On Predicting Transient Pressure in Vacuum Systems Featuring Getter Materials

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Abstract. Getter materials have been used to reduce pressure or partial pressures in a variety of vacuum applications ranging from vacuum tubes to space flight science instruments. Testing of getter materials has tended to emphasize the capacity of candidate materials to collect specific gas species in sufficient quantities to size them in these applications. When determining a getter material's capacity, it is typically subjected to enough excess target gas to ensure it sorbs as quickly as possible. However, when both the gas source strength and the getter's sorption rate exhibit transient decay behavior, such data is not sufficient to predict the targeted species' partial pressure within a vacuum system as a function of time.

Analytical solutions have been found that describe the transient influence getters have in countering the ill effects of outgassing and leaks in vacuum systems. They elucidate what have been vague intuitions regarding the complexity of interpreting contaminant outgassing rate measurements in a thermal vacuum test or in predicting the evolution of partial pressures in a sealed system.

In addition, development of these analytical solutions has revealed the existence of a characteristic critical target species pressure below which getter material sorption rates deviate from maximum rate behavior obtained in excess environments. Under such conditions, the impact of the getter's influence on species partial pressure becomes more complex. Finally, as a getter approaches saturation in a vacuum environment, system pressure may increase the possibility that it will revert to maximum sorption rate behavior before it reaches capacity.

INTRODUCTION

Getter materials consisting of metal alloys, molecular adsorber coating (MAC) zeolite materials, and organic polymers have been considered or employed in several spaceflight applications to scavenge gases under vacuum [1-5]. Applications include incorporation into a Hubble Space Telescope instrument for reducing the impact of volatile condensable material (VCM) contamination on optical surfaces [2], diminishing VCM contamination of the Perseverance Rover Sample Caching System during its transit to Mars (Fig. 1) [3], and abating total pressure of the Mars InSight Seismic Experiment for Interior Structure (SEIS) instrument [4]. Getter material was incorporated into the SEIS instrument after it breached its evacuated pressure requirement before launch, forcing delay of the InSight mission by 26 months [4].

In addition, MAC is increasingly being used during thermal vacuum testing of NASA science missions to reduce the threat of VCM deposition on sensitive optical and thermal control surfaces [6]. At the same time, these tests make use of high vacuum conditions to take measurements of VCM outgassing using quartz crystal microbalances (QCMs).

Often, the capacity of getter material used in such applications is determined by matching or exceeding an estimate of the amount of a particular target gas species anticipated to be produced in a system by the end of a mission's operational period. Such level of definition is insufficient to answer questions regarding anticipated total pressure, species partial pressure, or molecular flux measurements associated with meeting various mission requirements as a function of time when both molecular source rates and getter effectiveness are diminishing independently from one another. The purpose of this work is to develop expressions needed to describe such fluxes due to outgassing or leaks within an evacuated system in the presence of gettering material. Vessel pressure evolution will depend on whether molecular fluxes incident on the getter surface exceed its maximum rate of sorption, which here will be called the high immersion rate (HIR) limit. This behavior leads to the observation that for a given system there can be a critical pressure defining when the HIR limit has been reached.

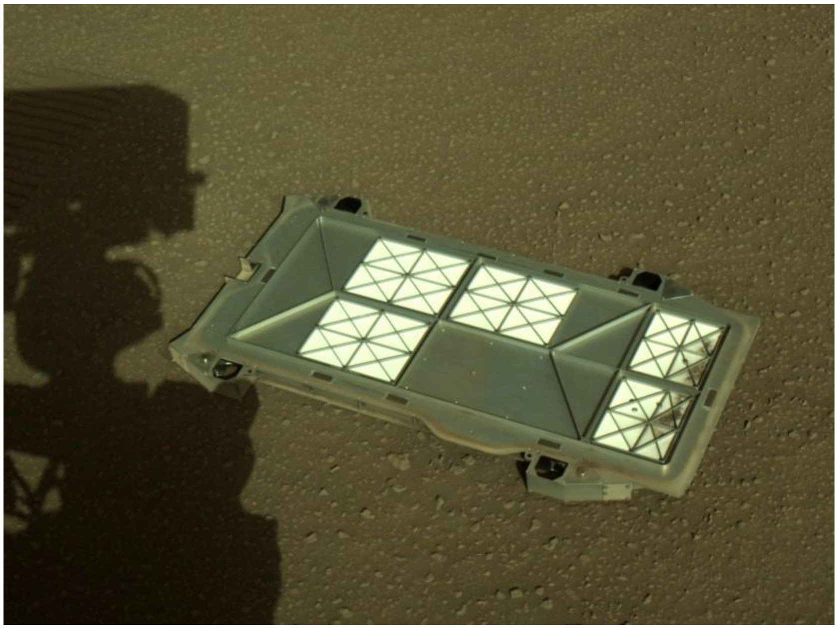

FIGURE 1. Mars Perseverance Rover Belly Pan featuring Tenax® organic polymer material, after release. (NASA/JPL-Caltech)

