

A Comprehensive Approach for Delivery of Low-Vapor-Pressure Process Chemicals

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Abstract:

A number of new challenges arise in the distribution technologies of chemicals for semiconductor manufacturing. They result on the one hand, from the introduction of larger wafer sizes and the consequent increase of chemicals consumption rate and, on the other hand, from the introduction of the new materials which are required at reduced device dimensions. We describe here recent developments in vapor phase chemicals supply technologies, which provide improved quality, reliability and safety, as well as optimized cost of ownership.

Introduction :

Vapor phase processing, eg, CVD, etching or dry cleaning, is ideally suited for the manufacturing of sub-micrometric, high-aspect-ratio thin films that are the building blocks of semiconductor (SC) devices. The controllability and quality of the vapor phase processes rely critically on the delivery of an "ideal" gas phase to the wafer surface in the process tool. Whereas this goal has been reached rather easily so far since manufacturing technologies used mostly high pressure process gases, special challenges are appearing for the emerging technologies : on the one hand, the introduction of larger wafer sizes , eg 300 mm wafers, involves significantly increased flow rates. When the precursors are liquefied gases stored at ambient temperature under their own vapor pressure, withdrawing high flow rate may entrain biphasic gas-liquid flow if the energy of vaporization is not properly supplied to the gas-liquid interface [1]. This, in turn, will induce manufacturing defectivity and loss of control of the fluid flow parameters. Separately, as dictated by the ITRS roadmap [2], at design rules below 100 nm, many new materials of specific physico-chemical and mechanical properties need to be introduced in the SC device structures. It is inconceivable that gas phase precursors under normal process conditions can be discovered for the deposition of these new materials. They will be in either liquid or solid phase at normal conditions, hence requiring the development of advanced distribution technologies for reaching the required vapor phase parameters at the wafer surface [3]. The trend to increasing vapor flow rates and usage of chemicals with very low vapor pressure under normal conditions is further motivated by COO (Cost of ownership) and ESH (Environment, safety and health) considerations.

We summarize here some recently developed solutions for delivering proper quality process chemicals of various physical and chemical properties to the process chamber. Specifically, we describe solutions for

- Localized supply of low-vapor-pressure gases such as WF₆, Me₃SiH, other Methyl Silanes, ClF₃, etc at flow rates of up to about 10 liters per minute,
- Centralized supply of low-vapor-pressure gases such as Cl₂, NH₃, Me₃SiH, other Methyl Silanes, etc, at flow rates greater than 10 liters per minute
- Localized supply of “very low vapor pressure” liquid chemicals such as TiCl₄, TDMAT, TEOS, PET, DMDMOS, TMCTS, etc at flow rates up to the order of 1 liter per minute.
- Centralized supply of “very low vapor pressure” liquid chemicals such as TCS, TEOS, DMDMOS, etc at flow rates greater than 1 liter per minute.

The above indicated flow rates represent typical orders of magnitude. Practical selection will be determined according to the local fab configuration, ie the process recipe and the number of tools to be supplied and by considerations of cost, space availability, and safety. The latter, as well as contamination risk, will be favorably affected by the reduced frequency of chemical container or gas cylinder exchanges.

Localized Supply of Low-Vapor-Pressure Gases: all vapor phase (AVP) cylinder Cabinet

Low-vapor-pressure gases are stored in liquefied state and vapor phase is withdrawn under “ambient” conditions to meet process requirement. External energy addition is needed to compensate for the heat of vaporization (typical value for currently used chemical gases is 5 to 20 W/slm to maintain a constant liquid temperature). The required energy input is normally provided by mere thermal conduction from ambient air. However, at high flowrates, this natural process becomes insufficient and further means of energy input is needed. Otherwise, the liquid temperature drops and accordingly the vapor pressure decreases, hence affecting the flow rate. In addition, violent boiling occurs in an overdrawn cylinder [1] and results in a mist of liquid droplets being introduced into the distribution network and, in some instances, into the process chambers. Such biphasic fluid emission prevents steady flow control.

A common solution uses a cylinder heating jacket to provide a constant heat flux or a regulated heat flux in order to maintain the cylinder wall at a constant temperature. However, under practical conditions, there is a considerable temperature difference between the liquid inside the cylinder and the outer cylinder wall due to poor thermal conduction of the heterogeneous biphasic chemical-cylinder container system [1]. As a result, with above procedure, insufficient heating is provided by the heating jacket [4]. Ideally, one would like to match precisely the required evaporation energy, based on the true temperature of the liquid inside of the cylinder, or more precisely on the one of the liquid-vapor interface since it is strongly heterogeneous. As it is not practical to install a temperature sensor inside of the cylinder, the liquid temperature is rather derived from the pressure measurement via the equation of state:

$$\text{Log } P = -A/T + B$$

Where P and T are pressure and temperature, A and B are constants known for various chemicals. Since in practice pressure is routinely monitored at the cylinder exit via a pressure transducer, the temperature of the liquid inside the cylinder can be continuously calculated from above relationship and used to control the heating device. A patented all vapor phase (AVP) cabinet [5,6] incorporates such control logic and an efficient heating device to ensure continuous, single phase, and stable supply of low-vapor-pressure gases (Figure 1).

The integrated heating device is controlled by the same PLC that controls the operation of the gas cabinet and is located at the bottom of the cylinder to exploit natural convection within the liquid phase for temperature homogeneity. Field data have shown that the AVP cabinet can increase the usable flow rate by 5X. In addition, the built-in heater eliminates liquid droplets and the consequent corrosion problems, thereby increasing reliability and reducing maintenance costs.

Figure 2 represents the delivery simulation of WF6 from a single cylinder to a 6-chamber, 300 mm tool (AMAT-Endura) with and without AVP technology. The flow rate reaches 2.4 slm when all chambers are in simultaneous operation. The AVP technology maintains a constant vapor pressure throughout the run, representing proper energy input management, whereas conventional cylinder supply clearly suffers from unacceptable pressure drop. Note that the heating device remains in operation after the scheduled process in order to bring the liquid temperature back to the set temperature for subsequent runs.

