High Flow Delivery Systems for Bulk Specialty Gases

Belgin Yücelen, Joseph Vininski, and Robert Torres
Matheson Tri-gas
Advanced Technology Center
Longmont, Colorado

Biography

Dr. Belgin Yücelen is a Senior Research Engineer at the Matheson Tri-Gas Advanced Technology Center. She received her Ph.D. in Chemical Engineering from the Colorado School of Mines. Prior to joining Matheson Tri-Gas, her industrial background included petroleum refining, fluid-bed combustion systems and phase equilibria. At Matheson Tri-Gas, Dr. Yücelen’s research involves developing heat and mass transfer models for corrosive gases, designing high purity gas distribution systems, and developing analytical techniques for the detection of trace gas impurities. She has been a member of AIChE since 1997.

Abstract:

Two independent high-flow bulk delivery systems were designed and built. These systems were employed to investigate the moisture and the temperature changes and to test the efficiency of the purification methods for hydrogen chloride and ammonia as a function of flow rate.

The moisture concentration in gas phase for hydrogen chloride and ammonia was measured by an FTIR spectrometer. The efficiency of Matheson Tri-gas’ Nanochem® series purifiers was tested at a wide range of flow rates. Heat was introduced to the Bulk Specialty Gas Unit (BSGU) and the distribution system during the purification experiments to ensure saturated vapor phase in the purifiers. The results from testing bulk specialty gas purifiers for ammonia and hydrogen chloride under severe moisture challenges and various flow rates are described.

The temperature changes were monitored throughout the delivery manifold and the BSGU to accurately characterize evaporative cooling and Joule-Thomson effects. A comprehensive model based on heat transfer concepts was developed to estimate the temperature profile within a BSGU. The temperatures predicted by the theoretical model were compared with the experimental data to assess the reliability of the heat transfer model. The results of the temperature measurements and the model predictions are reported for hydrogen chloride and ammonia for flow rates up to 900 and 500 L/min, respectively.

Introduction:

Bulk Specialty Gas Systems (BSGS) are now replacing the traditional cylinder delivery systems due to their lower cost, safety, product quality, consistency and reduced cylinder changes [1]. BSGS are also capable of high flow rates (up to 1500 slpm) which will be required by the semiconductor industry moving towards larger fabs along with 300 mm wafers. Information on the temperature and moisture variations at high flow regimes is critical to the design and operation of bulk distribution systems in order to ensure the supply of high purity gas to the process tools.

Hydrogen chloride is employed for the plasma and thermal etching of silicon and gallium arsenide wafer surfaces prior to epitaxial growth. A small amount of water may cause a reduction in the etching selectivity. Moisture in a corrosive gas such as hydrogen chloride also accelerates corrosion leading to metallic particulate contamination within the gas distribution system [2], [3]. These particles can be carried to the...
process tools and have a direct impact on the wafer yield. Ammonia is used for the deposition of silicon nitride layers in integrated circuits and for MOCVD growth of gallium nitride films in LED’s. Moisture can adversely affect the performance both processes.

Source gas and point of use purification (POU) of specialty gases minimize the effect of particulate contamination caused by corrosion [2] and reduce the chemical contamination to negligible levels. Therefore purification of gases is necessary to protect down stream components from corrosion and deterioration and to improve the process quality. Matheson Tri-gas’ Nanochem® series purifiers provide effective gas purification in multi-tool and single-source applications. Utilization of these purifiers for BSGS presents many challenges due to the problems associated with delivery of condensed gases at high flow rates. The effects of severe temperature drops, liquefaction of the gas, and large linear velocities must be considered to ensure optimal purifier performance.

Data:
Experimental Procedures
Two independent high flow gas distribution systems with 3/8" and 1/2" 316L stainless steel tubing were used for the experiments. The schematic of the gas distribution system for hydrogen chloride is shown in Figure 1 and for ammonia in Figure 2. Temperature changes were monitored throughout the delivery manifold and the BSGU using type K thermocouples interfaced to a computer. For the purification experiments the BSGU was heated with 5000 W and 5760 W heat blankets for hydrogen chloride and ammonia BSG units, respectively.

