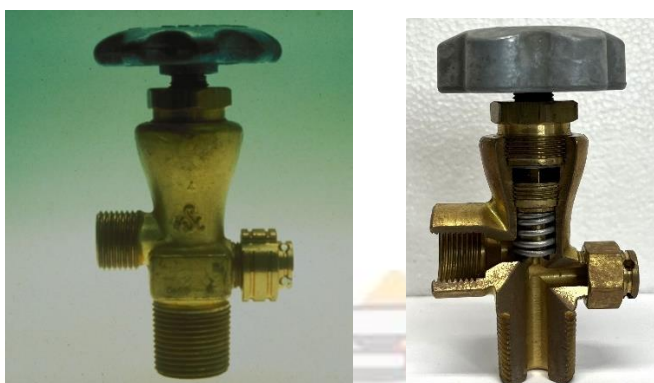


Development of an Electronic Specialty Gas Cylinder Valve

Aug, 2022

In the 1970's the dominant Electronic Specialty Gas cylinder valve was a brass spring loaded metal diaphragm valve from Superior Valve or Kerotest Corp in the US. This was because the Interstate Commerce Commission (ICC now DOT) at the time required the most leakproof valve available. Today the US DOT regulations 49CFR173.40 General packaging requirements for toxic materials packaged in cylinders (c) (2), requires a non-perforated metal diaphragm valve to be used for highly toxic and toxic Zone A and B gases such as arsine or phosphine.



Figs. 1 & 2: Brass Diaphragm Valves CGA 350 and 580 Outlet

Initially only a brass valve was available with a metal diaphragm. This was spring loaded design that will help lift the lower stem and valve seat to open it when the metal diaphragms are bowed upward. Closing the valve compressed the metal diaphragm forcing it to bow downward. This also pressed against the spring and lower stem to close it.

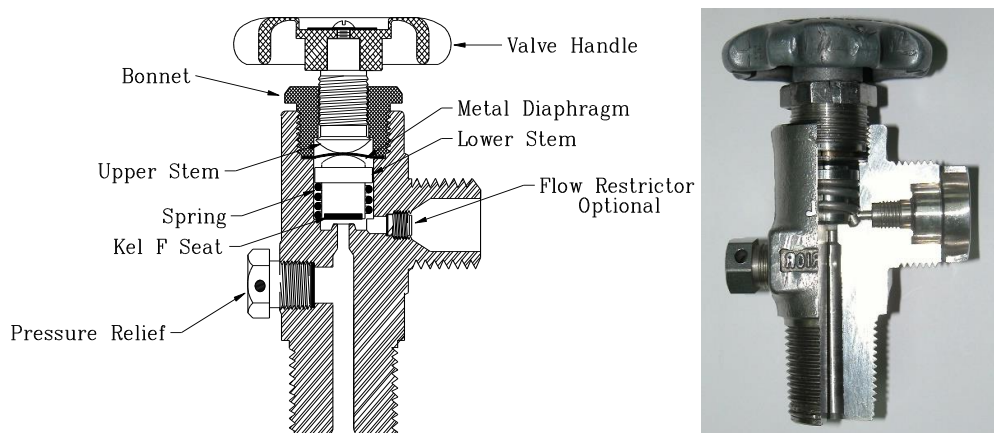
Highly toxic corrosive gases such as cyanogen chloride or phosgene can use packed valves if they have a seal cap over the packing nut to seal the stem.



Fig. 3: Packed Valve With Stem Cap



In the 1980's gas suppliers started to use a 303 stainless steel spring loaded metal diaphragm valve from Superior Valve Corp. for the higher purity Semiconductor gases such as arsine or phosphine.



Figs. 4 & 5: Superior Valve 303 Stainless Steel Diaphragm Valve with CGA 350 and DISS 632 Outlets

Metal Diaphragm Safety Issue

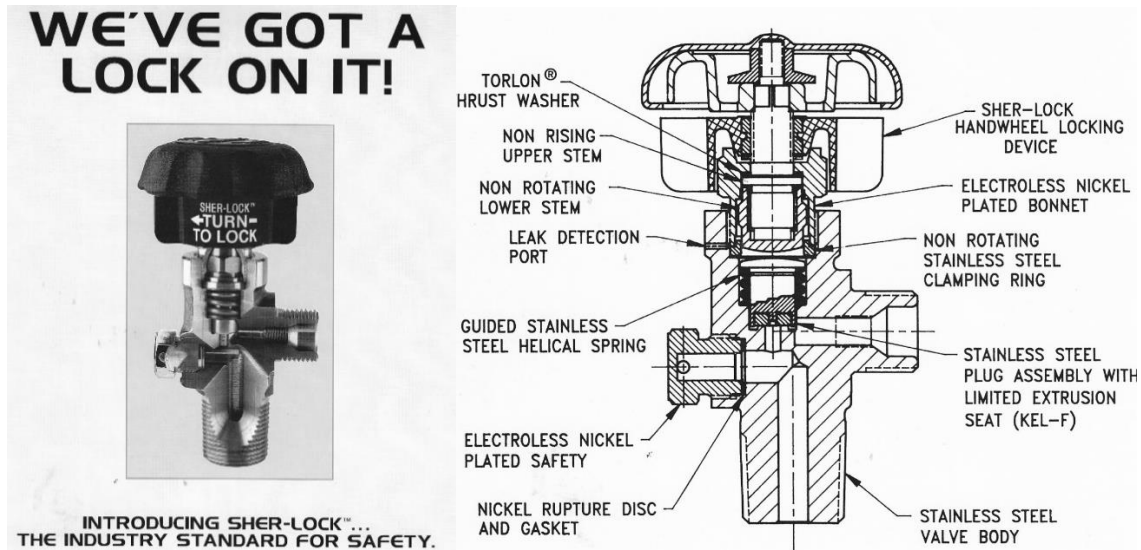
Spring loaded metal diaphragm cylinder valves under certain handling and transport conditions can vibrate open as demonstrated by the 1974 Asia Freighter arsine Incident where arsine cylinders leaked into the cargo container and caused many acute exposures (See Asia Freighter Arsine Incident) and the 1977 piggyback trailer on a train silane explosion.¹ Testing by the UK National Lab after the arsine incident demonstrated that a gas cylinder that is rolled horizontally 4 ft (1.25 m) impacting a wall and then rolled in the opposite direction and impacting the wall could torque the valve open in as little as 4 impacts. Even the most tightly closed valve opened after 21-25 impacts.² If cylinders are not properly braced in a container, the cylinders could easily break loose and fall to the floor where they would roll and impact numerous times during transit.

As a Best Practice, companies started tying the valve handle shut by using a metal wire or plastic zip tie to prevent it from vibrating open during shipment. Plastic shrink wrap around the valve provide additional securement of the handle.



Fig. 6: Cylinder Valve Tied Closed

Sherwood Valve Company designed a valve with a manual lock.³



Figs. 7 & 8: Sherwood Diaphragm Valve Lock (Sher-Lock)

The other reason for the leakage in both incidents was that the cylinder valve connection outlet caps were not designed to provide a gas tight seal. They were typically dust caps with a fiberboard washer. A CGA 350 outlet cap has a nipple in the center to form a seal with the outlet.

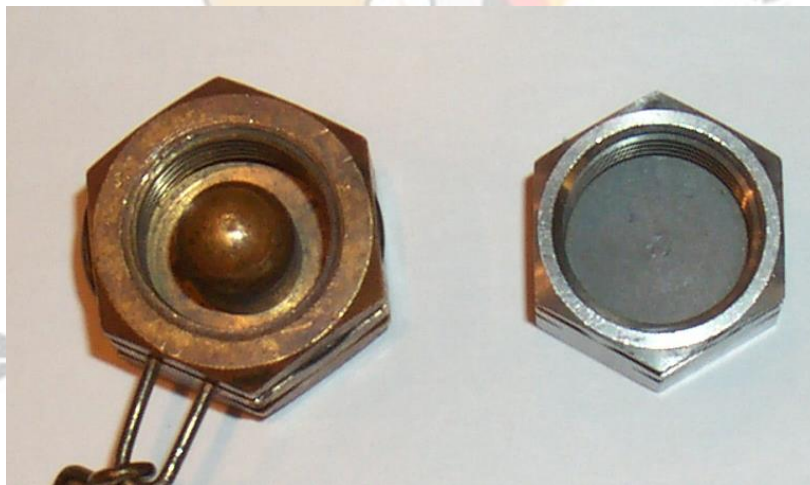


Fig. 9: CGA 350 Vapor Tight Cap and Dust Cap With Fiberboard Washer

The DOT regulations 49CFR173.40(c)(3) requires a vapor tight outlet cap on the valve outlet to provide a high pressure secondary seal for all highly toxic or pyrophoric gas cylinder valves

One major problem with spring loaded metal diaphragm valves is that positive closure is not always possible when there is high pressure in the cylinder. This pressure creates an upward force on the metal diaphragms creating significant physical resistance when closing the valve. The diaphragms are about an inch in diameter, but the gas pressure can be as high as 2,200 psig exerting an upward force of 1,725 lbs.



