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February 5, 1999

DEPARTMENT OF TRANSPORTATION
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DOCKET SECTION

Associate Administrator
for Hazardous Material Safety
c/o Director, Exemption and Approvals Branch
Research and Special Projects Admin. DHM-3 1
U.S. Dept. of Transportation
400 7th St. SW
Washington, D.C. 20590

RSPA-99 5160-1

RE: REQUEST FOR EXEMPTION

Dear Associate Administrator:

As identified in your records, our firm, North American Transportation Consultants, Inc. (NATC), is acting as agent for the applicant contained within this document. As such, this letter will serve as formal application for an exemption form those parts of 49 CFR identified herein and is submitted as set forth in 49 CFR 107.105.

In accordance with 49 CFR 107.105 the following information is provided.

a) Applicant is: Advanced Technology Materials, Inc.
7 Commerce Driver, Danbury, CT 0681 0-41 69
(203) 794-1100

b) The contact person for this application will be:
J. P. Gibbons, (NATC) at (609) 426-0555

c) This application, request the approval for transportation of gas molecules filled at sub-atmospheric pressure and packaged as a solid in pressurized containers other than approved cylinders.

d) This application request relief from those sections of 173.34, 173.301, 173.302, 173.304 and 173.315 as they relate to the packaging of gas molecules in DOT specification cylinders and the filling of such packaging under pressure.

e) This application pertains to the transportation of these containers by highway.

f) The specific details describing our proposed alternative packaging are contained within Section III of the attached technical information.

g) This application is requested for an indefinite period of time or until the regulations are revised to accommodate the technology involved within this method of gas molecule retention and transportation.

h) This application is submitted to allow the transportation and handling of regulated gas molecules which are retained during the transportation process in a method which changes the characteristics and dangers of the material during transportation and handling. The current regulations do not allow the flexible packaging necessary for economical distribution and utilization of this technology within the safety limits established by the Department of Transportation to protect the general public and those specifically involved in the transportation and handling of the altered materials.

i) The materials to be transported under this exemption will consist of materials currently described as Class 2.1 and Class 2.3 materials which have undergone alteration of their physical state from a gas to a solid for the transportation and handling phases. The initial list of gas molecules to be involved are identified in Section II of the attached technical information.

j) The proposed packaging requested under this exemption for the altered gas molecules is identified in Section IV of the attached technical information.

k) The documentation of quality assurance controls, package design, manufacturer, performance test criteria, in-service performance and service-life limitations are identified in Section IV of the attached technical information.

We believe the technical information attached will demonstrate that the safe guards established within the proposed packaging design, construction, and operation will achieve a level of safety at least equal to that required by regulation and is consistent with the public interest. In support of this statement the following additional information is provided.

- To date, there have been in excess of 1,200 shipments made under this technology without incident. These shipments included multiple containers per shipment and as such the number of individual containers exceeds over 10,000.
- It is our belief that any perceived increased risk to safety or property that may result if this exemption is granted, is offset by the substantial reduction in risk to the general public from an incident involving these materials when in their solid state for the transportation and handling phases. The technical data attached clearly demonstrates the safety risk and safety measures to be taken will provide the high level of public safety required by regulation.

It is our contention that the above information, along with the attached technical information, provides compliance with 49 CFR 107.105 and as such we respectfully request approval of this application for exemption.

Thank you for your time and attention in this matter and if you require additional information feel free to contact this office at your earliest convenience.

Sincerely,

J. P. Gibbons
Agent for applicant

ATTACHMENTS

cc: ATMI

TECHNICAL INFORMATION ATTACHMENT

I. General.

This information is submitted in support of the request of DOT exemption from ATMI, Inc.

Pursuant to a presentation and discussion on this subject on November 17, 1998, ATMI, Inc. formally requests an exemption for packaging its larger sub-atmospheric pressure gas source products. The exemption is specific to vessels with internal volumes of 100 liters or greater but less than 450 liters.

Currently ATMI, Inc. and its licensed afflliates ship all sub-atmospheric pressure products according to the requirements prescribed under Class 2.

