



Water Vapor and Carbon Nanotubes

Published technical papers on carbon nanotube fabrication point out the need to improve the growth rate and uniformity of Carbon Nanotubes. CNT faces major hurdles in its transfer from research to production. For repeatable and reliable CNT fabrication, tools are needed to control whether CNT are single or multi-wall, straight or bent, long or short, and clean or dirty. Water vapor addition to the process turns out to be the main control knob for all of these processes. Precise delivery of water vapor will determine what the CNT looks like, what the yield is, and how contaminant free the structure is. Water vapor is both the gas pedal and the steering wheel for CNT fabrication.

Water vapor controls:

- Length of CNT
- Structure of CNT
 - Branching
 - Single or Multi-wall
- Contamination of metals and amorphous carbon
- Continuity of tube wall
- Post CVD cleaning

Length

Water vapor is used to control the growth of CNT and remove contamination post growth. The formation of the carbon nanotube takes place at the catalyst site as the carbon is incorporated into the structure. However not all the carbon is used and some deposits as amorphous carbon and chokes off the reaction at the catalyst site. By adding a small amount of water vapor, the catalyst is kept free of debris and able to continue convert the carbon source in the CNT structures.

A small amount of water vapor introduced into the reaction chamber can combust the amorphous carbon, converting it into CO₂ which can then be purged from the chamber. Removal of the amorphous carbon allows the reaction to continue, leading to the longest CNT ever grown as report recently by the University of Cincinnati in *Small Times Magazine*. (1)

Structure of CNT

The ability of CNT to branch or turn has been attributed to catalyst particles contacting the assembly end of the CNT far from the CNT substrate. These particles can be removed by the addition of water vapor. In addition, water vapor was shown to change the growth structure from multi-walled to single wall. Metallic species are the sites for bends and branches of CNT. Addition of water vapor can react with metallic species to volatilize and remove them, which stops branching and bending. (2)



Contamination of metals and amorphous carbon

High resolution TEM (transmission electron microscope) has shown that single-walled nanotubes grown with water vapor are clean and free from amorphous carbon and metal particles. (3)

Continuity of tube wall

While small additions of water speed up the assembly process by keeping the catalyst site free, adding more water leads to breaks in the CNT walls. This leads to more perforations in the tubular structure, which is beneficial for applications such as hydrogen adsorption. Further addition ceases the process. Water vapor can be used to either perforate the CNT or stop further growth. (4)

Post CVD Cleaning

Once the tubes have been constructed, remaining amorphous carbon and metallic contaminants need to be removed by weak oxidizers. Standard processes using O₂, non-specifically attack the entire structure leading to CNT degradation. Generic semiconductor approaches such as SC1/SC2 cleaning or use of halogenated gases leads to non-specific degradation of the CNT. These and other aggressive wet cleaning technologies lead to large chemical usage and waste stream generation. The use of water vapor at temperatures above 200°C attacks only the amorphous carbon debris and metallic contaminants, so that they can be removed as CO₂ or easily washed away with water in an additional step. (5)

The RainMaker Humidifier System

The key to RASIRC technology is the precise delivery of water vapor that is free of dissolved gases including oxygen. This unique membrane technology allows the RainMaker Humidification System (RHS) to deliver water vapor into both atmospheric and vacuum process. No other technique can take industrial grade DI water and convert it directly in a single pass to the ultrapure degassed water vapor needed for CNT fabrication.

The **RainMaker** Humidifier uses a non-porous membrane to provide a barrier between the liquid source and the carrier gas to be humidified. The liquid source rapidly permeates across the membrane, while the carrier gas is excluded. This flow stops once the carrier gas has been fully saturated. Because the membrane has a known transfer rate based on pressure and temperature, **RainMaker** can be used as a flow control and gas delivery device.

A non-porous hydrophilic membrane within the RainMaker Humidification System purifies the steam, selectively allowing water vapor to pass. Selectivity is significant with up to 1,000,000 xs relative to nitrogen molecules. In the vapor phase, the membrane selectively passes water molecules. All other molecules are greatly restricted, so contaminants in water such as dissolved gases, ions, TOCs, urea, particles, viruses, bacteria, pyrons, and metals can be removed in the steam phase.

Molecular oxygen is the bad guy that stops all the good things water can do. If any molecular oxygen is in water, the oxygen will attack the amorphous carbon, the carbon matrix of the CNT and also the catalyst, so oxygen-free water vapor is important. RASIRC technology is the only

water purification that can separate oxygen from water vapor and deliver ultrapure steam under precise control to the process.

