Overview of Silane Incidents

April 2023

In over 40 years of silane manufacturing and use, there have been numerous incidents, most were minor, but a number were fatal. Root causes range from human error to system design, maintenance, lack of training, improper installation, etc. (Note: This is not a complete list of incidents, these are only the ones that I am aware of). The most significant incident was the Gollob explosion in 1988 which is reported in a separate summary.

Significant incidents involved gas cabinet explosions which have caused 7 fatalities.

Germany, 1976 – 1 fatality
Japan, 1989, 1 fatality & 1 injury (Leakage during cylinder purge)
Japan, Dec. 13, 1989 – 2 fatality & 2 injuries
US, Jan 1992 – 1 injury (Cylinder change)
Japan 1994 & 1996 – 2 injuries (disconnect wrong cylinder)
US, Feb 7, 1996 – no injuries (Corroded Cylinder)
Japan, Dec. 21, 1996 – 1 fatality (Cylinder change)
US Dept of Energy, Date Unknown – no injuries
US, 2003, no injuries
US Jan 16, 2005, 2 injuries
Taiwan, Nov 23, 2005 – 1 fatality (cylinder change)
India, March 2007 – 1 fatality (startup of new gas cabinet)
China, June 2009 - 1 injury (disconnect wrong cylinder)
China, 2010 - 1 injury (disconnect wrong cylinder)
Taiwan 2010 - 1 injury (disconnect wrong cylinder)
China 2011-14 – 5 injuries (disconnect wrong cylinder)

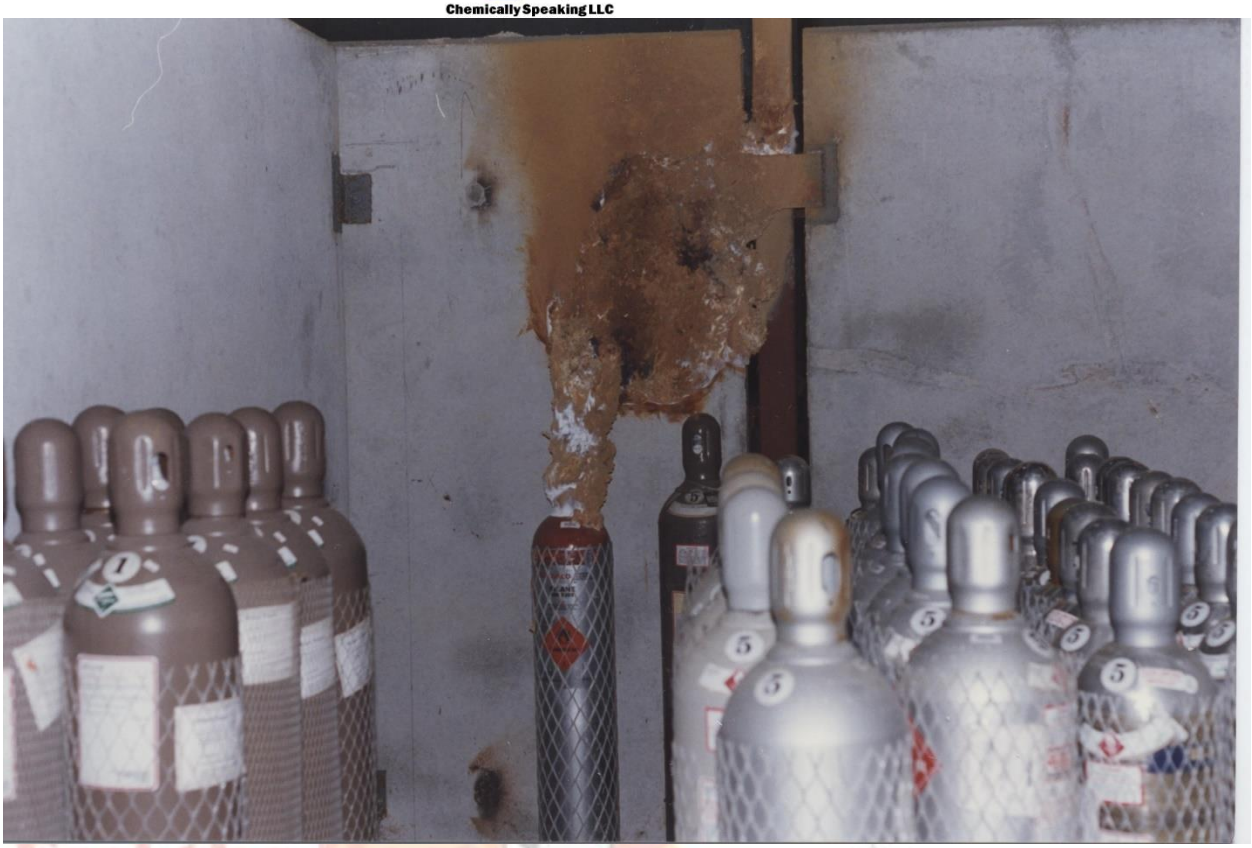
The number of incidents and their severity have been reduced at the traditional IC manufacturers as a result of training, equipment improvements and design changes. The most recent incidents are primarily at the Photovoltaic companies or Nano Fabs that are new to the use of silane.