Moisture experiments were run with BSGU containers of hydrogen chloride and ammonia that were prepared with known amounts of moisture. A Nicolet Magna FTIR bench was equipped with additional internal purge lines and an external purge box to assure low and constant background moisture levels in the beam path.

Purified nitrogen (< 1 ppb moisture) at 20 L/min was used as purge gas. Lines and valves were heated with heating tapes to avoid adsorption-desorption of moisture. A 10 m path length nickel coated cell with gold coated mirrors and IR quartz windows was used for gas sampling. The pressure in the FTIR cell was monitored with a MKS Baratron pressure gauge (0-1000 torr). Low noise levels and high sensitivities were obtained with a liquid nitrogen cooled MCTA detector. Sampling was performed at a resolution of 4 cm⁻¹ and Happ-Genzel apodization. A 1/8" 316L sample line was connected to the high flow manifold down stream of the purifier. This line flowed a continuous sample (at 2 L/min) to the FTIR. The 1/8" sample line was heated and held at a constant elevated temperature. The set up also allowed the purifier to be by-passed. All flows were adjusted with metal seated metering valves and measured with rotameters.
Moisture Concentration Measurements

**Hydrogen Chloride**

The moisture concentration in the gas phase was measured for a wide range of flow rates from 1 to 900 L/min. The concentration was stable throughout the experiments with a range from 0.24 to 1.22 ppm and was not a strong function of flow rate as seen in Figure 3. The average moisture concentration was 0.63 ppm.

![Figure 3. Change in the moisture concentration in gas phase hydrogen chloride as a function of flow rate. Moisture challenge: 10 ppm](image)

**Ammonia**

The moisture concentration in gas phase ammonia was measured at flow rates up to 500 L/min. The water concentration increases with flow rate, reaches a maximum, then declines as seen in Figure 4. This behavior was observed in two independent experiments and is believed to be a result of the combined effects of thermodynamics, fluid dynamics and heat transfer. It is difficult to model the water concentration as a function of flow rate but some theoretical explanations are under consideration to describe this interesting phenomenon.

![Figure 4. Change in the moisture concentration in gas phase ammonia as a function of flow rate. Moisture challenge: 40 ppm (liquid phase)](image)

**Purification Experiments**

**Hydrogen Chloride**

An 8L Nanochem® bulk hydrogen chloride purifier was tested at cylinder pressure (627.7 psia at 70 °F) for source gas purification applications. Heat was added both to the BS GU and the distribution manifold to ensure that hydrogen chloride was being introduced to the purifier as gas phase. With moisture challenges up to 10 ppm, the purifier performance was tested at three different flow rates and the results are shown in Figure 5.

![Figure 5. Moisture concentration in gas phase hydrogen chloride with high-pressure purification](image)
Ammonia
The efficiency of a Nanochem® bulk ammonia purifier was tested at flow rates of 2, 50, 100, 250, 500 and 700 L/min and a moisture challenge of 40 ppm (liquid phase). Heat was applied to the BSGU and the distribution manifold during these experiments. The results of the purification tests showed that the moisture concentration was reduced to below the FTIR detection limit of 100 ppb at all flow rates. Figure 6 shows the moisture concentration in the gas phase at each flow rate using a purifier together with the results at 400 L/min bypassing the purifier.

Figure 6. Moisture concentration in gas phase ammonia with purification

Heat Transfer Model
A model was developed to determine the temperature distribution in a tonner based on heat transfer concepts. Information on the temperature profile inside the tonner is essential for the understanding of the boiling mechanism and to estimate the pressure inside the BSGU in order to be able to maintain a constant flow.

It was assumed that there are three modes of heat transfer; heat loss due to evaporation of liquid ammonia, heat gain by convection from air and heat conduction within the liquid. The temperature distribution was determined from the solution of the one-dimensional, unsteady-state cylindrical heat conduction equation subject to a set of appropriate boundary and initial conditions. It was assumed that the system was cylindrically symmetric and that the volume of the liquid was the only variable. The finite difference method was employed to approximate the partial differential equations of heat conduction by a set of algebraic equations in both space and time domains at a number of nodal points. For the radial temperature profile 5 nodes were used and a total of 54 ordinary differential equations were simultaneously solved for 54 unknowns.

