

Materials Outgassing Rate Decay in Vacuum at Isothermal Conditions

Alvin Y. Huang*, George N. Kastanas, Leonard Kramer, Carlos E. Soares**, Ronald R. Mikatarian
The Boeing Company, 13100 Space Center Blvd., Houston, TX 77059-3556

** - Jet Propulsion Laboratory, 4800 Oak Grove Dr., Pasadena, CA 91109

ABSTRACT

As a laboratory for scientific research, the International Space Station has been in Low Earth Orbit for nearly 20 years and is expected to be on-orbit for another 10 years. The ISS has been maintaining a relatively pristine contamination environment for science payloads. Materials outgassing induced contamination is currently the dominant source for sensitive surfaces on ISS and modelling the outgassing rate decay over a 20 to 30 year period is challenging. Materials outgassing is described herein as a diffusion-reaction process using ASTM E 1559 rate data. The observation of $-1/2$ (diffusion) or non-integers (reaction limited) as rate decay exponents for common ISS materials indicate classical reaction kinetics is unsatisfactory in modelling materials outgassing. Nonrandomness of reactant concentrations at the interface is the source of this deviation from classical reaction kinetics. A diffusion limited decay was adopted as the result of the correlation of the contaminant layer thicknesses on returned ISS hardware, the existence of high outgassing silicone exhibiting near diffusion limited decay, and the confirmation of non-depleted material after ten years in the Low Earth Orbit.

Keywords: Materials Outgassing, ASTM E 1559, Reaction Kinetics, Diffusion, Space Environments Effects, Contamination

I. INTRODUCTION

Given the size of the International Space Station (i.e., about the size of a football field) and its use as a national laboratory for scientific research, maintaining an induced environment for contamination sensitive external payloads is challenging [1]. Whether it is the solar arrays or one of the International Partners' modules, external payload sites have views to ISS segments and therefore, may be in the field of view for volatile molecules generated by organic materials. If the environmental conditions are right, molecular contaminants may build on surfaces as these volatiles condense. Ultraviolet (UV) darkening or photochemical darkening of contaminant layers on optical or thermal control surfaces then proceeds potentially affecting optical or thermal performance. Spacecraft thermal control coatings utilize materials to achieve a balance between the heat absorbed and the heat emitted. Maintaining that balance to ensure that temperatures are regulated is an important issue for operations. Projections of optical property degradation are required to extend hardware life or procure new hardware. The ISS has been currently operating for approximately 20 years. Thus, the ability to conservatively predict molecular contamination levels and outgassing rate decay over a 20 to 30 year period is crucial.

*alvin.y.yuang@boeing.com; phone 1 281 226-8597; fax 1 281 226-6582

The present work seeks to characterize the materials outgassing, the release of volatiles, in vacuum at isothermal conditions using the ASTM E 1559 test standard. ASTM E 1559 is the standard U.S. test method for characterizing long term materials outgassing rates [2]. The test procedure incorporates a source temperature (the temperature of the outgassing material) and four different receivers (which simulates typical ISS operating temperatures). Although there is widespread use of ASTM E 595 as a screening test for mass loss, one of its main limitations is that the test measures initial and final mass after 24 hours and does not provide the variation of mass loss with time. This study will characterize the release of contaminants based on its surface reaction chemistry and diffusion kinetics. While solving Fick's law with boundary conditions assumptions for outgassing species is a powerful technique, it is often difficult in reality to identify each evolving species that desorb from commercial products or corroborate the initial and boundary conditions. Materials outgassing has been modeled as a first order process. This work seeks to describe the materials outgassing phenomena in vacuum as a diffusion or reaction limited process in heterogeneous media with ASTM E 1559 outgassing rate data. Its rate decay is described herein by a power law. For reaction limited processes, classical reaction kinetics has been shown to be lacking when the reactants are spatially constrained.