Of the many incidents reported, the following are the more common or severe.

1. **Pressure Relief Device**

   Pressure relief devices (PRD) have been one of the leading causes of silane incidents. These have caused considerable property damage but only minor injuries.

   Since a CG-4 combination (metal rupture disk and fuse metal) device is used, a defect or improperly assembled PRD may not be readily apparent. If the rupture disk is compromised or loose the fuse metal will hold back the silane pressure for a period of time. At pressures above 500 psig, the fuse metal will cold flow until the silane starts to leak and ignites. This fire will heat and melt the remaining fuse metal. Without the backing of the fuse metal, the rupture disk suddenly opens completely venting the contents of the cylinder in minutes. If this happens when nested with other silane cylinders, the fire will cause the other PRDs to activate.



All of the gas suppliers have experienced at least one event like this during the storage of cylinders. The largest incident of this type involved 215 silane cylinders in 1997 stored outdoors in one nest, all relieved in a period of 3-4 hrs.

Recognizing this as a key problem, the CGA member companies obtained a special permit in 2006 from DOT to make PRD's optional for cylinders of silane. This was extended to ISO Modules in 2010. In 2011 CGA S1.! Was changed to make PRD's optional. This was finally recognized by reference by DOT in Dec 2020.

a. **Design**
   A flaw in the design of an early pneumatic cylinder valve led to a premature PRD failure and fire. A second valve company used a platinum clad rupture disk which cracked over time due to H_2 embrittlement causing multiple failures. This has been the root cause of the failures that has caused the multiple cylinder incidents. It was also the cause for a recall of cylinders containing silane in the 1990's.

b. **Assembly**
   Incidents have occurred where the rupture disk is not install properly or not at all. Improperly machined surfaces or inadequate lubrication have damaged the disks during assembly. The pressure then causes the fusible metal to cold flow until it starts to leak.

c. **Vent tube failure**
   An ISO Module PRD vent stack seal cracked, allowing rainwater to enter the tube. This froze and the ice damaged the PRD. This was being transported across the US to a

customer. While on the interstate in South Dakota it began to leak. Motorist noticed a flame above the ISO Module and alerted the driver. Supplier had to perform an emergency cascade into an empty trailer

2. **Connection**

Cylinder outlet connections is another leading cause of incidents. Most of the fatal gas cabinet accidents were during cylinder change and may have been due to bad connections.

a. **CGA 350**

The CGA 350 connection was the primary connection used for silane in the 1970's and 1980's. This is a metal nipple that is deformed in the valve outlet. Stainless steel work hardens with each use, making it difficult to get a good seal with continuing use.

b. **Use of Elastomer Gaskets**

The DIN 1 (German) and JIS (Japanese) connections use a flat Teflon gasket for sealing. Under high pressures the gasket can cold flow and leak with time. Some users of DISS connections to save the cost of replacing nickel gaskets use Kel F gaskets which suffer from the same problem. These will leak after a day of pressurization.