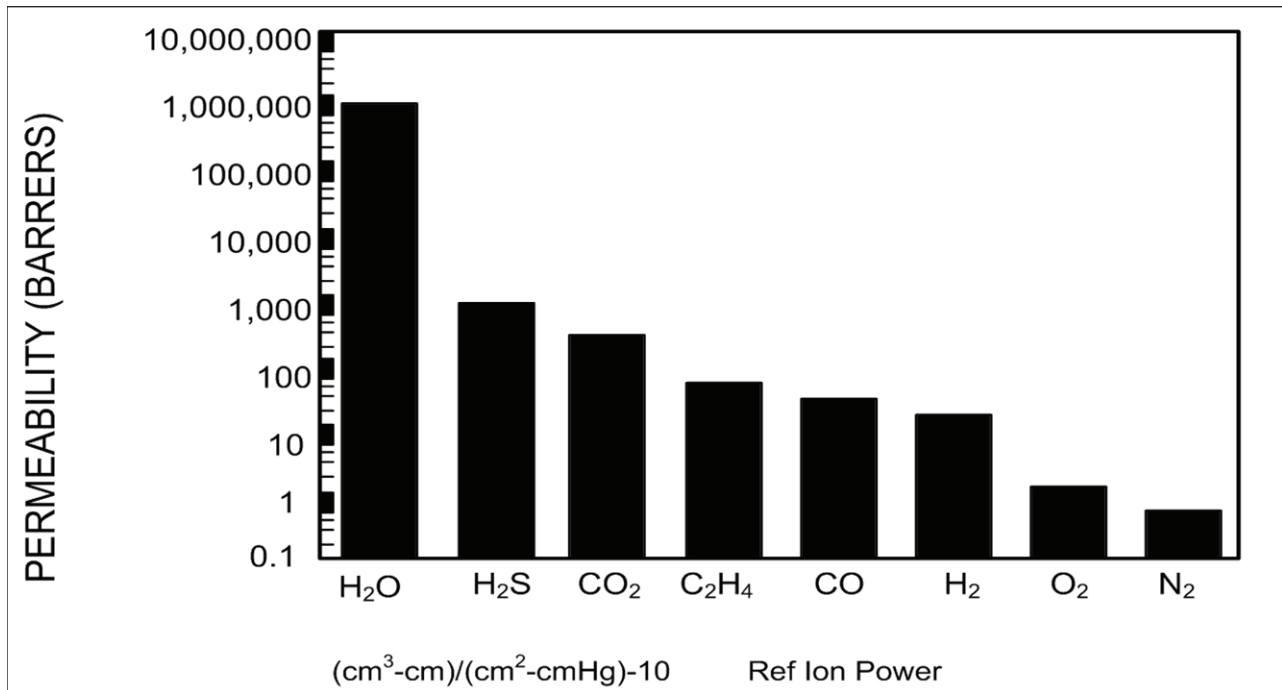


Figure 1: Permeability of the nonporous hydrophilic membrane used in RASIRC humidification technology.

The permeability of the nonporous hydrophilic membrane used in RASIRC humidification technology enables a diffusion rate of water to oxygen that is close to one million to one. This implies that in the time it takes one oxygen molecule to cross the membrane, one million water molecules will make the same traverse. Oxygen readily dissolves into water at the 5 to 10 parts per million level (ppm); the use of a RainMaker Humidification System will reduce this value to parts per trillion (ppt) levels.

The RainMaker Humidification System is the first closed loop humidifier to purify the water before it enters the gas stream. The nonporous membrane limits transfer of dissolved gases, particles, hydrocarbons, and ionic contaminants into the gas being humidified. While testing for 67 different metals with sensitivity levels to less than 1 ppt, 20 parts per billion (ppb) of total metals were found in the water supply. The humidified gas stream was also tested and shown to have less than 5 ppb, a reduction of 75% for metals.

