

Estimating Hydrochloric Acid and Ammonium Hydroxide Loss

Calculations suggest break-through from semiconductor bulk chemical distribution systems occurs in a matter of days and steady state permeation accounts for several milliliters of chemical loss each day.

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Permeability (P) and diffusion (D) coefficients were measured for hydrogen chloride and ammonia gas transport through a polytetrafluoroethylene copolymer, perfluoroalkoxy (PFA), using standard manometric techniques. These data were subsequently used to estimate the performance characteristics, such as break-through times and permeation rates, of a representative chemical distribution system that might be found inside a semiconductor wafer fabrication facility. Our findings suggest that break-through occurs in a matter of days and that steady state permeation can account for the loss of several grams of hydrochloric acid or ammonium hydroxide each day. This loss rate for hydrogen chloride would be equivalent to dumping five milliliters of concentrated hydrochloric acid on to the floor of a fabrication facility each day, or more likely into the secondary containment sub-system, and allowing the acid to dissipate over the course of a day. This equates to two liters per year. Everything else being equal, the loss rate of ammonium hydroxide is expected to be more than two times that of hydrochloric acid. To prevent accumulation of hydrogen chloride or ammonia, the secondary containment sub-system must be purged. The necessary purge rate can be estimated

using the mass transport data making this study useful to facility planners and operators.

Among melt-processable thermoplastics, tetrafluoroethylene (TFE) - perfluoroalkoxy copolymers, often abbreviated simply as PFA, have a unique combination of purity, toughness, and nearly universal chemical inertness. Therefore, PFA has been used broadly for the transport and storage of high purity chemicals in semiconductor wafer fabrication facilities or "fabs."^{1,2} Although much is known about the purity, mechanical, and thermal properties of PFA,³⁻⁵ less information is available regarding its permeation characteristics.

Some permeation testing has been performed on PFA,⁶⁻¹³ but most studies have not addressed two of the most widely used semiconductor process chemicals, hydrochloric acid and ammonium hydroxide. The active ingredient in both of these aqueous chemicals is dissolved gas, hydrogen chloride or ammonia, respectively. Thus, they are quite mobile and have caused concerns about unwanted permeation, cross-contamination, and corrosion.¹³ In this article, we explore break-through times and steady-state permeation rates of hydrogen chloride and ammonia for a PFA chemical distribution system. 

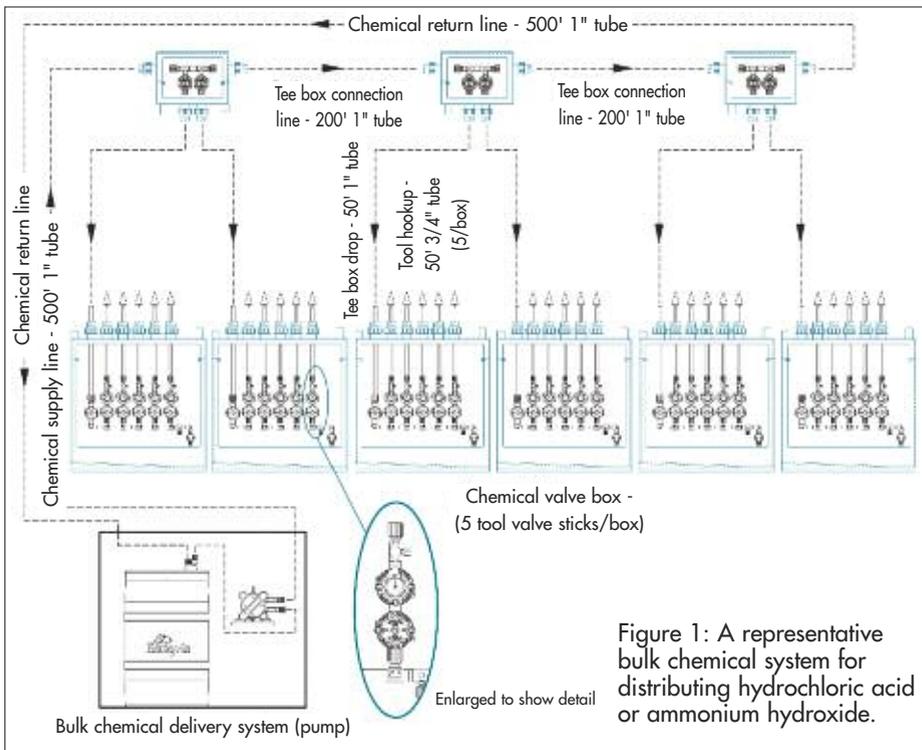


Figure 1: A representative bulk chemical system for distributing hydrochloric acid or ammonium hydroxide.