ATMI Inc., is making the request based on the belief that the sub-atmospheric pressure gas source storage and delivery system significantly reduces the risk of a gas release under conditions normally incident to transportation. The case for the increased safety is presented in the sections which follow.

The rapid acceptance of this technology by end users over the last several years is consistent with being recognized as a safer method of gas storage and use. The exemption, if granted, facilitates the expansion of applications using sub-atmospheric pressure gas sources.

Sub-atmospheric pressure gas sources have not been anticipated per se by the current codes and regulations. This exemption request addresses this situation and, if granted, is of direct benefit to end users by opening up more applications to this innovative technology.

II. Products withln the exemption.

Gases covered within this exemption request include:

Silane	SiH_4
Arsine	AsH_3
Phosphine	PH_3
Germane	GeH_4
Chlorine	Cl_2

III. Details describing alternative proposed packaging.

ATMI, Inc.'s gas source technology is based on reversibly adsorbing gases onto a high surface area, microporous substrate. The sorbents employed have surface areas of >1000 square meters per gram. The gas loading capacity is a function of the choice of substrate and properties of the individual gases. Loading densities [grams of gas per gram of adsorbent] of 15 to 100% are achieved. Reproducibility is quite good using sorbents which have been pre-qualified. Pill densities at 23°C and 650 torr for a number of gases are shown below.

Gas	% loading [wt]
AsH3	50
PH3	17
Cl2	60
SiH4	17
BF3	18

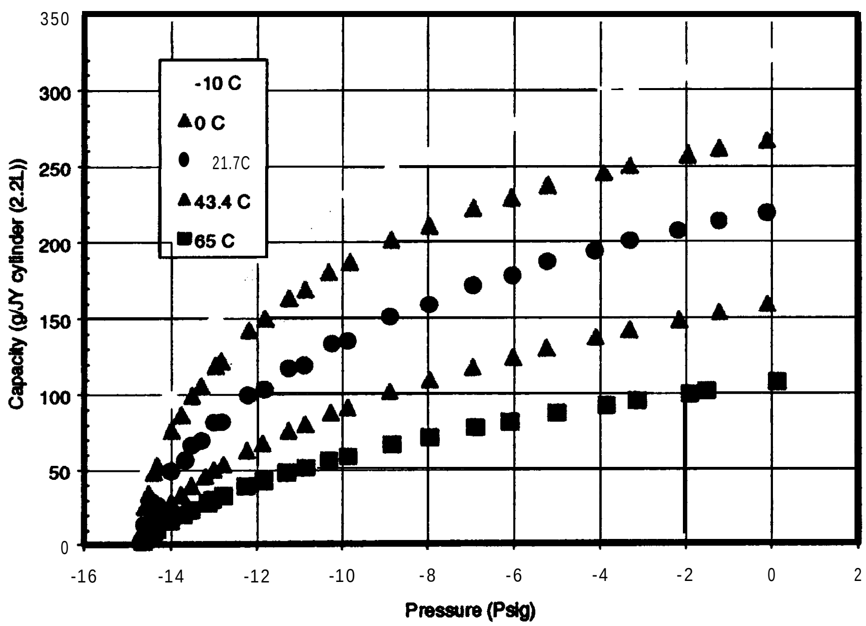
The adsorption process reduces the vapor pressure of the gas and gives it properties which are a hybrid between a gas and a solid We coined the term "gas source" to describe this process. The solid can become a source for the gas under certain conditions--typically reduced pressure is the motive force to withdraw the adsorbed gas from the vessel and deliver it to the process. The gases are literally pumped **from** the within pores of the adsorbent,

A sub-atmospheric gas delivery system begins with a vessel--typically a gas cylinder-- **filled** with an adsorbent prior to the additian of the gas. The valve and cylinder are identical to those used in high pressure service. A diagram of a sub-atmospheric pressure gas source is shown below.

