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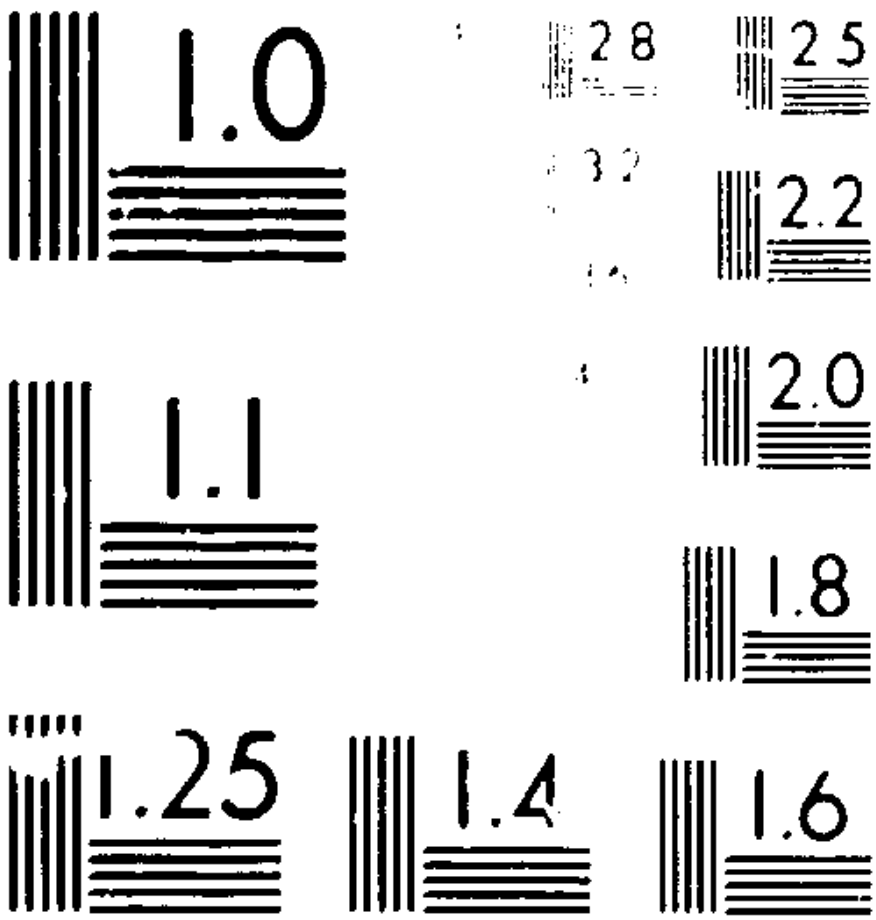
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SAFETY SYSTEMS INVOLVED IN HANDLING, STORAGE AND TRANSPORTATION OF LIQUID AMMONIA INCLUDING AMMONIACAL SOLUTIONS *

by

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I N T R O D U C T I O N

Ammonia is one of the largest products (in value) of the world chemical production. In 1980 the production of ammonia is estimated at about 80 · 10^6 t NH_3.

The storage and transportation of ammonia have become more and more important. On the one hand there is the demand of large scale storage for the big single train units of production itself. It is usual to cover 15 - 20 days by storage in case of shut down.
On the other hand ammonia is often transported, even over great distances, from the production units to the customers. In countries where liquid ammonia is directly used as a fertilizer large quantities must be stored for extended periods because the consumption of ammonia is, by nature, seasonal.

Referring to the large quantities of ammonia which are handled safe procedures for storage, transportation and handling are indispensable.

1. Storage of Liquid Ammonia

1.1. Methods of Liquid Ammonia Storage

There are 3 methods for the storage of ammonia:

a) The fully refrigerated storage at -33 °C and atmospheric pressure

b) The semi-refrigerated storage, where the temperature of ammonia is below ambient temperature, usually in the range of -5 to +8 °C.

c) The storage at ambient temperature.

The method used depends on the scale of the storage:
Smaller scale storage up to 500 t of capacity is at ambient temperature and consists of cylindrical pressure vessels up to 100 m^3 of volume.
Intermediate size storage from about 500 t to 5 000 t of capacity is still common in semi-refrigerated spheres

Above 5 000 t fully refrigerated storage is common. Insulated cylindrical tanks are used up to 50 000 m^3 of volume corresponding to 30 000 t of ammonia. Generally speaking fully refrigerated storage is the most economic method for large quantities.

The different methods described above are often combined in an extended storage comprising also all the facilities of loading and unloading.