MODEL DEVELOPMENT

The development described in this work considers high vacuum environments rather than ultrahigh or extremely high vacuum (UHV or XHV) systems of limited complexity. The main difference concerning gettering regards the types of gases to be sorbed. Gettering standard procedures are geared toward measuring effectiveness in removing molecular hydrogen and carbon monoxide, typically in small metallic vacuum chambers that may be heated to at least 150 °C for hours to days [7,8].

In contrast, scientific observation satellites are often relatively larger systems containing a variety of nonmetallic materials such as multilayer insulation (MLI) blankets and painted thermal control surfaces, as well as electronics assemblies, solar array panels, and mechanisms containing adhesives, wiring, potting compounds, and lubricants. These materials and assemblies produce much higher levels of outgassing than metallic surfaces in XHV systems, and generally cannot tolerate temperatures nearly as high as gettering performance conditioning procedures specify. The dominant species outgassed from such sources is water vapor, and usually removal of volatile organic species such as plasticizers are of interest for these satellite missions due to their molecular contamination potential on optical and thermal control surfaces.

For high vacuum systems, model development will tend to consider exposure in evacuated volumes such as for instance thermal vacuum chambers or sealed, evacuated vessels, with the goal of describing spatially-averaged species pressure evolution in the presence of outgassing sources, mechanical or cryogenic pumping, and a relevant getter material also sorbing those gases. It is assumed the Hertz-Knudsen equation describes the mass flux $\dot{\phi}$ incident on a surface associated with species pressure p at temperature T for VCM contamination environments [9]:

$$\dot{\phi} = \frac{p}{\sqrt{2\pi RT}} . \tag{1}$$

Mass Conservation Statement

The net rate of mass accumulation for a gas species of density ρ within a rigid volume V is given by the rate of generation $\dot{m}_{\text{gen}}$ due to outgassing and leaks minus the rate at which it is pumped at constant rate or sorbed.

$$\frac{d}{dt}\iiint\limits_V \rho\, dV = \dot{m}_{gen} - \dot{m}_{sorb} - \dot{m}_{pump} . \tag{2}$$

For ideal gas behavior under isothermal conditions, Eq. (1) may be recast in terms of gas load throughput Q for pressure p in a spatially-averaged system:

$$V\frac{dp}{dt} = \dot{m}_{gen}RT - \dot{m}_{pump}RT - \dot{m}_{sorb}RT = Q_{gen} - Q_{pump} - Q_{sorb} . \tag{3}$$

Outgassing Sources

Experience indicates it is often acceptable to assume $\dot{m}_{\text{gen}}$ may be described by classical, one-dimensional, diffusion-limited outgassing from a material having exposed area A, containing a trace volatile source substance initially present with uniform concentration c_0 within the parent material and having diffusivity ν. In this case, mass generation follows Fick's Second Law of Diffusion [10,11]. It is assumed the rate of pumping within the chamber is high enough to maintain high-vacuum, free molecule (FM) flow conditions such that the concentration of volatile material c_∞ in the background environment may be neglected or treated as approximately constant at some relatively low value. Let concentration differential $\Delta c \equiv c_0 - c_\infty$ and assume the source material has finite thickness L much thinner than the dimensions associated with A, so $\dot{m}_{\text{gen}}$ becomes [11]

$$\dot{m}_{\text{gen}}\left(\text{classical}\right) = \dot{\phi}A = \Delta c_0 A\sqrt{\frac{\nu}{\pi t}}\left[1 + 2\sum_{n=1}^{\infty}\left(-1\right)^n\left(\exp\left[-\frac{n^2L^2}{\nu t}\right]\right)\right] \approx \Delta c_0 A\sqrt{\frac{\nu}{\pi t}} \tag{4}$$

During thermal vacuum processing and testing, outgassing measurements indicate that the influence of a material's finite thickness typically does not appear, and so in using Eq. (4), the infinite series is ignored, and the classical transient outgassing rate exhibits a power-law decay with exponent η = ½ in the denominator.