Centralized Supply of Low-Vapor-Pressure Gases by gas phase distribution : Bulk evaporation purification systems (BEPS-G)

Centralized supply offers numerous advantageous features in terms of cost of ownership, enhanced safety and reduced contamination associated with reduced cylinder change-out, and improved operational efficiency. On the other hand, the selection of such a centralized supply solution requires a careful risk analysis according to specific local conditions, eg, regulations, space availability, necessary redundancy, distance from the bulk source to the process tools, etc. From the design aspect, the pressure needed to deliver the low-vapor-pressure gases over the entire distribution network to the point of use must be carefully evaluated for selection of the proper heat management solution. From the operational aspect, one needs to further consider purity assurance and system reliability indices, ie MTBF and MTTR, as the impact of out-of-specification chemicals would affect the whole fab production schedule.

The simplest solution for centralized supply of low-vapor-pressure gases is based on an extension of the AVP technology to a bulk container, eg, a ton unit equipped with a heating device of appropriate shape and using the same patented control logics [7,8]

(Figure 3). Figure 3 includes the time dependence of emitted pressure from a NH₃ bulk container with- and in absence of AVP on-demand heating. It is obvious that pressure cannot be maintained without proper heat input. If the NH₃ source container is placed in a temperature-controlled area, such a simple BEPS-G system can supply the whole fab with a total flow rate of up to several hundreds liters per minute.

Centralized Supply of Low-Vapor-Pressure Gases by liquid phase distribution : Bulk evaporation purification systems (BEPS-L)

An alternative design, BEPS-L, uses pressure-liquefied chemical gas distribution followed by vaporization at a location close to point of use [9]. It is of advantage for very low vapor pressure gases or whenever thermal management is difficult under local circumstances (Figure 4). A significant advantage is the reduced physical dimension simply because the density of liquid is orders of magnitude greater than that of vapor. Furthermore, a simple purification scheme can optionally be attached for removing heavy and light impurities by bottom and top purge respectively. It should be emphasized that the intent is not to place a chemical plant at a fab. But rather, through a simple scheme and a simple device housed in a 3-cylinder cabinet, (Figure 4), one has the possibility to eliminate some common contaminants often associated with handling ,eg, air originated contaminants (N₂/O₂/H₂O) in the light fraction and metals in the heavy fraction [10].

Table 1 summarizes the typical purification performance of a bulk evaporation purification system (BEPS-L) for Fe, B and H₂ impurities, as examples for dopant, metal and volatile impurities, in dichlorosilane. There are a number of species and forms in which the Fe and B contaminants may exist in either the liquid, vapor phase or as ultrafine particles in either the liquid or vapor phase, or even solid or particulate materials weakly adhered on the container and components surfaces that are subsequently entrained in the vapor flow. It is expected however due to the chemical nature of Fe and B that the majority of these impurities will be concentrated in the liquid phase relative to the vapor phase. This effect is expected to be much stronger for Fe than B. By contrast however, it is expected that H₂ will be strongly concentrated within the vapor phase. As a result, by appropriately adjusting the liquid and vapor phase purge rates it is possible to supply an ESG that is purified for both "heavy" impurities (e.g. Fe and B in DCS) and "lights" (e.g. H₂ in DCS) in a relatively small purification package that could supply the needs of an entire fab. Table 1 presents some results for the measured performance of a BEPS L for these three types of impurities in DCS.

Impurity	Impurity concentration in source product	BEPS-L Measured Performance
Boron (wtppb)	3.7	<0.16
Iron (wtppb)	40	5
H ₂ (vppm)	81	12

Table 1. Improved purity in DCS by BEPS-L technology

The most critical concern when using centralized supply technology arises from the high risk associated with any possible incident. For instance, an improperly purged connection could introduce ambient contamination into the whole fab and result in total production interruption. Hence, continuous quality control (CQC) tools, which have been standard to qualify high purity nitrogen (HPN) supply for years, become necessary for a centralized supply system for electronics specialty gases (ESG's) in order to guard against any potential irregularities, eg, leakage, corrosion, improper purging, etc. Moisture and particles detection provides an optimal and universal indication for such irregularities. Therefore, a mobile analytical cabinet (ALMAC) has been developed for monitoring onsite and in real time both moisture and particles in any chemical gas; in particular it uses diode laser hygrometry which allows for a moisture detection limit of 10 to 100 ppb in any chemical gas [11]. This technique allows to qualify both the distribution network and the chemicals supply with the actual process chemical prior to its introduction into the tools. (Figure 5)

Localized and Bulk supply of very low vapor pressure chemicals from liquid or solid phases

As already stated in the introduction, fulfillment of the need for new materials in semiconductor devices will involve increasing usage of liquid or solid phase precursors which need to be converted into vapor phase for CVD processing.

Despite an extensive history of research and development effort for the proper handling of such precursors, it is still considered poorly suited for high yield, high quality, advanced Si device production [3, 12, 13, 14]. Indeed, such liquid phase precursor handling has been in common usage in Silicon manufacturing technology for specific process steps, eg TEOS, TMP, TMB, etc CVD for SiO₂ base layers deposition or Chlorosilanes for Si epitaxy; liquid Ti, Ta, etc precursors were used recently for interface liner CVD deposition; also, in III-V and II-VI semiconductor processing, MO CVD using such liquid phase precursors at ambient conditions is common practice. Finally, much effort has been devoted recently to the precursor feed and vaporization techniques for high T_c superconductors CVD deposition, which are composed of the same elements (Y, Ba, Cu, etc) as the ones needed in future semiconductor devices and whose properties are highly sensitive to film quality, ie, composition, stoichiometry, morphology, etc.