II. THEORY

A. Materials Outgassing Modeling

Materials outgassing has been described as a diffusion and desorption process with the surface chemistry playing an important role. Molecules diffuse through the bulk material reaching the surface. Chemistry at the surface or interface is important in dictating whether the molecules desorb from the surface. Liu and Glassford expressed the transient diffusion of molecules through a solid with Fick's second law with boundary conditions assumptions for an infinite slab of thickness l for one dimensional flow in rectangular coordinates:

$$\frac{\partial C}{\partial t} = -D \frac{\partial^2 C}{\partial x^2}, \quad (1)$$

$$\dot{Q} = \frac{4DC_2}{l} \cdot \exp\left[-\left(\frac{D\pi^2}{l^2}\right) \cdot t\right], \quad (2)$$

where C is the concentration of the diffusing species in the medium, D is the temperature dependent diffusion coefficient, C_2 is the initial concentration of the desorbing species, and t is the time [3]. This approach requires identification of each species and knowledge of its diffusion coefficients and initial concentrations. Hughes espoused a simpler thermokinetic approach relating outgassing to classical chemical reaction kinetics:

$$\frac{dw}{dt} = -k \cdot w^n, \quad (3)$$

$$k = A \cdot \exp\left[-\frac{E}{RT}\right], \quad (4)$$

where w is the reacting weight, k is the temperature dependent proportionality constant, n is the reaction order, A is the temperature independent proportionality constant, E is the activation energy, R is the gas constant, and T is the temperature [4]. The French Aerospace Research Centre, National Centre for Space Studies, and European Space Agency have adopted a first order law for each desorbing species which depends on the residence times:

$$\frac{dm}{dt} = -\frac{m}{\tau}, \quad (5)$$

$$\tau = \tau_0 \cdot \exp\left[-\frac{E}{RT}\right], \quad (6)$$

where m is the desorbing mass, and τ is the temperature dependent residence time [5].

Two additional cases of one dimensional diffusion in a medium bounded by two parallel planes are considered besides those mentioned previously. A boundary condition for variable surface concentration is introduced for an infinitely thick sample and a sample with finite dimensions:

$$\dot{Q} = -D \frac{dC}{dx} \Big|_{x=0} = k_{des} [C_o - C_s] \quad (7)$$

where k_{des} is the desorption rate, C_o is the concentration required to maintain equilibrium with the surrounding atmosphere, and C_s is the surface concentration at any time. The desorption rate is the rate of exchange that is directly proportional to the difference between the C_o and C_s , the concentration gradient, at any time. For an infinitely thick sample, two additional boundary conditions are applied:

$$C(t=0, x) = C_2,$$

$$C(t, x = \infty) = C_2,$$

where C_2 is the initial concentration. For a sample with a finite thickness, l , and a cross sectional area, A , the initial concentration condition at $t = 0$ is applied instead of the boundary condition at infinite thickness. Crank shows the desorbing mass solutions for an infinitely thick sample and a sample with finite dimensions, respectively [6]:

$$M = \left(\frac{C_o - C_2}{h} \right) \cdot \left\{ \exp(h^2 \cdot D \cdot t) \cdot (1 - \operatorname{erf}(h\sqrt{D \cdot t})) - 1 + \left(\frac{2}{\sqrt{\pi}} \right) \cdot h\sqrt{D \cdot t} \right\}, \quad (8)$$

$$\frac{M}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{2L^2 \cdot \exp\left(\frac{-\beta_n^2 \cdot D \cdot t}{l^2}\right)}{\beta_n^2 \cdot (\beta_n^2 + L^2 + L)}, \quad (9)$$

where M is diffusing/desorbing mass flux at any time, M_∞ is the diffusing mass after infinite time, dimensionless h is the desorption rate divided by the diffusion coefficient, dimensionless L is the thickness times the desorption rate divided the diffusion coefficient, and β_n are the positive roots of $\beta \cdot \tan(\beta) = L$. Crank points out that the solution demonstrates the following for an infinite source having an uniform initial concentration and constant surface concentration [6]:

- 1) The distance of penetration of any given concentration is proportional to the square root of time.
- 2) Time required for any point to reach a given concentration is proportional to the square of its distance from the surface and varies inversely as the diffusion coefficient.
- 3) The amount of diffusing substance entering the medium through the unit area of its surface varies as the square root of time.

Thus, a square root time dependence is observed for an infinite source. This diffusion limited decay rate has been proposed [7]. The square root of time dependence has also been observed in drug release from inert, solid matrices [8-9]. An exponential time dependence falls out for a sample with finite dimensions. Since the solution for a sample with finite dimensions is a summation of exponentials, each exponential could potentially correspond to a desorption rate and a diffusion coefficient for each diffusing species.