Figure 1 gives an example:
A pressure ship is unloaded into a pressure sphere at ambient temperature; tank cars can be filled from the sphere. From the fully refrigerated tank a "cold ship" is loaded. The tanks are connected with the internal liquid ammonia network in both directions.

1.2. Fully Refrigerated storage of Ammonia

The atmospheric tanks normally operate in the range of 0.015 - 0.07 bar with a relief valve setting of 0.09 - 0.10 bar.

The tanks are cylindrical vessels with a fixed roof. The material normally used in Germany is so called fine grain carbon manganese steel with less then o.22 % C for low temperature service which corresponds to the German Eisen- und Werkstoffblatt G89, for instance, the materials TTSt E 26-36.

In the ANSI/ASTM code equivalent fine grain steel does not exist. It is necessary to use for example pressure vessel plates according to ANSI/ASTM-A 662 (carbon manganese steel for low temperature; -59 °C).

For safety conditions double wall tanks are erected. The annular space between the walls can be filled with perlite as insulation. Other insulation materials are styropor concrete, glass-fibre insulation or plates of foamed polyethylene which can be used for single wall and double wall constructions. Moisture with resultant corrosion can be prevented by a small flow of nitrogen in the annular space, which gives also an indication of any leak. If plate insulation is used at the outside of the inner wall and annular free space is left, leak detection and repair will be facilitated.

The type of foundation depends on the local soil conditions. Normally concrete ring walls are used. In the case of very poor load bearing soils piling is required.

1.3. Pressure Storage of Ammonia

Pressure vessels for ambient temperature are designed in Germany for a vapor pressure corresponding to 50 °C (or

40 °C with a reflecting paint). In tropical areas this temperature should be chosen higher. Refrigerated pressure vessels are designed for a vapour pressure corresponding to the highest operation temperature.

Material used is fine grain carbon manganese steel corresponding to German Stahl-Eisen-Werkstoffblatt 089 for instance StE 36 and StE 47 (down to -10 °C).
Qualified materials in the ANSI/ASTM code are for instance materials according to ANSI/ASTM-A 515.
The vessels, especially spheres, should be stress relieved in order to avoid stress corrosion during operation.

1.4. Safety devices and equipment for ammonia tanks

In the Federal Republic of Germany (BRD) the erection and the operation of an ammonia storage must be approved by the authorities. The safety regulations which are valid are the

Druckbehälterverordnung of 1980-which will replace the former UVV 16 and the Druckgasverordnung-concerning all kinds of pressure vessels and the

UVV 29 concerning gases.

On West European scale the APEA (Association des Producteurs Européens d'Azote) has presented safety recommendations for the stockage of ammonia in great quantities. Similar regulations exist in other countries.

The following principles for safe ammonia storage result from the existing regulations and recommendations:

Design and inspection according to the regulations for pressure vessels.

Equipment of the vessels:

1. Manometer
2. A couple of relief valves which can be operated only alternately. They must be designed that the pressure will never exceed 10 % of the operating pressure.

3. Two independent level indications. Moreover in BASF standard devices to prevent overfilling are provided.
4. Two independent devices to protect atmospheric tanks against vacuum (for instance shut down of the refrigerating compressors).
5. Two block valves at the vessel in the liquid and gas lines. Every main block valve must be distant controlled and has to shut automatically in case of auxiliary energie failure.
6. A dike with a volume of at least 85 % of the vessel. In case of a double-wall tank a dike is not necessary if the outer wall can resist the hydrostatic pressure of the liquid and if the containment is independent of the inner vessel. For instance the dike may be a conrete dike.

1.5. Location and equipment of the complete storage

Location and safety distances

The distance of an ammonia storage must be at least 25 m from a public road or railway and 100-200 m - for very large storage 500 m - to the next dwelling house.

Safety distances to the next installations inside the site should be provided according to the volume of the vessel. For instance UVV 29 in West Germany demands 20 m for > 5 000 m^3 of volume.

In an ammonia stockage, there should be sufficient hydrants and wind vanes located in a way that they can be well observed by the operating personal. At different places, there should be alarm buttons for producing an acoustic signal in dangerous situations. In the night the tank-farm must be well illuminated.

Pneumatic trip devices activated automatically and also by hand from a central control room should be provided for all important functions.

Electrical installations:
Ammonia vapour, in concentration between 16-28 vol.% in air, is flammable.
Electrical equipment is classified according to the international classification of hazardous areas.
As to the classification of an ammonia storage with devices of loading and unloading, the local conditions must be taken into account.
For instance in the BASF tank-farm at Ludwigshafen most electrical equipment is classified zone 2, only areas with bad ventilation, such as pits and deepenings are classified zone 1
The refrigeration capacity must be sufficient in case of a refrigerated stockage. In the event of a power failure, either an emergency generator must be installed to operate the holding compressors or an overpressure device is provided to lead the ammonia vapour to a flare where it is burnt.