Despite this extensive experience and much research for improvement, difficulties of the common distribution technologies are well recognized and improved robustness and process control is requested for the generalization of these techniques in Si manufacturing at < 100 nm design rule.

Current emphasis of development, as witnessed by the numerous published patents, focuses on the one hand on the improved distribution technology of liquid precursors, either in pure form or in solution or as molecular adducts, and on the other hand on the perfect vaporization into gas phase. The technical difficulties arising in particular from the risks of chemical reactivity, thermal or chemical decomposition, particle formation,

viscosity, etc and with the obtention of proper vapor phase are well documented in the literature.

Regarding the industrial structuring, chemicals and materials suppliers usually take direct responsibility for the delivery and distribution equipment logistics of the chemicals up to the process tool entrance; the vaporization equipment itself is normally incorporated into the process tool and hence the responsibility of the tool producer. However, development and construction of the total system is performed in close cooperation among chemicals suppliers, fluid control equipment producers and process tool manufacturers.

Liquid feed can be accomplished by pump or by gas pressure-feed technique. Generally speaking, the pressure-feed technique is preferred because pumps produce pulsating flow and require frequent services when dealing with chemicals of highly reactive nature. The three most important criteria for a chemical delivery system, ie, safety, reliability, and total availability, have been demonstrated for a number of state of the art commercially available systems. A fully automated delivery system for liquid precursors is represented in Figure 6. Since the delivery system is rigidly connected to the tool and cannot be easily modified after installation, it is designed to accept any type of chemical ampoule. A recharge tank with elaborate level sensors is connected in series to the mother tank. As the recharge tank is fixed in the delivery system and is designed with sufficient capacity, it can supply liquid precursors for several days while the mother tank is being changed. Cascade pressurization is used for the mother tank and the recharge tank. Therefore, the recharge tank can continuously deliver liquid precursors including when being refilled. Extensive purging procedure is automatically performed before and after changing the mother tank. An optional solvent purge module is available for high viscosity precursors which cannot be easily purged out.

Pressurization gas dissolved in the liquid precursors, which would affect the controllability of the MFC and of the vaporizer downstream, as well as possibly the deposit itself, is removed by a degassing module (Figure 7a). Judicial selection of proper membrane and laboratory verification of design parameters such as flow and pressure are critical to ensure proper performance of the degassing module. An alternative technique (Figure 7b), uses a flexible polymer container to separate the pressurization gas from the liquid. Since the pressurization gas is no longer in contact with the liquid, the bubble problems are completely eliminated [16] .

For some of the chemicals under consideration, it is desirable to include in line particle removal. Since filtration in liquid phase is far less efficient than in gas phase inclusion of a recirculation loop may represent the optimal means to reduce the particle level, especially in a centralized supply system. A continuous polishing loop (Figure 8, insert) successfully incorporates the recirculation nature into a pressure-feed system and is included in the bulk supply system.

The above techniques satisfy the short term needs of the manufacturing industry when associated with state of the art nebulization-vaporization techniques. However, for

further shranked devices and the subsequent higher aspect ratio structures, the need for improved vapor phase supply techniques is to be anticipated. Since the layers to be deposited will be thinner, deposition rates will become of less concern; major issues will concern control at atomic level of film quality, conformality and interfaces. Therefore, a number of new techniques are under research, such as laser ablation, supercritical solution CVD or photoactivated deposition techniques, for atomic layer controlled deposition process.

Optimized Total Cost of Ownership

Comparison of the total cost of ownership of the various delivery equipment options, includes consideration of all the details such as maximum flow rate and duration, distance from the source to the tools, ambient temperature, back-up solutions, etc. to insure that the required flow is delivered to the point-of-use with total quality and reliability. Next, one can compare the cost of the several delivery options. As an example of a newly introduced low vapor pressure gas precursor to be used at high flow rates one may cite trimethylsilane, 3MS, (1.6 bar at 20C), a chemical used for Si-O-C deposition as a low-k dielectric interconnect and other functional layers.

Table 3 summarizes the cost comparison for various delivery equipments: standard gas cabinet for which the material cost is set at X, AVP gas cabinet, BEPS-G at indoor, BEPS-G at outdoor, and BEPS-L at outdoor. Note that the cost of the container is not included in this analysis since it is typically included in the materials supply chain. Due to the low vapor pressure, the AVP system with integrated heating device gives better economics at low flow rates. Even though the cost of a BEPS-G is comparable to the AVP option at low flow rates, the significantly higher cost of the bulk container over a conventional cylinder would favor the AVP option. At higher flow rates, the bulk system (BEPS-G) provides a better choice if it can be placed indoors. However, if it is to be placed outdoors where the ambient can reach freezing temperatures, a bulk system with liquid delivery (BEPS-L) would be preferred.

Cost of Materials to Build for 3MS				
1 Hour maximum flow @ 19 psia				
System	100slm	50slm	16slm	8slm
Standard Cabinet	50X	25X	8X	4X
AVP Cabinet	6X	3X	1.5X	1.3X
BEPS-G, Inside 21C	4.2X	4.2X	1.3X	1.3X
BEPS-G, Outside -20C	6.9X	4.2X	4.2X	4.2X
BEPS-L, Outside -20C	3.5X	3.5X	3.5X	3.5X

Table 2. Delivery system cost comparison for 3MS where X represents the material cost of a standard gas cabinet

Beyond the construction cost of various delivery systems for a given chemical, facility design and layout can also be optimized with respect to the total cost of ownership. Figure 9 shows two designs: one with conventional delivery systems while the other with new delivery technologies such as AVP for low vapor pressure gases and BEPS for bulk ESG's, technology and bulk delivery systems. Even though the unit price for the new design is higher, it offers greater flow capability and therefore reduces the total number of units. Furthermore, certain common function such as purge gas for different systems can be centralized for additional cost reduction. As a result, a lower total cost of ownership was achieved.