Vaporizer Test for Trace Metals

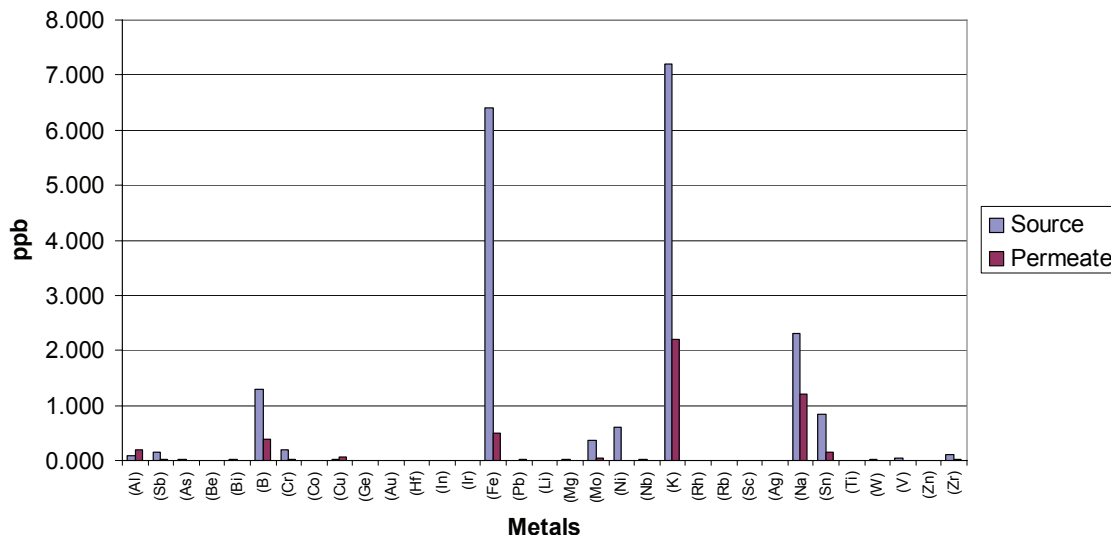


Figure 2: Results of metal transfer testing.

Flow Control Range

Published values for CNT imply that the amount of water vapor required in the process ranges from 0.1% to 4% depending on whether the water vapor is used to control growth or in the post process of the CNT. For process flow rates of 1 slm this implies the addition of water vapor ranges from 1 sccm to 40 sccm. Water is often added by exposing vessels containing water to bleed into the process chamber with the actual quantity of water delivered being unknown.

The RainMaker Humidification System allows tight repeatable control of low flow rates. The graph below illustrates the wide range of delivery rates possible with the RHS. For low flow below 10 sccm, we recommend using a 10 to 50 sccm flow controller for a wide stable delivery rate. For higher flow rates, flow up to 1000 sccm can be used in the same unit.

Water Vapor Flow Rate as Function of Carrier Gas Flow Rate

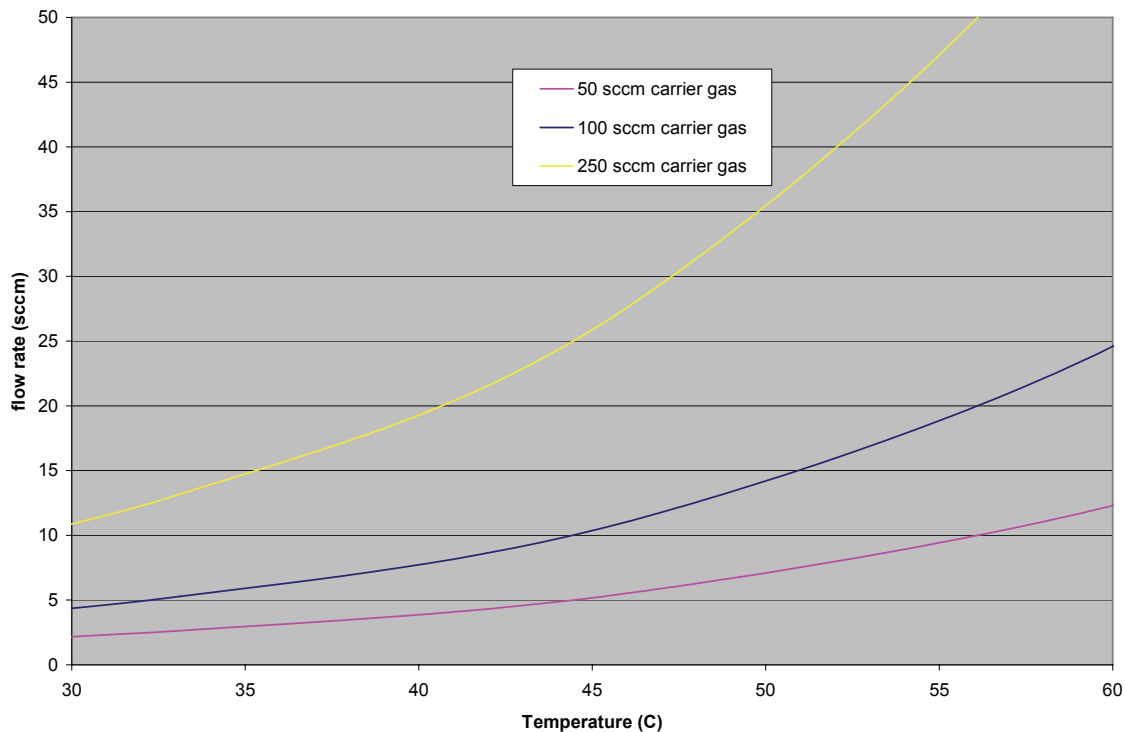


Figure 3: With the RHS, you can add a lot of water relative to flow rate and control water vapor for a specific flow rate by adjusting temperature.