As a result, gas tight closure is not always possible. To properly close the valve, operators must “double close” it. First it is closed as tight as possible and then the pigtail pressure is vented. This will remove the upward pressure on the metal diaphragm and the operator closes it again. Typically, the operator will get another 1/8 of a turn. This is a problem when a user is returning a full cylinder due to quality or other issues. In some cases, the vapor tight outlet cap is also not on wrench tight. These cylinders have leaked during handling or transport causing an incident.

Electronic Diaphragm Valve

As noted earlier, Superior Valve developed a 303 stainless steel diaphragm valve for Semiconductor gas service.

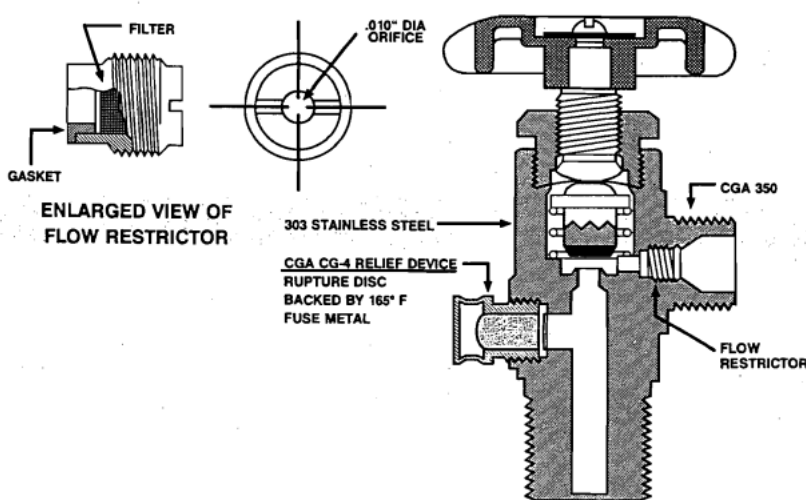


Fig. 10: Superior Valve 303 Stainless Steel Valve^{4,5}

While the Superior metal diaphragm valve provided very high purity and reliable service for non-corrosive gases, they quickly fail in corrosive (Cl_2 , HCl , BCl_3) gas service. Packed valves normally used for corrosive gases are poor designs for high purity service as the packing tends to leak or it can venturi air through the packing into the system during operation.

Attempts to use a spring loaded diaphragm valve for high purity corrosive gases have been a failure since they rapidly corrode the internal dead space parts such as the spring and lower stem making it inoperable in as short of a time as a single use. In addition, the valve dead space (2-3 cc) between the outlet connection and the valve seat is extremely difficult to clean or purge creating an area that generated significant particle contamination.

This was made even more difficult when an RFO is installed.⁵ The spring corrosion at times prevented the valve seat from opening.

The spring-loaded diaphragm valve also operated poorly when used for low vapor pressure liquefied gases such as boron trichloride or tungsten hexafluoride. There was inadequate pressure to lift the lower stem and diaphragm when they corroded.



The valve development projects first began in the early 1980's, a time when the semiconductor industry was experiencing tremendous growth. During this period there were numerous compressed gas incidents (explosions, fire or acute exposures). There was significant concern with uncontrolled leaks, especially with silane which was the cause of some major incidents. (See article *Development of a Cylinder Valve Restrictive Flow Orifice*)

In the late 1970's and early 1980's many US users of silane experienced numerous fires and explosions. IBM and AT&T launched internal research projects and created task forces to examine this issue. They also funded research studies by Hazards Research Corp., Battelle, Union Carbide, Intel.⁶

In the early 1980's there was considerable interest in designing the next generation valve ("State of the Art") to improve Electronic Gas safety and quality. The SEMI (Semiconductor Equipment Manufacturing Industry Association) Gases Safety Subcommittee Valve Task Force created a project to work with SSA (Semiconductor Safety Association, now SESA) and CGA (Compressed Gas Association) on this effort. A joint meeting was held on April 6, 1983 during the SSA annual conference which defined the following features for the valve:⁷

1. Better leaktight outlet connection (10^{-9} cc/sec, Replaceable Metal Gasket)
2. Right Hand Thread
3. Pneumatic Operation
4. RFO (In Valve)
5. 316 Electropolished Stainless Steel

Worldwide, many equipment, valve and gas companies initiated projects to work on developing a cylinder valve that could meet these requirements. Many equipment, valve and gas companies created projects to develop this cylinder valve. Key individuals and companies that took part in these efforts included:⁸

- Bill Korzenowski, Gary Johnson, Pat Taylor – Joint Project Linde (Now Praxair) & Veriflo
- Bill Koch - Nupro Valve
- Dick Martin - Martin Valve
- Bill Kalaskie - Superior Valve Corp
- Ceodux (Rotarex)
- BOC (Airco)
- Jim Proctor & Jerry Sameth – Matheson Gas Products
- Ted Bielli – Motorola
- Philip Schull - Texas Instruments

Superior Valve developed an electropolished 316 stainless steel spring loaded metal diaphragm valve with a DISS outlet connection.

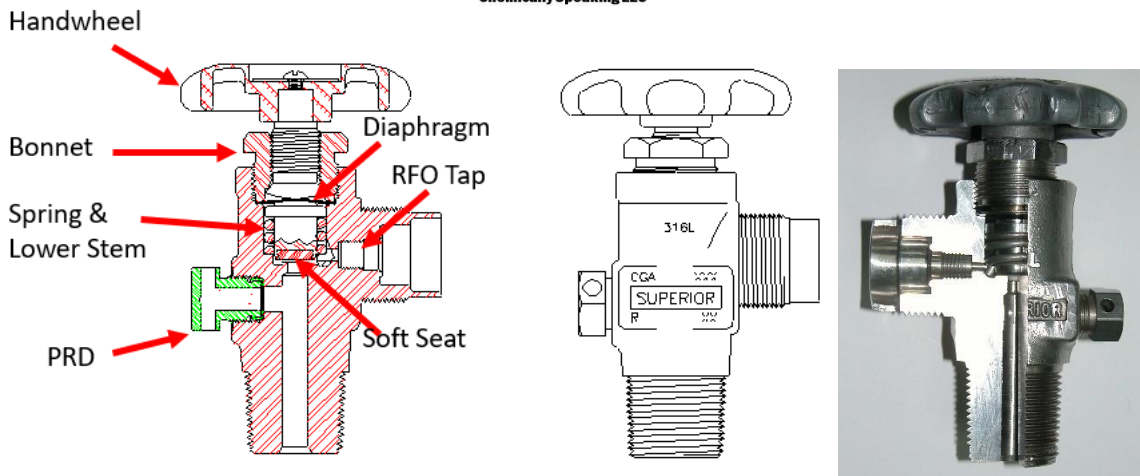


Fig. 11: Superior 316 Stainless Steel Spring Loaded Metal Diaphragm Valve

During this time, tied diaphragm valves were introduced. These had smaller dead spaces, less wetted parts and no spring. These were ideal for low vapor pressure gases since it no longer relied on a spring and pressure to lift the lower stem to open the valve.

Ceodeux and Superior both developed prototypes that were tested

Tied Diaphragm Assembly

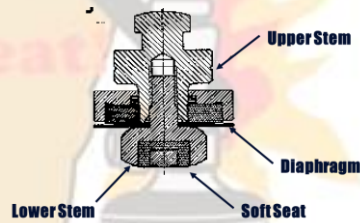


Fig. 12: Tied Diaphragm Assembly

An issue with a tied diaphragm is that metal diaphragm is drilled through so that the lower stem can be attached to the upper stem. The diaphragm is then welded to seal it. Did this meet the DOT requirement for a non-perforated diaphragm? The industry consensus was that it did due to the welding of the diaphragms. There were concerns with the flexing and possible cracking of the weld the so lift for the initial version was small limiting flow to a 0.25 Cv. A leak check hole is also provided above the diaphragm to monitor for diaphragm leakage.