Conclusion

The above described new distribution technologies of vapor phase process chemicals provide improved quality, reliability, safety and cost of ownership for the emerging semiconductor manufacturing processing . Specifically, the optimized supply of enhanced flow rate chemical gases from pressure liquefied gas containers is described. Distribution solutions for the liquid or solid phase precursors which will increasingly be needed to satisfy the physico-chemical properties required at shrunked device dimensions are introduced. Clearly, further development efforts are required in the latter area for high throughput, high quality routine manufacturing; these are in progress through close partnership among all the partners of the value chain, ie, the process and equipment developers, the fluid control equipment suppliers and the materials and chemicals suppliers.

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Biography

Jean M. Friedt is the Director of Technology Development of Air Liquide, Electronics Division; he is a fellow of Air Liquide group. From 1995 to 1998, he hold similar function based in San Francisco; from 1988 to 1995 he was in charge of corporate electronics R&D in Tsukuba. Prior to joining Air Liquide he held an academic carrier as a materials scientist specializing in solid state spectroscopies, with international assignments around the globe.

Hwa-Chi Wang is the Manager of Electronics R&D at Air Liquide and has been involved in the research of gases and chemicals for the semiconductor industry since 1987. He is also an Adjunct Professor at the Department of Chemical & Environmental Engineering, Illinois Institute of Technology, Chicago, IL. He earned a PhD from the University of Illinois at Urbana-Champaign in 1984.

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Herve Dulphy is the Manager of the Development Department of Air Liquide Electronics Systems. He has many years of experience in ultrapure gases and chemicals dispense systems or on-site generation systems design and manufacturing, as well as in management and operation. He also has several years of experience in chemical engineering from his work with an oil company as a research scientist. He received a Ph.D. in Organic Chemistry from the University of Aix/Marseille.

FIGURE CAPTIONS

Figure 1 : AVP gas cabinet for low vapor pressure gases such as WF₆, 3MS, and DCS

Figure 2 : Time dependence of Pressure from a WF₆ cylinder using respectively a standard gas cabinet and an AVP cabinet. The gas flow schedule includes 5 cycles of 25 process steps, each having an average flow rate of 400 sccm and a maximum of 2400 sccm, followed by 25 minutes flow interruption.

Figure 3 : Schematic representation of the BEPS G supply technology. Time dependence of NH₃ pressure emitted from such a ton container with- and without AVP heat regulation. The average flow demand was 160 slm over 680 minutes, with a practical schedule ranging between 300 slm and 25 slm.

Figure 4 : Schematic representation of the BEPS L distribution technology and on-site purification equipment.

Figure 5 : Mobile analytical cabinet for real time, on site continuous quality control of moisture and particles in chemical gases.

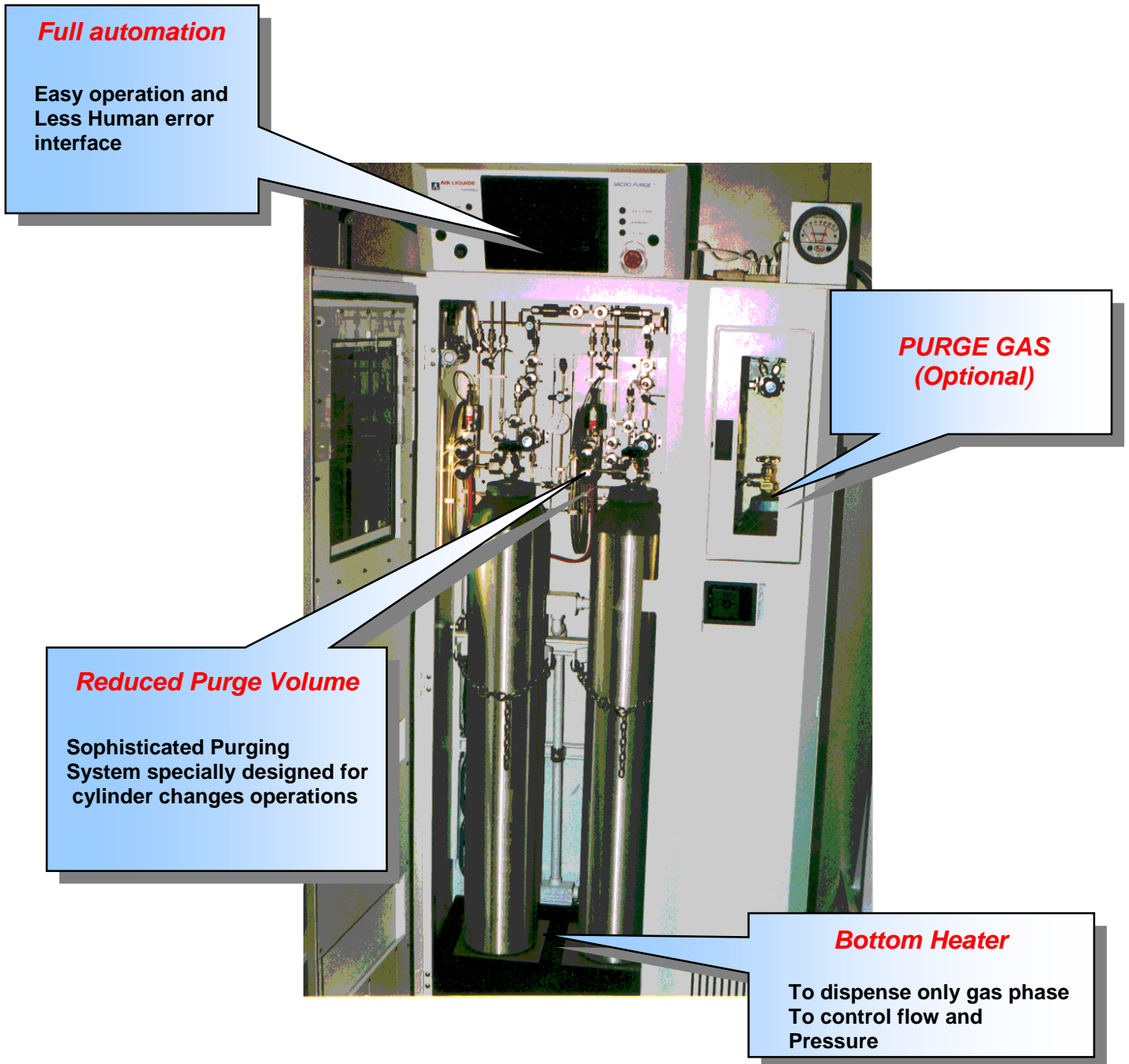
Figure 6 : Liquid chemicals dispenser equipment

