Drying Technology: Microporous vs. Nafion

Materials that are microporous have been used for drying for many years; some examples are molecular sieves and films such as Gortex®. These materials work by selectively removing water from other gases (usually air) based purely on the physical size of the molecule.

Using air as an example, water molecules are much smaller than nitrogen or oxygen molecules. When air is exposed to a material containing very small pores, water vapor penetrates the pores much more rapidly than nitrogen or oxygen. Consequently most of the water vapor enters the pores while a much smaller percentage (but not negligible) of the nitrogen and oxygen enter the pores. If the material is a solid chunk, such as a molecular sieve used as a desiccant, the pores will eventually fill, and the water must be removed before the material can be used again for drying. This is done by heating the material (for example placing it in an oven), or by reducing the pressure of the air surrounding the molecular sieve.

Molecular Sieve Drying

Often molecular sieves are treated as a disposable item. Our DM-Series dryers use molecular sieve surrounding our Nafion tubing to absorb water after it permeates through our tubing. Once the molecular sieve has absorbed its fill of water, it can be removed and regenerated or simply replaced.

It is possible of construct drying devices using molecular sieves that can operate continuously. This is done by providing two chambers of molecular sieve desiccant, and switching operation from one while the other is regenerated. If the molecular sieve is regenerated by heating it, the device is described as a “temperature-swing” dryer. These are usually very large devices with very high flow capacity. If the molecular sieve is regenerated by reducing the pressure surrounding it, the device is described as a “pressure-swing” dryer or “heatless” dryer. These can be made in smaller sizes. Perma Pure offers what we believe is the smallest one of these in the industry. When confronted with an application requiring air to be dried at modest flow rates (up to 60 liters per minute with our smaller model, and up to 100 liters per minutes with our larger model), our heatless dryer is an excellent solution as long as the air is available at a pressure of 60-100 psi (4-7 bar).

Microporous Hydrophobic Filters

It is also possible to construct drying devices using microporous plastic. Sometimes this is done with a sheet of the material; hydrophobic filters are examples. These filters will let gases of all types through, but the pores are too small for liquids to pass. “Knockout” filters are an example of this type of filter used in our industry. They can protect an analyzer from damage due to liquid water. They serve the same function as a coalescing filter, but are sometimes more complete in removal while giving lower pressure drop. Perma Pure offers a small hydrophobic filter for medical use only in combination with our Nafion dryers.

Microporous Tubing Dryers

If the microporous plastic is formed into tubing instead of a sheet, it is possible to remove water vapor from gases (usually air). The pores in the tubing wall are smaller, and function like the pores in the molecular sieve mentioned above. The dryer functions by supplying a total pressure differential between one side of the tubing and the other. Either the sample is supplied to the inside of the tubing at an elevated pressure, or a partial vacuum is applied to the outside of the tubing. Because of the pressure difference, small molecules such as water vapor are forced through the pores in the tubing wall. Larger molecules such as nitrogen or oxygen move slowly through the pores, while water moves quickly. Consequently most of the water is removed while a small percentage of the other gases is removed. When drying air, it is worth it to lose a bit of the oxygen and nitrogen in order to get rid of most of the water. Perma Pure does not offer any products based on this principle.

Nafion Dryers

Nafion tubing dries using an entirely different principle than microiporous materials. Nafion has no small pores, and it does not remove gases based on their molecular size. Instead Nafion removes gases based on their chemical affinity for sulfuric acid. Nafion is basically Teflon® with sulfuric (sulfonic) acid groups interspersed within it. Sulfuric acid has a very high affinity for water, so it absorbs water into the Nafion. Once absorbed into the wall of the Nafion tubing, the water permeates from one sulfonic group to another until it reaches the outside wall of the tubing, where it perevaporates into the surrounding gas (air or other gas).

The driving force here is that water vapor pressure gradient, not total pressure. It is not necessary to supply the sample under pressure or to supply a vacuum to the outside of the tubing in order for Nafion to function as a dryer. In fact, Nafion can dry gases even when they are at lower pressure than their surroundings. The only issue is whether it is wetter inside or outside. If the gases inside Nafion tubing contain more water (have a higher water vapor pressure) than the gases outside, the water vapor will move out. If the gases outside contain more water, water vapor will move in (acting as a humidifier rather than as a dryer).

More generally, any gas that associates strongly with sulfuric acid will permeate through Nafion based on this chemical affinity. Gases that are basic in character (as opposed to acidic in character) associate strongly with sulfuric acid (acids react strongly with bases). Fortunately for us, most bases are solids at the temperatures of interest to us. Bases usually have an hydroxyl group (-OH) as part of their molecular composition. Water (H-OH), organic bases called alcohols (general formula R-OH), and ammonia (when water is present ammonia forms ammonium hydroxide by the reaction $NH_3 + H_2O = NH_4\text{-}OH$) are the main gases that are basic in character and consequently permeate through Nafion. Most of the gases of interest for environmental or process control monitoring are oxides as products of some combustion process. These oxides do not permeate through Nafion, or at least extremely slowly. For example, oxygen (O_2), ozone (O3), carbon monoxide (CO), carbon dioxide (CO2), nitrogen oxides (NOx), and sulfur oxides (Sox) do not permeate through Nafion tubing. Consequently, dryers constructed from Nafion tubing can be used to remove water from gas streams while losing only negligible amounts of any of these compounds. Perma Pure is the sole supplier of Nafion tubing and Nafion gas dryers to the world.

Ionic Pores in Nafion

Nafion is really composed of two chemical groups of quite different chemical character. Most of the material is tetrafluoroethylene, the same compound that forms Teflon. This material is ver corrosion resistant and chemically inert. It is hydrophobic (reject water) and non-polar. Its bonds are covalent rather than ionic in character. It has a crystalline polymer structure.

In Nafion, interspersed throughout this Teflon matrix are sulfonic acid groups. These are hydrophilic (are drawn to water), polar, and ionic in character. Chemicals that are hydrophilic, covalent (literally, they are oil and water). Consequently, the sulfonic acid groups in Nafion associate with each other within the Nafion. They form long ionic chains extending through the Teflon surrounding matrix. These ionic chains often extend from the external surface of the inside wall of Nafion tubing to the outside wall. When water strikes the sulfonic acid at the inside surface, it binds to the sulfonic acid there, then moves to the adjoining sulfonic acid down inside the tubing. This process continues until the water reaches the sulfonic acid group at the outside wall where it is released to the surrounding gas (as long as there is still more water inside than outside). This is the way that water molecules move through Nafion. The process is a First-Order kinetic reaction, and proceeds very quickly, so Nafion dries gases very quickly.

Because the sulfonic acid groups are thoroughly embedded within a surrounding Teflon matrix, they are not exposed to chemical agents that might break them away from the matrix. Consequently Nafion is extremely resistant to chemical corrosion.

These chains of sulfonic acid groups leading through the Nafion tubing walls are sometimes called ionic pores. Unlike molecular sieves and microporous tubing, there is no physical hole. There is instead a region of ionic groups embedded within the Teflon matrix. This type of material is quite unusual and is more properly called an ionomer rather than a polymer. Nafion is the primary example. These ionic channels are about 11 angstroms in cross-section (they can be very long and branching. “Pore size” regarding Nafion refers to this dimension.