B. Reaction Kinetics

When Hughes developed an approach relating outgassing to chemical reaction kinetics, he suggested that outgassing is primarily a first order reaction [4]. For a first order reaction (i.e., $n = 1$), the reacting weight solution has an exponential dependence on time. The reaction rate constant is dependent on temperature, is independent of time. Classical reaction kinetics has been shown to work quite well in the laboratory and industrial homogeneous reactions. Homogenous reaction involves only one phase. However, classical reaction kinetics has been shown to be lacking for heterogeneous reactions in which the reactants are geometrically constrained. A heterogeneous reaction involves more than one phase

and the reaction typically occurs at or near the interface. Experimental studies and Monte Carlo simulations have shown that the reactant distributions in low dimensional geometries are the source of time dependent reaction rate constant and anomalous reaction orders [10-14]. The studies have investigated an elementary, irreversible bimolecular reaction, $A+B \rightarrow 0$, which would also be applicable in materials outgassing. The appearance of a $t^{-1/2}$ dependence and non-integer reaction orders are indications that classical reaction kinetics is lacking. Diffusion is not an effective mixing or homogenization mechanism in low dimensions, which results in nonrandom reactant concentrations.

III. MATERIALS AND METHODS

Samples of the black 3M™ Dual Lock™ recloseable fastener SJ3441 were procured by the Boeing Company and sent to Outgassing Services International for ASTM E1559 Method B testing. 3M™ describes the SJ3441 as having a plain backing with no adhesive constructed of polypropylene stems with mushroom shaped tops. SJ3441 has 400 stems per square inch and a thickness of 0.160 inches when the strip is mated. A short strip (i.e., three inches long by an inch wide by 0.1 inches thick) was tested at 62°C, 121°C, and 149°C. Each isothermal outgassing test is run for six days or 144 hours. Each sample was typically 1.65 grams and had a sample area of 19.7 cm². Figure 1 shows a schematic of the ASTM E 1559 test setup [3]. Chamber pressures were maintained between 10⁻¹⁰ to 10⁻⁸ torr. The sample is placed in a temperature-controlled effusion cell and outgassing flux leaving the cell orifice impinges on four Quartz Crystal Microbalances (QCMs). One of the QCMs is maintained at 80K to collect essentially all of the impinging species. The vacuum chamber walls surrounding the QCMs and effusion cell are liquid nitrogen cooled to ensure that the molecular flux impinging on the QCMs is due only to the sample in the effusion cell. Applying the sample to QCM view factor (415.02 cm²) and the QCM sensitivity (4.43x10⁻⁹ g/cm²/Hz) for a 10 MHz crystal, the sample outgassing rate can be determined as a function of time from mass deposited at the 80K QCM. A mass spectrometer is inserted into the vacuum chamber to monitor each individual species in the outgassing flux.