Fig. 13: Spring Loaded Diaphragm Valve and Tied Diaphragm Dead Space

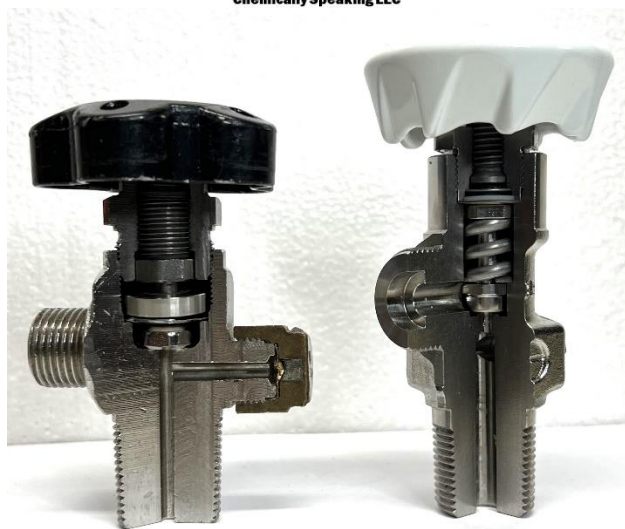


Fig. 14 Tied Diaphragm versus Spring loaded Metal Diaphragm

The tied diaphragm valve however was better suited for Electronic Gas Service since the upper stem and lower stems were tied together allowing positive action. This worked well with low vapor pressure gases such as boron trichloride, dichlorosilane, monochlorosilane, etc.

The lift was also increased to provide a much higher Cv of 0.55

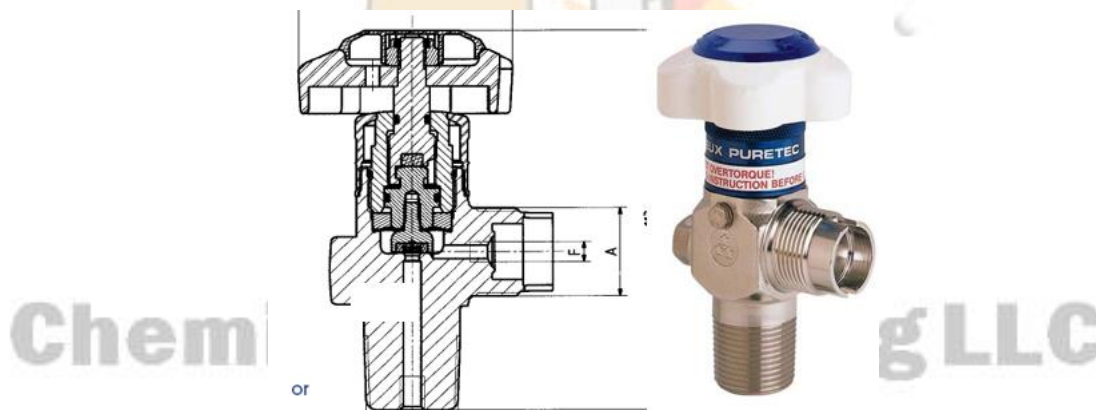


Fig. 15: High Flow Ceodeux D335, Cv 0.55

Mechanical Valve Closers

The International Fire Code (IFC) requires an automated shutoff valve as close to the cylinder as possible for highly toxic, toxic or pyrophoric gas systems. As a result, a pneumatically operated pigtail valve has typically been installed to comply with this requirement. A pigtail valve however would be effective with the most likely leak point since it is close to the cylinder valve outlet connection. There have however been numerous incidents involving the types of connections and their failure high pressure cylinders where the Teflon (PTFE) or Kel F™ (PCTFE) gasket is used for the valve outlet connection has failed.



Under high pressure it will cold flow and then leak. For a pyrophoric gas like silane or phosphine there would be an immediate fire at the connection and the heat from the fire will melt the gasket creating an even bigger leak.

The UVIR detector will immediately detect the fire and shut the pigtail valve. It will not stop the leak as the outlet connection is before the pigtail valve.

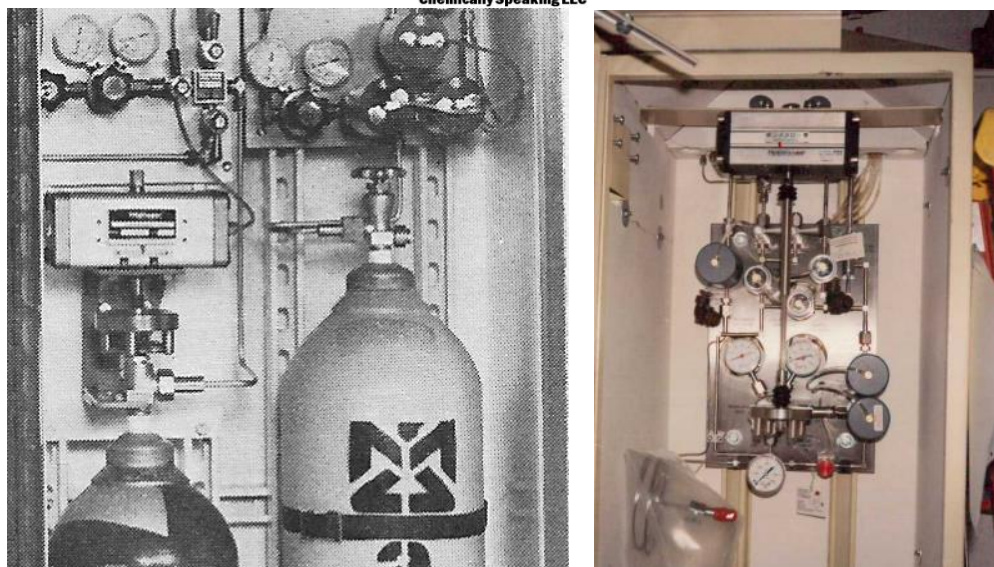


Fig. 16: Silane Leak at Outlet Connection, Pigtail Valve Has Automatically Closed

In this case the operator or Emergency Responder must reach in and manually close the cylinder valve exposing their hand and arm to the flames. In some cases, the valve handwheel may have melted preventing easy closure. This type of incident has happened many times throughout the world with pyrophoric gases such as silane, phosphine or diborane.

In the 1980's there were several manual cylinder valve closers that could be attached to a cylinder valve handwheel that will turn and shut off the valve in an emergency. While a pneumatic actuated cylinder valve would provide the optimum solution these other options were offered since the pneumatic cylinder valve had not been fully developed in the 1980's. It is also expensive.

For example, a double acting piston activated device that clamped onto the cylinder valve handwheel was available from Matheson.⁸ It could open and close the cylinder valve.



Figs. 17 & 18: Matheson Piston Actuated Valve Opener and Closer

These valve shutoff devices were flawed in that there was no way to adjust the rotation of the cylinder valve to fully open or close. As a result, they could over torque the valve causing the valve handle fingers to distort or not open fully. There were also others available from gas cabinet suppliers that were similar in design.

Better shutoff valve devices are the Tomoe "Shutboy" or Festo which are spring loaded devices that are manually activated. The operator uses a handwheel to crank the valve open and unwinding the spring. If there is a problem the spring is released via an electronic signal shutting the valve.^{9,10}



Figs 19 & 20: Tomoe Shutboys



Fig. 21: Festo Valve Shutoff

In Asia these valve shutoff devices continue to find wide use despite the availability of pneumatic cylinder valves which are more costly.

Pneumatic Cylinder Valves

A pneumatic cylinder valve that will automatically isolate the cylinder due to leak or fire detection is a best practice for many US companies, but they are expensive. A key problem is there is limited house N₂ pressure at most user sites, so the highest actuation pressure was limited to 80 psig. Springs that can be compressed by 80 psig pressure to open the valve can chatter when closed due to vibration during transportation and handling this will cause leakage across the valve seat that will be trapped by the vapor tight outlet cap/plug.

The challenge in designing this valve is the force against the metal diaphragm must be overcome by the springs to properly close the valve.

Many designs were introduced. Ceodeux finally was able to develop a valve that could meet all the requirements.

During handling and transportation all pneumatic cylinder valves must have a manual interlock to hold the valve shut. This manually compresses the valve seat so that it cannot vibrate open. All pneumatic cylinder valves had manual locks that would prevent a valve from chattering opened due to transportation vibration or physical impact. These must be unlocked before the valve can be opened pneumatically.

