Jet Propulsion Laboratory
California Institute of Technology

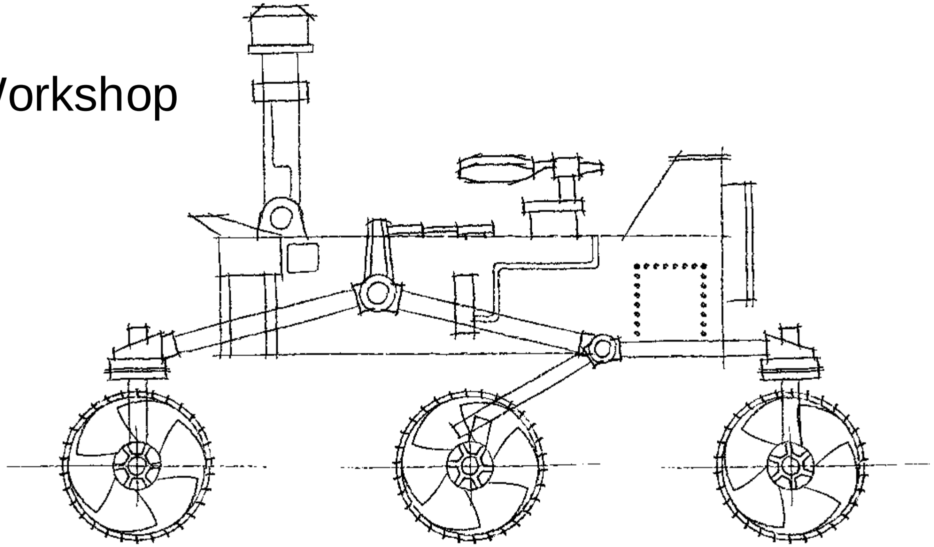
Mars 2020 Return Sample Cleanliness Molecular Transport Model

Ira Katz, Brian K. Blakkolb, Kristina A. Kipp, Mark S. Anderson, John R. Anderson, and Lauren M. White

2017 NASA Contamination, Coatings,
Materials, and Planetary Protection Workshop

NASA GODDARD SPACE FLIGHT CENTER
Greenbelt, Maryland

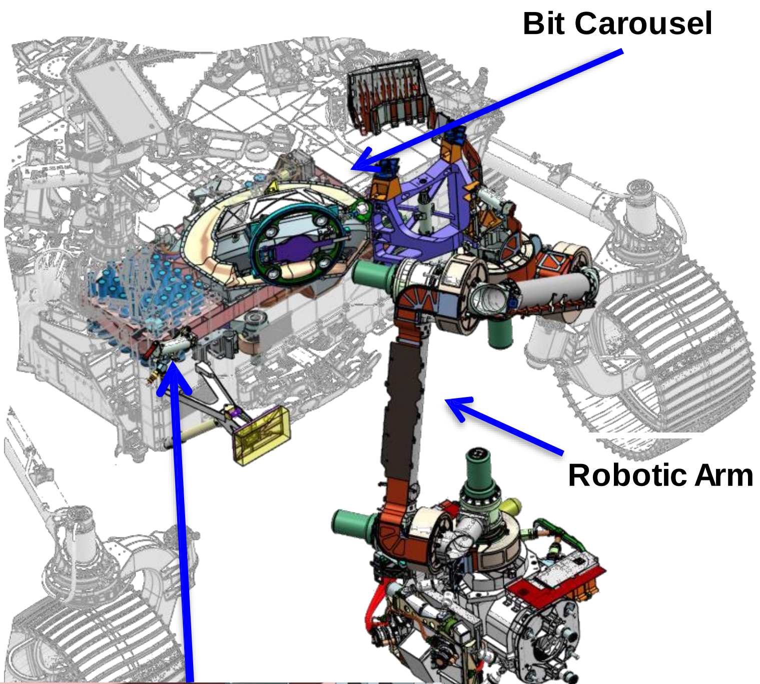
July 18, 2017



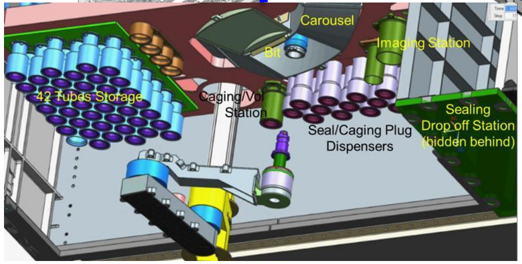
Mars 2020 Project

Mars 2020 Mission has an Objective to Assemble Returnable Cached Samples for potential future Return to Earth

Sample tubes are stored in the Adaptive Caching Assembly (ACA)



Turret
(Robotic Arm End Effector)
Corer & other instruments



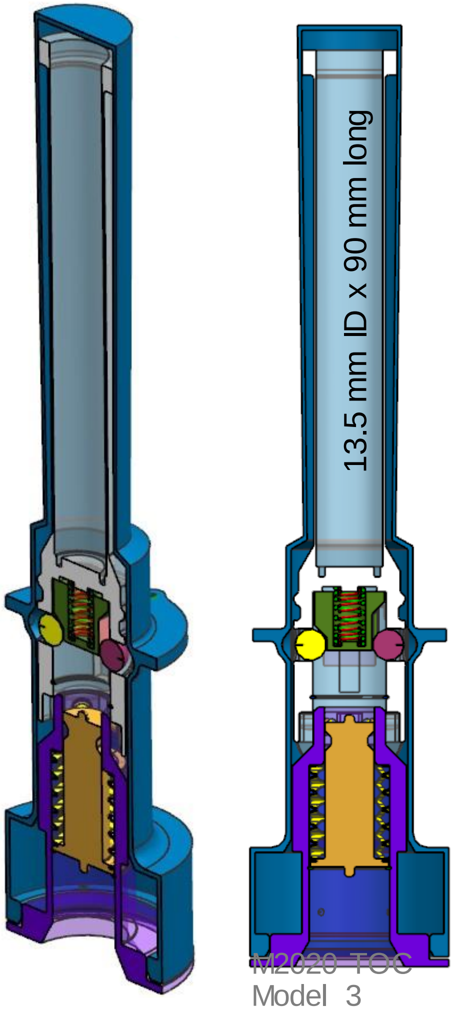
Adaptive Caching Assembly (ACA)

Returnable Sample Cleanliness Requirement

- Mars 2020 Level 1 Requirement: For returned samples **less than 10 ppb total organic compounds** (TOC) and less than 1 ppb of any of a set of special organic compound known as "tier one" compounds
  - PPB estimates are made assuming a 15 g sample. For a 15 g sample, 10 PPB corresponds to a **Requirement = 150 ng per Sample Tube**
- Sample Tube interior and the Cap
  - Tube and cap sample contacting surface area ~50 cm^2. TOC surface density must be < 3 ng/cm^2
  - **TOC Requirement << Molecular Monolayer**
- Implementation Approach is Comprehensive
  - Extensive outgas testing, hardware bakeouts (with low $ng/cm^2/hr$ TQCM exit criteria), use of witness coupons, both chemical and thermal cleaning treatments, chemically inert coatings, sealed container storage, molecular absorber, T-0 purge, a Fluid Mechanical Particle Barrier (FMPB) protecting the sample return tubes and a hermetic seal on tubes with collected samples.
- Modeling Approach
  - Identify and model TOC sources (Materials in the ACA are the largest source of TOC)
  - For each M2020 Mission phase, model TOC transport from sources to sample contacting surfaces (tube interior and cap below the seal)
  - Combine into an end-to-end model to evaluate TOC and sensitivity to assumptions

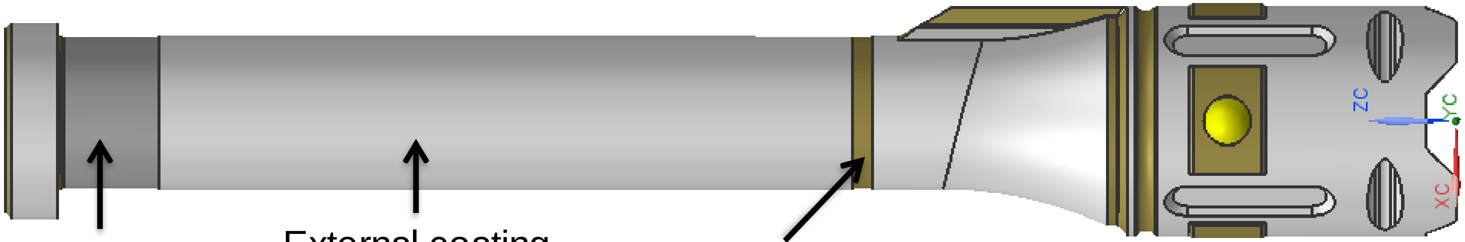
Sample Tube inside "Fluid Mechanical Particle Barrier"

