Interaction of Molecular Contamination with Surfaces

Junpin Yao, Asad Iqbal,Harpreet Juneja and Farhang Shadman

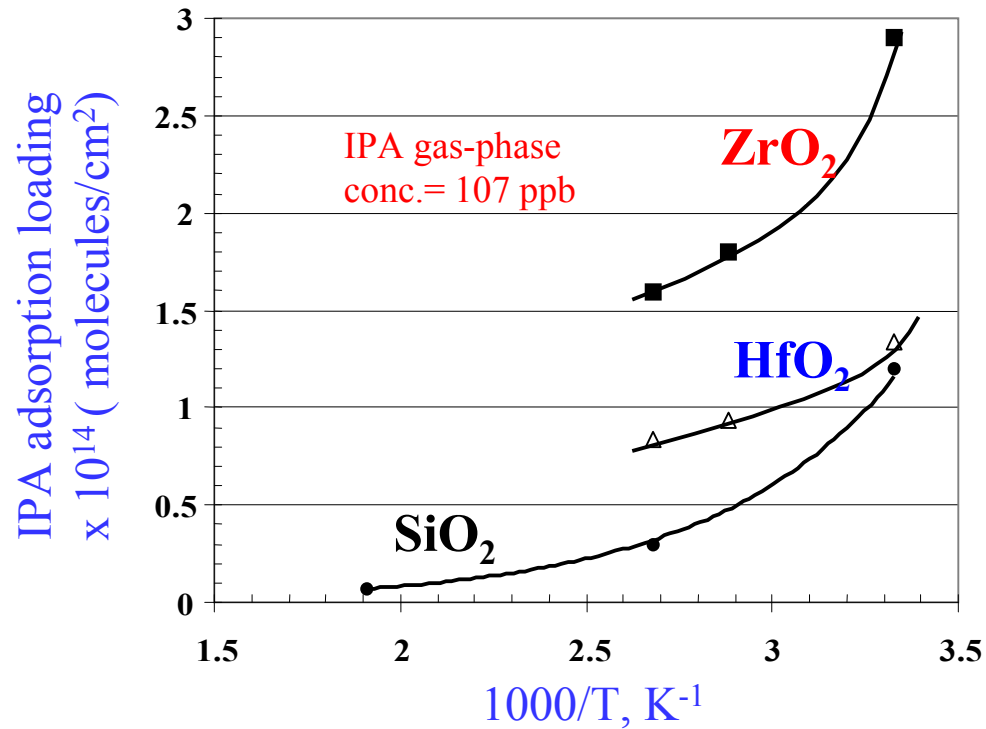**Chemical and Environmental Engineering, University of Arizona**

ERC Teleseminar

Thursday, October 18, 2007

Interaction of Molecular Contamination with High-k Dielectric Films

IPA Adsorption Loading

IPA gas-phase conc.= 107 ppb

ZrO$_2$

HfO$_2$

SiO$_2$

Y-axis: IPA adsorption loading x 10^{14} (molecules/cm^2)

X-axis: 1000/T, K^{-1}

➢ HfO$_2$ and ZrO$_2$ have higher IPA adsorption loading than SiO$_2$

➢ IPA loading order: ZrO$_2$ > HfO$_2$ > SiO$_2$

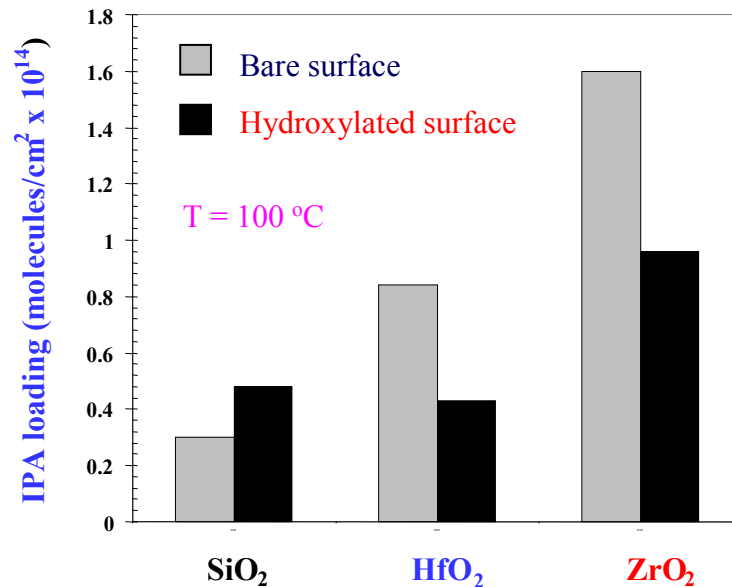➢ Same trend was observed over a wide range of concentrations