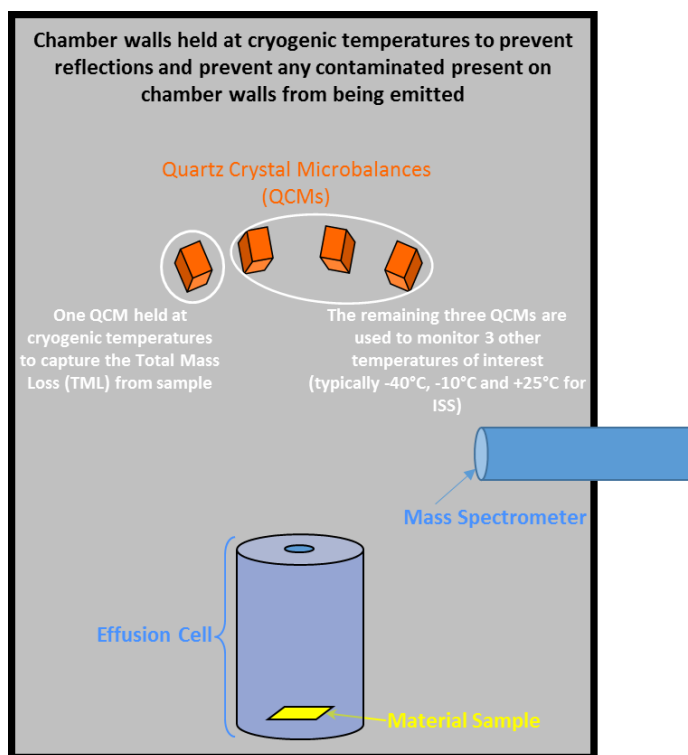


Figure 1. Adapted schematic of the Quartz Crystal Microbalance (QCM) collection measurement method used for ASTM E 1559 [3].

IV. RESULTS AND DISCUSSION

A. Evolution of a Fastener Outgassing Rate

Black 3M™ Dual Lock™ recloseable fastener SJ3441 was tested at 62°C, 121°C, and 149°C for a duration of 144 hours. Figure 2 shows a log-log plot of the measured outgassing rate of Dual Lock SJ3441 as a function of time at three different temperatures (62°C - red, 121°C - green, and 149°C - blue).

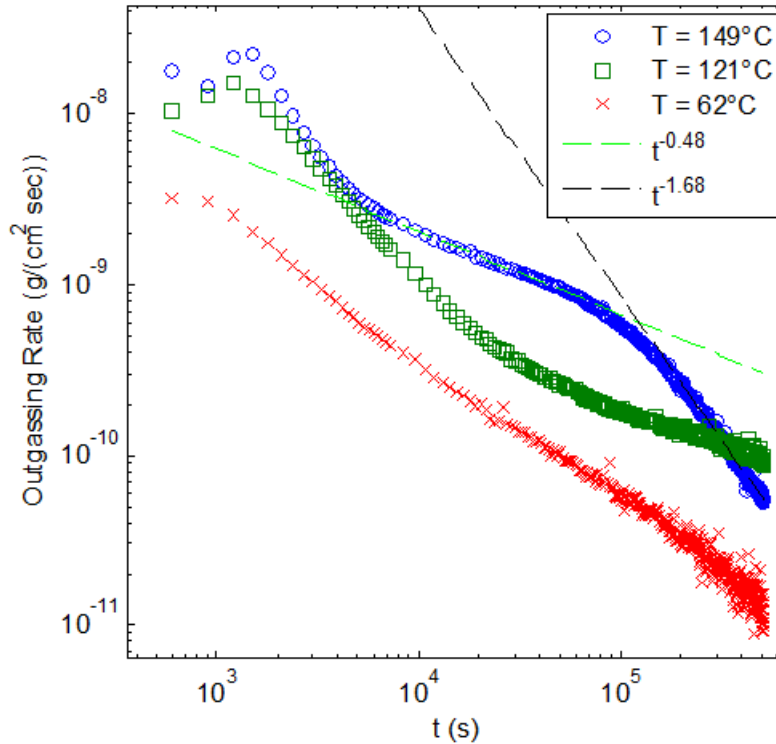


Figure 2. Evolution of Dual Lock™ fastener SJ3441 outgassing rate at three temperatures (62°C, 121°C, and 149°C) as a function of time.

The rates show an expected trend of higher rates at higher temperatures except for the end of the data at 149°C. The decay rate is defined by an exponent from a power law similar to Equation 3. The rate data at 149°C is distinct as it shows square root of time dependence from 5000 to 80000 s and then, a steep drop off in rate at longer times with power law decay exponent of 1.7. There is an inflection point around 24 hours. At the end of 144 hours, the rate at 149°C has dropped below that at 121°C. The fastener initially acts like an infinite source and then, shows a decay similar to a sample with a finite thickness. The 149°C rate crossing below the 121°C rate is an indication that the diffusion front has reach the sample edge and the diffusing species is now being depleted due to the combination of a higher tested temperature and a test duration of 144 hours. Mass loss at the three temperatures as a function of time is also shown in Figure 3. It shows an expected trend of greater mass loss at higher temperatures.