*Sub-atmospheric pressure gas **source cut** away.*

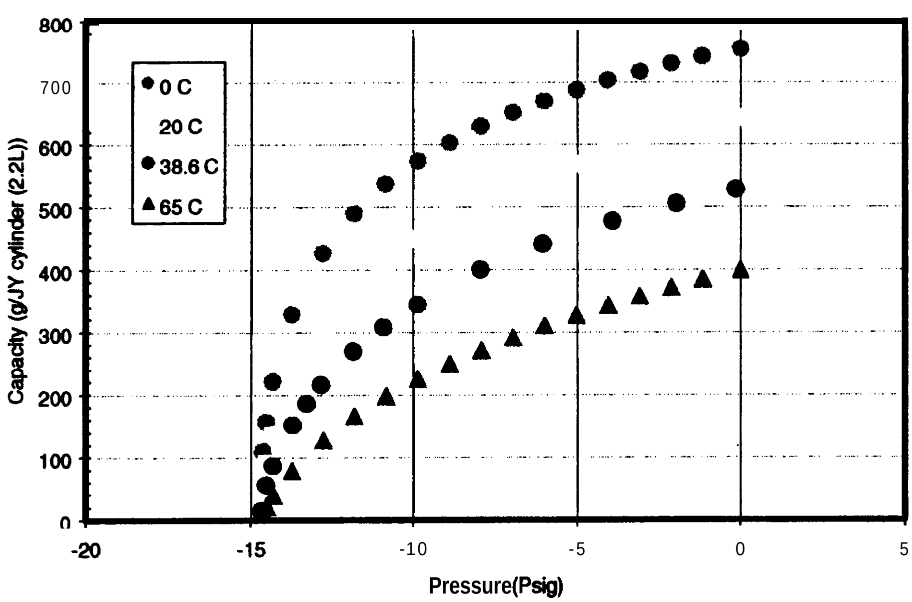
Gas is loaded on to an adsorbent and the pressure gradually increases **from** a vacuum **[0.01 torr]** to just below atmospheric. **The** relationship between the pressure of the gas and its mass loaded onto an **adsorbent** is called an isotherm. From the isotherm, the gas loading as a function of pressure is determined. Isotherms for several gases are presented. At a fixed temperature, the amount of material adsorbed as a function of pressure is also constant.

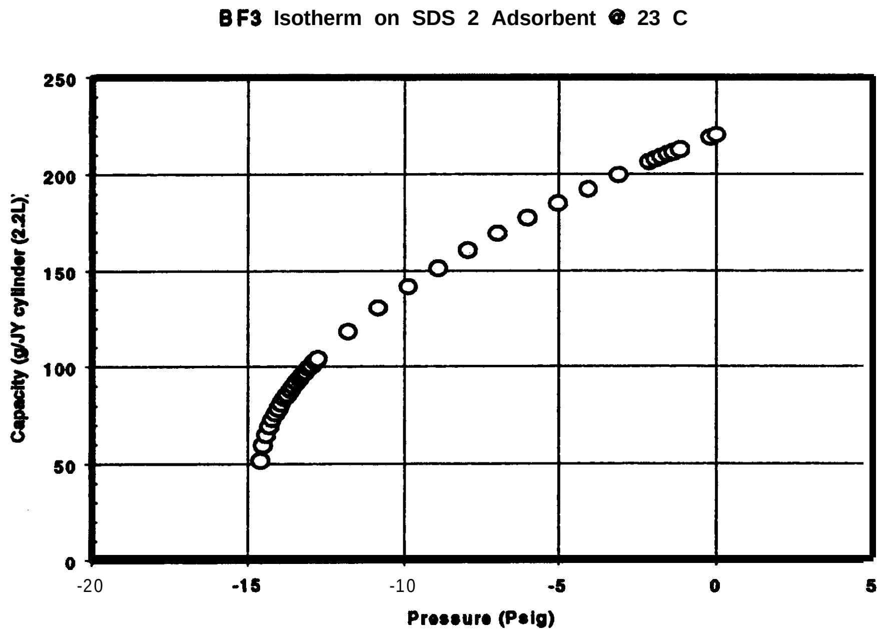
PH3 Isotherm on SDS 2 Adsorbent @ Various Temperatures



The amount of gas which is adsorbed on a given adsorbent can be varied by altering the **temperature.** At lower **temperatures** more gas is adsorbed and higher fill densities are achieved. The isotherms for several gases at different temperatures are presented below.