Effect of Pre-Adsorbed Moisture on IPA Loading

Experimental Procedure

Step 1. Moisture challenge (conc: 56 ppb)

Step 2. IPA challenge (conc: 107 ppb)

- Presence of one contaminant can affect adsorption/desorption characteristics of other

- Moisture hydroxylates oxide surfaces; the hydroxyl groups change the nature of the surface

- Pre-adsorbed moisture enhances IPA adsorption on SiO_2, but reduces IPA adsorption on HfO_2 and ZrO_2

- IPA is more attracted to bare HfO_2 and ZrO_2 surfaces than to hydroxylated surfaces. Presence of H_2O reduces their affinity for IPA
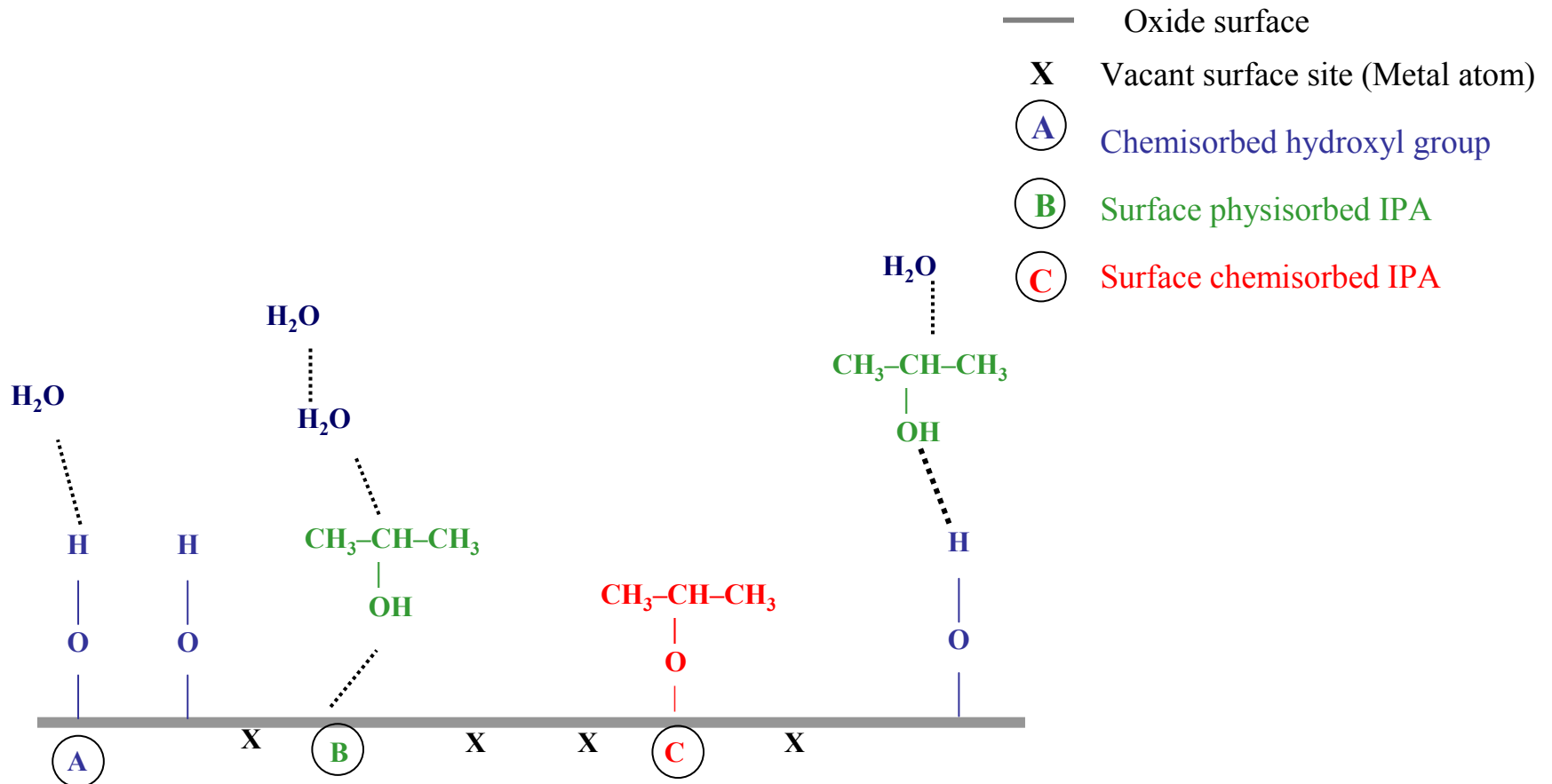
Interaction of IPA with Hyroxylated Surfaces