Superior

In the 1980's Superior Valve Corp sold most of the electronic specialty gas cylinder valves in the US. A decision was made that in order not to obsolete a cylinder that already had a spring loaded cylinder valve already installed. The actuator was installed on the existing valve by simply removing the

handwheel and bonnet nut and replacing them with the actuator housing. The design also had to fit under the cylinder cap.⁷

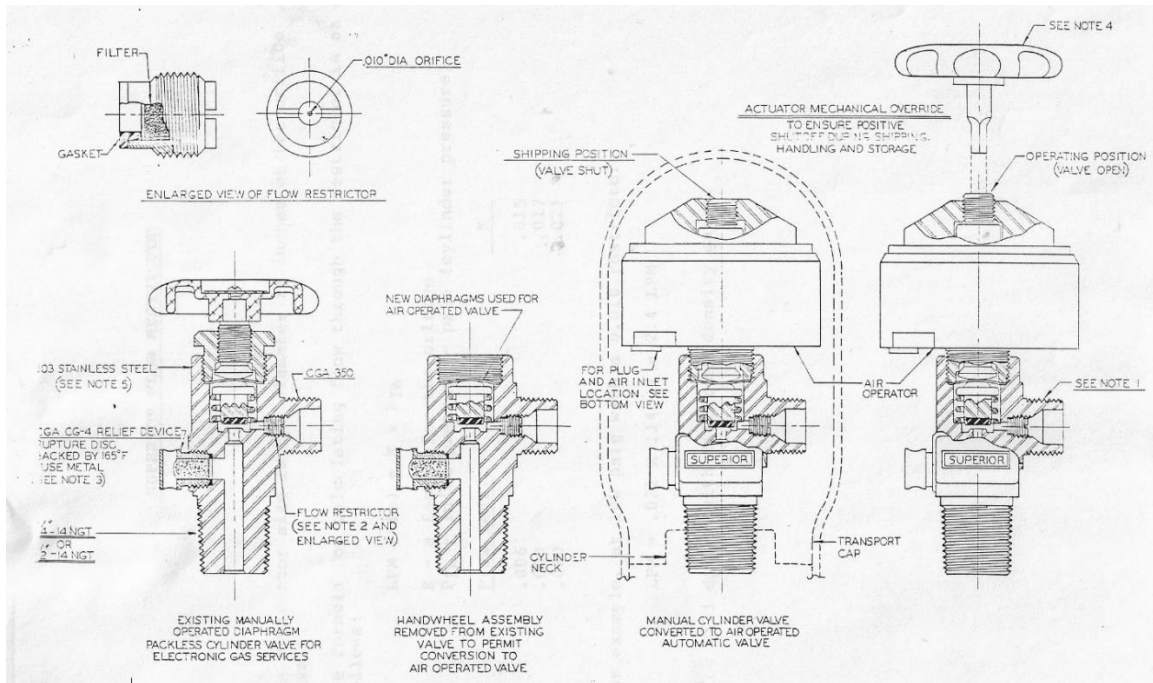


Fig 22: First Generation Superior Valve Pneumatic Actuator

This design was very heavy due to the large springs and thick pneumatic actuator housing since an actuator pressure of 200 psig was required to open the valve. This made the housing incredibly top heavy and the cylinder unstable.

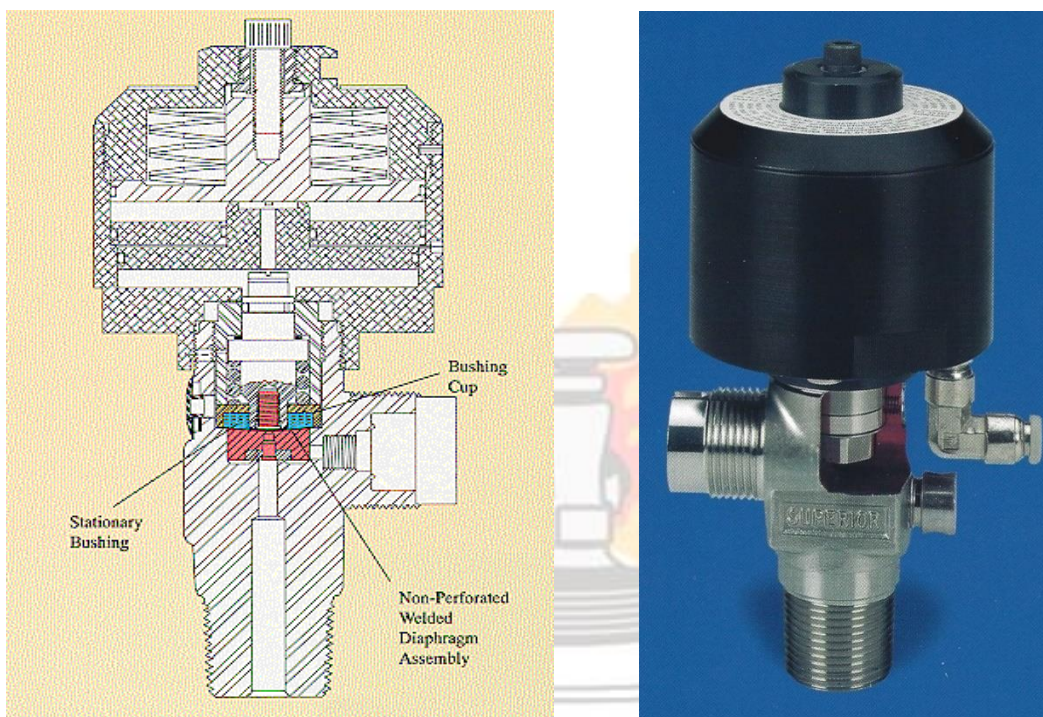


Fig. 23: Superior 1st Generation Pneumatic Valve



A major safety problem with this design was if the cylinder was to topple over, the sudden physical impact onto the ground tended to loosen the pneumatic housing that compressed the diaphragms. This will cause a leak when the valve was opened. Since it was initially used for silane, it was dangerous to open the valve since an explosion or fire would occur. Many gas suppliers experienced incidents like this. One gas supplier had silane cylinders in India with this leak problem that had to be mitigated in the 1990's. Other gas suppliers had similar problems in house. These incidents caused this design to be abandoned since they were impossible to safely control.

Superior Valve then designed a pneumatic tied diaphragm valve which had a much lower actuation pressure.



Figs.24 & 25: Superior Pneumatic Tied Diaphragm Cylinder Valve

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It never had widespread use and was discontinued.

Neriki Valves

Neriki introduced a valve that could be operated manually or with a pneumatic actuator that could be mounted on top of their valves by the user. As the pneumatic actuator was not shipped with the cylinder, the valve fit the existing cylinder caps.¹¹



DS-3L

(スプリングレス仕様アクチュエーター分離タイプ)

- 特徴
- デッドスペース極小でガス置換が容易である
 - アクチュエーター分離式構造
 - ◇アクチュエーターはキャビネット内に常設し、
 - 容積交換時はワンタッチで脱着可能
 - ◇容積弁はコンパクトでランニングコストを低減
 - 安全構造
 - ◇ノルマルクローズ式
 - ◇グラウンド部2重シール構造

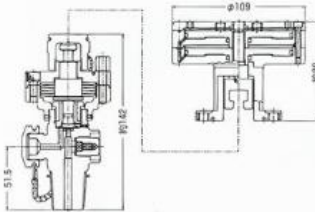


Fig. 26 & 27: Neiriki Valve Without Actuator Attached and Pneumatic Actuator

Feel the

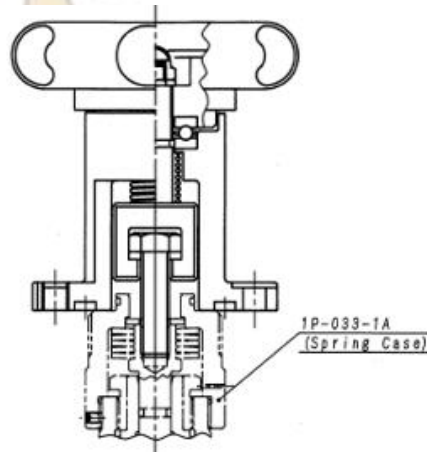
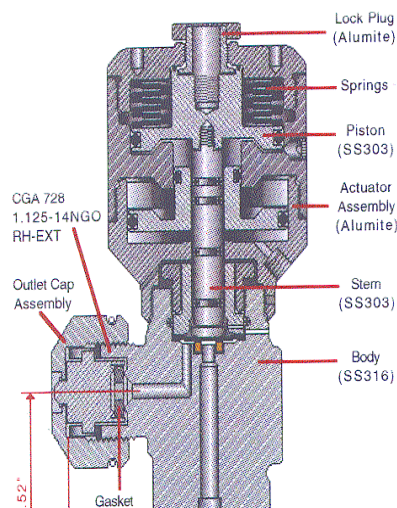
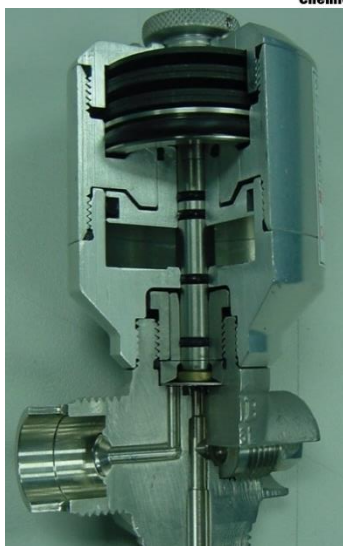


Fig. 28: Manual Actuator

This is a much less expensive option for the user.