AsH3 Isotherm on SDS 2 Adsorbent @ Various Temperatures





During manufacture, subatmospheric pressure gas sources are filled at room temperature [nominally **23°C]** to a final pressure of 650 torr **[760** torr = 1 atmosphere] or -2.2 psig. **The** filling process typically takes 12 to 24 hours to accomplish. Under these conditions, the gas is held on the substrate and, should the cylinder valve be inadvertently opened, air would be pulled into the cylinder until the pressure was equalized to ambient.

Sub-atmospheric pressure gas sources are installed and operated below atmospheric pressure. During the course of use, the cylinder pressure **decreases from** -2.2 psig to about -14 psig. The stored gas is literally pumped from the substrate and drawn to the process. Typical semiconductor processes **which** employ this technology operate at 100 torr or much less.

Storing and using gases under sub-atmospheric conditions has significant risk reduction implications for the end user. Leaks normally associated with the use of pressurized gases are all but eliminated and include leaks at the valve to cylinder neck [neck leakers] and leaks across the cylinder valve and/or through the dust cap [valve leakers]. Leaks **from regulator** failures, piping and plumbing, downstream component failures [mass flow controllers, **valves,** pressure transducers] and faulty connections are virtually eliminated. As will be shown below, even if a leak occurs, the rate of gas egress from the cylinder is very low and below a harmful concentration **[TLV].** Since its introduction in 1994, about 12,000 **sub-**atmospheric pressure cylinders have been manufactured and sold worldwide--all into the semiconductor industry.

ATMI, Inc. conducted **full** scale release tests at Roy F. Weston's "fate and effects" environmental facility. During these tests, cylinders were fully opened to the environment and the discharge rate monitored. Restrictive flow orifices were not used. The release rates at 600 torr [-3 psig] are reported below in **mg/min** and also converted to a ppbv concentration.

Gas Source	Release Rate (mg/min) Avg.	Max.	Exposure Level (ppbv) Avg.	Max.
AsH3	**<0.03**	0.50	**<6**	108
PH3	0.12	0.50	57	248

The release rate for cylinders at 50 torr r-13.7 psig] was considerably less than at **600 torr** and **non-**detectable. The full report is available to the DOT upon request.

Gas release rates can be approximated using diffusion models. From sub-atmospheric pressure gas sources, release rates are very slow and in general the gas would rather stay adsorbed and remain in the container.

Behavior at Elevated Temperatures

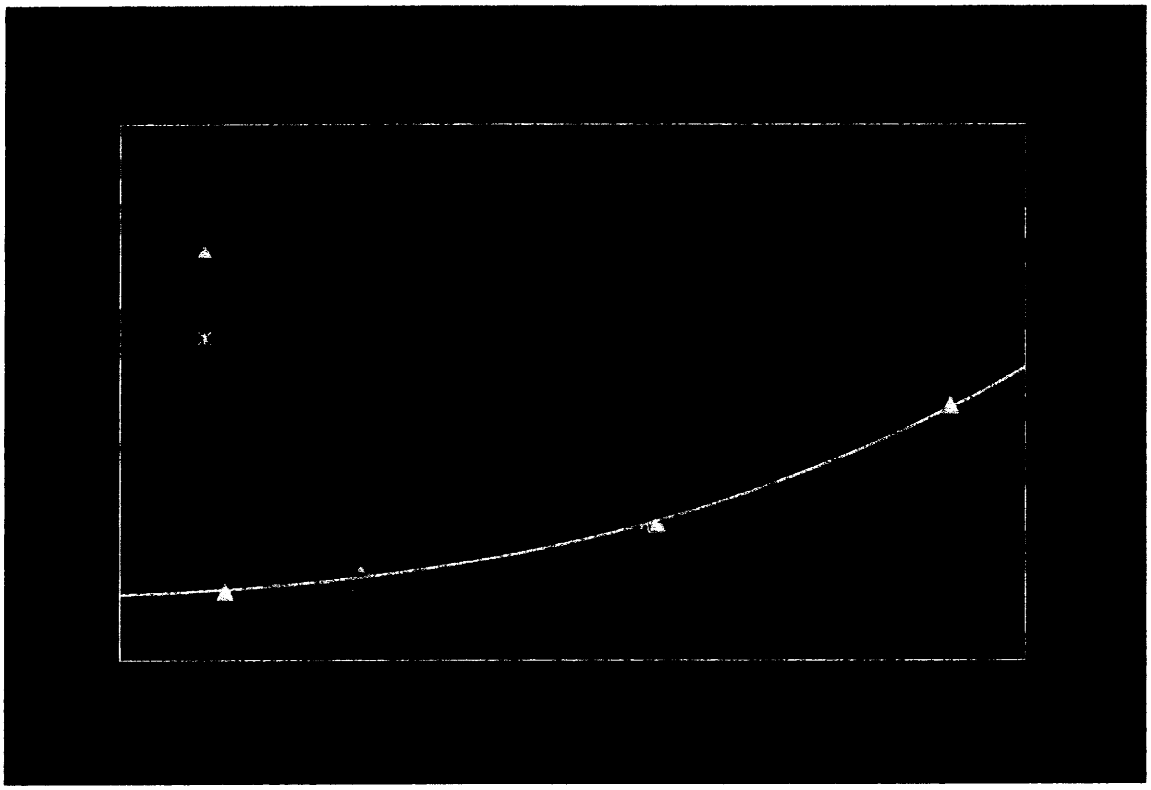
The room temperature equilibrium between the adsorbed phase [molecules held on the substrate] and the vapor phase [free or **unadsorbed** gas] varies with the gas, but in general constitutes a small amount of the available gas inventory. For a cylinder filled under normal conditions, 23°C and 650 torr, the pressure in the cylinder increases with increasing external temperature and **decreases** as the temperature is reduced. At elevated temperatures, the pressure will become positive, but the pressure is nominally in the range of 25 to 30 psig at **140°F [60°C].**

Percentage of "Unadsorbed Gas" as a Function of Temperature.

	0°F	**70°F**	**140°F**
AsH_3	0.2	0.5	1.4
PH_3	0.2	0.6	2.2
SiH_4	0.3	0.9	1.9
Cl_2	0.1	0.4	1.0

Cylinder pressure returns to its normal sub-atmospheric state when the temperature is returned to 23°C.

If a cylinder was opened [cylinder wall breached] at temperatures much above room temperature, the gas volume which could be released would be on the order of 0.5 to 2 percent of the total cylinder inventory. Once the pressure was equalized, however, the release rate would again become diffusion controlled and the rate significantly less by 3-4 orders of magnitude.



Isotherms showing pressure as a function of temperature are shown above. The maximum pressure observed is 30 psig at **140°F**. The pressure returns to sub-atmospheric levels as the cylinder cools back to room temperature **[23°C** or **73°F]** and the gas is re-adsorbed. **The** extent to which gases are desorbed at elevated temperatures has been **factored** into the overall pressure rating of our proposed packaging for larger sub-atmospheric pressure vessels; nominally 100 to 450 **liter** internal volumes.

Risk Comparison

During normal **transportation** and even under extreme temperature conditions, sub-atmospheric gas sources are safer than standard high pressure gases because:

--at or below **80°F,** the vessel is sub-atmospheric and leaks, should they occur, are inboard. Loss of hazardous **materials** is limited to **diffusion.**

--**between** *80* and **140°F,** the vessel is at varying degrees of positive pressure but generally not exceeding **25--30** psig.

High pressure gases on the other hand run anywhere **from** 200 to 2000 psig at **room** temperature. If they are heated to **140°F,** the pressure increases accordingly.

Another important distinction between a sub-atmospheric pressure gas source and a high pressure cylinder is *a high pressure* ***cylinder*** *can* lose ***its*** *entire contents* in the case of a leak. The sub-atmospheric pressure cylinder can only lose a small **fraction** of its contents **[<2%]** until the pressure is equalized Once the pressure is equalized with the environment, the rate of gas loss is controlled by diffusion--a very slow process.

A sub-atmospheric pressure cylinder typically contains between 20 and 35% of the mass of material **[gas]** of an equivalently sized high pressure gas cylinder. High pressure gases can be liquified or stored at high pressures while the sub-atmospheric system is constrained by the amount of gas which can be adsorbed. Wherever same sized cylinders are compared, the sub-atmospheric pressure vessel will always have considerably less hazardous material stored.

Specifically **ATMI,** Inc. would propose an **operating** design pressure of 75 psig with a burst pressure of 300 psig for any vessels covered in the exemption.

Cylinder History Recap	Pressure [psig]	Temperature [°F]
Normal operating	-2 to -13	room (68-72)
Maximum during transport	**25 to 30**	140
Burst conditions	**300+**	**>>140**

ATMI, Inc. believes these design pressures provide a safe and adequate working margin between normal operating pressure and failure for the containers.

IV. Packaging Design Goals

The sub-atmospheric-pressure vessel design and construction requirements are unique. A separate fill port through which the adsorbent can be added is critical to the construction of 100 to 450 liter packages. The adsorbent needs to be purified separately and conveyed hermetically to the package. This **transfer** is done under inert gas [typically nitrogen or helium] and accomplished without contaminating the sorbent with atmospheric impurities such as oxygen, water, carbon monoxide or carbon dioxide---all of which are detrimental to the manufacture of semiconductor devices.

The sorbent cannot be added via the opening used for the cylinder valve because the aforementioned contamination requirements, but also because the discharge **port** has a metal **frit (filter)** intended to contain the sorbent in the vessel and catch any small particles.

The fill port would be double sealed using **[1]** a **conflat** flange (bolted flange with metal seal) and **[2]** a cap over the flange. The cap would be sealed, since it is not to be used by the customer.

A pneumatically operated valve would be specified for the gas delivery port.

A collar ring with a hinged cover would protect the valve and fill port from incidental impact damage.

The use of safety devices requires some discussion. ATMI, Inc. believes that safety devices should be used with both corrosive [acid] and poisonous [arsine, phosphine] gases as authorized in 49 CFR at present. Rupturing the safety device does not necessarily mean that the entire contents would be lost to the environment; with subatmospheric pressure gas sources only a portion of the material would be vented. Once the internal pressure has been **equalized,** losses are diffusion limited.

In a fire condition, we believe it is best to vent a portion of the contents rather than risk rupturing the vessel. A controlled release of poisonous or flammable materials [e.g., arsine, phosphine, silane] to the environment is preferred and it would be expected that any material expelled be combusted upon release.

Description and specifications for 100450 liter (26-l 19 gallon) packaging.

The 100 - 450 liter SDS package is designed to be a portable, transportable, approved shipping container for gases stored on an SDS adsorbent. It is fitted with wheels to facilitate movement, primarily at the customer's site. All connections are located on the top of the vessel inside a welded protective ring of such a height that all connections are below the top of the ring. The ring is fitted with a hinged lid that can be bolted or locked. The vessel will have one of two types of heating/cooling device installed internally: 1) a passive system of baffles to conduct energy through the outside wall; 2) an active system consisting of a coil of tubing which would be connected to an external source of heated or cooled liquid. The entire unit will be constructed of carbon steel. While the vessel is normally operated a subatmospheric pressure, provision is made for handling the pressure that might be attained in the vessel if it is subjected to a temperature of **140°F** when completely filled.

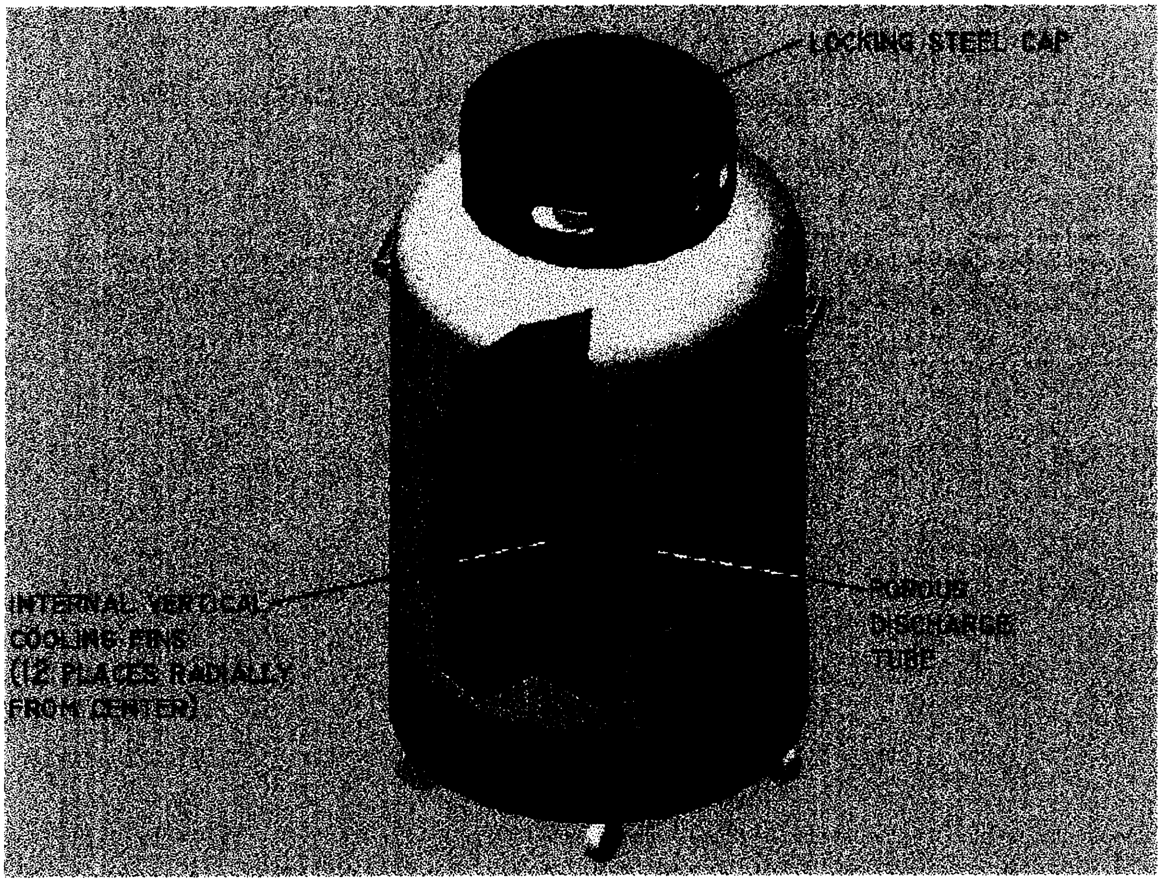
<u>450 liter **package**</u>

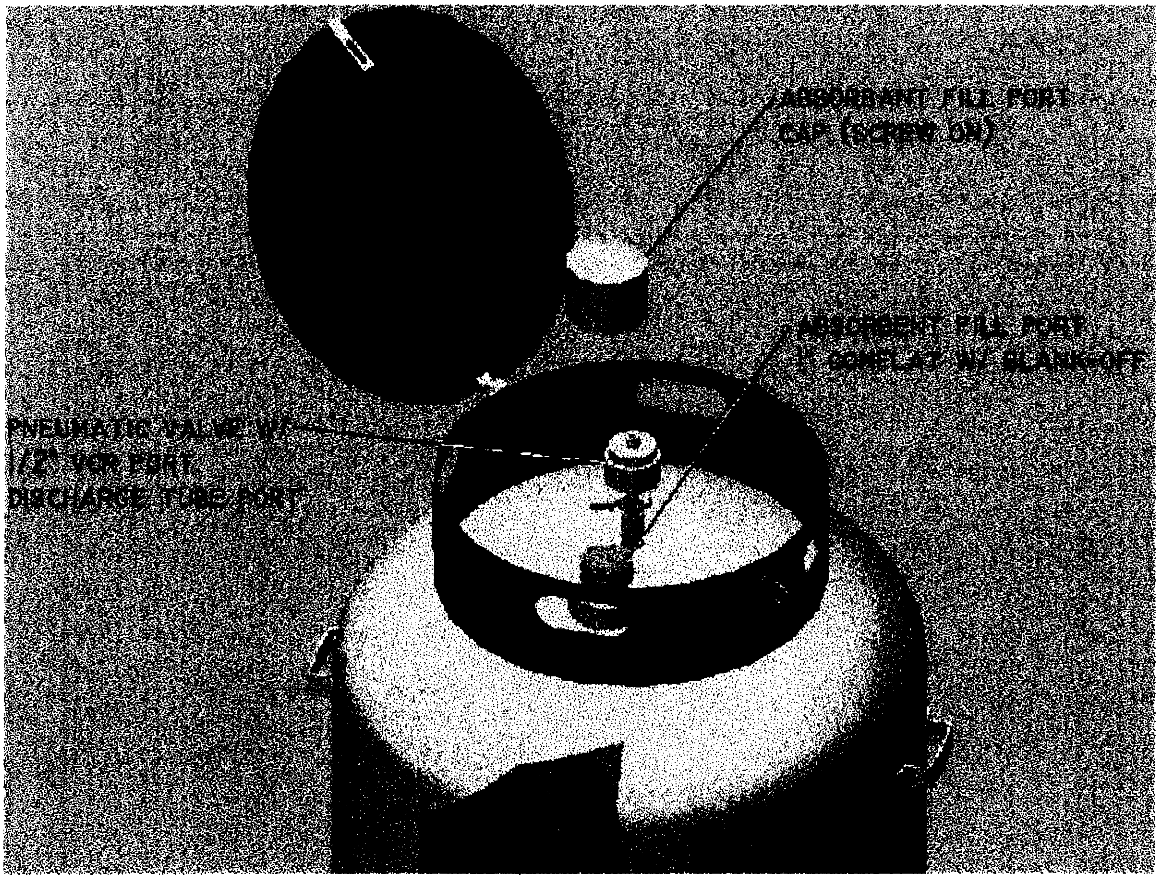
- 30" **dia x** 46" high vertical tank
- 0.187" wall thickness
- internal baffles to dissipate heat (welded to the outside cylindrical wall)
- material - mild steel (carbon steel)
- full vacuum rated
- 75 psig working pressure
- porous center fill/withdrawal tube extends full height of vessel
- air actuated valve with **1/2"** VCR fitting (Ceodeux valve)
- 1" fill port with **Conflat** bolted blind flange with metal seal
- 5 wheels attached to bottom skirt (all castored)
- top protective ring with hinged, lockable lid; ring to be same thickness as vessel wall
- handles on two sides

For 450 liter vessel with internal cooling coil:

- same specifications as above
- internal heating/cooling coil installed (replaces internal **baffles)**
- coil to be **½ "** diameter tubing
- self-sealing, quick-disconnect fittings
- fittings are located inside protective ring

estimated weight: vessel only – 310 lbs
vessel filled with adsorbent – 805 **lbs**


LOCKING STEEL CAP
INTERNAL VERTICAL COOLING FINS (12 PLACES RADIALLY FROM CENTER)
POROUS DISCHARGE TUBE



Close-Up View of Connections Inside Protective Ring

V. Conclusion

ATMI, Inc. believes the introducticm of sub-atmospheric pressure gas sources and delivery systems heralded a new **era** in gas handling safety. The exemption request included herein permits ATMI, Inc. to **extend** this technology to new applications and materials which are only economically viable using **larger** packaging.

ATMI, Inc. believes that the gas delivery systems as outlined in this request represent an **equivalent** or **higher** level **of** safetv and reduced risk for end users during transportation, storage and use of these materials compared to current practices based on high pressure gases.