Figure 7 : Distribution of dissolved gas-free liquid chemicals by gas pressurization : principle for removal of dissolved gas by membrane technology; polymer film separation of the liquid phase from the pressurizing gas phase.

Figure 8 : Double tank liquid chemical distribution equipment for particle-free supply via recirculation

Figure 9. Incorporating new gas delivery design for reduced total cost of ownership.

Fig 1



Full automation

Easy operation and Less Human error interface

PURGE GAS (Optional)

Reduced Purge Volume

Sophisticated Purging System specially designed for cylinder changes operations

Bottom Heater

To dispense only gas phase
To control flow and Pressure

Fig 2

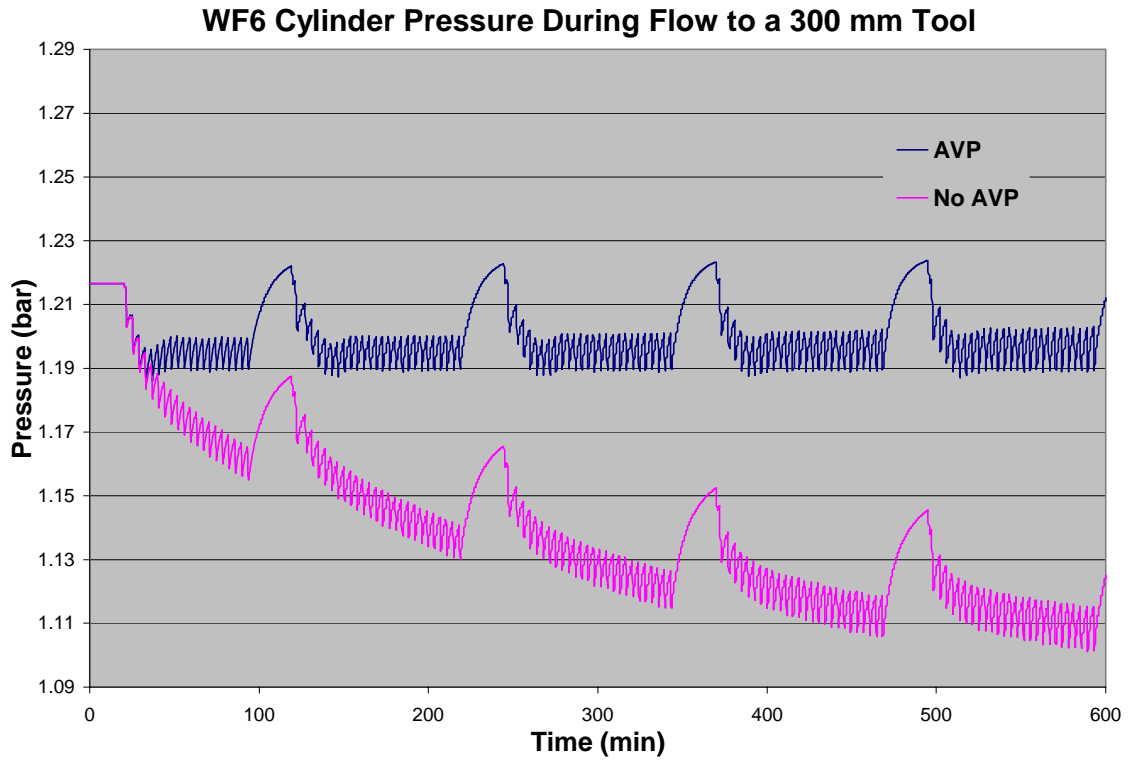


Fig 3

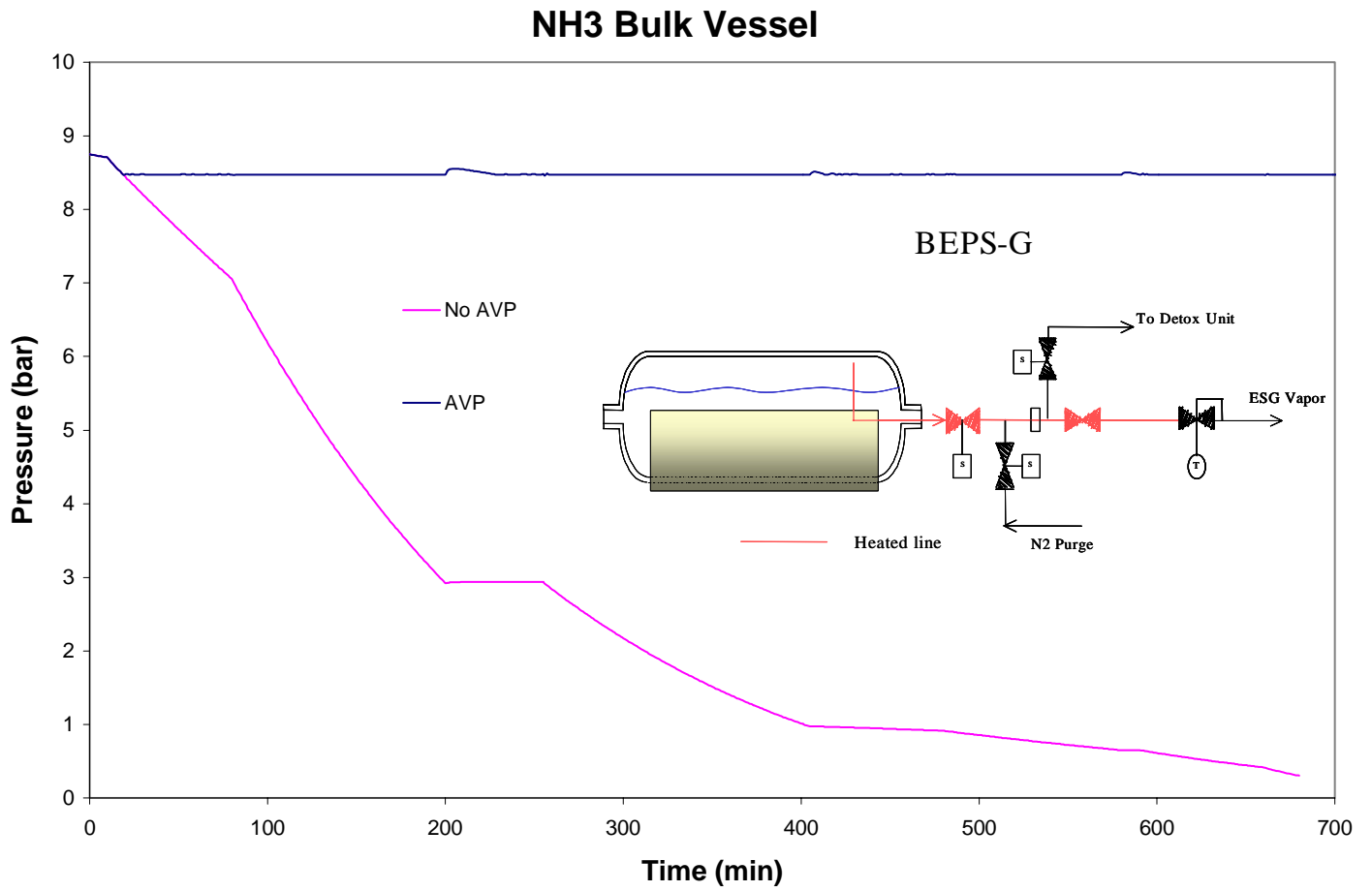


Fig 4



BEPS-L

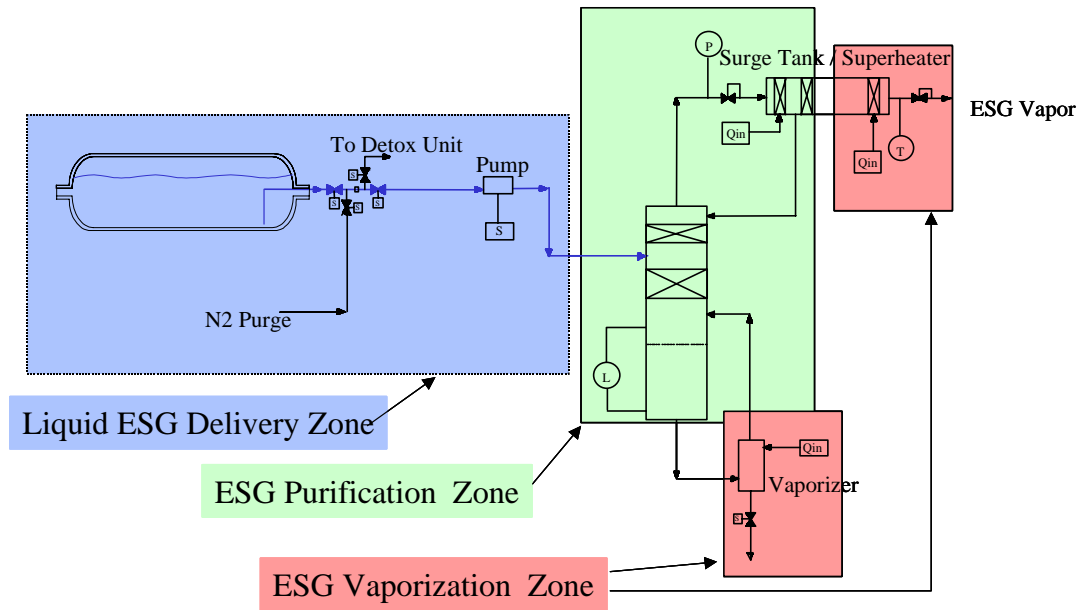


Fig 5



Fig 6

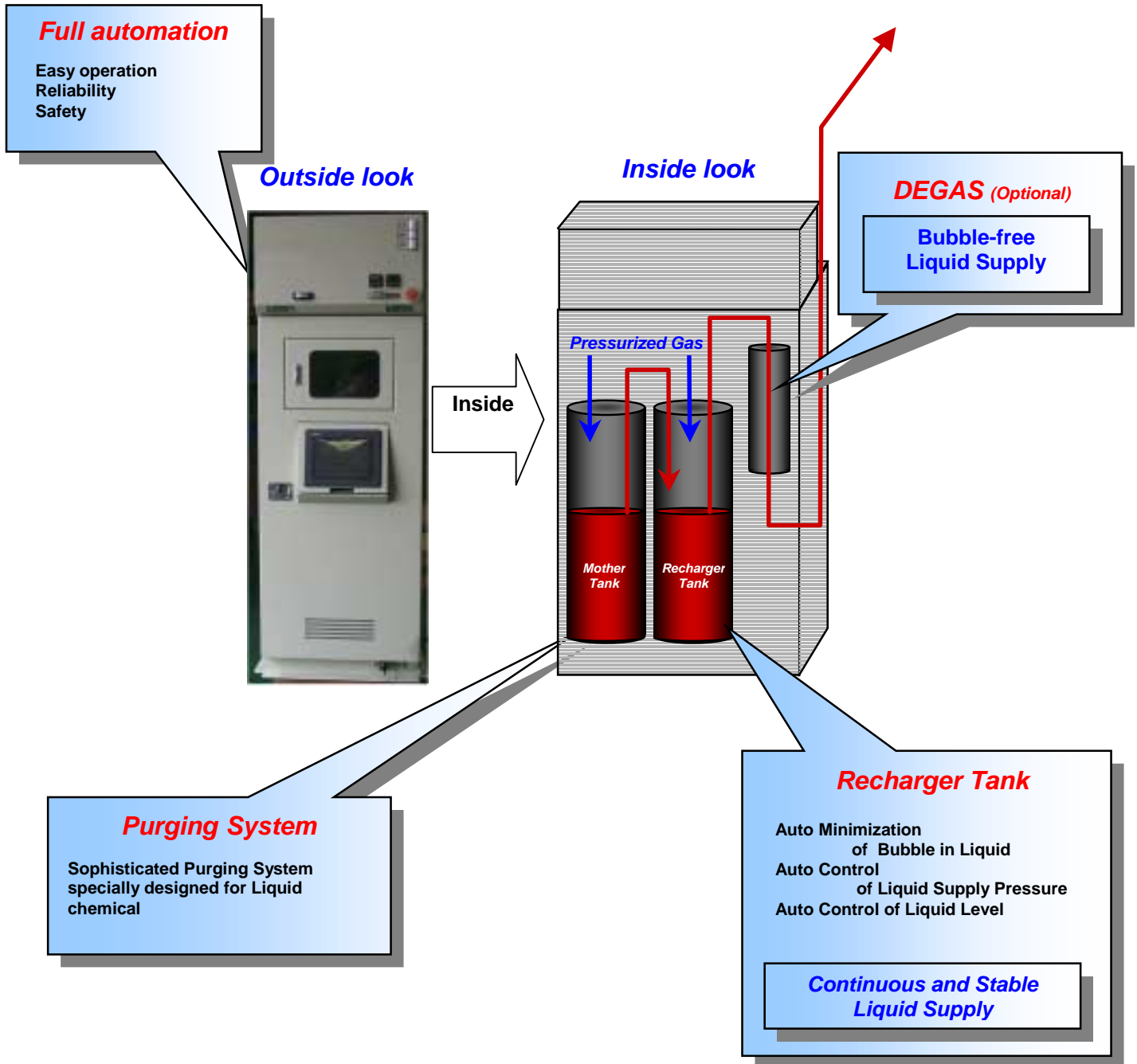


Fig 7

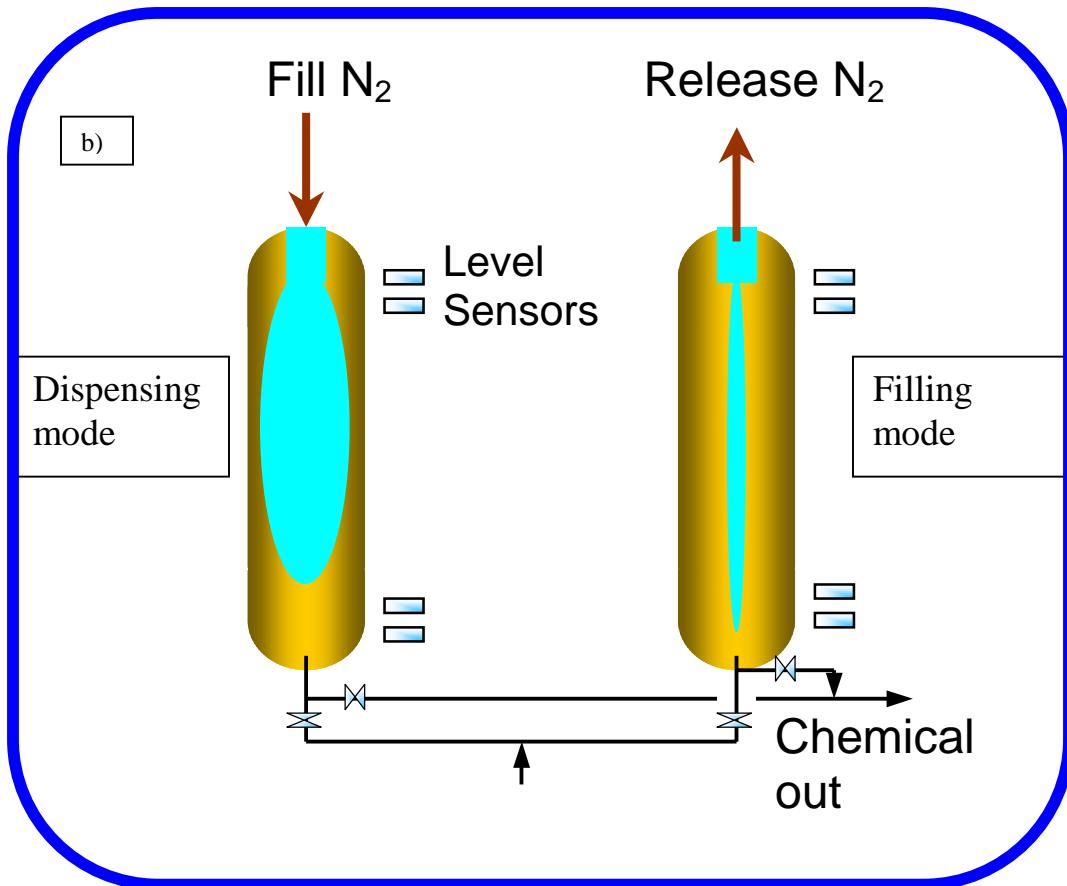
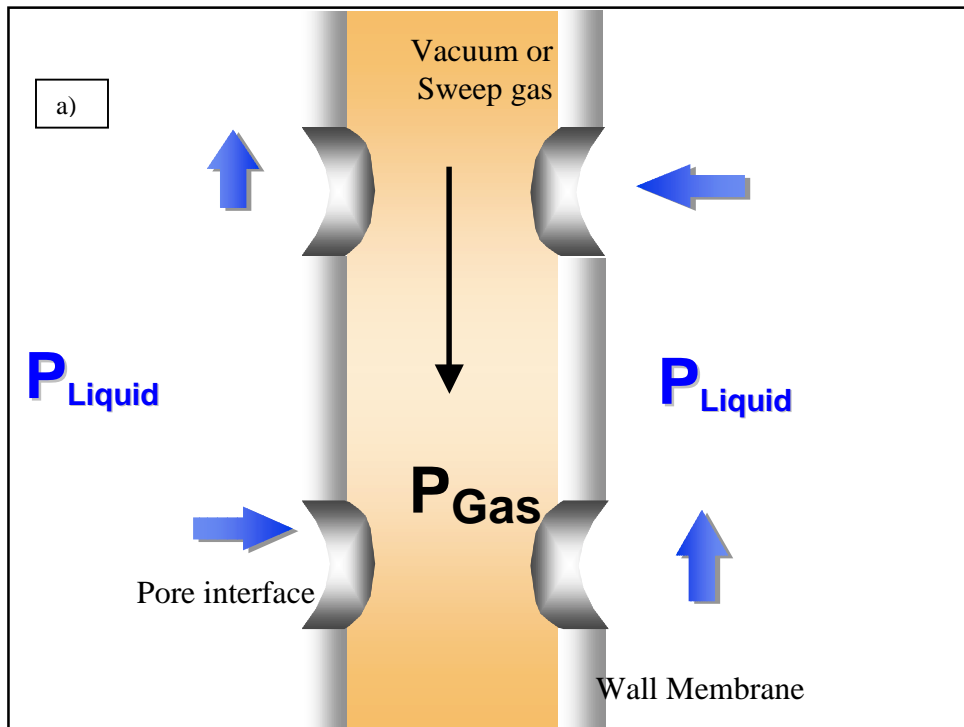
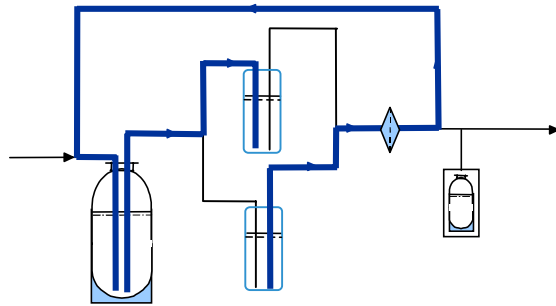