A REPRESENTATIVE BULK CHEMICAL SYSTEM

In the following examples, we use a representative bulk chemical system that could be used for distributing hydrochloric acid or ammonium hydroxide. It is shown schematically in Figure 1. The distribution system consists of a bulk chemical container, a pump, tubing, pipe, and valves. The various PFA components are tabulated in Table 1. The valves are mounted inside containment boxes. The chemical, hydrochloric acid or ammonium hydroxide, is pumped from a chemical container through a one inch (25 mm) PFA supply line to three tee boxes that each contain two PFA drop valves. The drop valves feed six valve boxes that in turn distribute the chemical to 30 points of use via 3/4 inch (19 mm) PFA tubing. Unused chemical is sent back to the storage container through a one inch PFA return line. For simplicity, we assume that all components are constructed from PFA.

Tee and valve boxes would typically be fabricated from polypropylene (PP). The tee boxes shown here have dimensions of 48 cm x 42 cm x 24 cm. The valve boxes are larger, approximately 90 cm x 80 cm x 30 cm. Although not

shown, a typical system would also have secondary containment around the runs of pipe and tubing, often two inch (50 mm) poly vinyl chloride (PVC) pipe.

Table 1 also includes quantities and dimensions of the chemical distribution components: length (L), thickness (B), surface area (A), and fractional surface area (f_A) relative to the entire system. The total surface area is 660,529 cm², which can inconspicuously allow chemical to escape the PFA via permeation. This system has a large surface area that is approximately equivalent to one side of a volleyball court (66 m² or 710 ft²). The total length of the system is one kilometer, so it is not surprising that most of the surface area is from the tubing and pipe, which accounts for >98% of the total surface area. Almost all of

that area (97%) lies outside the tee and valve boxes. The remainder of the wetted surface area listed in Table 1 is from the valve diaphragms. We also estimated the area of the valve bodies, a total sum of 12,600 cm². This is much larger than the area associated with the diaphragms (1,660 cm²).

COMPONENT	TYPE	QUANTITY	L (m)	B (cm)	A (cm ²)	f _A (%)
OUTSIDE THE VALVE BOXES						
Chemical supply line	1" tube	1	152.400	0.157	114,070	17.27
Return line	1" tube	1	152.400	0.157	114,070	17.27
Tee box line 1	1" tube	1	60.960	0.157	45,628	6.91
Tee box line 2	1" tube	1	60.960	0.157	45,628	6.91
Tee box drop	1" tube	6	91.440	0.157	68,442	10.36
Tool hook-up line	3/4" tube	30	457.200	0.157	251,003	38.00
INSIDE THE TEE BOXES						
Pipe	1" pipe	3	0.925	0.338	873	0.13
Valve	Diaphragm valve	6	1.000	0.050*	1,527	0.23
INSIDE THE VALVE BOXES						
Tee box drop	1" tube	6	2.089	0.157	1,564	0.24
Tool hook-up line	3/4" tube	30	6.507	0.157	3,573	0.54
Pipe	3/4" pipe	6	4.153	0.305	3,082	0.47
Tee box drop valve	Diaphragm valve	6	1.000	0.050*	1,527	0.23
Tool hook-up valve	Diaphragm valve	60	10.000	0.040*	9,543	1.44
TOTALS			1,001.000		660,529	100.00
L= Length; B=Thickness; A=Surface area; f _A = Fractional surface area relative to the entire system						
*Thickness is for valve diaphragm; valve body is much thicker, ~0.5cm.						

Table 1: Bulk chemical distribution components, quantities, and dimensions.

