pressurization from inside, obtaining the characteristic "pillow like" shape.

The plates obtained in this way are very strong mechanically thanks to their shape, and reliable, thanks to the automated manufacturing process, that, once tuned, produces all identical units. The plates are suitable and already used for steam generation or gas heating.

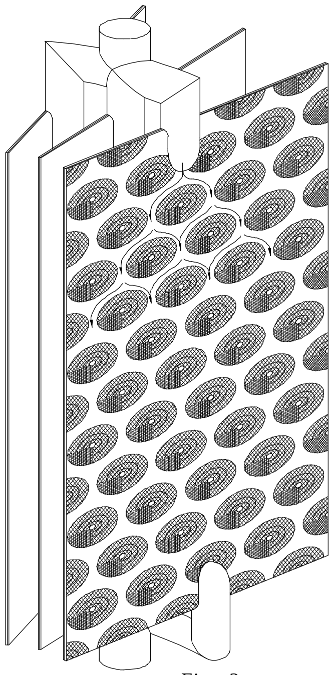


Fig. 2

Fig. 8 – Hollow Plates

5. Industrial Experiences of IAC

The first industrial experience of IAC reactor type is the replacement of the existing two converter internals in the PCS Nitrogen O3 ammonia plant in Trinidad.

The 03 ammonia plant is an original C.F. Braun design erected in 1965 in Brea, California. The plant was relocated to Trinidad in 1994. The design capacity at that time was 680 MTD. Some minor modifications increased the plant's production rate to 753 MTD.

Fig. 9 - Photo of IAC Converter Basket being lifted into place

Ammonia Casale engineered a complete plant revamp in 2004 and the modified plant started up in April 2005.

The plant production is now 953 MTD with a reduction of energy consumption of about 4.2 MMBtu/St (0.96 Gcal/MT).

Many sections of the plant have been modified and among them the revamping of the two ammonia converter is the most innovative.

The plant is fitted with two ammonia converters operating in parallel. The revamp of the synthesis section demanded a very significant efficiency improvement because of:

1. The large capacity increases (+26%) and
2. The higher concentration of inerts in the circulating gas due to the front-end transformation.

The new IAC design (Fig. 9) allowed a significant reduction in the circulation flow and consequently a considerable decrease in the specific duties of the exchangers. The lower recycle flow resulted in a smaller heat recovery in the synthesis waste heat boiler. To overcome this, an additional BFW pre-heater was installed and now it recovers 50 mmBTU/hr (12.6 Gcal/h). Additionally, the increased ammonia conversion, to 17%, in the synthesis loop translated into no additional load on the refrigeration system, which in turn meant no modification to the refrigeration compressor.

Only few months later, Casale modified one reactor operated by Canadian Fertilizers Limited in Medicine Hat, Alberta, Canada.

The original 1135 MTD reactor was previously revamped adopting two adiabatic beds with interchanger layout with capacity increasing up to 1600MTD and changed again to an Isothermal design by using the Casale IAC technology.

The reactor internals were modified by inserting plates where the reaction heat is removed by the incoming syngas.

It has to be mentioned that, while for PCS O3 plant, two complete new cartridges, with the internals already installed, were supplied, for CFL, the internals were supplied in pieces and installed “in situ” during an extended plant turn-around.

The following table summarizes the converter performances before and after the revamping:

		Before	**After**
Converter capacity	**MTD**	**1’600**	**1’630**
Ammonia content at converter inlet	% mol.	1.65	1.25
Ammonia content at converter outlet	% mol.	15.7	17.5
Converter outlet pressure	Bar g	142	137

6. Applications of Isothermal Ammonia Converter and AmoMax-10

Amomax-10, thanks to its higher activity at low operating temperature is the “ideal partner” for the new Casale Isothermal Reactor.

In these advanced reactor (see Fig 10), it is possible to keep under very good control the temperature of the whole catalytic mass, therefore enhancing the performance of the AmoMax-10 to get higher conversion per pass

The cooling medium, used inside the plates, is the same circulating gas before being fed to the catalytic bed. Some technical solutions, like cold gas bypasses, are used to control and optimize the catalyst temperature along the reacting gas flow and during all the catalyst life in order to be always as closer as possible to the maximum reaction curve, optimizing, at any moment the reactor performances.

The incoming gas flows inside the plates and removing the reaction heat as soon as it is generated, it is heated up to the required catalyst inlet temperature.

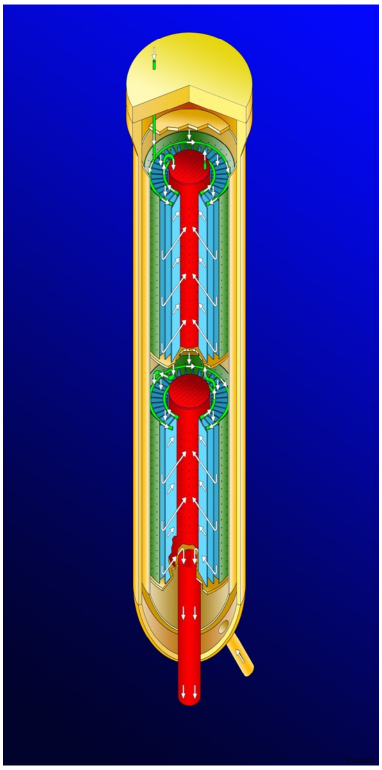


Fig. 10 - Isothermal Ammonia Converter

To evidence the advantages coming from the joint application of IAC and AmoMax-10 Casale has studied in details two cases:

The first one is a revamping case; the second one is the design of a new ammonia loop.

For both the cases, the following scenarios have been investigated:

A) Base Case - Casale Axial-Radial 3 beds, adiabatic reactor with magnetite catalyst

B) IAC and magnetite catalyst

C) IAC and AmoMax-10

The cases have been studied keeping all the main parameters constant like: same catalys age, same inerts concentration, etc.

The results are shown in the following tables:

1 - Revamping Case:

		1-A **Base Case**	**1-B** **IAC** **&** **Magnetite**	**1-C** **IAC** **&** **AmoMax**
Converter capacity	**MTD**	**1'600**	**1'600**	**1'600**
Ammonia content at converter inlet	% mol.	1.3		
Ammonia content at converter outlet	% mol.	15.5	17.4	18.3
Converter outlet pressure	Bar g	140	138	138
Energy				
Total Energy Saving	kcal/MTD	---	50'000	70'000

'

2 - New Loop Case:

		2-A Base Case	2-B IAC & Magnetite	2-C IAC & AmoMAx
Converter capacity	**MTD**	**2'000**	**2'000**	**2'000**
Ammonia content at converter inlet	% mol.	4.4		
Ammonia content at converter outlet	% mol.	20.5	21.3	22.3
Converter outlet pressure	Bar g	158		
Energy				
Total Energy Saving	kcal/MTD	---	50'000	70'000

7. Conclusions

Among the technologies nowadays available for revamping and for new plants, two new "entries" have to be taken into consideration:

- The innovative Casale Isothermal Ammonia Converter.
- The highly active and highly performing Süd-Chemie AmoMax-10 catalyst;

The combination of these two "players" can boost the plant performances in a significant way, improving plant capacity at the same or lower energy consumption or reducing energy consumption of about 70'000 kcal/MT.

The application of these two technologies is now well established, with several applications operating since years.

When planning a revamping, or a new plant construction, the combination of the two advancements together is an important factor to be considered for maximizing plant efficiency.

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