Although many materials exhibit classical diffusion-limited outgassing, generally one must contend with data that is best fit empirically with

$$\dot{m}_{gen}\left(\text{non-classical}\right) = \frac{bA}{t^\eta} = \frac{B}{t^\eta} , \tag{5}$$

where b represents a flux magnitude for the material under consideration and $0.5 \leq \eta \leq 1.0$, although this parameter range does not represent hard limits [12]. Of course when η = ½, $b = \Delta c_0\sqrt{\nu/\pi}$. Surface desorption of moisture from a metallic surface often follows an inverse time relationship (η = 1) [13].

For external leaks into an evacuated vessel under high vacuum, mass flow rate $\dot{m}_{leak}$ is essentially constant, governed by a sonic constraint under atmospheric continuum conditions or orifice flow under FM conditions dictated by a characteristic dimension associated with an effective leak area across the vessel wall. In Eq. (5), $\eta = 0$ and $B = \dot{m}_{leak}$.

Pumping

Pumping gas load Q_{pump} is given by the product of vessel pressure p and effective pumping speed S_{eff}. Under FM, equilibrium conditions S_{eff} is constant, given by $A_{p,eff}\sqrt{RT/2\pi}$, where $A_{p,eff}$ represents the installed, effective area of the pump presented to the system being modeled, accounting for its duct network separating it from the vessel.

Sorption

The sorption effectiveness of getter materials is often obtained in a manner to establish how much gas may be collected for a given mass or surface area of material [7,8]. Results are usually displayed in a sort of phase portrait diagram presenting the rate at which gas is sorbed as a function of how much a sample has already collected (Fig. 2).

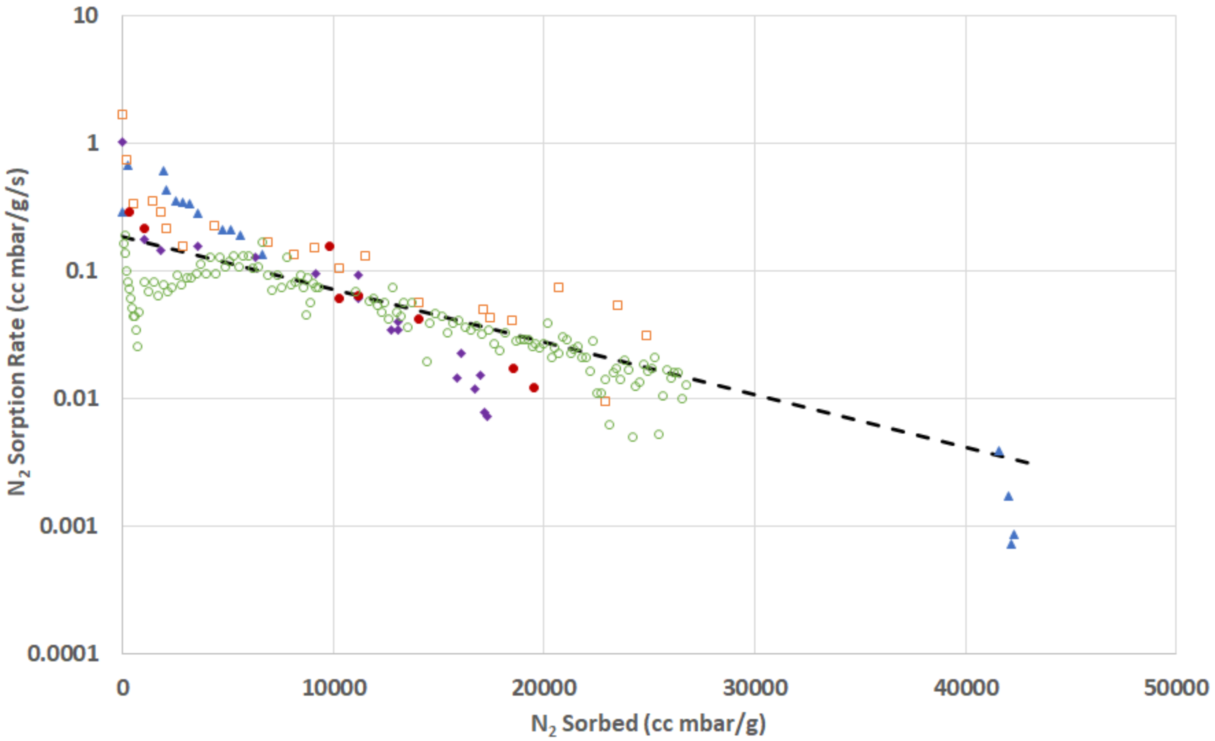

FIGURE 2. Sorption flux data of N_2 vs. quantity sorbed at 1.33 mbar and 300 K for $BaLi_4$ pellet samples, various runs [14].