Neriki also designed a pneumatic valve DS-3H. The manual opener however can still be used.



Figs. 29 & 30: Neriki Pneumatic Cylinder Valve

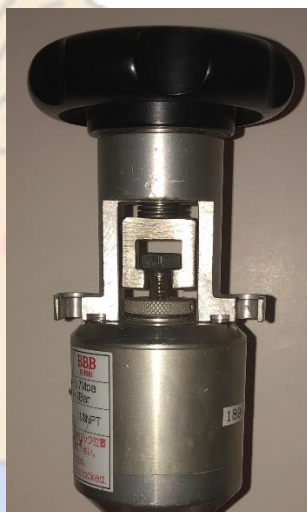


Fig. 31: With Manual Actuator Attached

The Neriki valve seat is a ring recessed in the housing. The Kel F valve seat elastomer is compressed by the metal diaphragm so that very little is exposed when the valve is shut. This prevents reaction during handling with reactive gases such as chlorine trifluoride (ClF_3). If handled or moved in a horizontal position the liquid ClF_3 can suddenly slosh into the valve and cause a reaction with the Kel F. This is the reason why gas suppliers require the cylinder to be shipped in a vertical position.

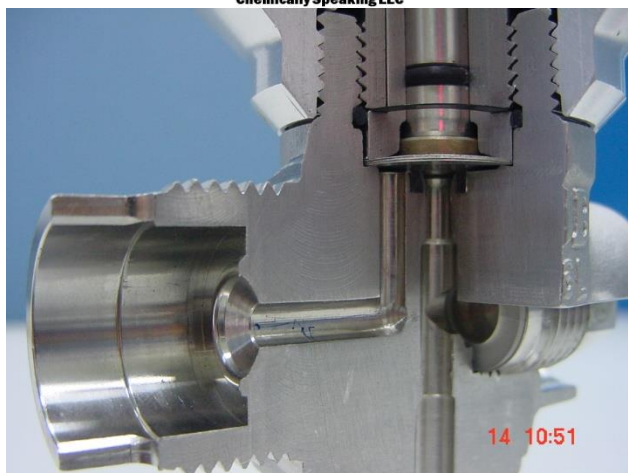
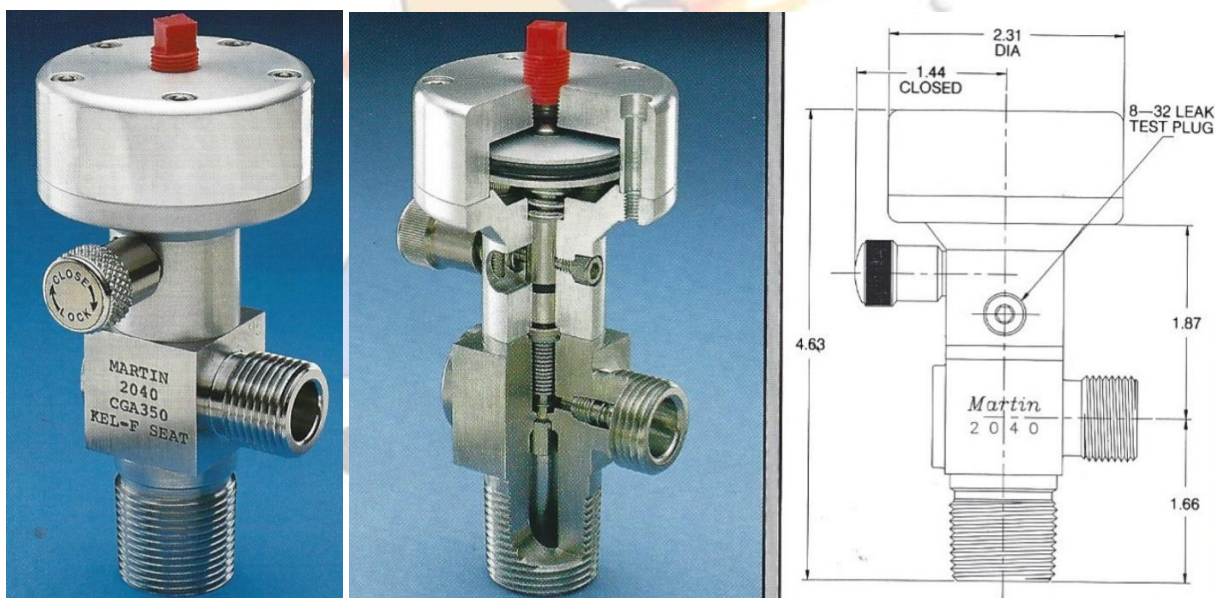


Fig. 32: Neriki Valve Seat Embedded in Housing

Martin Valve

Developed by Dick Martin. Company was acquired by Sherwood Valves. It was a metal bellows valve with a reverse acting seat.¹²

First generation



Figs. 33 & 34: Martin Pneumatic Cylinder Valve

Reverse acting metal bellows valve. The valve closes by pulling up the seat which is the opposite of the typical cylinder valve. Since the seat is threaded onto the actuator one could envision it unscrewing and falling off causing an uncontrolled release.

Incident:

In 1989 a silane cylinder PRD popped when the plastic shrink wrap around the valve was removed at a user site. Leak occurred due to a damaged metal rupture disk. There was concern that the silane fire

would fully melt the fusible metal that would allow the metal rupture disk to open fully. The onsite gas supplier ER team quickly offloaded the cylinder.

After an investigation by Martin Valve and the gas supplier a second generation valve was designed.¹³

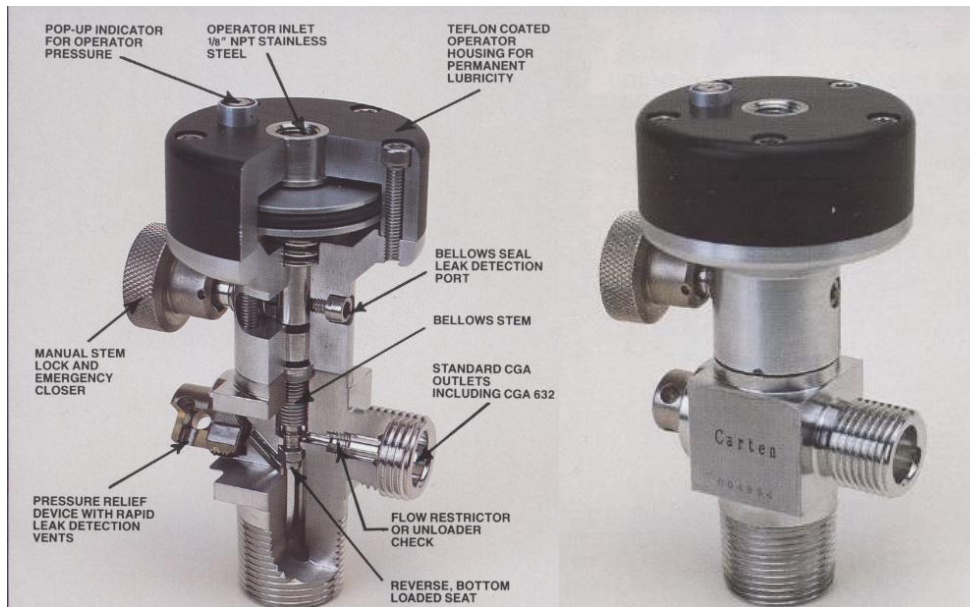


Fig. 35: 2nd Generation Martin Pneumatic Cylinder Valve

Linde/Veriflow Valve

Linde (Praxair) and Veriflo jointly developed a pneumatic cylinder valve. This also combined an internal pressure regulator that reduced the pressure.^{5, 14, 15, 16}