FMPB



Sample Tubes, Seals, Coring Bits

Tube Exterior
(unsealed)

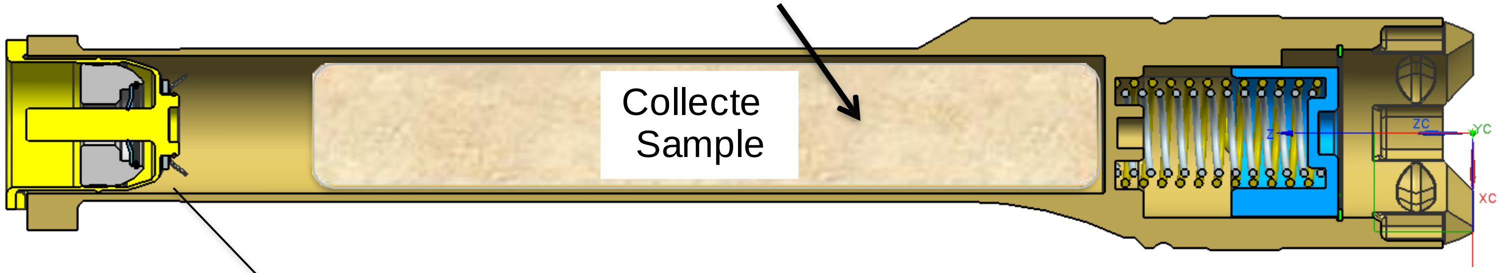


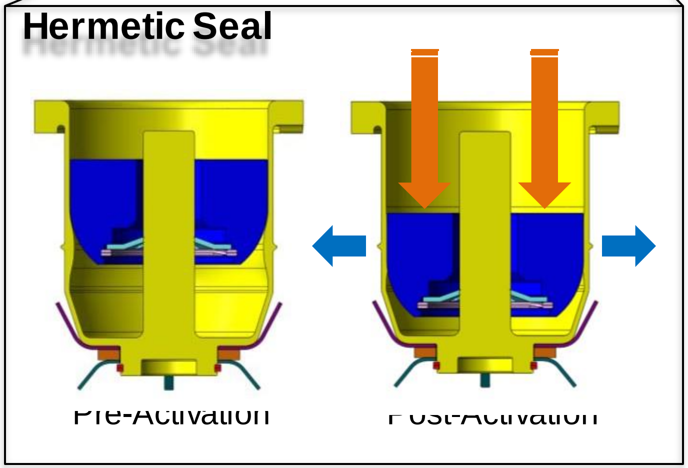
Bare Titanium

External coating
(Alumina)

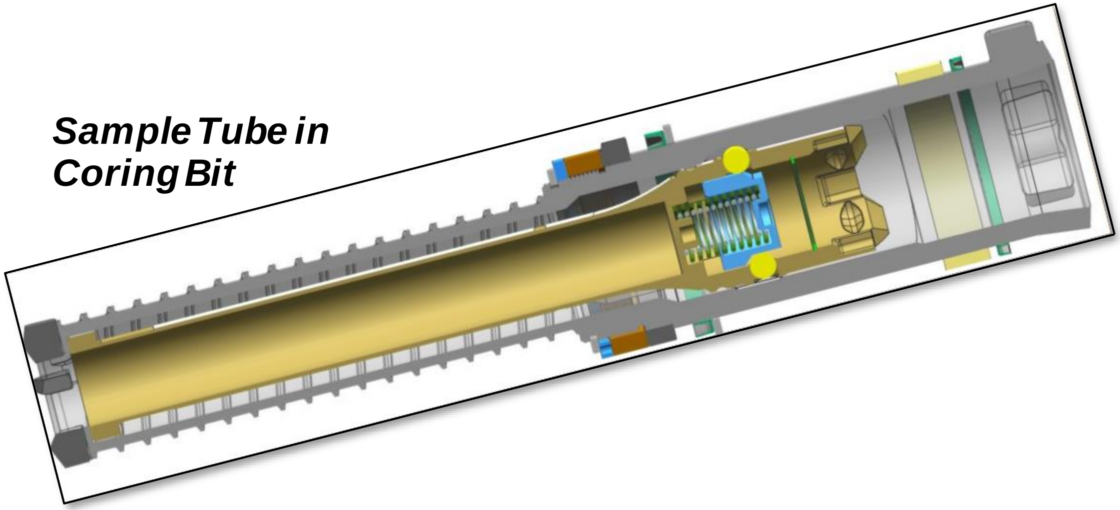
Tube Body
(*Nitrided Ti-6Al-4V*)

Tube Interior
(sealed)

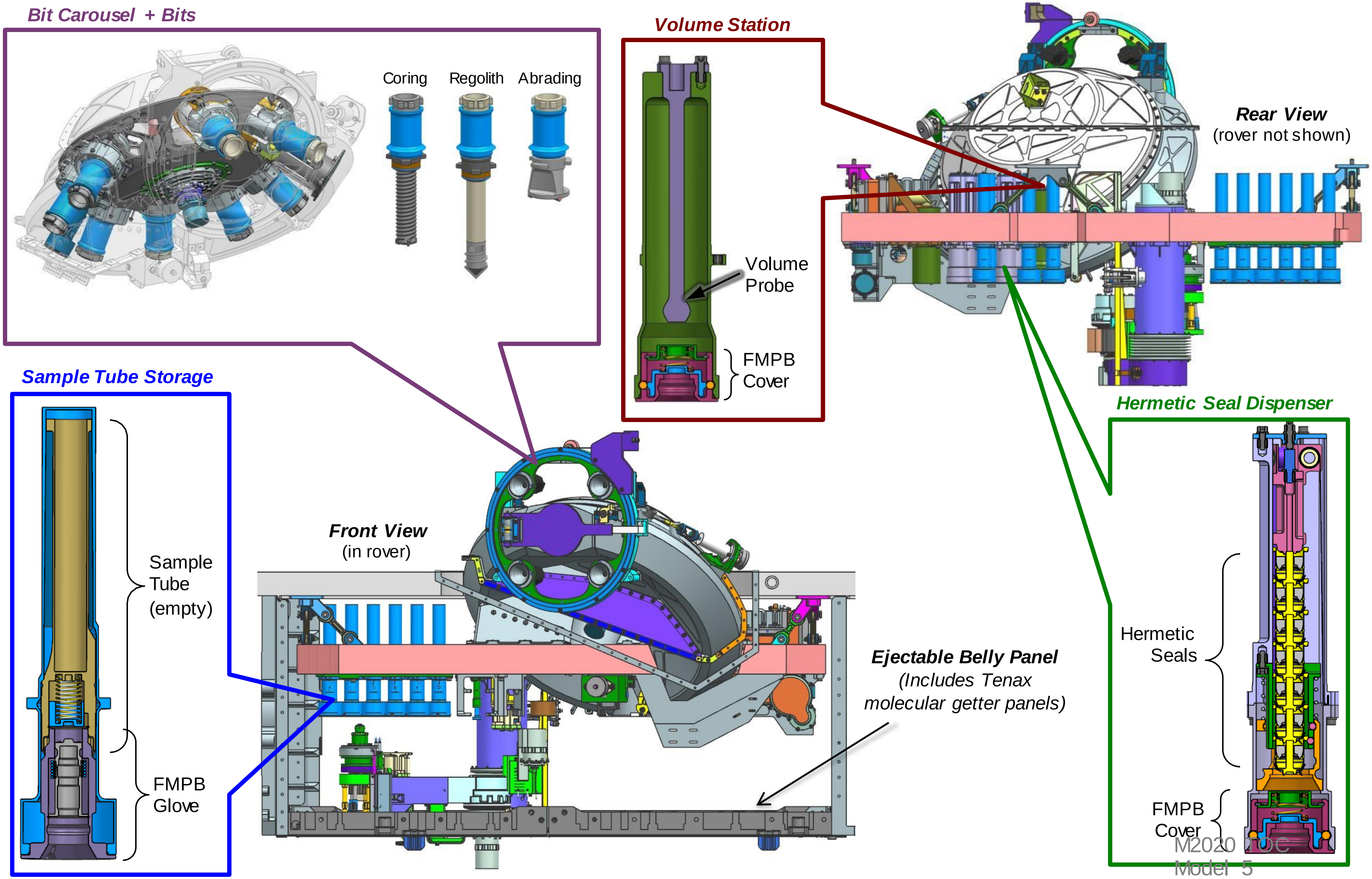




Sample Tube in Coring Bit



Adaptive Caching Assembly (ACA) Hardware Details



Bit Carousel + Bits

Coring

Regolith

Abrading

Volume Station

Volume Probe

FMPB Cover

Rear View

(rover not shown)