Mechanical equipment
Piping must be designed for at least 25 bar in West Germany
BASF practice is a design for 40 bar
Adequate material for tubes and pipes is carbon steel for example ST 35 corresponding to ANSI/ASTM-A 106 qualities and for low temperatures RST 25 (up to 6 bar) corresponding ANSI/ASTM-A 333. Joints may be flanged or butt welded; BASF uses seamless tubes and pipes for liquid ammonia.

If welded pipework is used it should be stress relieved.
BASF uses for flanged liquid ammonia lines the so called Hahnsche Dichtung as sealing (a metallic ring with a soft

sealing - compressed asbestos fibres - in a groove). Steel castings should be used for the cases of pumps and pumps should be equipped with slide ring packings. It is desirable to provide sections in a large liquid ammonia network which can be cut off by pneumatic shut down valves in case of leaks.
To avoid pressure by thermal expansion of liquid which may be trapped, small relief valves must be installed. The discharge of all relief valves in an extended stockage should be given into a purge network which goes to the suction side of the compressors of the atmospheric tank.

2. Transport of Liquid Ammonia

Ammonia is transported in larger quantities by pipelines, by ammonia tankers, by tank cars and by road tankers.

2.1. Transport by pipelines

In Western Europe only over short distances. There is however a pipeline system in USA linking the Louisiana Gulf Coast and Texas with the Midwest.
The material used for ammonia pipelines is carbon-manganese steel. The operation temperature is normally between 0 °C - 25 °C. The pipeline is divided up in sections by automatically closing cut off valves in case of a large pipeline rupture. In such a case also the upstream and downstream pump stations will be shut down.

2.2. Transport by ship

There are pressure vessel tankers for 400-2 000 t NH_3 and fully refrigerated tankers for 1 000-20 000 t NH_3.

On the river Rhine in Europa pressure vessel tankers can hold 400-600 t and fully refrigerated tankers about 1 000 t NH_3.

The tanks of the ships are also designed and equipped in the same way as the non-mobile storage tanks but there are special regulations for the river and sea transport in the different countries. The APEA (Association des Producteurs Européens d'Azote) has given recommendations for loading and unloading of ammonia tankers, especially at sea-ports.

The first sea-going tanker for the transport of refrigerated ammonia, the W.R. Grace, was launched in 1964 with a capacity of 8 600 t NH_3 arranged in 4 double wall tanks.

2.3. Transport by tank car

Ammonia is transported by pressure vessel tank cars in the range of 20-50 t NH_3.

In Western Europe tank cars with 4 axles and a capacity of about 50 t NH_3 are mainly used now.
The tanks are designed for the vapor pressure of +50 ^{o}C and for a minimum temperature of -20 ^{o}C; the minimum test pressure is 26 bar. Adequate materials is carbon steel according to Stahl und Eisenwerkstoffblatt 089. The tank cars have no relief valve and no manometer. The lines for the gas and liquid phase are arranged at the bottom equipped with automatic oil hydraulic shut down valves governed by a steel cable, fixed at the rail in order to shut by displacement of the car. This valves can be activated by the control room of the filling station and shut also by other automatic trip devices. There are manual handled valves at the nozzles. The tank cars have openings for an inner control.

At the end of the nozzles the tank cars are usually equipped with flanges of 80 mm for the liquid and 50 mm for the gas phase which are shut during the transport. The maximum filling corresponds to 0.53 kg/l. Main regulation for Europe and some countries of North Africa and the Middle East is the "RID" concerning the railway transport of dangerous goods.
Furthermore in Germany the above mentioned Druckbehälterverordnung und the TRG is concerned.

2.4. Transport by road tankers in pressure vessels of ambient temperatures.

Besides of national regulations there are the following international agreements:
"ADR", regulation concerning the transport of dangerous goods for the most European countries and
APEA (Producteurs Européens d'Azote), recommendation concerning the design of road tankers.
Adequate material is carbon manganese steel (according to Stahl und Eisenwerkstoffblatt 089).
There are some extracts of the above mentioned agreements:
The design of the tanks corresponds to the following test pressures:

diameter of tank [m]	with insulation [bar]	without insulation [bar]
≤ 1.5	33	33
>1.5	26	29

The maximum filling amounts to 0.95 X density of the liquid at 50 ^{o}C. The tanks should be designed in addition for an acceleration of 20 m/s^{2}. The tanks must be equipped with inner situated shut down valves for the liquid and gas phase activated from the bottom or distant controlled. They must shut automatically if any troubles should arise. These valves, plus 1 or 2 nozzles with block valves and end flanges, have a diameter of 80 mm for the liquid phase and of 50 or 80 mm for the gase phase. The end flange of the gase phase however has a diameter of 50 mm. It must be

prevented by bolts that the valves can open during the transport. Furthermore the tanks must have an inspection opening and an indication of the maximum level.
For electric motor driven ammonia pumps only plugs with earth must be used.