Outgassing Services International detected Irgafos® 168 via the in situ mass spectrometer as the major outgassing flux species for the test at 149°C. Irgafos® 168 is a stabilizer added to prevent oxidation of the polyolefins and olefin copolymers [15]. Irgafos® was also identified as one of major species for the test at 121°C; however, it was not detected at 62°C. Different species may be dominant at different operating temperatures and the concentrations may be time variable boundary conditions. This is an example of one of the complexities faced in materials outgassing.

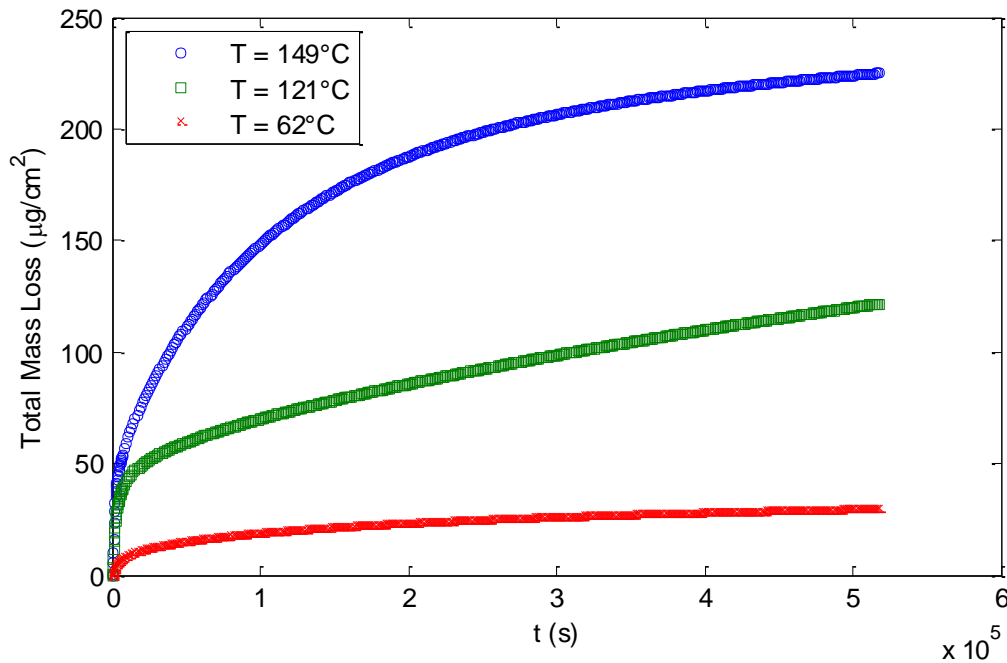


Figure 3. Mass Loss for Dual Lock™ fastener SJ3441 outgassing rate at three temperatures (62°C, 121°C, and 149°C) as a function of time.

B. ASTM E 1559 Outgassing Rates of Common ISS Materials

Outgassing rates of Dual Lock™ SJ3441 are compared with those of some ISS materials in Figure 4. Table 1 shows the power law decay exponents determined from a linear least squares fit to the data at the end of 144 hours (last 54 hours) in Figure 4. The decay in the first 24 hours is typically different than that at the end of test. A majority of the power law decay exponents are near one, but only the Beta cloth at 125°C shows an exponent of one. Thus, ISS materials typically have non-integer power law exponents. In addition, Dual Lock™ SJ3441 at 149°C exhibits an exponent of 0.5 acting like an infinite source for a period of time. These kinetics suggest that ISS materials outgassing in vacuum is mainly a diffusion-reaction process with geometrical constraints occurring at the interface.

The top four materials with the highest outgassing rates are silicones. While silicones has tremendous material properties, they are a significant concern for contamination. The Room Temperature Vulcanization silicone and silicone rubber exhibit high outgassing rates and a slower “infinite source” like decay at the end of the ASTM E 1559 test. Due to these characteristics, the materials are expected to be the drivers for materials outgassing induce contamination over the long term on ISS.

The last two entries in Table 1 compares the decay of a flown and an unflown solar array netting and the corresponding outgassing rates are shown in Figure 5. The netting was flown for a period of ten years on Mir space station and returned as part of the Mir Solar Array Return Experiment on STS-89 mission in January 1998. The flown and unflown netting tested according to ASTM E 1559 test standard. The flown netting shows a slower rate of decay and has not exhibited any signs of depletion even after ten years during the tested duration of 144 hours.