Fig 8

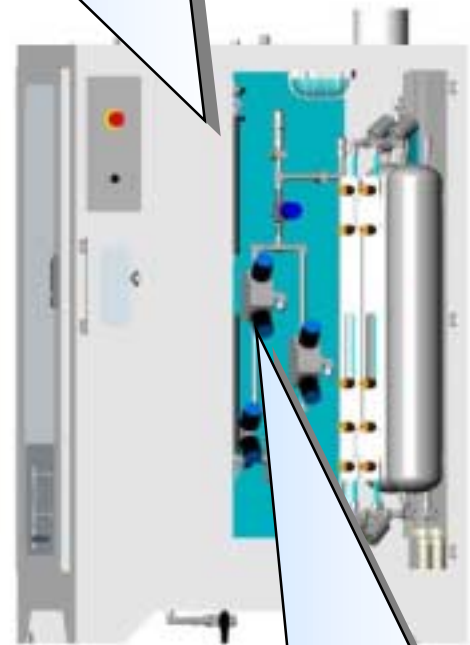
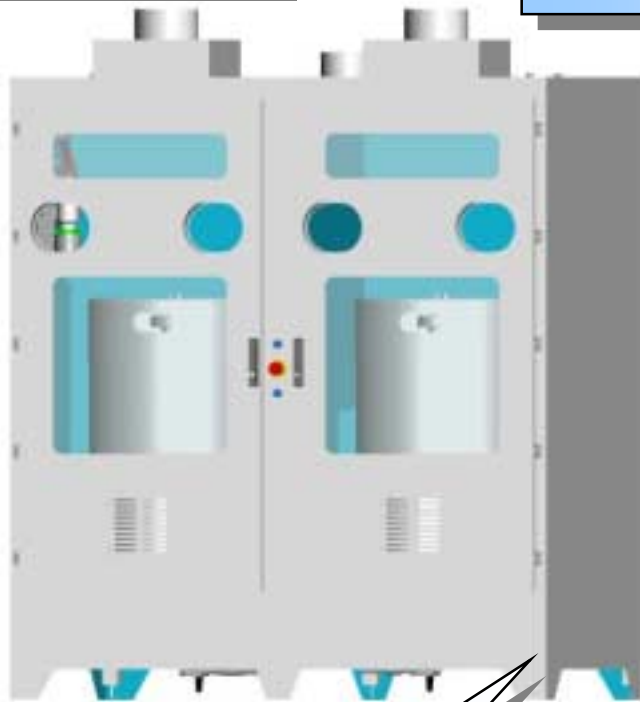


Full automation

Easy operation
Reliability
Safety

OPTIONS

Degas module
Continuous polishing loop



Dual Mother Tank Unit

Various sizes of mother tank
are available from 20L to 200L

Distribution Unit

Dual receiver tanks allows continuous supply
Accurate Control of Liquid Level

Up to 40 tools

Fig 9