3. Safety in Handling of Ammonia

3.1. Physiological properties of ammonia

Vapour of ammonia is already perceptible in the range of 1-10 vol ppm. The MAK (maximum admissible concentration during a shift of 8 hours) is 50 vol ppm in West Europe. In the range of 100-400 vol ppm irritation of the mucous membrane and the eyes is caused. Tissue will be damaged or destroyed above about 1 500-3 000 ppm. Above 10 000 vol.ppm of ammonia vapour direct killing is caused (the skin can resist only for seconds).
Liquid ammonia causes burns and strong attacks on the skin.

3.2. Protection of the personal

Personal protective equipment should comprise gas-tight goggles and gloves, breathing sets and full protective clothing and boots. Furthermore filter hoods as escape sets. This equipment must be readily available and the personal must be trained in its use and limitations. The breathing sets are hoods fed by compressed air or self contained breathing apparatus which have a nominal duration of at least 30 minutes. As to the clothing, some sorts of rubber as for example clorobutyl rubbers are adequate materials.
For emergency operations in areas of nigher ammonia concentration, self contained breathing apparatus and clothing offering complete protection against vapour are indispensable.

For routine operations a breathing set and light protective clothing will be normally sufficient.

3.3. Personal qualification and Safety instructions.

Operators charged with handling of ammonia must be well instructed. They should be familiar with the safety instructions and the operating manuals which must be always kept up to da e. Lessons, in order to repeat the instructions, must be periodically arranged by the management. During every operation men never should be completely alone.

3.4. Maintenance

In an ammonia storage daily inspections of the installations should be carried out. Machines, as for instance compressors, should be inspected in longer periods as to the recommendations of the suppliers. If repairs must be carried out the section of repair must be completely cut off from the rest of the installation, depressurized and purged. Repairs must only be started if a written permission is given by a reponsable person. The permission should comprise the precautions which have to be carried out before starting and the safety equipment during the repair. There are national regulations for the inspection of pressure vessels. In the Federal Republik of Germany:
Outside inspections every 2 years, internal inspections every 5 years and hydraulic testing every 10 years.
Inspections are prescribed for the vessels of road tankers every 6 years and for tank cars every 8 years.

3.5. Operation

A filling station should be equipped with automatic trip devices to cut off the flow in case of abnormal conditions. The admissible filling weights of tank cars and road tankers must be carefully respected in order to avoid overloading. Flexible hoses should be avoided as far as possible for connections. They must be inspected regularly.

3.6. Emergency procedures

The leak of fully refrigerated ammonia will fall to the ground and form pools. Evaporation will be slow. A small leak of ammonia at ambient temperature from a pressure vessel will produce ammonia vapour while a large leak will form an aerosol.

Pools of liquid ammonia should be pumped into a vessel. Water must be avoided because the sensible heat of the water and the heat of solution will increase the rate of evaporation in a large scale.

In an atmophere with low ammonia concentration a water spray will reduce the concentration. On the other hand, water spray against an ammonia aerosol is only effective if large quantities of water compared with the quantity of ammonia in the air will be used. In any case emergency plans should be worked out. As to the transport of ammonia by tank cars or road tankers the suppliers should be prepared to give assistance to the local Fire and Police Services.