Permeant	P [10 ⁻¹⁰ cm ³ ·cm/cm ² ·s·cmHg]	D [10 ⁻⁸ cm ² /s]
Hydrogen chloride	1.60 ±0.07	0.92 ±0.15
Ammonia	2.83 ±0.07	0.99 ±0.24

Table 2: Hydrogen chloride and ammonia permeability coefficients (P) and diffusion coefficients (D) for PFA at 25°C (77°F).

MASS TRANSPORT PROPERTIES OF PFA

Permeability (P) and diffusion (D) coefficients of PFA for both hydrogen chloride and ammonia gas were measured at 25°C by standard manometric techniques.¹⁴ Gas pressures for hydrogen chloride ranged between 15 and 25 cmHg or for ammonia, from 42 to 47 cmHg. Values of P and D did not depend on gas pressure in these ranges. Their averages are summarized in Table 2. The diffusion coefficient describes the mobility of a molecule in a material, while the permeability coefficient is an inherent material property that describes the normalized “flow” rate through a material. Greater solubility of ammonia in PFA led to a permeability coefficient (P) that was nearly two times larger than for hydrogen chloride. The measured values agreed with the few published values found in open literature.^{9,13}

PERFORMANCE OF THE BULK CHEMICAL SYSTEM

Break-through times. If hydrochloric acid or ammonium hydroxide were introduced into our representative distribution system, how much time would pass before hydrogen chloride or ammonia gas would begin to appear at the outer surface of our PFA components? The break-through time (t_b) depends on the sample thickness (B) and the diffusion coefficient (D) of the material,¹⁵

$$t_b = \frac{B^2}{6D}$$

Assuming we have a perfectly sealed system, break-through of hydrogen chloride or ammonia would occur first in the thinnest wall sections of the valve diaphragms (7-8 hours). These gases would begin to emerge from the tubing in t_b = four to five days.

Steady state permeation rates. Once break-through occurs, steady state is generally reached after $3t_b$.¹⁵ For the tubing in this system, that would happen approximately three weeks after introduction of hydrochloric acid or ammonium hydroxide into the dry system. If we assume the concentration in the surrounding atmosphere (tee boxes, valve boxes, and containment sub-systems, etc.) is effectively zero and is kept there, then volumetric loss rates (Q) due to permeation can be estimated from each component using the following equation,^{15,16}

$$Q = \frac{q}{t} = \frac{P \cdot A \cdot p_b}{B}$$

where q is the volume of gas at standard temperature and pressure ($T_0 = 0^\circ\text{C} = 273\text{ K}$ and $p_0 = 1\text{ atm} = 76\text{ cmHg}$) that permeates, t is time, P is the permeability coefficient, B is the component thickness, A is the area (A), and (p_b) is the internal partial pressure of the gas. In turn, the volumetric loss rates can be converted into mass loss rates (\dot{m}) using the ideal gas law,

$$\dot{m} = \frac{Q \cdot p_0 \cdot M}{R \cdot T_0}$$

where M is the molar mass of the gas in question (36.46 g/mol for HCl and 17.03 g/mol for ammonia) and R is the ideal gas constant (6236.6 cm³·cmHg/K·mol). Steady state permeation rates depend on the vapor pressure of hydrogen chloride and ammonia, which are determined by the concentrations of hydrochloric acid and ammonium hydroxide. In the calculations, we used 22.5 cmHg for hydrogen chloride and 47.0 cmHg for ammonia as vapor pressures. These numbers represent 37% hydrochloric acid and 25% ammonium hydroxide, respectively.

Considering one of the components as a scenario—the chemical supply line is comprised of 152 m of one inch PFA tubing. Under steady state conditions, it would be expected to lose 225 standard cm³ of hydrogen chloride gas per day to permeation or 832 standard cm³ per day of ammonia. On a mass basis, this equates to 0.37 g or 0.63 g per day, respectively. Steady state mass loss rates are listed in Table 3 for all components. Since most of the area available for transport is found in the tubing, it accounts for most of the steady state gas loss. The daily totals are 2.1 g/day for hydrogen chloride and 3.6 g/day for ammonia. These loss rates of hydrogen chloride and ammonia can be converted into the amount of hydrochloric acid and ammonium hydroxide using concentration and density. The loss rate for hydrogen chloride would be equivalent to dumping five milliliters of concentrated hydrochloric acid on to the floor of a fab each day, or more likely into the secondary containment sub-system, allowing the acid to dissipate over the course of a day. This equates to two liters per year. Everything else being equal, the loss rate of ammonium hydroxide is expected to be more than two times that of hydrochloric acid.

