

FACTS Database with hazardous materials used for industrial safety maintained by the Department of Industrial Safety of TNO Coded Accident Abstract	Accident Nr. 13371
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Identification

<u>Type</u>	<u>Value</u>	<u>Text</u>
Class	* * * *	-
Abstr	Extended abstract english	
Address	Lar	
Adate	1988	
Activ	Processing	Normal operation
Loctn	Chemical factory	Ammonia plant
Dtype	Chemical industry	Ammonia plant
Dchem	Ammonia (prod.)	-

Cause

<u>Type</u>	<u>Value</u>	<u>Text</u>
Cause	Technical-failure	-

Description

<u>Type</u>	<u>Value</u>	<u>Text</u>
Occur	Penetrate/Puncture	Mercury penetrated into steel
Eqinv	Separator	Multi shell
Weight		48000/Kg
Eqmade		Steel
Temp		-5/c
Press		298/Bar
Chem	Ammonia	-
State	Liquid	-
Occur	Chemical reaction	Electro chemical
Occur	Corrosion	Stress corrosion
Occur	Crack	Newly formed cracks
Occur	Release	Leak
Tmrel		15-20/Sec
Occur	Stench-emission	Smell of ammonia
Dist		75/m
Occur	Chemical reaction	Mercury-nitrogen or ?
Occur	Chemical reaction	Mercury-nitrogen-oxygen ?
Occur	Explosion	-
Occur	Fire	-
Occur	Blast-wave/Shock-wave	-
Occur	Blow-away	-
Eqinv	Fragment	81
Weight		42000/Kg
Eqinv	Fragment	-
Weight		23600/Kg
Dist		150/m
Weight		769/Kg
Dist		63/m
Weight		665/Kg
Dist		113/m
Injurs	Worker	>1
Cost	Loss-of-property	40.350e+6 usa dollars
Lesson		See extended abstract
Photo		11
Drwng		1

Scene

<u>Type</u>	<u>Value</u>	<u>Text</u>
Scene		Explosion of a mulitshell

Scene		Ammonia separator caused
Scene		Minor injuries

EXTENDED ABSTRACT ENGLISH

After 10/years operation an ammonia separator in a 1.000/metric tons per day plant ruptured. The process is based on steam reforming of natural gas, followed by CO-shift, CO₂-scrubbing, methanation, compression and ammonia synthesis coupled with a compressor refrigeration unit. Materials of construction are according to normal practice, e.g. no aluminium components are used anywhere in the plant.

The separator is of the multi shell design with a 22/mm thick core layer and 13 wrapping layers of 7.1/mm thickness each, operated at 29800/kPa and -5/C. The wrapping layers failed in a ductile manner and approximately 90%, heavily deformed, weighing 23600/kg were thrown 150/m away. The blast wave was directed to the opposite side. The rest of the separator, i.e. core layer and both hemispherical heads, failed predominantly in a brittle manner leading to fragmentation.

In total 81 fragments could be identified weighing altogether 42000/kg whereas the total vessel weight was 48000/kg. Some fragments reached a distance of up to 500/m. Many uncounted small pieces (shrapnels) have punched walls of the reformer section 50/m away and the feed gas heater including the coil. The feed gas heater burnt out and suffered also from the blast wave as did the reformer. Walls buckled, steel profiles were bent and the refractory was affected to an extent that complete replacement was required. The immediate neighbourhood of the separator showed damages from nil to minor up to complete indicating that flying fragments are mainly responsible for the damages in this area, whereas the reformer area suffered heavily from the blast. The fire originating from the blow out added not too much to the total damage. There were no fatalities and only minor injuries.

In case mercury is accepted as a factor of influence, then the events can be explained in a way rather consistent with all observations and findings.

Mercury collected at the bottom of the separator changing the electrochemical behaviour of the system steel/liquid ammonia to the effect that stress corrosion becomes possible similar to the SCC in ammonia storage tanks (mercury instead of oxygen?).

The fact that mercury has penetrated into the steel has to be taken as such. Perhaps somebody is able to calculate from the given figures the time for which it must have been present.

The leak was observed 15-20/sec. before the rupture, ammonia smell was sensed by an operator in a distance of 75/m. When he started to move to the synthesis the blast released from the exploding vessel knocked him down.

Therefore it may well be that the leaking occurred earlier than observed.

However, the developing crack must have reached a critical size, but not to explain the fragmentation. This time a critical crack size is necessary only to explain pressure built-up between the different wrapping layers, especially behind the most outer one. Estimating calculations show that the pressure can reach at this point the bursting pressure of the thin wrapping layer, because the size of the weep holes limits the possible pressure reduction over the length of the weep holes. As in case of the first route the wrapping layers will then rupture successively under overload conditions.

As mentioned earlier it is not unlikely that mercury may form explosive Hg-N or Hg-N-O compounds with high detonating violence.

Indeed, it was reported that during cleaning of a valve in the ammonia

storage area some small mercury bubbles rolled out and the attempt to scrape off some scale led to small explosions.

Experts told me that 1 kg of such compound is equivalent to approximately 2/kg/TNT or 9.2/MJ. With the feed 60-72/kg Hg are introduced per year. If we assume 10/kg to have been present at the time of rupture at the bottom of the separator we have a charge of 473/MJ for 11/m³ gas volume calculated.

Whatever assumptions are made with respect to blast or missile energy it can be postulated, that the range where fragments were found is smaller than it should be based only on the stored energy. This leads to the speculation that within seconds a steep depressurization may have occurred before final rupture. It has been estimated that a crack 2/cm wide and 2/m long would depressurize the system within approximately 6/seconds, sufficiently short to happen within the mentioned 15-20/sec. Assuming for example that the pressure dropped to below 2000/kPa then the remaining stored energy is reduced to approximately 50/MJ, not sufficient to explain the fragment distribution.

Would there be still any need for the vessel to explode?

There is no answer to that question. However, the steep pressure fall and the percussions would be sufficient to release the detonation of an explosive Hg-N-compound which is said to be violent and would destroy the vessel wall. The contribution to fragment distribution on the other hand is considered to be small. To assume that the final rupture of the vessel was accompanied by such an internal explosion is consistent with:

- . the complete fragmentation of both heads,
- . formation of many shrapnels of bullet size,
- . the suspicion from fracture path studies that unstable brittle crack growth may also have been launched from the bottom head,
- . the fact that a specific nozzle was not found.

Lessons learned (conclusion)

The conclusion to give in the form of messages and they consider as usual all possible effects which may have lead to failure.

1. Message

Weep holes are designed for the release of diffusing hydrogen and to indicate small leaks. Large leaks (crack size larger than weep hole size) can lead to pressure built up between the wrapping layers and subsequent failure.

2. Message

Repair of a core layer of a multi shell may be performed successfully, if the core layer needs no heat treatment (no experience available). In case heat treatment is required for the material, a reliable repair cannot be performed, because:

- a. with a heat treatment the composite structure of the multi shell is affected,
- b. with no heat treatment the required material properties cannot be established.

3. Message

A required multi shell vessel should be considered as a safety risk and be replaced as soon as possible.

4. Message

It is suspected that mercury in liquid ammonia changes electrochemical behaviour of the system steel-liquid ammonia and makes the steel prone to SCC similar to ammonia storage tanks.

5. Message

It is further suspected that mercury and liquid ammonia form explosive compounds of the type Hg-N or Hg-N-O which detonate under a stroke, a rapid pressure fall or a concussion and decompose slowly under normal conditions.

6. Message

If mercury is detected in the feed it should be removed to the lowest possible level.