When the sorption rate is relatively low compared to its initial measurement, it becomes evident the sample's sorption capacity is being approached, and this capacity is what historically has been used to establish the amount of sorbing material needed to counteract the undesirable buildup of unwanted gases in sealed or insufficiently vented spaceflight systems [2,4].

However, when attempting to determine time-dependent variables such as the evolution of pressure in these same systems (see Eq. 3), or how to relate a transient QCM mass flux measurement to payload outgassing in a thermal vacuum chamber in the presence of a sorbing material, the information directly obtained from a phase portrait is insufficient.

When a sorbing sample is placed in a surfeit of test gas, it can only collect at the maximum rate it can achieve given its time history of exposure to that gas. In Ref. 14, the sorption flux performance of samples at 1.33 mbar depicted in Fig. 2 was similar to their exposure 13.3 mbar. In this high immersion rate (HIR) limit, sorption performance is independent of pressure. This data will serve as an example for the development that follows. For the environment depicted in Fig. 2, it appears the limiting behavior follows

$$\frac{Q}{Q_{ref}} = \frac{\dot{m}}{\dot{m}_{ref}} = \exp\left(-\frac{m}{m_{ref}}\right). \tag{6}$$

It may happen that not every sorbing material will exhibit the same relationship, but in this case an exponential fit appears to work reasonably well. Continuing, one may obtain the sample's transient sorption mass buildup in the HIR limit by integrating Eq. 6:

$$m(t) = m_{ref}\ \ln\left(1+\frac{\dot{m}_{ref}\,t}{m_{ref}}\right) = m_{ref}\ \ln\left(1+\frac{t}{t_{ref}}\right). \tag{7}$$

In the HIR limit, the pressure-independent, transient collection rate of sorbed gas within a sample exhibiting the behavior of Fig. 2 becomes

$$Q_{sorb,HIR} = \dot{m}_{HIR}RT = \frac{t_{ref}}{t+t_{ref}}\dot{m}_{ref}\,RT\ . \tag{8}$$

Outgassing and Sorption in HIR Limit

In this case, we imagine getter material is activated in an evacuated vessel under pumping, and then the vessel is sealed. After pumping is terminated, if the getter is operating in its HIR limit, substituting Eqns. 5 & 8 into Eq. 3 produces

$$V\frac{dp}{dt} = \frac{bART}{t^{\eta}} - \frac{t_{ref}}{t+t_{ref}}\dot{m}_{ref}\,RT\ . \tag{9}$$

While under FM flow conditions which will depend on particular details of the evacuated system, straightforward integration yields

$$p(t) = p_0 + \frac{bART}{V(1-\eta)}t^{1-\eta} - \frac{m_{ref}\,RT}{V}\ln\left(1+\frac{t}{t_{ref}}\right) \qquad (\eta \neq 1)\,. \tag{10}$$

It is apparent that the presence of sorbing material operating in the HIR limit reduces the impact of the outgassing or leaking source independent of its magnitude. If enough material is present to diminish partial pressure $p(t)$ under consideration, the assumption of HIR limiting behavior will become violated before $p(t) \to 0$ since gas can only be sorbed based on its impingement rate upon the sorbing surface.

Outgassing, Pumping, and Sorption in HIR Limit

When pumping is included with the previous configuration, Eq. 3 may be written as

$$V\frac{dp}{dt}=\frac{bART}{t^{\eta}}-pA_{p,eff}\sqrt{\frac{RT}{2\pi}}-\frac{t_{ref}}{t+t_{ref}}\dot{m}_{ref}RT\ . \tag{11}$$

In this case, solution involves use of an integrating factor which complicates matters. Let

$$\tau\equiv\frac{V}{A_{p,eff}}\sqrt{\frac{2\pi}{RT}}\quad \&\quad s\equiv\frac{t}{\tau}\ . \tag{12}$$

After some rearrangement, integration reveals

$$p(t)=p_0e^{-s}+\frac{bART}{V}\tau^{1-\eta}\left(e^{-s}\int_0^s\frac{e^s}{s^{\eta}}ds\right)-\frac{m_{ref}RT}{V}e^{-(s+\xi)}\int_{\xi}^{u}e^{e^u}du\qquad(\eta\neq1)\ . \tag{13}$$