Removal of permeants from the secondary containment sub-system. If we assume the secondary containment sub-system for a hydrochloric acid or ammonium hydroxide line is sealed and isolated from the ambient fab environment, it should be purged periodically to prevent accumulation of errant

hydrogen chloride or ammonia. At the other extreme, if it were required to maintain levels of either gas in the secondary containment below the Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL), then constant purging of the sub-system would be necessary.

Again, let us use hydrogen chloride to make a few estimates. Without purging, the rate of accumulation will vary throughout the system. Hydrogen chloride levels will rise more slowly in the large valve boxes and more quickly in the confines of the tubing secondary containment. Therefore, to minimize hydrogen chloride concentration rise in the secondary containment sub-system, it is sufficient to address the smallest annular volume surrounding the tubing outside the boxes.

The daily hydrogen chloride loss at 25°C from a unit length of one inch tubing is 0.016 cm³ per day, while the annular volume of a unit length of secondary containment is 15 cm³. The OSHA PEL for hydrogen chloride is 5 ppm.¹⁷ In order to dilute the hydrogen chloride gas to this level, the air volume inside the containment sub-system should be turned over roughly 200 times per day. This corresponds to a residence time of seven minutes. Thus, the purge gas flow rate through the containment sub-system (0.8 m³) should be 0.1 m³/min (3.5 ft³/min). The highest purge gas velocities would occur in the PVC conduit containing the one inch PFA tubing. With an annular cross-sectional area of 15 cm², the average velocity in the conduit would be 75 m/min (4.5 km/hour = 3 mi/hour).

CONCLUSIONS

Permeability and diffusion coefficients of hydrogen chloride and ammonia gas were measured for PFA and then used to estimate the performance of a representative bulk chemical distribution system in a semiconductor wafer fab constructed from PFA. Our calculations suggest that for real systems, break-through occurs in a matter of days and steady state permeation accounts for several milliliters of chemical loss each day. Most of that loss comes from the long runs of tubing that transport chemical throughout fabrication facilities. To prevent accumulation and maintain very low levels of hydrogen chloride or ammonia, the secondary containment sub-system must be purged. The purge rate can be estimated using mass transport data.

COMPONENT	TYPE	HCl		NH ₃	
		\dot{m} [g/day]	f_i [%]	\dot{m} [g/day]	f_i [%]
OUTSIDE THE VALVE BOXES					
Chemical supply line	1" tube	0.367	17.38	0.633	17.38
Return line	1" tube	0.367	17.38	0.633	17.38
Tee box line 1	1" tube	0.147	6.95	0.253	6.95
Tee box line 2	1" tube	0.147	6.95	0.253	6.95
Tee box drop	1" tube	0.220	10.43	0.380	10.43
Tool hook-up line	¾" tube	0.807	38.24	1.392	38.24
INSIDE THE TEE BOXES					
Pipe	1" pipe	0.0008	0.06	0.001	0.06
Valve	Diaphragm valve	0.004	0.18	0.006	0.18
INSIDE THE VALVE BOXES					
Tee box drop	1" tube	0.005	0.24	0.009	0.24
Tool hook-up line	¾" tube	0.011	0.54	0.020	0.54
Pipe	¾" pipe	0.005	0.24	0.009	0.24
Tee box drop valve	Diaphragm valve	0.004	0.18	0.006	0.18
Tool hook-up valve	Diaphragm valve	0.026	1.23	0.045	1.23
TOTALS		2.110	100.00	3.641	100.00

Values were estimated assuming concentration solutions with $P_h = 22.5$ cmHg for hydrochloric acid and $P_h = 47$ cmHg for ammonium hydroxide.

Table 3: Permeation rates (\dot{m}) and fractional contribution to the total system permeation (f_i) of the various distribution components.

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