c. **Pigtail rotational torque**

VCR connections are commonly used to connect the pigtail to the gas panel. During cylinder changes the pigtail is physically pushed away from the cylinder to remove it. This applies rotational torque or stress to the VCR gasket, causing it to leak

d. **Gaskets**

Reuse of metal gaskets, double gasket or no gasket. Under or over torque

e. **Thermal Expansion/Contraction**

During high flow conditions the cylinder valve or RFO can act as an expansion nozzle and liquid silane will be formed (<-100^{o}F). This cold liquid has caused VCR and DISS connection leaks due to thermal contraction of dissimilar metals

f. **Vibration or impact**

VCR gaskets can easily be damaged by vibration or impact. Connection to diaphragm compressor leaked

g. **Physical Support of Pigtail**
Insufficient mechanical support of the pigtail damaged the DISS gasket

3. **Operator Error**
A number of incidents have occurred when the operator attempted to remove the wrong cylinder of silane when there are two in a gas cabinet in order to provide uninterrupted flow. The operator tries to disconnect the in use cylinder rather than the “empty”. This has happened despite physical, visual safeguards and training. In 2 cases (2009 and 2010) the operator and cylinder were thrown to the ground after the explosion. In 2012 the operator tried to disconnect a full Tonner, since it was an outdoor location the explosion only damaged his eardrum.
In another incident when the operator removed the valve handle wiretie he inadvertently opened and locked the valve handwheel open. Thinking it was closed he tried to remove the vaportight cap and it immediately ignited. Another operator came to assist and checked the handwheel, since it was locked open he thought it was closed. He loosened the vaportight cap and got an even larger flame. The cylinder vented for 110 minutes and when the flames died down, they tightened the vaportight cap.

4. **System failure**
   a. **Backflow of gas into cylinder**
   Users may have backflowed contaminant gas such as nitrous oxide into cylinder through the purge gas systems. Incidents in 1988 (Gollub Analytical) and 1991 (Osaka University) where this happened caused 5 fatalities, nitrous oxide flowed into a silane cylinder that was online, creating an explosive mixture.
   b. **Checkvalve failure**
   Tonners manifolded together for higher flow in a 2 x 2 arrangement. Problem with one of the pigtails caused the user to isolate one side. Maintenance guy disconnects the

pigtail of the bad side and silane immediately flows out from the adjacent tonner creating a large fire. This impinges on the tonner PRD causing it to fail.

5. **Venting**
   a. **Venting into exhaust duct**
      A common practice in the 1970's and 1980's was to vent silane into the exhaust duct above the gas cabinet. During system purging high flow rates of silane occurs. Many incidents of duct explosions caused the industry to move away from this practice. The PV industry has not learned this. A recent incident in Dec 2011 blew up a 20' section of 10" dia duct and threw the fan off the roof.
   b. **Shielding vent stack**
      User build shield around vent stack to "hide" it. The "confinement" was enough to increase the amount of metastable mass during venting and the ensuing explosion was like a cannon damaging the roof below it.

6. **Cylinder filling system**
   Leaks in cylinder filling systems have cascaded into events that caused the tube and the cylinders to vent their contents. Multiple safeguards did not work or are missing. Serious fire damage to fill systems and cylinders. Fill room is destroyed and building severely damaged. In a few cases the fire burned uncontrolled for days because there is no way to isolate the cylinders. Venting silane is unlike other gases since it forms a tube of SiO_2 that slowly chokes off the flow. Then the SiO_2 suddenly falls off and it vents at full flow again only to repeat the formation of SiO_2 again. This becomes worse as the pressure decays.

7. **Valve Design/Maintenance**
   Silane will oxidize to form silicon oxide particles which will embed in the soft valve seats. This will allow some silane to leak past the seat and be trapped behind the valve gastight outlet cap. Over time this can develop as much pressure as the cylinder. When the operator removes the gastight outlet cap to prepare the cylinder for service they will experience a flash or bang when the silane is released. (aka popper) Valve design and maintenance has improved. In the 1970's this was almost 50% while today it is 1 in 10,000

8. **Bullplug Leak**
   Proper machining and polishing of bullplug mating surfaces is critical for seal. A few incidents of leaks on ISO Modules have occurred at the bullplug