The general solution of the parenthetical expression has been described elsewhere [15]. For η = ½ it is given by Dawson's Integral $D(x)$ where $x=\sqrt{s}$. More generally for η, as $t >> \tau$, the expression relaxes to

$$\frac{bART}{V}\tau^{1-\eta}\left(e^{-s}\int_0^s\frac{e^s}{s^{\eta}}ds\right)\to\frac{bART}{S_{eff}t^{\eta}}=\frac{\dot{m}_{gen}RT}{S_{eff}}\quad(s\to\infty)\ . \tag{14}$$

The second integral has the form [15,16]

$$\int_{\xi}^{u}e^{e^u}du=\mathrm{Ei}(-e^{\xi})-\mathrm{Ei}(-e^{u});\quad\text{where}\quad u\equiv\ln\left(\frac{t+t_{ref}}{\tau}\right)\quad\&\quad\xi\equiv\ln\frac{t_{ref}}{\tau}\ . \tag{15}$$

Outgassing, Pumping, and Sorption, Below HIR Limit

When operating below the HIR limit, it is still possible to describe the sorption gas load in a more general sense. Under FM conditions,

$$Q_{sorb}=p(t)A_{sorb}(t)\sqrt{\frac{RT}{2\pi}}\ . \tag{16}$$

For the sorption description connected with Fig. 2 data, let

$$A_{sorb}(t)=A_{sorb,ref}\exp\left(-\frac{m(t)}{m_{ref}}\right);\quad\text{where}\quad m(t)=\int_0^t\dot{m}(t)dt=\int_0^t\frac{Q_{sorb}(t)}{RT}dt\ . \tag{17}$$

The normalization factor $A_{sorb,ref}$ is associated with the minimum pressure $p_{sorb,crit}$, which in turn is related to $\dot{m}_{ref}$ in the HIR limit. Just as the HIR limit is reached from below, this condition may be expressed as

$$\dot{m}_{ref}\sqrt{2\pi RT} = p_{sorb,crit} A_{sorb,ref} \,. \tag{18}$$

The reference area is a parameter associated with a given physical vacuum system configuration, while the critical pressure is a getter property that appears to be independent of that configuration. It also appears that sorptive materials are generally not tested to find this property. Without other information to act upon, perhaps as a first approximation for finding $p_{sorb,crit}$ where gettering behavior switches to the HIR limit, one could assume the material is one hundred percent effective and substitute its projected, exposed area for $A_{sorb,ref}$. Although the development leading to Eq. 18 has been based upon a curve fit to the data of Ref. 14, it should be possible to perform analogous developments for getters that exhibit different phase portrait behavior.

For an evacuated vessel with an outgassing source undergoing pumping and sorption following the data of Ref. 14, Eq. 3 becomes

$$\frac{dp}{dt} = \frac{bART}{Vt^{\eta}} - \frac{p}{\tau}\left[1 + \frac{A_{sorb,ref}}{A_{p,eff}} \exp\left(\frac{-1}{m_{ref}\,RT}\int_0^t Q_{sorb}\left(t\right)dt\right)\right]. \tag{19}$$

The second bracketed term indicates how the presence of a getter modifies the influence of pumping. The loading history integrand is also a function of pressure, so it appears one must resort to numerical quadrature to solve for the pressure in a given system environment.

When a getter is exposed under test to a continuous excess atmosphere of gas, or when sorbing moisture or VCM from a thermal vacuum payload having thick enough material, as residual sorptive capacity diminishes its performance will eventually degenerate to HIR limit behavior as total capacity is reached even if started out operating well below that limit.

CONCLUDING REMARKS

The addition of sorptive materials to evacuated systems requires awareness of which species need removal along with their magnitudes, however phase portrait diagrams do not directly indicate their performance in terms of predicting transient quantities such as partial pressures or surface impingement rates associated with interpretation of molecular contamination measurements.

A framework has been presented for overcoming this omission. By integrating a curve fitted to a particular set of phase portrait plot data obtained in an excess of gas (“HIR limit”), one may estimate the transient performance of a getter in terms of sorbed mass and collection rate. This description may be used to determine spatially-averaged mass transport properties in an evacuated system in the presence of gas sources with or without mechanical pumping or cryopumping.

When operating below the HIR limit, transient sorption behavior becomes dependent on the time history of previously collected gas, which will give rise to different behavior than when collecting in that limit. Sub-HIR limit behavior points to existence of a critical pressure parameter as a getter property that may not have been previously identified. Finally, this development indicates that when a getter is exposed long enough to relevant sources under sub-HIR limit conditions, its ever-diminishing residual capacity will eventually cause it to degenerate to HIR-limiting behavior.

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