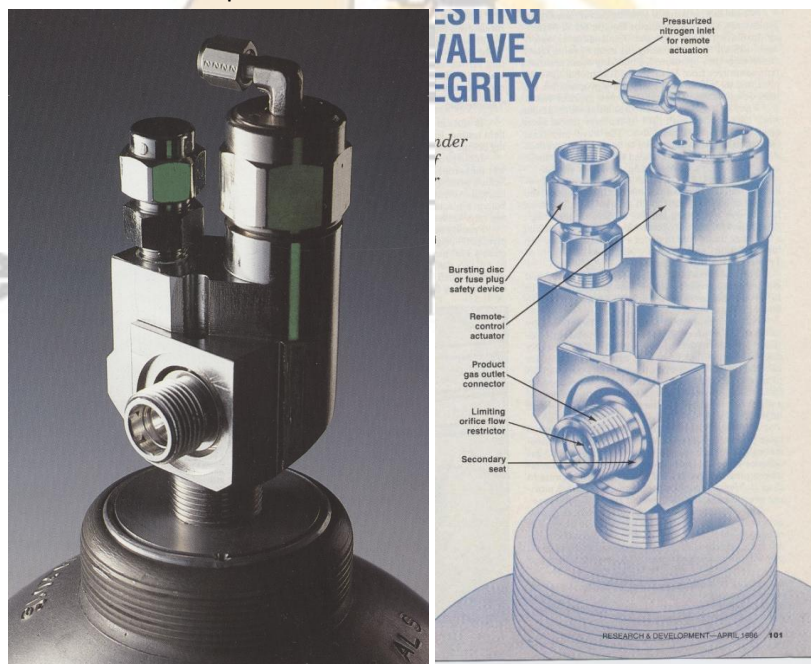


Fig. 36: Linde/Veriflo Pneumatic Cylinder Valve

Nupro Valve.

Nupro Inc, a Swagelok company known for their VCR connections entered the market by introducing a cylinder valve with a VCR type connection. Like the Superior valve it was a spring loaded metal diaphragm valve. The VCR outlet had 2 keys that rotated around the outlet face to create a unique connection.



Fig.37: Nupro Valve¹⁷

The initial design had only 6 different outlet connections. This was redesigned to expand the number of connections (See *Development of a DISS Cylinder Outlet Connection*)

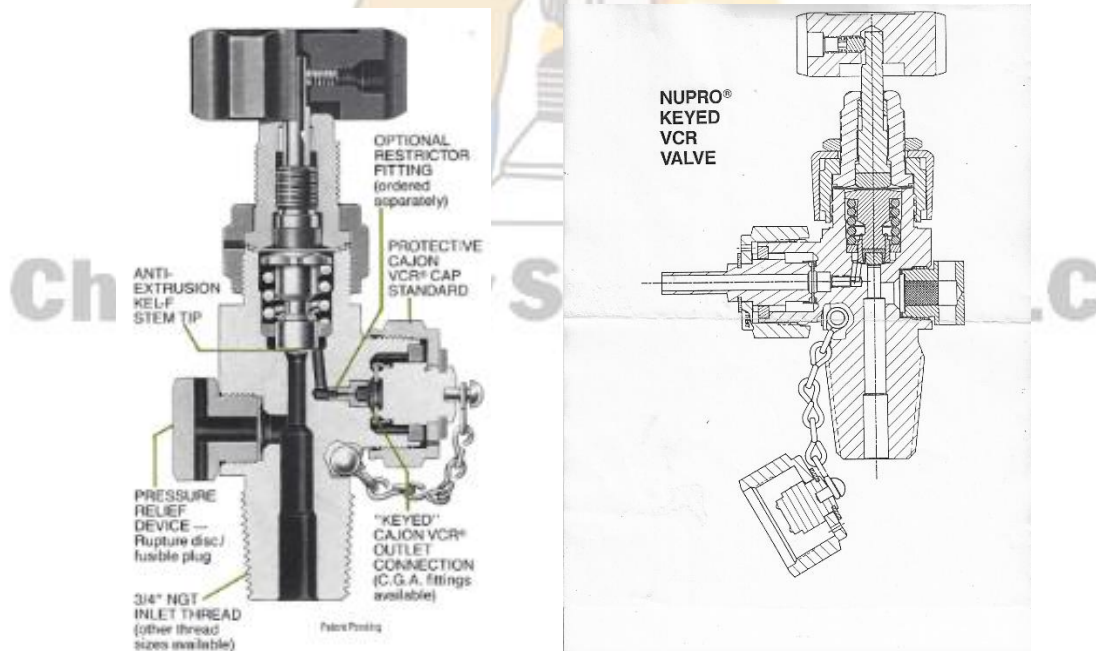


Fig. 38: Nupro Valve

One gas supplier tested the valve using anhydrous hydrogen chloride by



1. Inserting a new valve into a cylinder and filling it with high purity HCl
2. With the vapor tight outlet cap on the valve is opened allowing the HCl to fill the valve dead space for 8 hrs
3. Shut the valve and remove the vapor tight outlet cap and allowing it to be exposed to air overnight
4. Repeat step 2 and 3 every 3 days over a period of 30 days
5. After 30 days allow the cylinder to sit without the vaportight outlet cap on for 60 days
6. After this period connect the cylinder to a pigtail and see if the connection seals and the valve is operable

The Ceodux and Nupro valves pass the test. The Superior and Martin valves did not.

There was also a pneumatic version.



Fig. 39: Nupro Valve With Pneumatic Actuator

The gas supplier had over 500 cylinders in service for a major US Fab. The problem was that a new valve had to be installed each time due to cleanliness concerns. There was no cleaning procedure or rebuild kits.

Significant regulatory issues with using the valve. They offer only a rupture disk or fuse metal pressure relief device. These do not conform to the CGA V-9 requirements which are referenced by DOT. In addition, the outlet connections are not CGA connections and are proprietary.

BOC Pneumatic Valve

British Oxygen Corp, (Airco in US) developed an electronic valve. Not much information is available for this.¹⁹

Ceodux Pneumatic Valves

By mid 1990's, Ceodux (Rotarex) was making inroads into the Electronic Specialty Gas Valve business and would replace Superior as the primary Semiconductor valve supplier worldwide.