Depth profiles of contamination layers on returned hardware from ISS, the existence of high outgassing silicones exhibiting near diffusion limited decay, and the confirmation of non-depleted material after a long duration in the space environment have led to the assumption of a $t^{1/2}$ decay rate for materials outgassing. Good correlation between this decay

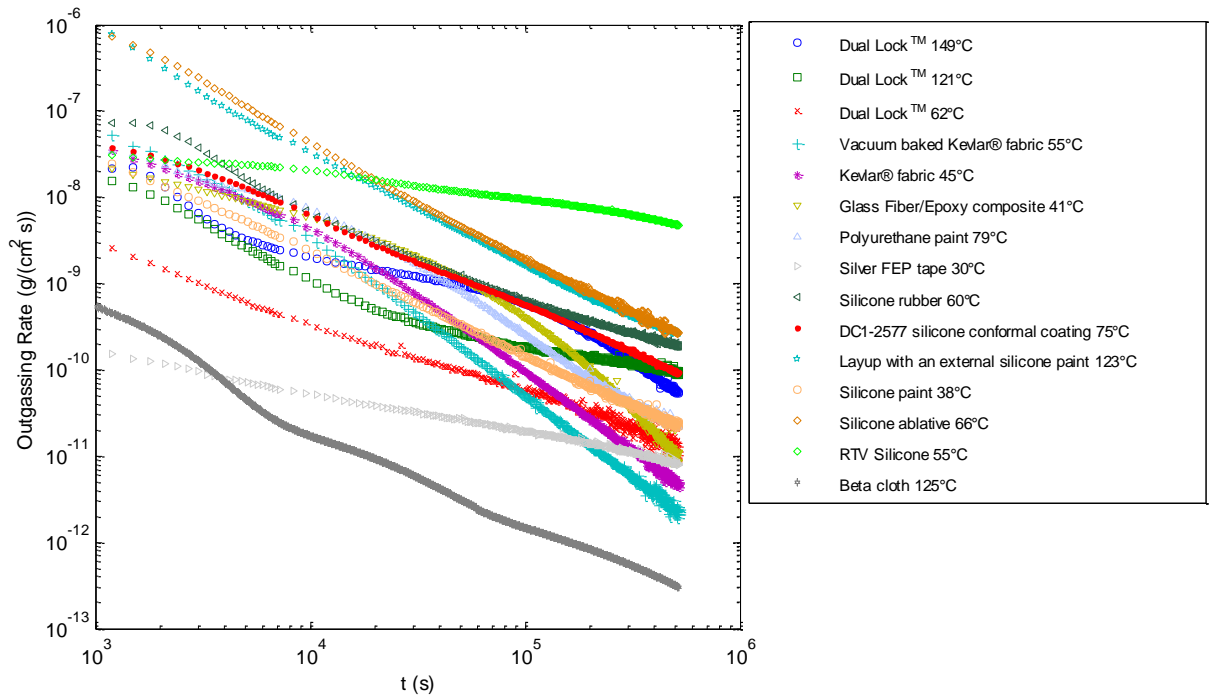


Figure 4. ASTM E 1559 outgassing rates for International Space Station materials.

Table 1. Observed ASTM E 1559 Outgassing Rate Decay for ISS Materials at End of Test.

Sample	Tested Temperature (°C)	Power Law Decay Exponent
Dual Lock™ SJ3441	149	-1.7
Dual Lock™ SJ3441	121	-0.84
Dual Lock™ SJ3441	62	-0.84
Vacuum baked Kevlar® fabric	55	-1.9
Kevlar® fabric	45	-1.9
Glass fiber/epoxy composite	41	-2.7
Polyurethane paint	79	-1.3
Silver FEP tape	30	-0.64
Silicone rubber	60	-0.67
DC1-2577 silicone conformal coating	75	-1.2
Layup with an external silicone paint	123	-1.2
Silicone paint	38	-1.2
Silicone ablative	66	-1.3
RTV silicone	55	-0.56
Beta cloth	125	-1.0
Solar Array Netting	80	-1.1
Flown Solar Array Netting	80	-0.90

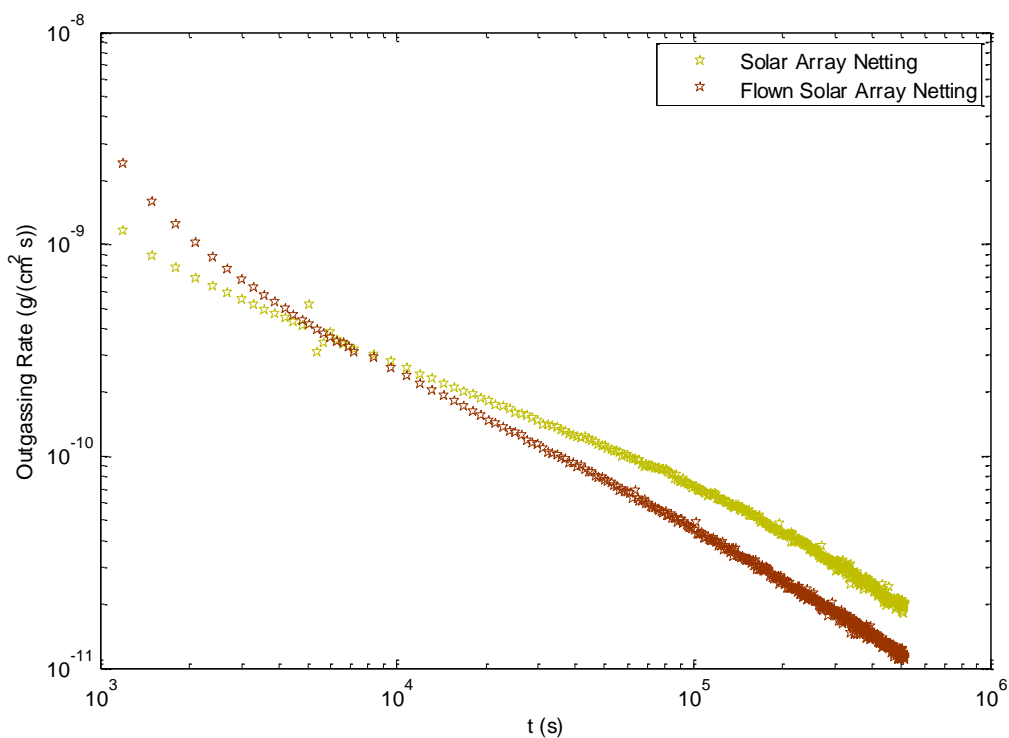


Figure 5. ASTM E 1559 outgassing rates for Flown and Unflown ISS Solar Array Netting.

model and contamination layer measurements from the Japanese Micro-Particle Capturer and Space Environment Exposure Device on the Service Module and the Materials International Space Station Experiment 2 on the United States Airlock were demonstrated over a period of several years [1, 16]. The returned showed that materials outgassing products are the dominant source on ISS with the exception of the areas near the ISS attitude control thrusters. Fuel Oxidizer Reaction Products (FORP) from thruster firings were determined to be the primary source for contamination on the adjacent areas around the attitude control thrusters [17-18].

V. CONCLUSIONS

Material outgassing is considered herein as a diffusion limited process or a reaction limited process with geometric constraints at the interface. The diffusion and release of materials outgassing induced contaminants at isothermal conditions is modeled as a power law decay with the use of ASTM E 1559 data. The power law exponent is related to a diffusion limited decay for an infinitely thick sample or reaction order kinetics at the interface. The appearance of a $t^{-1/2}$ (diffusion limited or “infinite source”) dependence and non-integer reaction orders for common ISS materials indicate that classical kinetics for homogenous reactions is unsatisfactory in describing ISS materials outgassing. Deviation from integer reaction orders originate from the nonrandomness of reactant concentrations in low dimensions. Correlation of contamination layer thicknesses on returned ISS hardware, the existence of high outgassing silicones exhibiting near diffusion limited decay, and the confirmation of non-depleted material after a long duration in the space environment have led to the adoption of a $t^{-1/2}$ decay rate for its materials outgassing.

VI. ACKNOWLEDGEMENTS

The authors gratefully acknowledge Jeff Garrett and Outgassing Services International for conducting the ASTM E 1559 testing and the species identification in the mass spectrometer analysis.

REFERENCES

- [1] Soares, C.E., Mikatarian, R.R., Olsen, R.L., Huang, A.Y., Steagall, C.A., Schmidl, W.D., Wright, B.D., and Koontz, S.L., "External Contamination Control of Attached Payloads on the International Space Station," Proceedings of 12th International Symposium on Materials in the Space Environment, Noordwijk, the Netherlands, September 24-28, 2012, ESA SP-705.
- [2] Garrett, J.W., Glassford, A.P.M., and Steakley, J.M., "ASTM E 1559 Method for Measuring Material Outgassing/Deposition Kinetics," Journal of the Institute of Environmental Sciences and Technology, pp. 19-28, January/February 1995.
- [3] Liu, C.K., and Glassford, A.P.M., "Kinetics data for diffusion of outgassing species from RTV 560 silicone rubber," Journal of Vacuum Science and Technology, 15(5), pp. 1761-1768, September/October 1978.
- [4] Hughes, T.A., "Outgassing of Materials in the Space Environment," Proceedings of the USAF/NASA International Spacecraft Contamination Conference, NASA-CP-2039, AFML-TR-78-190, pp. 13-29, March 1978.
- [5] Roussel, J-F., Faye, D., Van Eesbeek, M., Tondu, T., Migliore, R., Rampini, R., and Paulmier, T., "A New Frontier for Contamination: Reaching the Molecules," Proceedings of 11th International Symposium on Materials in the Space Environment, Aix-en-Provence, France, September 15-18, 2009.
- [6] Crank, J., *The Mathematics of Diffusion* (Oxford Univ. Press, London, 1975), 2nd ed., pp. 28-61.
- [7] Girard, T.J. and Payton, R.M., "A method of conservatively predicting long term outgassing and deposition levels based on diffusion limited outgassing theory," Proc. SPIE 2261, 150 (1994).
- [8] Higuchi, T., "Mechanism of sustained-action medication. Theoretical analysis of rate of release of solid drugs dispersed in solid matrices," Journal of Pharmaceutical Sciences 52, 1145 (1963).
- [9] Flynn, G.L., Yalkowsky, S.H., Roseman, T.J., "Mass Transport Phenomena and Models: Theoretical Concepts," Journal of Pharmaceutical Sciences 63, 479 (1974).
- [10] Kopelman, R., "Fractal Reaction Kinetics," Science 241, 1620 (1988).
- [11] Toussaint D., and Wilczek, F., "Particle-Antiparticle Annihilation in Diffusive Motion," Journal of Chemical Physics 78, 2642 (1983).
- [12] Kang, K., and Redner, S., "Scaling Approach for the Kinetics of Recombination Processes," Physical Review Letters 52, 995 (1984).
- [13] Sancho, J.M., Romero, A.H., Lindenberg, K., Sagues, F., Reigada, R., and Lacasta, A.M., "A + B - 0 Reaction with Different Initial Patterns," Journal of Physical Chemistry 100, 19066 (1996).
- [14] Zhao, X., Yen, A., and Kopelman, R., "Monte Carlo Simulation of Surface Adsorption-Diffusion-Reaction Kinetics," Journal of Physical Chemistry B 52, 995 (1984).
- [15] <https://www.ulprospector.com/en/na/Coatings/Detail/479/216437/Irgafos-168>.
- [16] Steagall, C.A., Smith, K.A., Soares, C.E., and Mikatarian, R.R., "Induced-Contamination Predictions for Micro-Particle Capturer and Space Environment Exposure Device," Journal of Spacecraft and Rockets 46, 39 (2009).
- [17] Schmidl, W., Mikatarian, R., Lam, C., West, B., Buchanan, V., Dee, L., Baker, D., and Koontz, S., "N-Nitrosodimethylamine Release from Fuel Oxidizer reaction Product Contaminated Extravehicular Activity Suits," Journal of Spacecraft and Rockets 43, 557 (2006).
- [18] Alexeenko, A.A., Wadsworth, D.C., Gimelshein, S.F., and Ketsdever, A.D., "Numerical Modeling of ISS Thruster Plume Induced Contamination Environment," Proc. SPIE 5526, 125 (2004).