D$_2$O-covered surface exposed to IPA
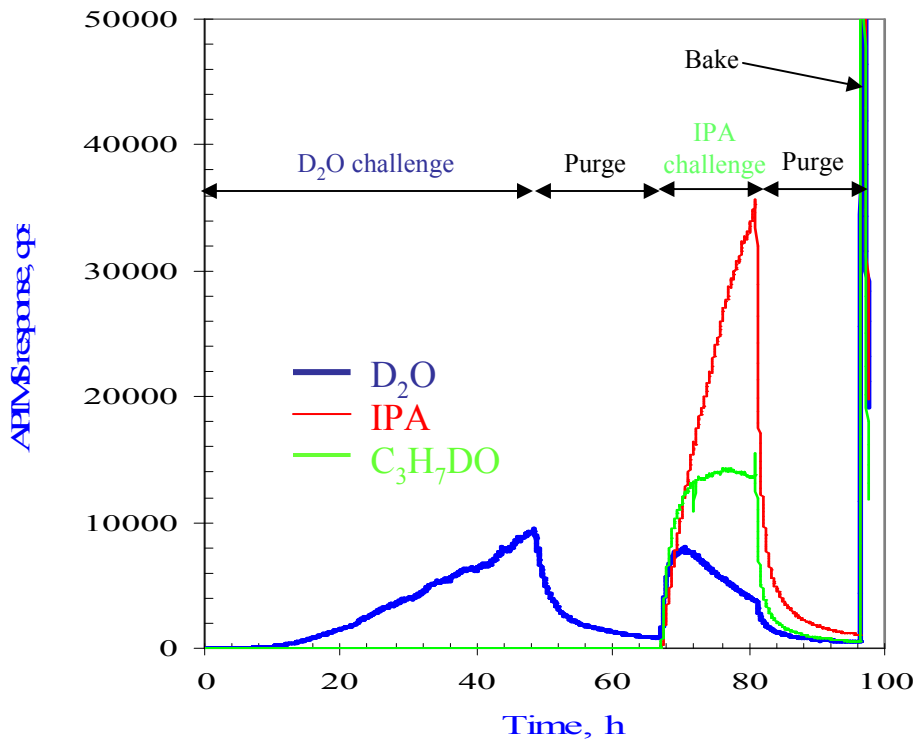
C$_3$H$_7$DO

m/e = 46

- ➢ C$_3$H$_7$DO (m/e = 46) formed when IPA is introduced on D$_2$O-covered ZrO$_2$

- ➢ C$_3$H$_7$DO may be formed by surface interactions between IPA and D$_2$O

- ➢ C$_3$H$_7$DO is also formed in the APIMS plasma (source) from interactions between IPA and D$_2$O

- ➢ Sample-gas ionization in the APIMS is accomplished by electron impact at atmospheric pressure

- ➢ Extensive collisions among molecules in the APIMS plasma source produce intermediate species (for example, C$_3$H$_7$DO)

- ➢ A technique was required to characterize and separate post-reactor interferences due to plasma effect

Low Concentration Multicomponent Adsorption Model

—— Oxide surface

X   Vacant surface site (Metal atom)

(A)   Chemisorbed hydroxyl group

(B)   Surface physisorbed IPA

(C)   Surface chemisorbed IPA

Conclusion

❑ **ZrO_2 was shown to form the strongest metal-hydroxyl (M-OH) bond and adsorb IPA stronger than SiO_2 and HfO_2**

❑ **ZrO_2 should not be the material of choice from the standpoint of molecular contamination**

❑ **Isotope labeling with D_2O indicated chemisorption of IPA on hydroxylated surfaces via an esterification reaction**

Interaction of Molecular Contamination with Low-k Dielectric Films

Contamination Behavior of Low-k Materials

• Low-k inter-layer dielectrics (ILD) are highly prone to molecular contamination, especially if it porous

• Potential issues associated with molecular contamination of low-k materials:

  - Their ability to absorb chemicals, such as contaminants containing polar O-H bonds due to their porous structure
  - Increase in k values, create adhesion problems, and cause reliability issues.
  - Signal propagation delays and cross-talk between interconnects