Ceodux D350

First generation design D350 had a low lift tied diaphragm, Cv 0.25

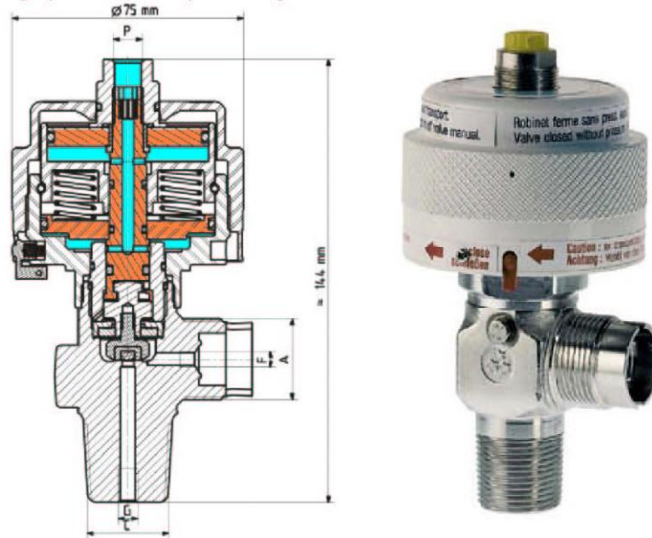


Fig. 40: First Generation Ceodux Cylinder Valves D350

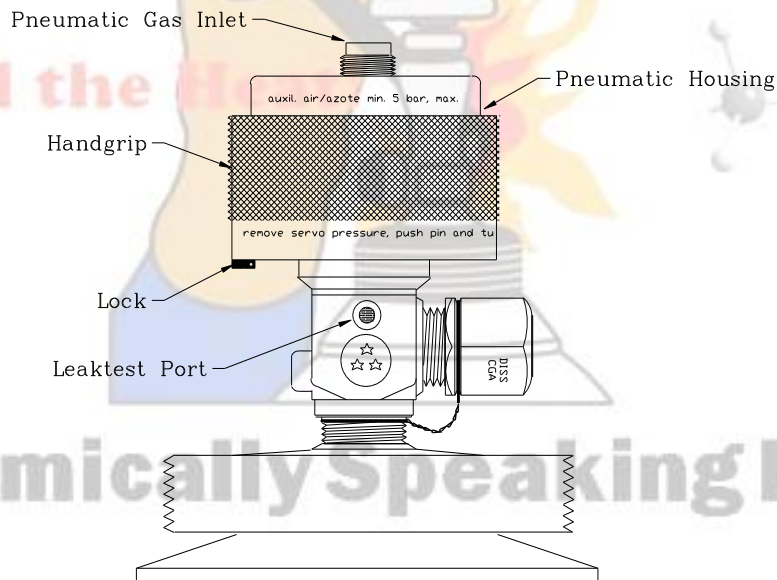


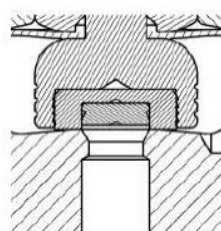
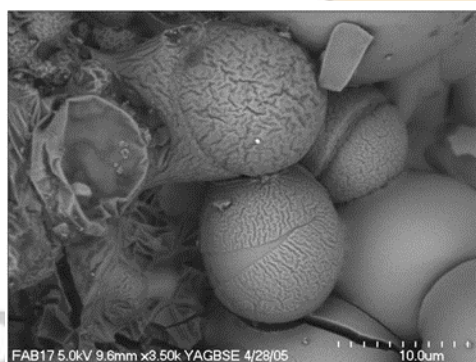
Fig. 41: Ceodux Pneumatic Cylinder Valve

Higher lift D385 Cv 0.55

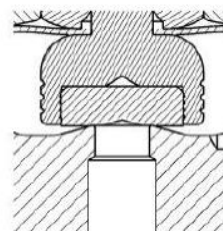


Fig.42: High Lift Ceodeux Pneumatic Valve

For gases that oxidize or hydrolyze to form solids like diborane or silane. These particles embed themselves under the soft valve seat causing leakage across the flat seat. For these gases the D-388 pneumatic valve was designed. It had a knife edge that reduced the potential for the particles to interfere with the positive closure of the valve.



SERIES D385
 Standard seat design



SERIES D388
 Knife edge seat design
 for silane

Fig.43 & 44: Knife Edge Seat Reduces the Effect of Particles Under Valve Seat

Knife edge seat increases the specific force on the edge and guarantees a tight closure.

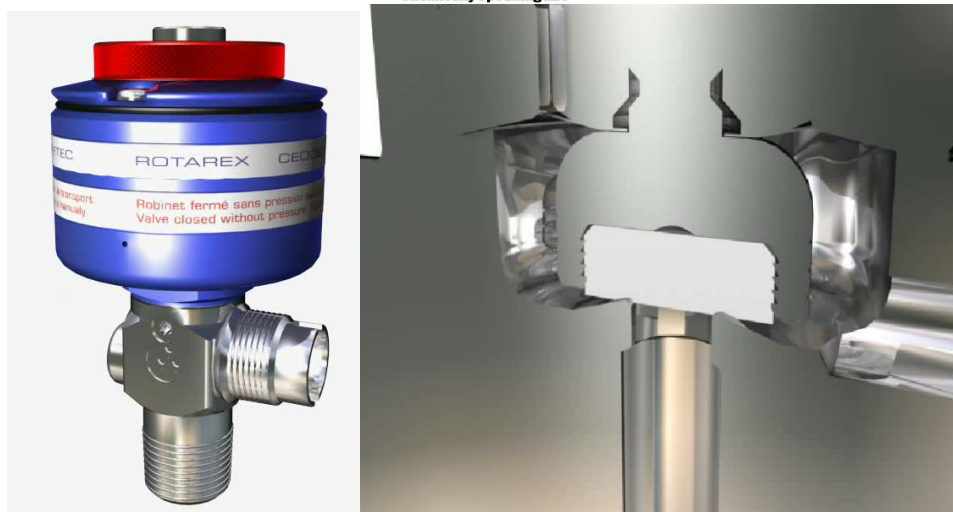


Fig. 45 & 46: Ceodux D-388 Pneumatic Cylinder Valve For Silane, Diborane

Manual openers for Ceodux Pneumatic Valves



Figs.47 & 48: Regular and High Lift

Excess Flow Valves for Cylinder Valves

Periodically excess flow valves for cylinders have been introduced as a must have safety device. These are activated if a cylinder valve is sheared off in an accident.

An inventor in New York State had his good friend a NY state Senator propose Assembly Bill No. 10078 in 1986 mandating the use of one for all compressed gas cylinders.

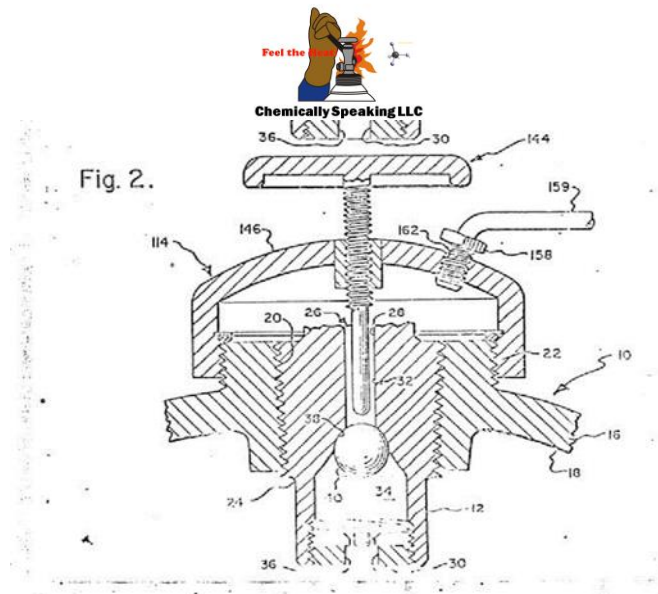


Fig.49: Brit Valve

The Brit Valve was debated for over a year but the bill never got passed.

A second valve like this was made by Whalen Corp in 1991. He advertised this at many trade shows, SSHA (Semiconductor Environmental Safety and Health Association) as well as SEMICON West and the Compressed Gas Association. He lobbied the Fire Code officials to mandate the use for pyrophoric and highly toxic gases

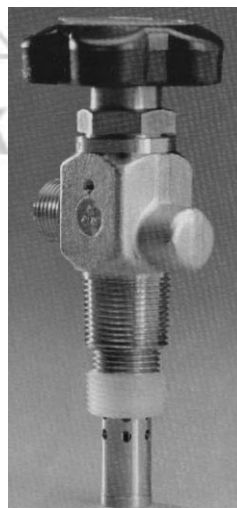
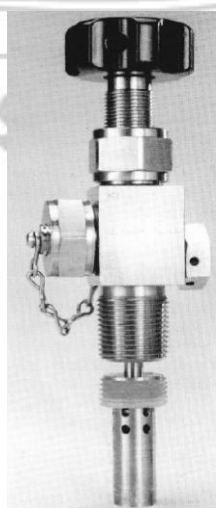
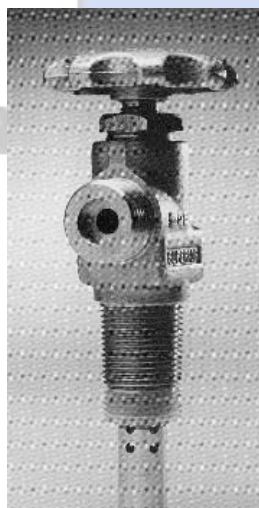
This device is inserted into the bottom of a cylinder valve and relies on the cylinder valve threads for operation. The operation is simple, a pure ceramic rod holds a spring assembly and compresses it against an elastomer seat. If the cylinder valve is bent or sheared the ceramic rod would break allowing the spring to slam the elastomer seat shut. It is critical for the valve threads to engage with the cylinder as they will withstand the cylinder pressure in the event of a valve shear.^{20, 21}

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Fig. 50: Whalen Valve Cross Section

1. How do you know it activated?
2. The valve requires 2-3 threads in the cylinder. This will prevent it from being used with older cylinders
3. The additional device would require additional cleaning
4. Increases the cylinder conditioning times
5. The device was sized for only 3 valve designs, would not fit a Martin Valve
6. The additional space taken by the device prevents it from being used for any PRD gases, therefore only Zone A
7. How to dispose of a cylinder if it activates?