The RHS can deliver from 2 sccm to 500 sccm with the same mass flow controller. By using a 500 sccm full scale carrier gas mass flow controller and controlling the flow from 50 to 500 sccm, the RHS has the ability to load from 2% to 100% of carrier gas flow.

Water Vapor Flow Rate as Function of Carrier Gas Flow Rate

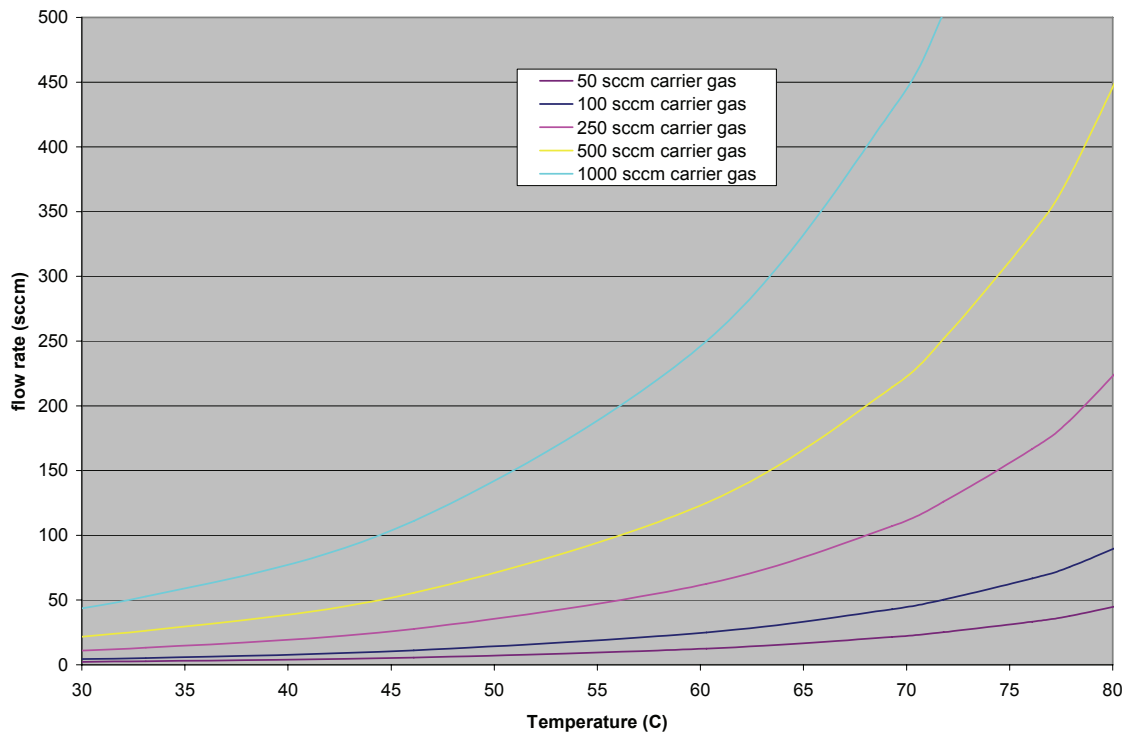


Figure 4: The RHS can deliver from 2 sccm to 500 sccm with the same mass flow controller and load from 2% to 100% of carrier gas flow.

Conclusion

Carbon Nanotube fabrication requires tight control of water vapor addition. The water vapor can affect all aspects of the final product including length, shape, and purity. The RainMaker Humidification System can precisely control the amount of water vapor added to the process for CNT assembly and post-assembly cleaning. The unique technology not only has the ability to control the wide range of water vapor flows, but can remove molecular oxygen and other contaminants from the water supply, so the process is repeatable and stable.

RASIRC focuses on cutting-edge applications where the ability to deliver ultrapure steam is critical to film performance. RASIRC product lines, including the RASIRC Steamer direct water vapor delivery system and the RainMaker Humidification System, are designed to provide ultrapure water vapor precisely to critical processes. These safe and low cost techniques are appropriate for applications that include CNT, photovoltaic cells, MEMS, and semiconductor.



References

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