4. Storage and Transport of water / ammonia solutions

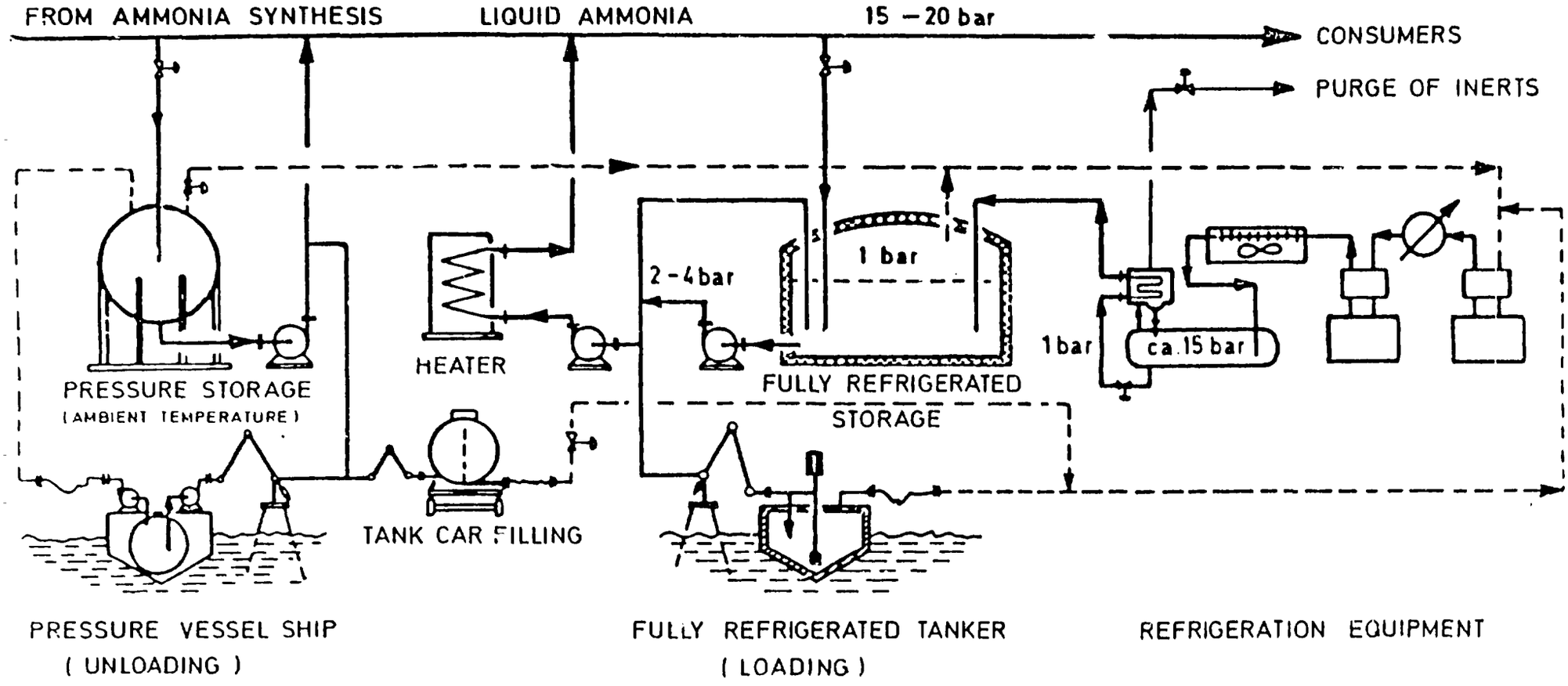
Liquid ammonia is completely miscible with water. Ammonia gas is extremely soluble in water. Solutions >35 weight % NH_3 must be stored in pressure vessels. They are handled in the same way as anhydrous ammonia. As to the transport of these solutions by tank car or road tanker they are considered in Europe as dangerous goods of the class 2 as anhydrous ammonia and the above mentioned regulations "RID" and "ADR" are applied to these solutions. The design and filling conditions for tank car and road tanker vessels are less severe than for anhydrous ammonia in the follwing cases:

NH_3 content weight %	Minimum test pressure [bar]	Maximum Weight/l volume [kg/l]
>35 and ≦ 40	10	0.80
>40 and ≦ 50	12	0.77

Usually only the transport of solutions with less than 35 weight % has practical importance. For instance BASF often supplies 25 weight % ammonical solutions.

These solutions can be stored at ambient temperature and at atmospheric pressure in vessels equipped with a pipe open to the atmophere. On the other hand for the transport pressure vessels are used equipped with a little relief valve. Although carbon steel is an adequate material stainless steel is often used for the installations of the storage and for the tanks of the tank cars and road tankers. The reason is that many consumers want a product with a very low content of iron.

For the handling of ammonical solutions the personal protective equipment should be the same as above described.



AMMONIA STORAGE

R E F E R E N C E S

RID = Reglement international concernant le transport des marchandises dangereuses par chemin de fer

ADR = Accord européen relalif au transport international des marchendises dangereuses par route

TRG = Technische Regeln Druckgase

Druckbehälterverordnung 1980

UVV = Unfallverhütungsvorschriften (Berufsgenossenschaft der Chemischen Industrie)

APEA = (Association des Producteurs Européens d'Azote)

- Sicherheitsempfehlungen für die Lagerung von Ammoniak in großen Mengen
- Empfehlungen für das Be- und Entladen von Ammoniaktankern (Seehäfen)
- Sicherheitsempfehlungen für den Bau von Ammoniak-straßentankwagen

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