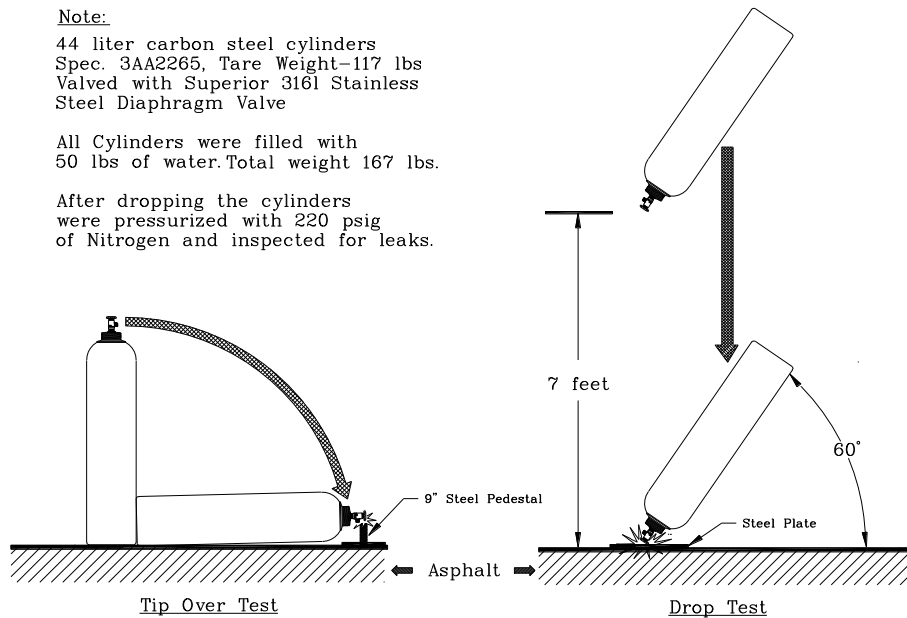
Figs 51, 52, 53: Whalen Inserted into Superior, Nupro and Ceodux Valves

Due to the expense the only gas cylinders that could justify its use were expensive Electronic Specialty Gases such as silane or arsine. As a test a US gas company installed a dozen of them in silane cylinders and shipped them across the country. 2-3 of them activated I assume due to vibration or impact. Now they were stuck having to drill into the cylinder to remove the silane. A second test had a similar problem. They abandoned the program after that. The Whalen Valve was not adopted.

In 2019 another company designed a similar type of valve but they stopped marketing them after I recapped the history for them on the Brit and Whalen Valves.

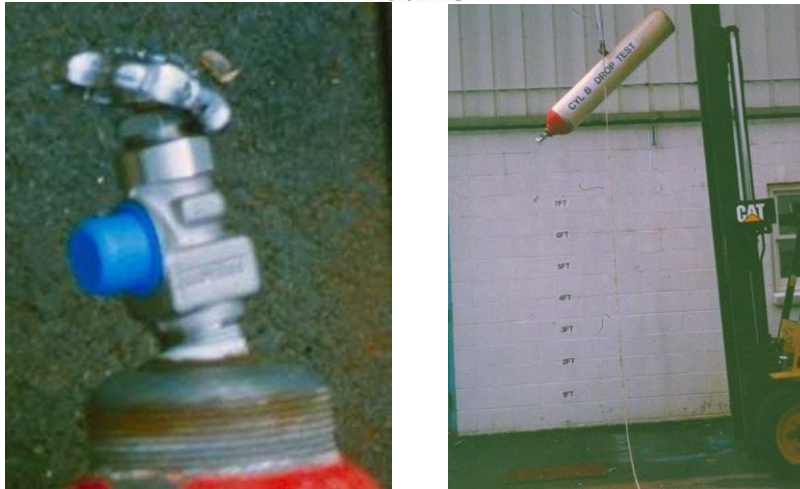
Electronic Specialty Gas cylinders use stainless steel valves rather than brass for cleanliness. As a result, they can take a greater physical impact. I did drop testing of cylinders filled with water to 150 lbs without the valve protection cap on from 7' impacting directly onto the valve. I could never crack the stainless steel valve but sheared the brass or aluminum silicon bronze valve every time.

This is due to the use of a stainless steel valve, which has greater than twice the tensile strength of brass. In 1995, four cylinders were tested in this manner with the same results.



DROPTEST WITHOUT CYLINDER CAP

Fig. 55: Cylinder Drop Test No Cap



Figs 56 & 57: Valve Damage After Drop and Drop Test

Further testing was done in May and June 2000. In this case the height of the drop was increased to 8' and the total cylinder weight was a minimum of 250 lbs to reflect the new CGA cylinder cap testing guidelines. This resulted in a final impact force of two times that of the earlier drop testing. To fill a cylinder to this weight, steel shot was placed in the cylinder since water alone could not fill a cylinder to the desired weight.

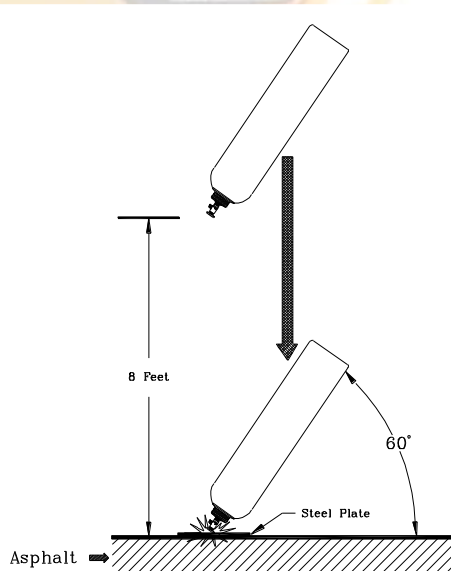


Fig 58: Higher and Heavier Drop Test

The test results confirmed the earlier testing and highlighted the differences between stainless alloys. The weaker 303 Stainless cracked at the thread interface in one of the two cylinders dropped while the 316 Stainless both had small leakers (<10 cc/min)

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References:

1. Britton, L., *Combustion Hazards of Silane and its Chlorides*, Plant Operations Progress, Vol. 9, No. 1, Jan 1990, pg 21-22
2. Report *Test of Cylinders Involved in the Arsine Gas Incident Aboard MV Asia Freighter*, National Engineering Laboratory for the Dept of Trade, 1974.
3. Sherwood Product Brochure, *We've Got A Lock on It!*, A-CG11B93
4. Larson S., *The Flow Restrictor Orifice in the Outlet of the Compressed Gas Cylinder Valve*, SSA Journal, November, 1990.
5. Quinn, W.E. and D. Rainer, *Flow Restricting Devices Used with Semiconductor Process Gases*, Solid State Technology, July, 1986
6. Sarma/Meyerson Task Force *Final Report and Guidelines for Small Quantity Silane Users*, IBM Corp, Aug 1984.
7. Kalaskie, W., *A Superior Automatically Operated Cylinder Valve for the Semiconductor Industry*, SSA Newsletter Vol 8, No. 1, 12-14, Jan 1986
8. SSA News Update 1984
9. Valve Shutter VS-100Mark II Product Brochure, Tomoe Shokai Co. LTD
10. Valve Shutter FSC Instructions, Festo
11. Cylinder Valve Product Brochure, BBB Neriki
12. Martin Technology Product Brochure for Remote Operated, Stainless Steel, Bellows Seal, Cylinder Valve, 1988
13. CLA Series Remote Operated, Stainless Steel Bellows Seal, Cylinder Valve, Carten Controls Inc, Sept 1991
14. Linde, Union Carbide Product Brochure, *Advanced Cylinder Valve For Electronic Gases.*, L5968, 85-0011
15. Johnson G, L., Korzeniowski W. F., *Product Testing Confirms Valve Design Integrity*, Research and Development, April 1986, 101-103
16. *All-New Linde Valve*, Spectrum, Linde Division, Union Carbide Corporation, 1986
17. Nupro Technical Bulletin No. 42, *DC Series Gas Cylinder Valves*, 9-86-25M-IP, MS-01-50
18. Koch, U., *Nupro Cylinder Valve & Connection – An Update*, SSA Newsletter Vol 8, No. 1, 15-17, Jan 1986
19. Pilgrim, D., *BOC Cylinder Valves – An Update*, SSA Newsletter Vol 8, No. 1, 15-17, Jan 1986
20. *The Whalen Shut-off Valve for Compressed Gas Cylinders*, Product Brochure for Safety Assurance Corp, 1991
21. *The SAC Safety Shutoff Valve for Compressed Gas Cylinders*, Product Brochure Safety Assurance Corp, 1991