# High Temperature Hydrogen Attack (HTHA) in Ammonia Plants

**Abstract**

High temperature hydrogen attack (HTHA is a problem which concerns steels operating at elevated temperatures in hydrogen environments. It is not to be confused with hydrogen embrittlement or other forms of low temperature hydrogen damage.

HTHA is a time-temperature-pressure function. These, basically means the longer that a piece of equipment is exposed to temperatures above its resistance limit in certain hydro-process environment (see API941-NELSON Curve), the more damage to the steel will accumulate; and the higher the temperature rises above the limit of the steel, the more rapidly the damage will occur.

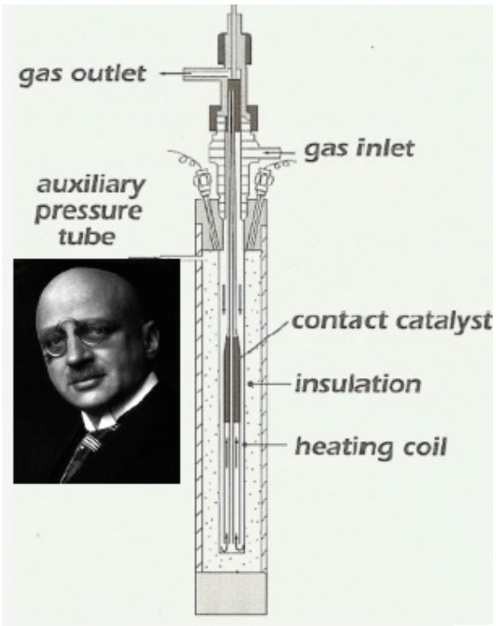
Monitoring the integrity of equipment in HTHA-Service is necessary to avoid accidents, especially if one of the following reasons are true:

- HTHA in many old plants -is true for many ammonia plants- can occur especially after a long onstream-time, if the incubation time ended.
- However, there have been several cases where HTHA was found, even though operating conditions were below the Nelson Curve.
- There are new findings since 2016: After explosion in the TESORO refinery with 7 dead, it must be assumed that HTHA in C steel can already be expected at > 204 °C and a hydrogen partial pressure of $pH_2$ > 3.45 bar.

It is strongly recommended to monitor the integrity of HTHA vulnerable equipment!
Due to the age of many ammonia plants, a lot of equipment may need to be replaced.
For avoiding HTHA of new equipment, use the recommendations for fabrication of new equipment in the hydrogen service according API 941 and API 934A!

## Introduction

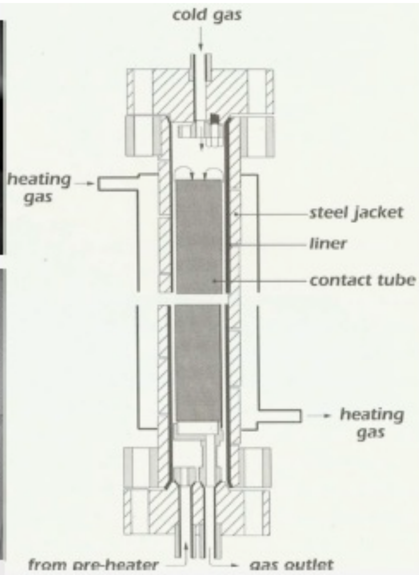
Fritz Haber developed from 1904 to 1908 the "process for the synthetic representation of ammonia from the elements". He applied for a patent at the Patent Office in Berlin on October 13, 1908. On June 8, 1911, it was granted: Patent No. 235,421. In the meantime, Haber was an employee at BASF. He has left the patent for the economic exploitation of BASF.
However, the ammonia synthesis could not be used industrially. There were no vessels, that would not let hydrogen through and withstand the high temperatures and especially the pressure.
The equipment had to be dense and resistant to the slightly diffusing and easily combustible hydrogen at high temperatures and pressures.
The pressures required by Haber of 100 to 200 atmospheres at the temperature of incipient red heat of the iron had to mastered.
The company technician Carl Bosch, who also worked for BASF, was responsible for mastering this challenge.



Haber's Experiment Converter for Ammonia Synthesis 1909

At first, one failure followed the other: Several equipment vessels exploded.
The carbon steels of conventional type were not resistant to the combined attack of heat, pressure and hydrogen gas (failure by cracking).
Haber found that the hydrogen could penetrate carbon-free iron without damage at these temperatures.
Carl Bosch had the idea to solve this problem by inserting a liner made from low-carbon, soft iron.
The penetrating hydrogen escaped through holes in the pressure-bearing steel jacket (this idea is still applied today).
By the development of Cr-Mo-steels later this problem could be solved and the liner-shell construction is no longer required.
Finally, in 1913, the Haber-Bosch trial finally took place in Oppau near Ludwigshafen (Germany). The annual capacity of ammonia was initially 4000 tonnes (syngas from lignite).
Even today, there are limits. The challenges of material and technology in the hydrogen service are enormous.


A high-pressure reactor is installed in the ammonia factory



Bosch's first reactor with liner and external heater (1911)
The so-called liner-hole concept

**Basics[1)]**

*First the Knowledge of the HTHA mechanism*

High temperature hydrogen attack (HTHA) is a treacherous damage mechanism

- It can occur in hydrogen atmosphere at elevated temperatures (at least 400 ºF or 204 ºC).
- The atomic hydrogen diffuses through the pressure and the temperature in the steel.
- This atomic hydrogen then reacts with unstable carbides in steel and forms methane ($CH_4$) gas, resulting in cracking and failure of the vessel

*Second Recognize the potential danger of HTHA*

- HTHA is a time-temperature-pressure function that basically means:
- The longer a part of the equipment is exposed to the temperatures, the more accumulated damage it will cause in the steel.
- The higher the temperature rises above the limit of the Nelson curve, the earlier the damage will occur.

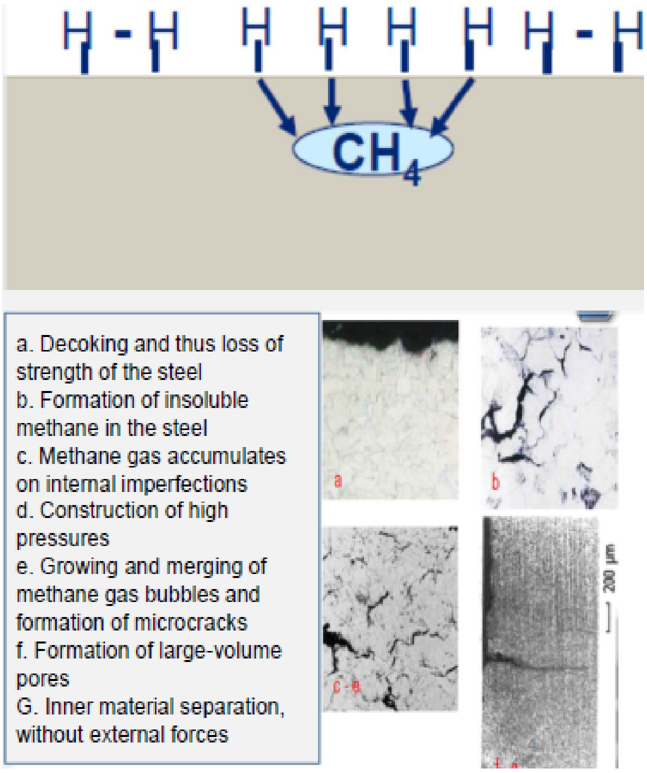
Picture from explosion due too HTHA
*The 2nd International Conference on Technical Inspection and NDT (TINDT2008)- October 2008 - Tehran, Iran*

*Thirdly the Knowledge of vulnerable locations*

- HTHA is most commonly found in equipment made from carbon steel and carbon-½Mo steel
- There is evidence that carbon steel, as well as carbon ½Mo, can also be damaged under the current Nelson curve
- Damaged areas are often near the outlet nozzles of catalytic equipment or in the hot area of the inlet chamber of WHB.

## Explanation to the principle of HTHA

- High-temperature high-pressure hydrogen attack (HTHA) as a chemical-physical process is a damaging mechanism at elevated temperatures.
- He can attack steels in two ways:
  a) surface decarburization,
  b) internal decarburization and cracking which eventually leads to cracks.
- The activation occurs above t> 204 °C and $pH_2$ = 3.45 bar hydrogen partial
- Thermal dissociation produces atomic hydrogen: $H_2 \rightarrow H + H$
- The resulting atomic hydrogen is dissolve in the steel. These small hydrogen atoms diffuse into the steel (physical process)
- With the carbon or cementite ($Fe_2C$) phases responsible for the strength of the steel, the hydrogen reacts and forms methane (chemical process):
  $Fe_2C + 4H \rightarrow CH_4 + 2\ Fe$
- The methane cannot escape, the steel is decarburized. It leads to cracking and in case not recognized to the failure of the vessel
- Already from stage a (refer to figure) the integrity of the vessel is impaired




*$CH_4$ formation and decarburization (means the loss of strength)*
C (from the steel) + 4 H atoms → $CH_4$
Trapped in the micropores or grain boundaries under pressure methane is the cause of HTHA.

This results in cracks parallel to the surface: Most commonly affected are C-steel and low-alloy steel (C-½Mo steel). Alloy elements such as Cr, Mo and V can counteract by carbide formation. Affected equipment is those that operate above or near the Nelson curve.
Particularly affected areas are the hot areas near the outlet area of pressure vessels with catalyst and inlet area of process heat exchangers.

**Basically, the longer a part of the equipment is exposed to temperatures near or above its resistance limit in a hydrogen environment, the more damage can accumulate.**

**Please contact us (mark.brouwer@ureaknowhow.com) if you would like further information on the following topics in terms of HTHA in ammonia plants:**

- Explanations to Rules against HTHA
- Explanations for requirements of monitoring for HTHA damage
- Explanation of API 941 approved testing techniques
- Evaluation of publications: HTHA in ammonia plants (summary literature research)
- Results of NDT with damage-classification for equipment in ammonia plants
- Example for a HTHA test report
- Evaluation of mechanical fitness for service of high temperature hydrogen attacked steel
- Failure cases in ammonia-plants due to HTHA
- Recommendations for prioritizing of NDT in ammonia plants
- Recommendations for fabrication of new equipment in the hydrogen service according API 941 and API 934A

References

1) https://inspectioneering.com/blog/2014-01-13/3804/three-tips-for-addressing-high