9. **Reactive Silicon Oxides**
   a. **In Exhaust Duct**
      Partially oxidized silicon oxides have accumulated in ducts. These are still reactive and flammable, trapping silane and hydrogen. In one case a maintenance worker disturbed the mass in a duct and it exploded throwing him off the ladder
   b. **In System Vacuum**
      Vacuum pump outlets may accumulate reactive silicon oxides and nitrides plugging the line. During system maintenance this is exposed to air and a violent reaction occurs. Sometimes during a purge sequence, air is introduced into the system. This has led to

explosions in the vacuum system. Some users have surrounded the vacuum pumps with blast shields.

c. **In Baghouse**

Silicon oxide particles can develop a very high static charge and can still be flammable. In one case workers were using a HEPA vacuum cleaner to clean a cyclone and baghouse. The vacuum cleaner exploded enveloping both workers in flames.

10. **Loss of Purge Gas**

To prevent plugging of vent lines and scrubbers and air intrusion, a continuous flow of inert gas is used. In a few cases the flow was stopped or inadequate. Wet and dry scrubber have exploded in some cases when air backflowed into the system. Silane has a very wide flammable range and some scrubbing reactions also create hydrogen as a byproduct.

11. **Reactor Explosion**

Improper sequencing of valves has allowed silane and an oxidizer gas to be flowed into the reactor at the same time. This caused an explosion in the quartz reactor

12. **Expansion cooling**

Expansion of high pressure silane liquefies a portion of the silane. This can cause thermal contraction or embrittlement of system components. Leaks and system failures have occurred with improperly designed systems. Regulators which are typically where the expansion occurs have had diaphragm failures due to cold temperature embrittlement of the sealing gasket. During system startup of a 1,000 meter supply line, the flowrate into the line which was under a vacuum was extremely high, the expansion cooling through the RFO caused the connection to leak.

Expansion cooling in silane ISO Module manifold caused DISS connection to leak.

13. Supplier Incidents

A supplier was offloading cylinders inside a 10,000 ft^2 warehouse without cylinder protection or valve outlet caps on. One dropped off the dock and the valve opened. The fire caused over 200 silane and ethylene cylinder PRDs to activate. Killed 2 operators and destroyed the warehouse.

A supplier was venting silane through a water bath. The employees decided to bring it indoors because of the weather. The explosion severely injured both operators and destroyed the 100 ft x 100 ft building.

While transporting full Y cylinders on an open truck, it took a sharp turn. A Y broke free from a strap and impacted another Y. The welded cylinder cap broke and damaged the valve causing a fire. ER team had to offload the other Y's while the Fire Dept sprayed water to cool the cylinders.

車上固定式鋼瓶猛烈燃燒，產生濃濃的黃煙。吳傑沐攝

14. Miscellaneous

Other incidents have occurred due to regulator diaphragm failures, improper lockout of vent lines, cylinder corrosion, stress crack corrosion of aluminum, valve diaphragm leakage.

15. Unbelievable Category

Devalving a cylinder while it still contains silane. Happened at least three times (US, Malaysia, UK). Fortunately, they discovered the mistake when flames came out of the valve threads and resealed it immediately.

A user thought silane was a liquefied gas so they immersed the cylinder in a heated water bath. To control the algae that grew in the heated bath they mixed sodium hypochlorite in the water. The carbon steel cylinder corroded over time forming pinholes. During a holiday shutdown the exhaust ventilation was shutoff. The gas cabinet exploded during the evening. Gas supplier ER Team had to remove the cylinder while silane was popping from the sidewall of the cylinder.

16. Truly Unbelievable Category

A silane distributor operated his business out of a motel in the 1970's. At least 3 major US Semiconductor Companies knew they were shipping to a Motel! In 1998 when the Motel was being demolished, they found 18 full cylinders in a basement storage room. The Fire Marshal gave these to a local hydrotest company who was going to simply open the valves and vent them!

In 2016, during demolition of a mixed used building a silane mixture cylinder from the 1980's was found. The contractor opened the cylinder valve and a huge flame came out. He proceeded to bury the cylinder in a mound of dirt.

By the time I had HazMat dig up the cylinder, it had emptied.

Emergency Response to a cylinder connection leak due to the use of a Kel F gasket. Gas supplier ERT had to shut the cylinder valve and disconnect the cylinder.

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