Sample Tube Storage

Sample Tube (empty)

FMPB Glove

Front View

(in rover)

Ejectable Belly Panel

(Includes Tenax molecular getter panels)

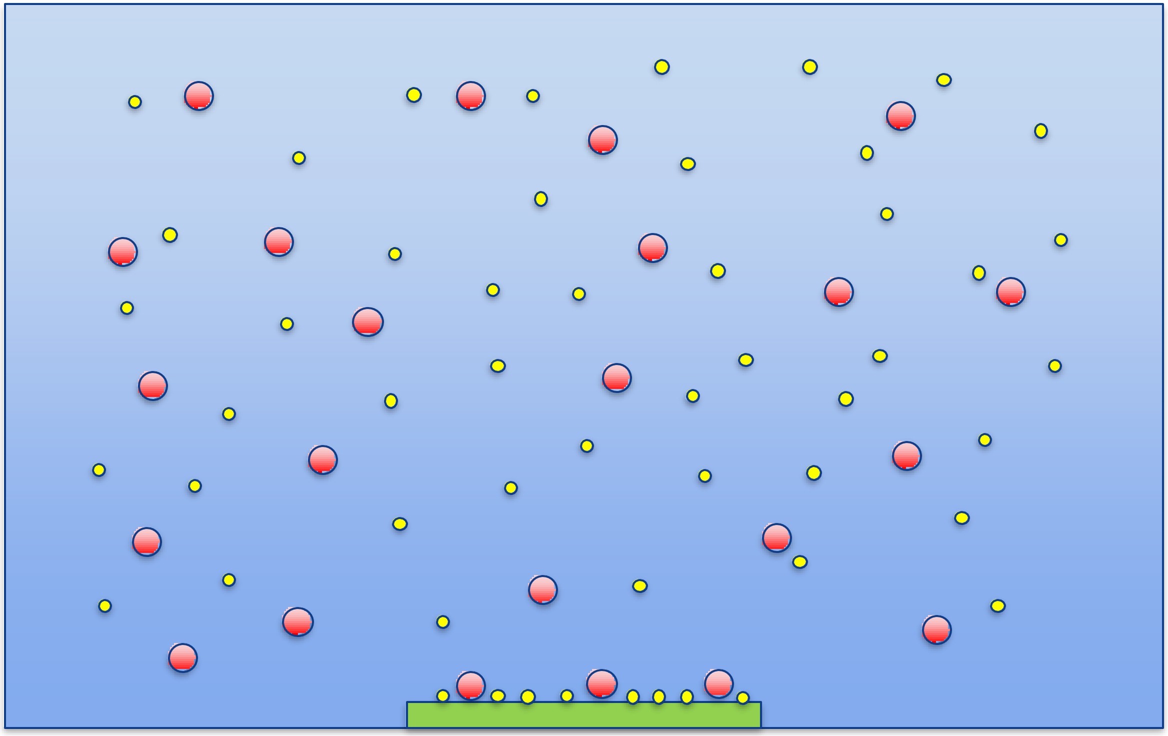
Hermetic Seal Dispenser

Hermetic Seals

FMPB Cover

TOC Requirement Not Met Without Mitigation

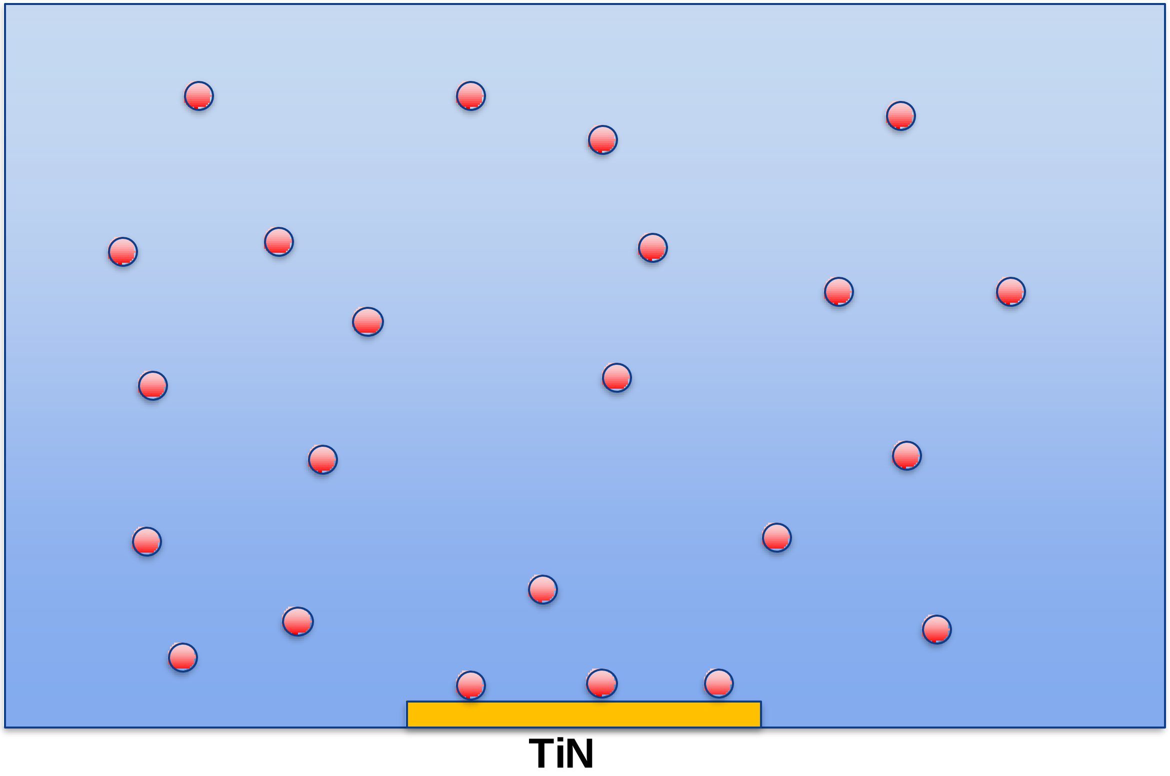
- Large number of organic molecules in the environment
- Light molecules with hydroxyl and other polar groups can chemisorb on oxide surfaces (e.g. Ti, or Al)
- Adventitious Carbon (AC) accumulation asymptotes in about a week to ~100 ng/cm^2 on a Ti-6Al-4V surface exposed in a clean room
- A Sample Tube would launch with ~ 50 x 100 = 5000 ng <u>TOC > 30X the requirement</u>



Ti-6Al-4V

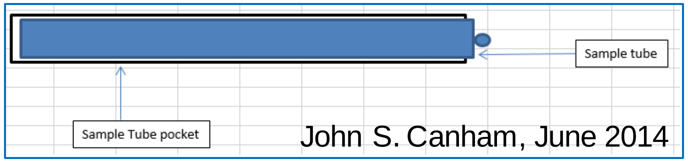
Mitigation #1: Stop Light Organic Molecules from Sticking using Titanium Nitride (TiN) Surface Treatment

- TiN suggested by Prof. Francisco Zaera, UC Riverside
- Vapor pressure decreases exponentially with Molecular Weight → low concentration of large organic molecules (MW > 200 amu)
- Molecules can only physisorb on surfaces that are chemically inert (e.g. Au or TiN)
  - Residence time for low MW molecules is very short
- AC accumulation asymptotes in about a week to ~20 ng/cm^2 on a TiN surface
- A Sample Tube would launch with ~ 50 x 20 = 1000 ng TOC > 6X the requirement

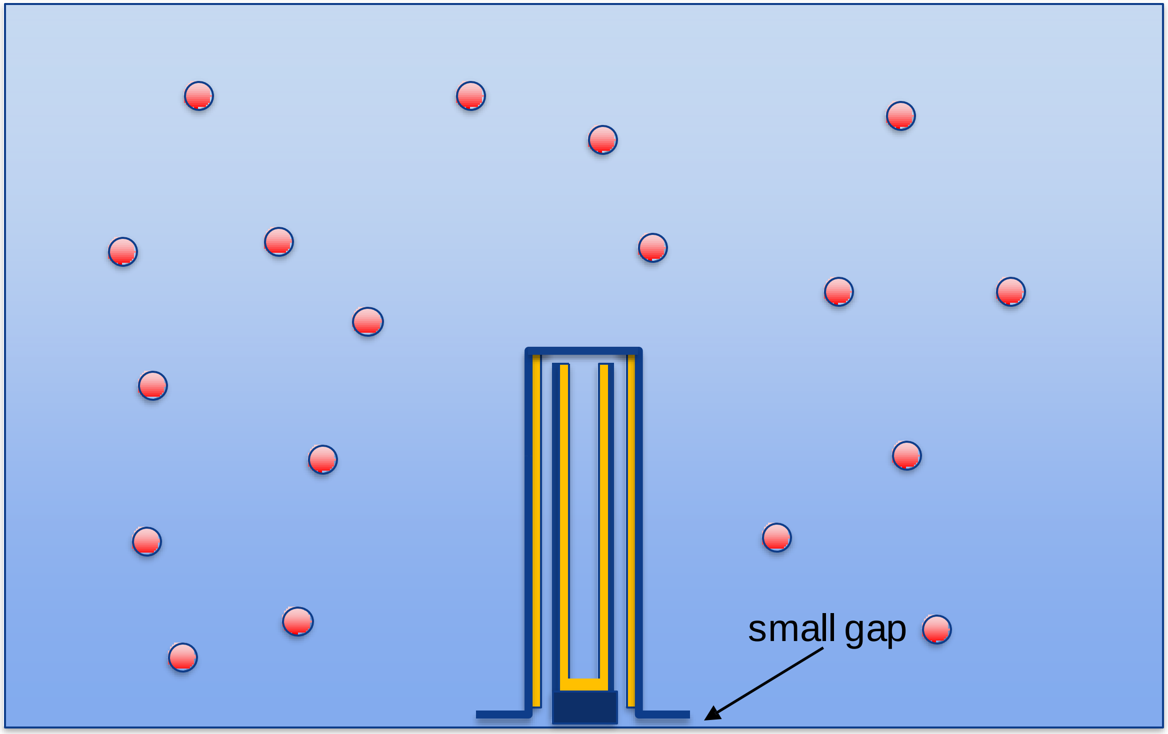


Mitigation #2: Reduce AC Accumulation Rate with a Small Opening and a Torturous Path

- Accumulation rate proportional to molecular flux reaching the interior surface of the sample tube
- Fluid Mechanical Particle Barrier (FMPB) reduces opening to <1% of the tube interior surface area
  - inspired by John Canham, “Contamination rate tube in pocket.xls”, June 2014
- FMPB sleeve provides another ~100 cm^2 to act as a “getter”



John S. Canham, June 2014



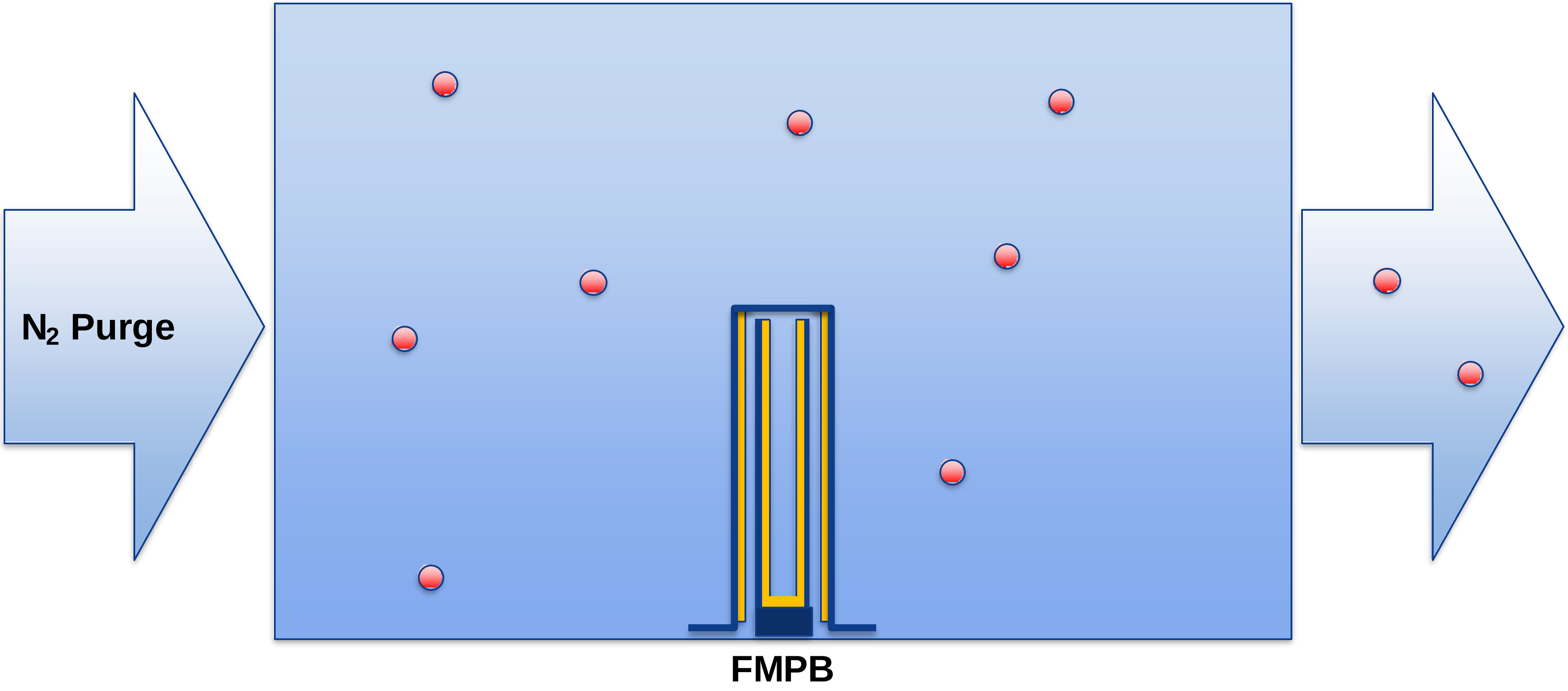
FMPB

FMPB

Mitigations #3 & #4: Minimize TOC Density with Low Outgassing Materials and Big TOC Sinks

- Accumulation rate proportional to molecular density near the gap at the bottom of the FMPB
- Sources: Low outgassing materials in the ACA
- Sinks: Purge in ATLO, Molecular Absorber during Cruise & Commissioning, Mars wind during Surface Operations

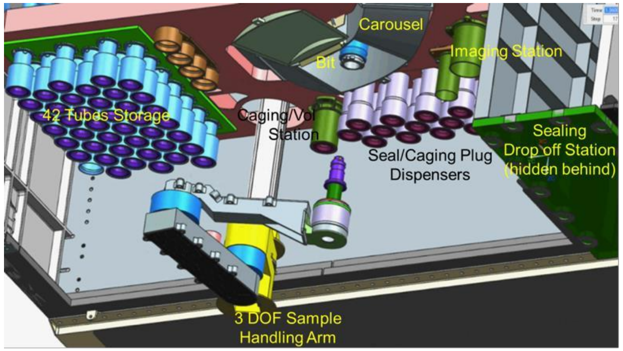
Mission Phase	TOC Sink
ATLO	N_2 Purge
Cruise	Molecular Absorber
Commissioning	Molecular Absorber
Surface Operations	Advection & Diffusion

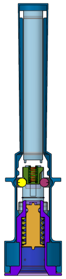


TOC in Mars 2020 Sample Tubes: Basic Model

- Contamination
  - Sources
  - Transport
  - Sinks
- **Basic Model: Flux Balance**
  - Density of TOC molecules in the ACA near the FMPB flange is determined by a balance of the flux of outgassed molecules and those leaving the ACA or hitting the Molecular Absorber.
  - The flux into the FMPB is a tiny fraction of the total ACA outgassing

ACA (Adaptive Caching Assembly)





FMPB
into the gap and up to the top of the sample tube

Sources
ACA outgassing
Airborne in ATLO

Transport
Atmospheric Advection & Diffusion
Free Molecular during cruise

Sinks
Purge in ATLO
Molecular Absorber during cruise
Mars wind – surface Ops

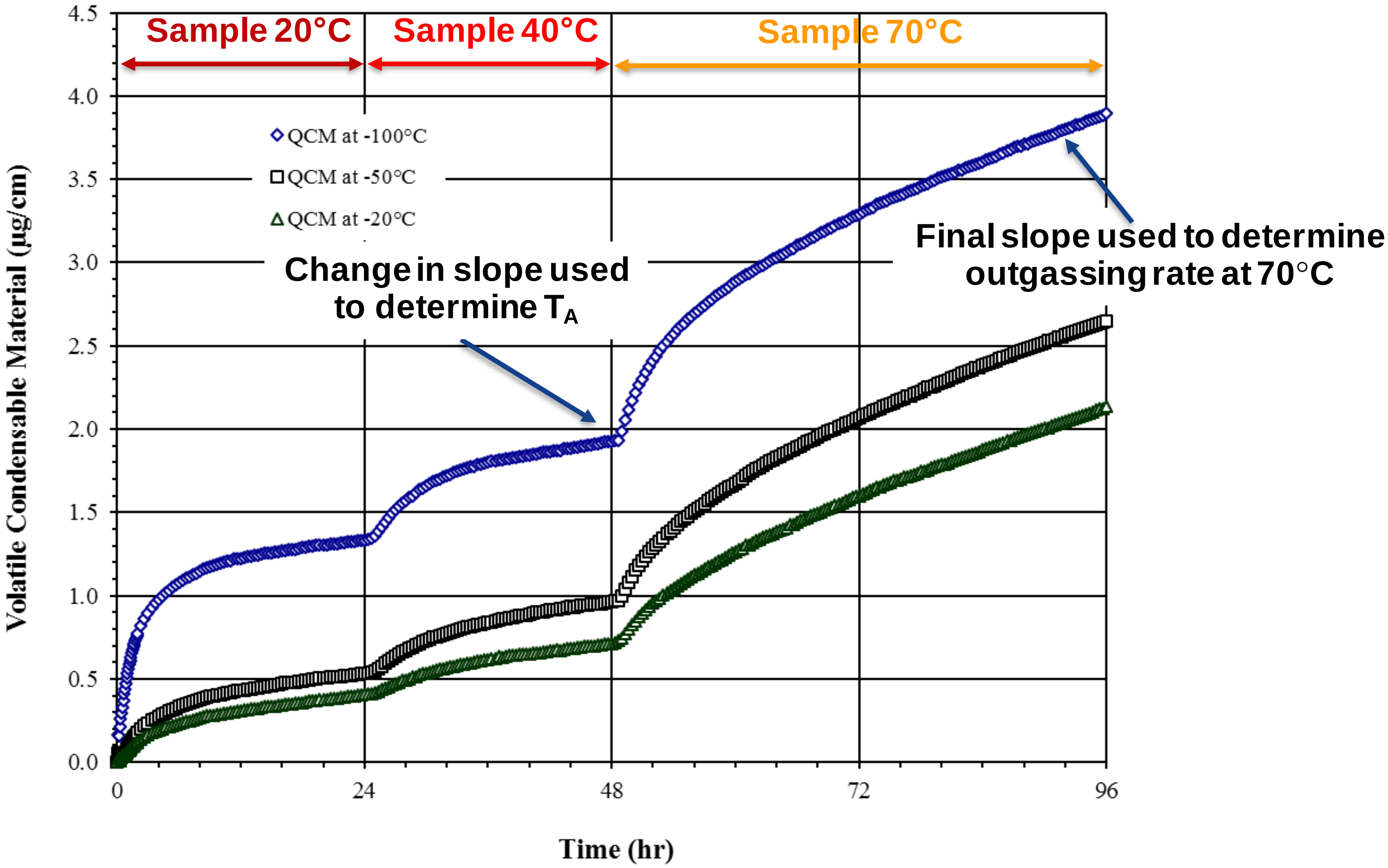
$$\dot{m}_{TOC} = \rho_{TOC} \dot{V}$$

ASTM E 1559 Outgassing/Deposition Kinetics Tests performed by Outgassing Services International (OSI)

Sources

Sample Data

External MAHLI Harness Cable at 20°C, 40°C, and 70°C.



Change in slope used to determine T_A

Final slope used to determine outgassing rate at 70°C

Outgassing Source Rates Used in TOC Analysis

Sources

- Rates derived from the -100°C QCM
  - Accumulation on QCM is much greater than a mono-layer
  - Only data that I have seen has binding energy of the second layer about 2/3 of the first (360 K vs 523 K)
  - Molecules that can form a monolayer on a 20°C (293 K) surface, can form multiple layers on a -70°C (203 K) surface
  - Suggests using outgassing rates derived from the -100°C QCM
- Outgassing inputs to end-to-end model example

	QCM→	T -100°C		T -50°C		T -20°C	
Materials	**unit**	**Γ (70°C) (ng/unit/hr)**	**T_A(K)**	**Γ (70°C) (ng/unit/hr)**	**T_A(K)**	**Γ (70°C) (ng/unit/hr)**	**T_A(K)**
Flex Cable	**cm²**	**5.4**	**12767**	**2.40**	**11554**	**1.8**	**13616**
Round Wire Cable	**cm²**	**6.2**	**9246**	**5.7**	**8340**	**5.8**	**9838**
Connectors	**unit**	**257**	**9493**	**191**	**9770**	**113**	**8682**
Motors	**unit**	**14025**	**13697**	**14035**	**13417**	**13683**	**13890**

- Outgassing Source Term in the end-to-end model

$$\dot{m}_{TOC} = \sum_{sources} A_i \Gamma_i(T)$$

$$\Gamma(T) = \Gamma(T_0)\frac{\exp\left(-\frac{T_A}{T}\right)}{\exp\left(-\frac{T_A}{T_0}\right)}$$

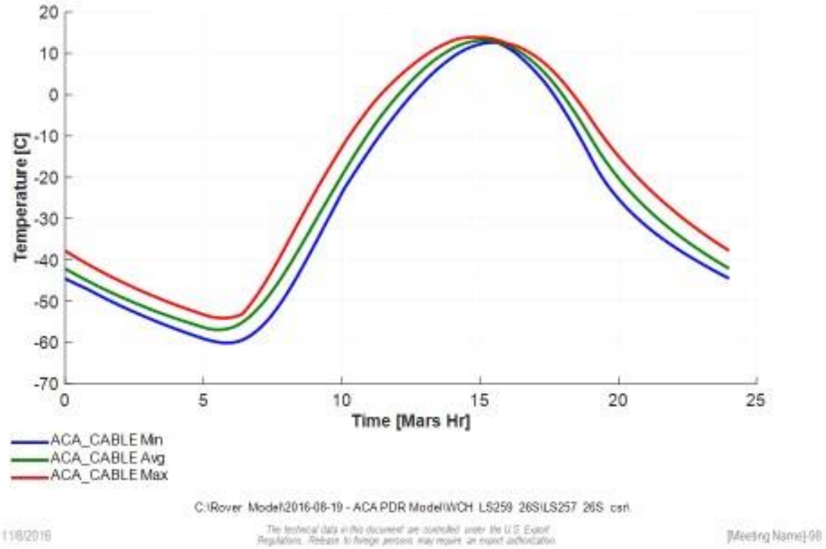
ACA Temperatures: Surface of Mars

Sources

- Matt Redmond & Eddie Farias, “H_Section_CCMD and Sealing Station - 2016-09-06.pptx”
- Cables produce a large fraction of ACA outgassing
- Spreadsheet model adds +10°C for margin

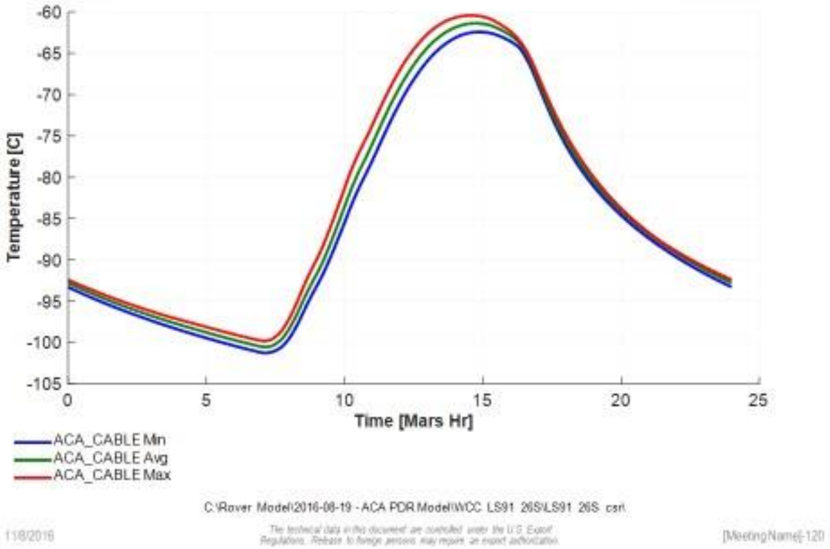
Case	WCH/BPoff	WCC/BPoff
T_max(°C)	25	-55
T_min(°C)	-50	-90

Worst Case Hot (WCH)



C:\Rover Model\2016-08-19 - ACA PDR Model\WCH LS259 26S\LS257 26S csv

Worst Case Cold (WCC)



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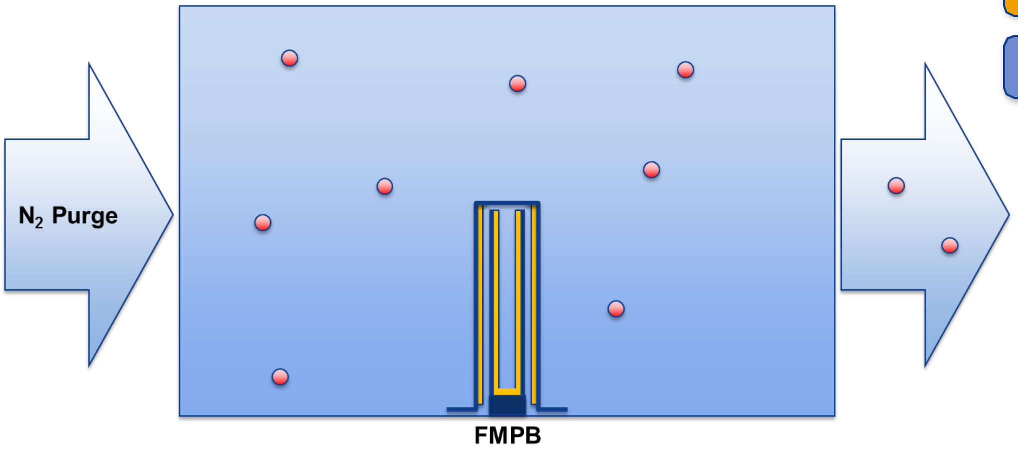
Transport & Sinks by Mission Phase

Transport
Sinks

Density of TOC molecules in the ACA is determined by balancing the flux of outgassed molecules with those leaving the ACA

$$\boxed{\rho_{TOC} = \frac{\dot{m}}{\dot{V}}}$$



Mission Phase	TOC Transport	TOC Sink
ATLO	Advection/Diffusion	N₂ Purge
Cruise	Free Molecular	Molecular Absorber
Commissioning	Diffusion	Molecular Absorber
Surface Ops	Advection/Diffusion	Mars Atmosphere

$$\dot{V} = \dot{V}_{purge}$$

$$\dot{V} = \frac{\bar{c}}{4} A_{MA}$$

$$\dot{V} = u_{dif} A_{MA}, \quad u_{dif} \approx \frac{D_{Mars}}{\square}, \quad \square \approx 0.2\ m$$

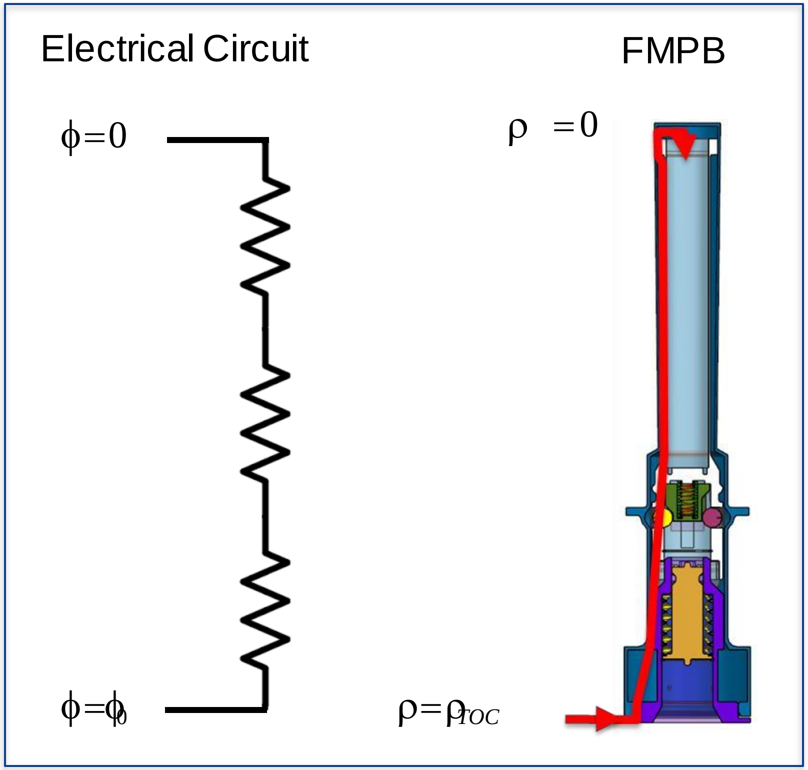
$$\dot{V} = u_{wind}^{effective} A_{bellypan}, \quad u_{wind}^{effective} \approx 0.02\, u_{wind}$$

TOC into the FMPB: Flow Resistances Add

Transport

- Ohm's Law is a diffusion equation
- Torturous path modeled as a series of flow resistances

	Ohm's Law	Mass Diffusion
basic equation	$j=\sigma\nabla\phi$	$j=D\nabla\rho$
	$\nabla\phi=\eta j$	$\nabla\rho=\frac{1}{D}j$
	$\Delta\phi=R\,I$	$\Delta\rho=R\,J$
series resistance	$\phi=I\sum R$	$\Delta\rho=J\sum R$
circuit current	$I=\frac{\phi}{\sum R}$	$J=\frac{\rho}{\sum R}$



Diffusion Rate into the Sample Tube

- Mass diffusion equation

  $j = D\nabla\rho$ where *j* is the mass flow density

- Mass flow through a single gap

  (assuming nothing sticks to the walls)

  $J = 2\pi r\, h\, D\frac{\Delta\rho}{L}$ where r is the tube radius, h the gap height, and L the gap length

- Flow resistance, η, through a gap is

  $\Delta\rho = \eta J$

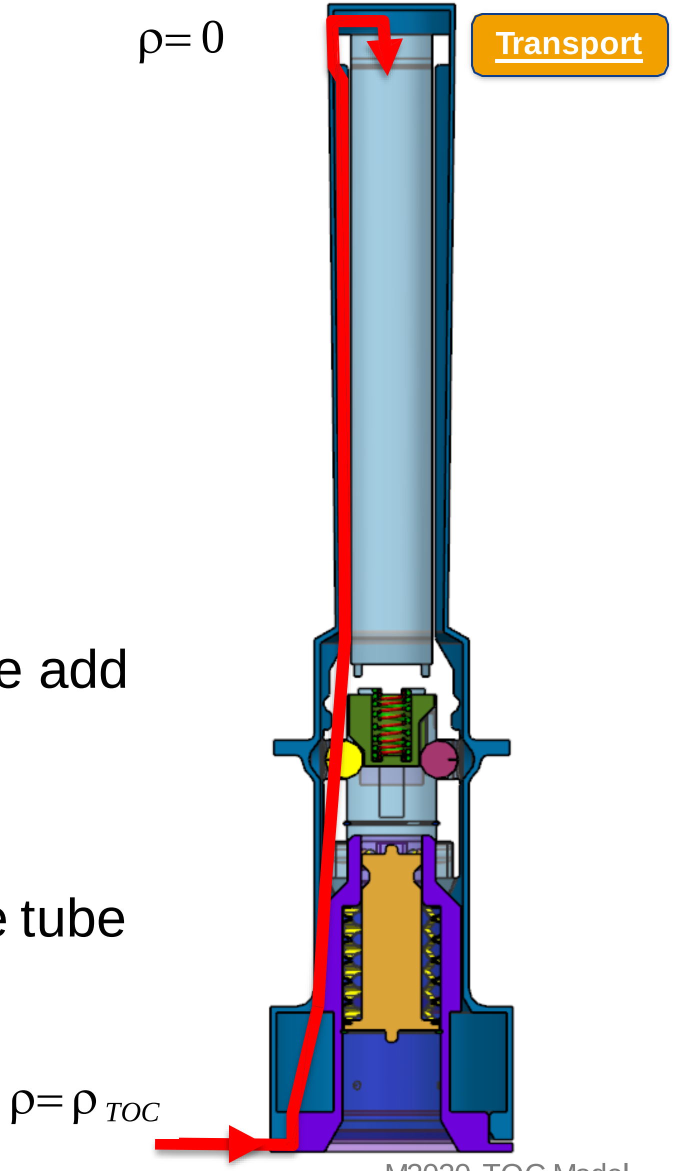
  $$\eta \equiv \frac{L}{2\pi r\, h}\frac{1}{D}$$

