

Understanding The Effects of Air Exposure

All vacuum systems are subject to the buildup of water vapor on surfaces during air exposure. It's now possible to quantify and compare the amount of water buildup under varying conditions of exposure.

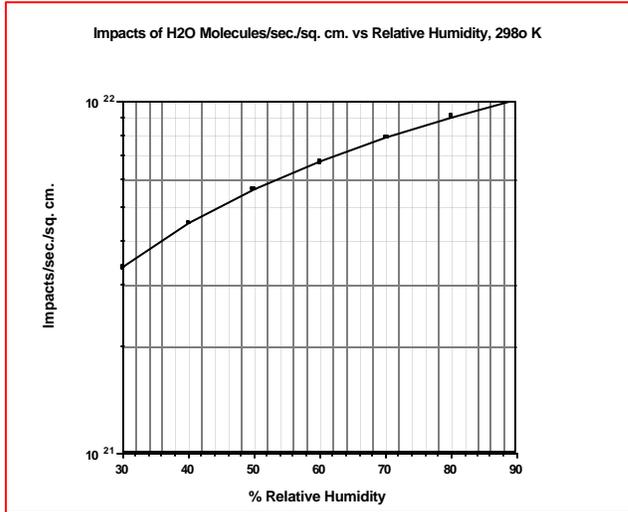
Every high vacuum practitioner has had to fight the battle of the drydown zone where the water vapor molecules are slowly desorbing from the system's internal surfaces and totally dominating the makeup of the system's residual gases. As the system slowly claws its way through the gradually decreasing desorption rate, the question always arises as to when the pressure will finally reach the level required by the process specifications. There is no fixed answer to this question because the amount of water desorbing from the internal surfaces will vary under a constantly changing set of parameters that are often beyond the practitioner's control. So, what do we really know?

We know these two things: the longer the chamber is exposed to ambient air, the slower the pumpdown will be, and the more humidity is present in the ambient air, the slower the pumpdown will be. These two observations lead us to the conclusion that the decay in pumpdown performance is not totally traceable to either time of exposure or of humidity. In fact, it's traceable to the number of impacts of water vapor molecules with the chamber's internal surfaces. A long exposure to fairly dry air can result in the same number of impacts as a short exposure to fairly humid air. A larger number of impacts means more water adsorbed, and the more water adsorbed means more time to desorb it. If we can gain a better understanding of the adsorption and desorption dynamics, we can use that understanding to maximize system performance.

Adsorption Dynamics

When a vacuum chamber is opened to ambient air, the exposed surfaces will be constantly bombarded by the various gas molecules making up the gas mixture. The number of water vapor molecules that make up a percentage of the impacting gas molecules will depend upon the relative humidity (rh). A percentage of the water molecules that impact the surface will form weak water-to-surface bonds. Since all of the molecules are in constant thermal motion, any water molecules that are depleted by bonding, are immediately replaced by the continual mixing process within the gas. This means that the percentage of water

molecules impacting the surface will remain constant as long as the humidity and temperature are constant.



The number of impacts of humidity-borne water vapor molecules on a surface provides a first step basis for understanding the buildup of water vapor during air exposure, but requires the addition of sticking coefficients to complete the picture.

Knowing the rate of impact can be useful in terms of assessing the effects of exposure to varying times and humidity in terms of subsequent pumpdown performance. It won't, however, get you any further than differences in terms of a "little" or a "lot." Since every molecule that strikes a surface doesn't stick, we have to go further in attempting to form a more quantitative measure of the effects of water adsorption. The water (H₂O) molecule is composed of an oxygen atom with two hydrogen atoms bonded to it 105° apart. The effect is that the oxygen atom will be negative relative to the hydrogen atoms being positive. This polarity means that the water molecule

will bond to surfaces and to other water molecules in varying configurations and with varying bonding energies.

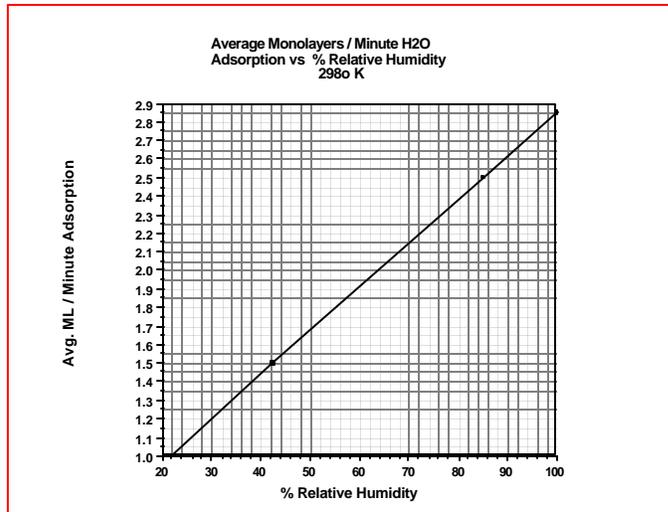
When a water molecule adsorbs onto a metal surface, it will form a bond with an energy of about 23 kcal/mole. The next few layers that form will have an energy slightly less, and further layers will have bond energies of slightly less than 10 kcal/mole. Since strong bonds will form more easily than weaker bonds, we can see that the chances of an impacting molecule adsorbing will be dependent upon the character of the surface it impacts upon. This brings us to the concept of sticking coefficient.

Sticking Coefficient

The term sticking coefficient is used to describe the probability of an impacting molecule sticking, or adsorbing, on a surface. A sticking coefficient of unity (1) means that every impacting molecule will stick. When a vacuum chamber is exposed to ambient air, the water molecules will begin to adsorb onto the surfaces, but the sticking coefficient will be very low.

The first monolayers that adsorb will have the highest sticking coefficient, but it will depend upon the cleanliness of the surface since many processes don't require a total removal of all of the water molecules adsorbed on the surface. As further monolayers form, the sticking coefficient becomes even lower as the

nature of the surface changes and the subsequent bonds become weaker. As the bed of adsorbed water monolayers builds up and becomes more and more disordered, the sticking coefficient becomes lower and lower but highly variable. This becomes even more variable with small temperature variations.



Experimentally determined buildup rate of monolayers of water vapor provide the ability to quantify the amount of water vapor that will require pumping away.

Taken together, the variations in sticking coefficient make it virtually impossible to calculate the amount of adsorbed water molecules based on the calculated number of collisions upon a surface. Although helping our understanding of the adsorption process, the vacuum practitioner still needs a measure of the amount of adsorbed water in order to estimate the effects of the desorbing water on the pumpdown performance of the system. We have to turn to actual measurements.

Measuring Monolayer

Buildup

As a chamber is evacuated from atmospheric pressure, there isn't much desorption of water vapor until the pressure reaches about 20 torr. Although this pressure is within the volume zone where volume gas predominates, substantial water vapor desorption starts to occur.

If the water partial pressure is measured as the total pressure falls through the volume zone, into, and through the drydown zone where water vapor predominates, we can form a water vapor pumpdown curve. Knowing the system's pumping speed for water vapor and the total surface area, we can calculate the total amount of water vapor that's been desorbed in terms of monolayers/cm².

When enough data has been assembled from repeated pumpdown curves at both varying exposure times and rh exposure, it becomes possible to graph average monolayer adsorption rates at various rh conditions. The rate of formation times the total exposure time will easily yield the total number of monolayers of water vapor to be desorbed during the subsequent pumpdown.

There are some limitations to the accuracy and precision to be accepted. We already know that the rate of formation for very short and very long exposures will be susceptible to inaccuracy. Slight changes in temperature will also have an

effect on the adsorption rate. The inaccuracies encountered with this method, though, don't interfere with its use as a practical measure for estimating the amount of water vapor adsorbed under varying conditions. The day-to-day variations in pumpdown performance can be monitored in terms of water desorption variations.

If a log book is kept of pumpdown curves, comparison of suspicious curves with a "standard" curve can often be interpreted in light of variations of water vapor buildup as part of a troubleshooting process. Additionally, pumpdown curves calculated from the adsorption data will usually yield pressure vs. time performance points within a few minutes, and this variation easily falls within the scatter due to pressure reading error envelope.

The number of monolayers of water vapor sorbed on a system's surfaces is a useful measure of relative performance, but it is only half of the story. It's the starting point for a pumpdown, but that pumpdown will depend upon desorption rates. The second half of the story will be covered in the next column in the June issue.

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