The validity of the model developed was established by comparing the predictions with the experimental data for both ammonia and hydrogen chloride. The data were taken using a thermocouple placed on the BSGU wall below the liquid level. No heat was supplied for these experiments. This model can also be used to predict the efficiency of heat transfer of various methods by simply measuring the temperature of the BSGU surface.

Hydrogen Chloride
The comparison of the model predictions with the experimental data for hydrogen chloride is given in Figure 7 for 100, 500 and 900 L/min. These results show that the model can predict the surface temperature of the BSGU for hydrogen chloride with an average deviation of ±0.3°C between the calculated and the measured values.

Figure 7. Model predictions and experimental data measured on the BSGU surface below the liquid level line for hydrogen chloride
The predicted temperature profile at 5 nodal points for 900 L/min is illustrated in Figure 8. The temperature at the center of the tonner goes down to temperatures below \(-110^\circ\text{C}\) (hydrogen chloride freezing point) after 15 minutes. These results may suggest the formation of hydrogen chloride ice. However, it should be noted that at high flow rates, the vigorous boiling mechanism may increase the mixing process and decrease the temperature gradients. As a result, the temperature distribution may be more uniform and the possibility of having hydrogen chloride ice inside the tonner will be reduced. But, the pressure calculated from the predicted average temperature correlates very well with the experimental pressure at all flow rates. This also confirms the validity of the model.

![Figure 8. Temperature profile for hydrogen chloride BSGU at 900 L/min](image)

**Ammonia**

Figure 9 shows the model predictions together with the experimental data measured at the BSGU surface for ammonia at 100, 250 and 500 L/min. The model predictions were generally in very good agreement with the data and the average deviations between the calculated and the measured values were \(\pm0.4^\circ\text{C}\) throughout the course of the experiments.

![Figure 9. Model predictions and experimental data measured on the BSGU surface below the liquid level line for ammonia](image)

The predicted temperature profile at 5 nodal points for 500 L/min is illustrated in Figure 10. The calculations were made until there was no more pressure inside the tonner to provide flow.

![Figure 10. Temperature profile for ammonia BSGU at 500 L/min](image)

These predictions show that running only for 90 minutes may cool the center temperature to below \(-200^\circ\text{C}\). These results may suggest the formation of ammonia ice (freezing point of ammonia \(-77.7^\circ\text{C}\)) assuming the mixing process does not effect the temperature gradients. However, the fact that the measured and the calculated pressures agree for all flow rates indicates that the effect of mixing is negligible.
Conclusions:
Water is differently distributed between the liquid and the vapor phase for each gas. Both hydrogen chloride and ammonia are gases in which water is very soluble, yet they have dramatically different flow rate dependence of moisture. The hydrogen chloride moisture level was not a strong function of flow rate. The performance of Matheson Tri-gas' Nanochem series purifier was consistent for all flow rates tested at both low and high pressures. At high moisture the average moisture obtained downstream of the purifier was reduced significantly for low and high-pressure purification.

The ammonia moisture concentration increased with flow rate reached a maximum then declined at higher flow rates. Further studies are under development in order to explain this behavior with the combined effects of thermodynamics, fluid dynamics and heat transfer. A cylinder is being built to observe the boiling mechanism and model the boiling regimes of ammonia as a function of flow rate. Matheson Tri-gas' Nanochem series purifier reduced the moisture to a level that would not be detrimental to stainless steel [4]. The purification of the gas lowered the moisture level to below the FTIR detection limit at all flow rates tested, with high moisture challenges.

An integrated approach combining experimental and modeling techniques was presented to characterize the thermal and physical properties of a bulk delivery system. The heat transfer model showed good agreement with the experimental data for both hydrogen chloride and ammonia at all flow rates. The mixing effects due to temperature gradients and evaporative boiling were not taken in to consideration but this model allows us to predict the average pressure inside the BSGU and the efficiency of heat transfer for various methods.

Acknowledgements:
We would like to thank to Scott Thompson and Sean Williamson from the La Porte branch of Matheson Tri-gas and to Joe Giagnacova and his group from the Montgomeryville branch of Matheson Tri-gas for their assistance in building the distribution systems used in this study.

We also would like to acknowledge Ehrich Diede of Diede Precision Welding, Inc. for welding and assembly of the distribution manifolds.

References:

