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By Phil Danielson

From THE VACUUM LAB

Pumpdown Effects of Water Vapor Buildup

The pumpdown performance in traversing the drydown zone can be quantified by calculating the monolayers of adsorbed water molecules and determining the subsequent desorption rate graphically.

When a vacuum chamber, following exposure to ambient air, is evacuated, the resultant pressure vs. time curve will show a fairly simple first stage where the pressure drop is a function of chamber volume and pumping speed. This stage is called the volume zone where the non-condensable gas filling the chamber is being removed. As the pressure reaches about 20 torr, water vapor that has been adsorbed on the chamber's internal surfaces begins to slowly desorb, but the residual gas is still dominated by the volume gas filling the chamber. As the pressure drops further to about 10^{-3} torr, the seemingly linear pressure drop declines in rate and seems to hit a wall.

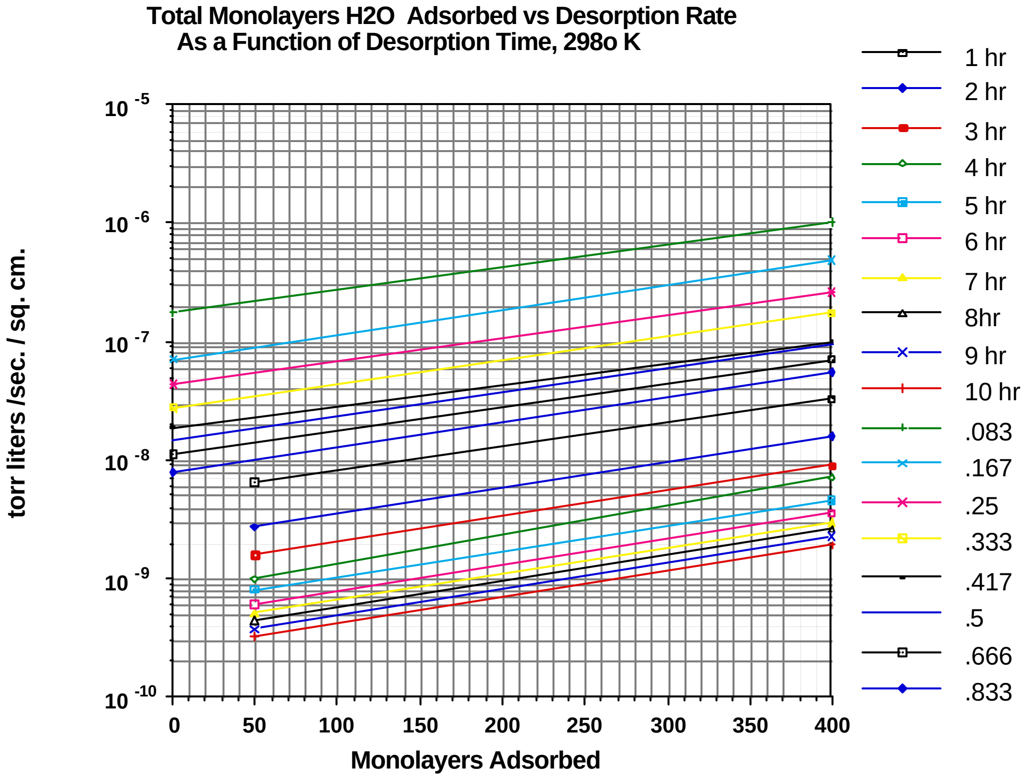
That wall is exemplified by the chamber wall since the residual gas is now dominated by water vapor desorbing from the chamber's internal surfaces. This stage is called the drydown zone, and it's the main source of pumpdown time extension in reaching a high vacuum process pressure specification.

The time spent in traversing the drydown zone is a direct result of the desorption rate of the water molecules adsorbed on the surfaces. This rate, in turn, is a result of the amount of water vapor adsorbed, and the amount adsorbed is a direct function of the conditions of air exposure. The amount of water vapor buildup is proportional to the number of impacts of water molecules on the exposed surfaces, and the number of impacts depends upon the air's relative humidity, the exposure time, and the probability (sticking coefficient) of an impacting molecule being adsorbed. Once the amount of adsorbed water vapor buildup is determined, ("Understanding the Effects of Air Exposure", R&D, April, 2005) the second half of the pumpdown rate puzzle can be examined as we consider desorption.

Desorption Dynamics

As the adsorbed water vapor molecules begin to desorb, the rate is fairly high. The high rate is due, in part, to the fact that these molecules are adsorbed in water-to-water bonds that are relatively weak (10 kcal/mole), and subsequently break easily. This initial bond breaking is not the desorption rate we are considering here. Instead, we are considering the net desorption rate, and that is the rate at which the water molecules are removed from the chamber. The initial desorption from the bed of adsorbed water molecules is only the first step in a long process.

Initial desorption times of microseconds to milliseconds are to be expected, but the desorbing molecule will almost certainly impact another surface instead of entering the pump. The chances, at this point, of the molecule re-adsorbing, are very much lower than unity. This means that even though the molecule will bounce around inside the chamber for an hour or so, there is still a better chance of its being pumped away than of its being re-adsorbed.



The desorption rate of the adsorbed water molecules at various times during a pumpdown can be determined once the total monolayers of adsorbed molecules are known. Each straight line represents a given pumping time and used as an intersection point to read out the desorption rate at that time.

As desorption continues, the rate will fall off as molecules are pumped away and slowly replaced by other desorbing molecules. As the bed of adsorbed molecules erodes by desorption, the exposed monolayers will be reduced to the last few that are adsorbed on The chamber's surfaces. These layers will have much higher bond energies (23 kcal/mole for water-to-metal) and will desorb much more slowly. The sojourn time for a water molecule adsorbed onto metal is about 25 hours at room temperature. As the initial desorption rate falls, there are fewer molecules available for pumping and the net desorption rate falls as well. Additionally, the probability of a molecule re-adsorbing (sticking coefficient) rises and fewer molecules are pumped away.

All this provides the vacuum practitioner with a resultant pressure vs. time pumpdown curve that is dependent upon a number of parameters that are traceable to the amount of water molecules, in terms of adsorbed monolayers, at the time of the onset of pumping and the effective pumping speed.

Pumping Speed Considerations

The effective pumping speed has little effect upon the rate of initial desorption, but it comes into play when we determine the effects on a practical pumpdown in terms of the net desorption rate. The effective pumping speed is a function of the pump's actual speed for water vapor and the conductance losses encountered in the pumping line between the pump and the chamber. Obviously, the higher the effective pumping speed, the higher the rate of removal of desorbing water molecules. There are a number of problems in calculating the effective pumping speed. Water vapor pumping speeds are seldom available from manufacturers of turbo pumps, but they are available for most cryopumps. Additionally, the formulas used for conductance calculations don't take into account water vapor's "stickiness" caused by its desorb-sorb-desorb cycles.

We can, however, work around this to some extent. If we calculate an effective pumping speed for nitrogen, we can establish a pumping parameter in terms of liters/sec. of pumping speed/ cm^2 of surface area. There is a critical pumping speed of 0.01 L/sec./cm^2 that provides a practical limit to work from. Below this limit, the net desorption rate falls off rapidly with decreasing pumping speed, but massive increases are required to affect the net rate. Heroic means such as large cryogenically-cooled panels within the chamber are required.

If we work within the limits of the constraints of the critical pumping speed, we can establish a graphical method of picking off net desorption rates at various points in time during a pumpdown as a function of the monolayers of water molecules adsorbed on the chamber's surfaces following air exposure.

If the pumping speed for water vapor is calculated, we can use the Q=SP relationship to calculate the expected pressure at any point in time. Q (torr L/sec. of desorption rate) = S (L/sec. of pumping speed) X P (torr). An actual pumpdown curve can be modeled by taking enough points to graph a curve.

Conclusions

It's possible to understand the effects of exposure to humid air on the pumpdown performance of a system in terms of adsorption rate during exposure, and then graphically determining the subsequent desorption rate(s).

Effective Pumping Speed Simplified

Calculating the effective pumping speed can be complicated, but a practical method is available that's fairly straightforward. Roughing pumps, operating mostly in viscous flow conditions are the easiest to deal with by using the conductance(C) formula:

C in liters/sec. = F x (avg. pressure in torr x diameter^4/ length)

F= 2,950 for inches or 180 for centimeters

The effective pumping speed is then calculated by this formula:

Effective Speed in liters/sec.= 1/((1/S_p) +(1/C))

where S_p is the rated speed of the pump in liters/sec.

Calculating the effective pumping speed in the molecular flow regime[2] can be a good deal more complicated, but in a well designed system where the connecting tubulation is short, the same diameter as the pump, and the same diameter from chamber to pump, a simple method is to use the following system. This method uses the conductance of the pumping line's entry orifice and the transmission probability of molecules down the line to the pump.

Maximum Orifice Conductance($C_{Orifice}$) in liters/sec.

Gas	l/sec/cm^2	l/sec/in.^{2}
H_2	44.01	283.9
He	31.23	201.4
H_20	14.72	94.9
N_2	11.81	76.1
Air	11.61	76.1
O_2	11.05	71.3
A	9.89	63.8
Xe	5.45	35.2

The conductance of the tube is C (liters/sec) = $C_{orifice}$ x a
Where a (transmission probability) is calculated from the formula:

a = 1/ 1+(L/D) x ((3L/D + 10)/(4L/D) + 10))

where length(L) and diameter(D) cab be in any units as long as they are consistent since a is based on ratios.

Once the conductance of the pumping line is calculated, the same formula for effective pumping speed as shown above can be used.

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