- Since the FMPB has multiple gaps in series, we add the flow resistances

  $$\eta_{FMPB} \equiv \frac{1}{D}\sum_i \frac{L_i}{2\pi r_i\, h_i} \equiv \frac{1}{D} R_{FMPB} \qquad R_{FMPB} \equiv \sum_i \frac{L_i}{2\pi r_i\, h_i}$$

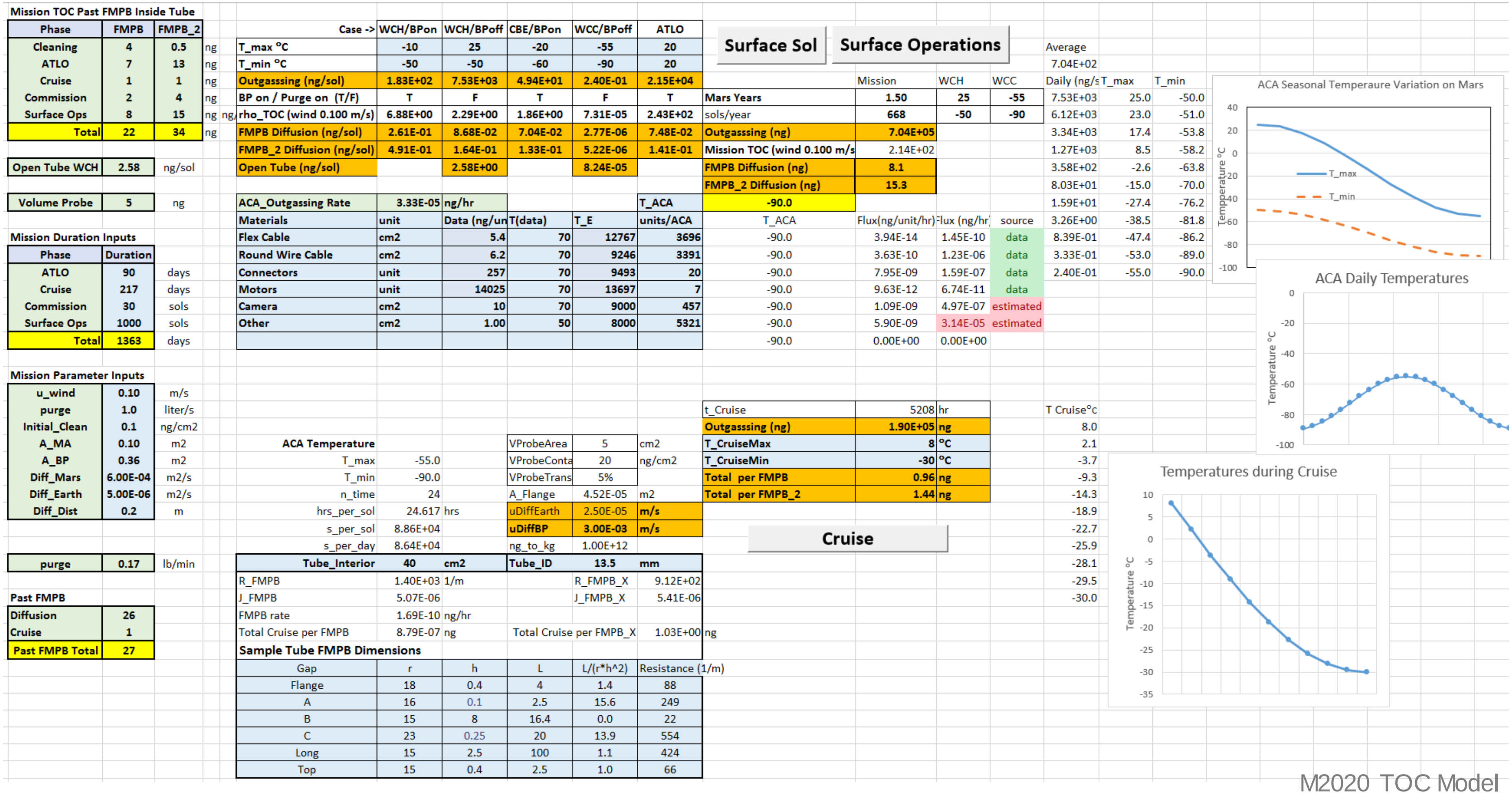
- The mass flow rate to the interior of the sample tube

  $$\boxed{J_{FMPB} \equiv \frac{\rho_{TOC}}{\eta_{FMPB}} = \frac{D}{R_{FMPB}}\rho_{TOC}}$$



Data and Analysis Combined in the M2020 TOC End to End Spreadsheet

- Values and formulas in the spreadsheet are described in this presentation
- Light blue cells are Inputs, e.g. **purge** | **1.0** | liter/s
- Buttons perform calculations, e.g. **Cruise**



Mission TOC Past FMPB Inside Tube

Phase	FMPB	FMPB_2	
Cleaning	4	0.5	ng
ATLO	7	13	ng
Cruise	1	1	ng
Commission	2	4	ng
Surface Ops	8	15	ng
Total	22	34	ng

Open Tube WCH	2.58	ng/sol
Volume Probe	5	ng

Mission Duration Inputs

Phase	Duration	
ATLO	90	days
Cruise	217	days
Commission	30	sols
Surface Ops	1000	sols
Total	1363	days

Mission Parameter Inputs

u_wind	0.10	m/s
purge	1.0	liter/s
Initial_Clean	0.1	ng/cm2
A_MA	0.10	m2
A_BP	0.36	m2
Diff_Mars	6.00E-04	m2/s
Diff_Earth	5.00E-06	m2/s
Diff_Dist	0.2	m

purge	0.17	lb/min

Past FMPB

Diffusion	26
Cruise	1
Past FMPB Total	27

	Case ->	WCH/BPon	WCH/BPoff	CBE/BPon	WCC/BPoff	ATLO
	T_max °C	-10	25	-20	-55	20
	T_min °C	-50	-50	-60	-90	20
	Outgasssing (ng/sol)	1.83E+02	7.53E+03	4.94E+01	2.40E-01	2.15E+04
	BP on / Purge on (T/F)	T	F	T	F	T
ng/	rho_TOC (wind 0.100 m/s)	6.88E+00	2.29E+00	1.86E+00	7.31E-05	2.43E+02
	FMPB Diffusion (ng/sol)	2.61E-01	8.68E-02	7.04E-02	2.77E-06	7.48E-02
	FMPB_2 Diffusion (ng/sol)	4.91E-01	1.64E-01	1.33E-01	5.22E-06	1.41E-01
	Open Tube (ng/sol)		2.58E+00		8.24E-05	

Surface Sol **Surface Operations**

	Mission	WCH	WCC
Mars Years	1.50	25	-55
sols/year	668	-50	-90
Outgasssing (ng)	7.04E+05		
Mission TOC (wind 0.100 m/s	2.14E+02		
FMPB Diffusion (ng)	8.1		
FMPB_2 Diffusion (ng)	15.3		

ACA_Outgassing Rate	3.33E-05	ng/hr			T_ACA	-90.0			
Materials	unit	Data (ng/un	T(data)	T_E	units/ACA	T_ACA	Flux(ng/unit/hr)	Flux (ng/hr)	source
Flex Cable	cm2	5.4	70	12767	3696	-90.0	3.94E-14	1.45E-10	data
Round Wire Cable	cm2	6.2	70	9246	3391	-90.0	3.63E-10	1.23E-06	data
Connectors	unit	257	70	9493	20	-90.0	7.95E-09	1.59E-07	data
Motors	unit	14025	70	13697	7	-90.0	9.63E-12	6.74E-11	data
Camera	cm2	10	70	9000	457	-90.0	1.09E-09	4.97E-07	estimated
Other	cm2	1.00	50	8000	5321	-90.0	5.90E-09	3.14E-05	estimated
						-90.0	0.00E+00	0.00E+00	

Average		
7.04E+02		
Daily (ng/s	T_max	T_min
7.53E+03	25.0	-50.0
6.12E+03	23.0	-51.0
3.34E+03	17.4	-53.8
1.27E+03	8.5	-58.2
3.58E+02	-2.6	-63.8
8.03E+01	-15.0	-70.0
1.59E+01	-27.4	-76.2
3.26E+00	-38.5	-81.8
8.39E-01	-47.4	-86.2
3.33E-01	-53.0	-89.0
2.40E-01	-55.0	-90.0

t_Cruise	5208	hr
Outgasssing (ng)	1.90E+05	ng
T_CruiseMax	8	°C
T_CruiseMin	-30	°C
Total per FMPB	0.96	ng
Total per FMPB_2	1.44	ng

Cruise

T Cruise°c
8.0
2.1
-3.7
-9.3
-14.3
-18.9
-22.7
-25.9
-28.1
-29.5
-30.0

ACA Temperature		
T_max	-55.0	
T_min	-90.0	
n_time	24	
hrs_per_sol	24.617	hrs
s_per_sol	8.86E+04	
s_per_day	8.64E+04	

VProbeArea	5	cm2
VProbeConta	20	ng/cm2
VProbeTrans	5%	
A_Flange	4.52E-05	m2
uDiffEarth	2.50E-05	m/s
uDiffBP	3.00E-03	m/s
ng_to_kg	1.00E+12	

Tube_Interior	40	cm2	Tube_ID	13.5	mm	
R_FMPB	1.40E+03	1/m		R_FMPB_X	9.12E+02	
J_FMPB	5.07E-06			J_FMPB_X	5.41E-06	
FMPB rate	1.69E-10	ng/hr				
Total Cruise per FMPB	8.79E-07	ng	Total Cruise per FMPB_X		1.03E+00	ng

Sample Tube FMPB Dimensions

Gap	r	h	L	L/(r*h^2)	Resistance (1/m)
Flange	18	0.4	4	1.4	88
A	16	0.1	2.5	15.6	249
B	15	8	16.4	0.0	22
C	23	0.25	20	13.9	554
Long	15	2.5	100	1.1	424
Top	15	0.4	2.5	1.0	66

Mars 2020 Return Sample Cleanliness Molecular Transport Model: Summary

- Molecular Transport Model Approach
  - Identify and model TOC sources (Materials in the ACA are the largest source of TOC)
  - For each M2020 Mission phase, model TOC transport from sources to sample contacting surfaces (tube interior and cap below the seal)
  - Combine into an end-to-end model to evaluate TOC and sensitivity to assumptions
- Model is Data Driven
  - Measured outgassing rates for Sample Handling System materials
  - Temperature models validated with MSL flight data
  - Diffusion coefficients from the open literature
  - Mars wind speeds based on Viking observations
  - Laboratory tests of Tenax molecular absorber
- Model results show 10 ppb TOC requirement is achievable

Backup

TiN Chosen for Sample Tube Surfaces Because it Accumulates Low Levels of AC

- TiN suggested by Prof. Zaera
- TiN collects much less TOC than other surfaces
- A small percentage of organic molecules in the air stick to TiN
- Asymptotic accumulation much lower on good TiN surfaces
- TiN will oxidize at high temperatures
  - Tests show TiN layer significantly degraded after heating to 500°C in air
  - Peer reviewed literature (from Zaera) and shows TiN oxidizes at 500 °C but should be stable at 350°C

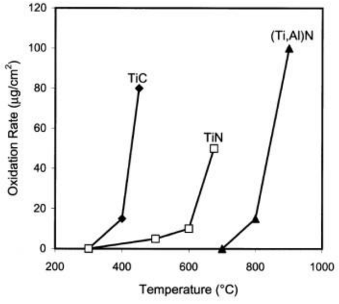


Fig. 12. Oxidation rate of hard coatings in step stress tests [51].

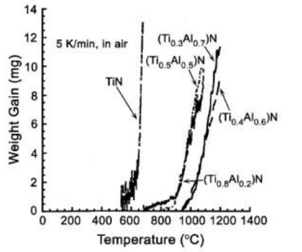
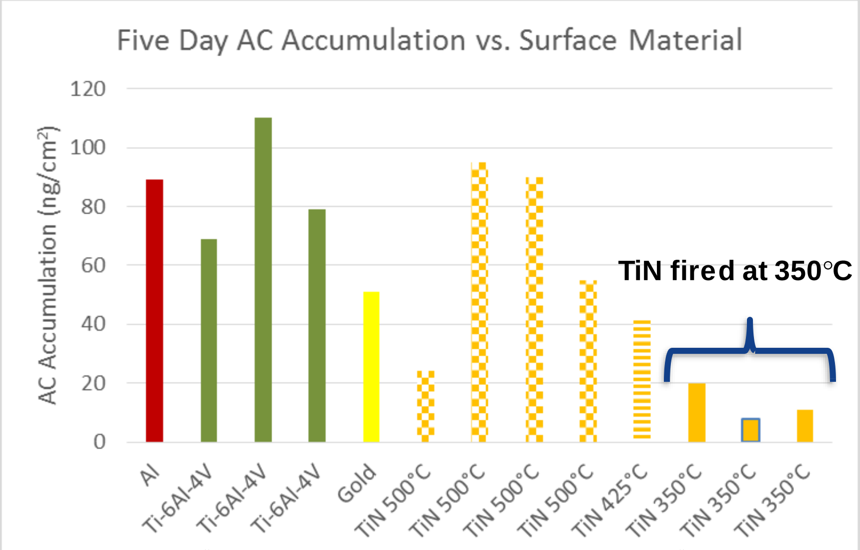
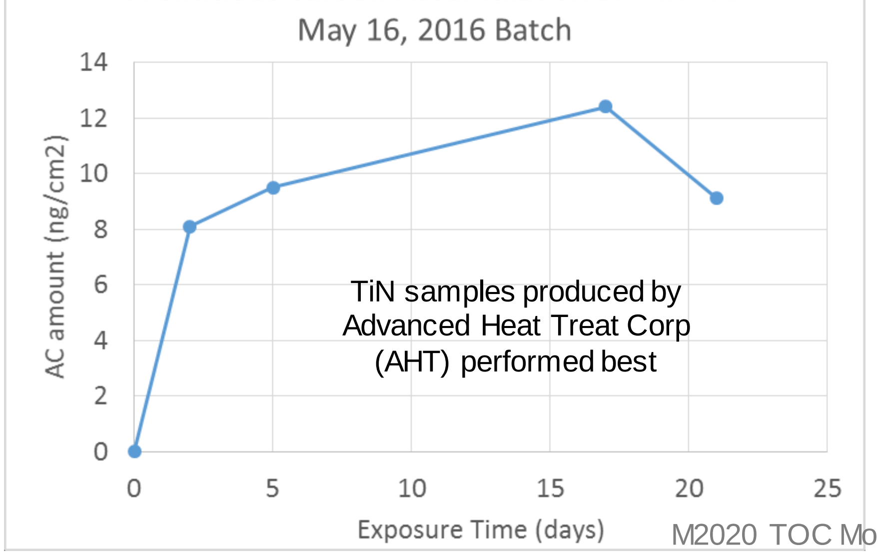


Fig. 13. Oxidation curves as a function of the Al concentration in the $(Ti_{1-x}Al_x)N$ films [29].

PalDey & Deevi, “Single layer and multilayer wear resistant coatings of (Ti,Al)N: a review”, Materials Science and Engineering A342 (2003) 58-79



Mark Anderson, “Tube_TiN_Status_3-29-16.xlsx, Mark Anderson, “Adventitious Carbon Accumulation on TiN –AHT May 16, 2016 Batch”, 6/7/2016



TiN samples produced by Advanced Heat Treat Corp (AHT) performed best