• Characterization of sorption behavior of new low-k films will assist in deciding their potential for successful integration in semiconductor processes
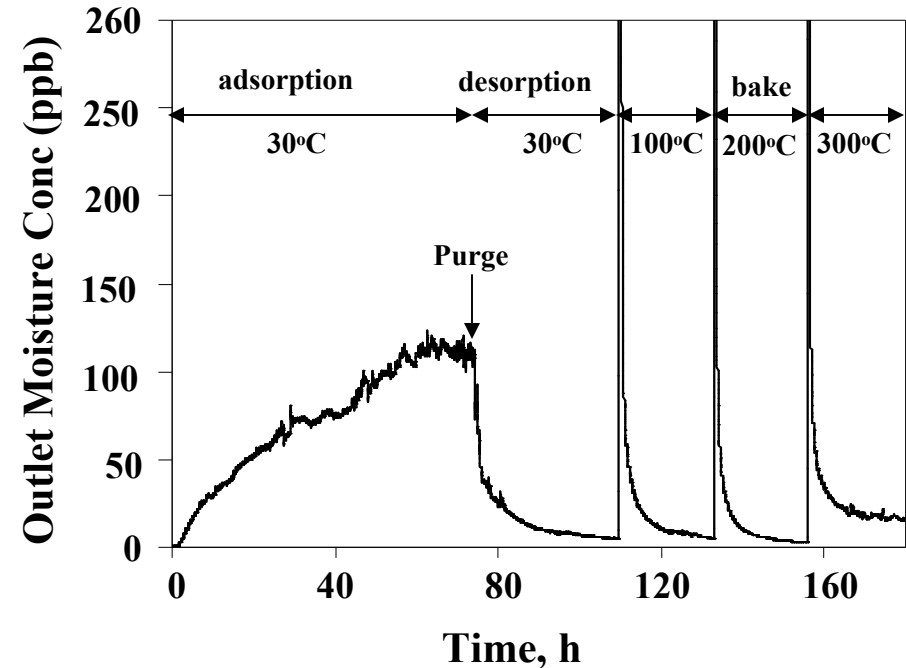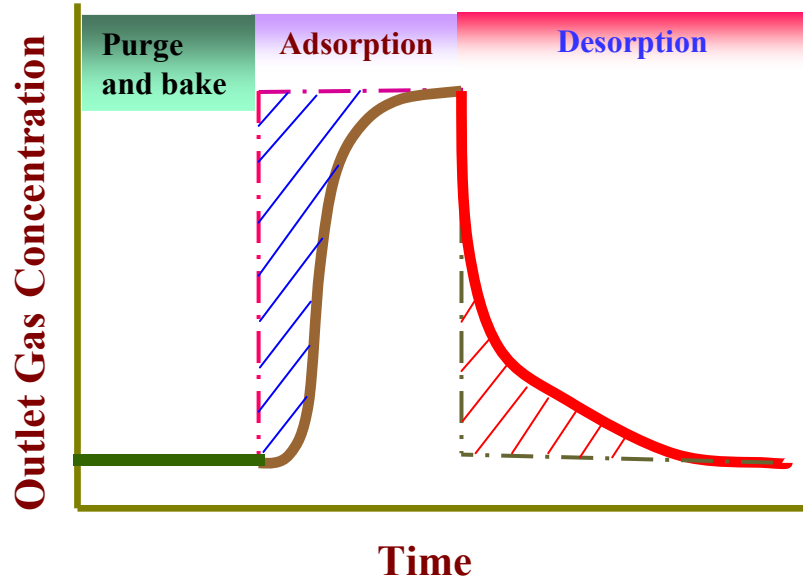
Research Objectives

- **Determine the fundamentals of moisture interactions and outgassing in both uniform and non-uniform porous low-k films:**

  - **Loading**

  - **Transport, incorporation and removal of moisture in all forms in the matrix**

  - **Mechanism of interactions of moisture and organics with wafer surfaces**

- **Develop experimental and process modeling techniques for minimizing the chemical and energy usage during cleaning and purging of low-k films**

Experimental Setup

- **Atmospheric Pressure Ionization Mass Spectrometer (APIMS)**

- **Cavity Ring Down Spectroscope (CRDS)**

- **Electron Impact Mass Spectrometer (EIMS)**

- **Fourier Transform Infrared Spectrometer (FTIR)**

Experimental Procedure

Experimental procedure

Isothermal adsorption and desorption
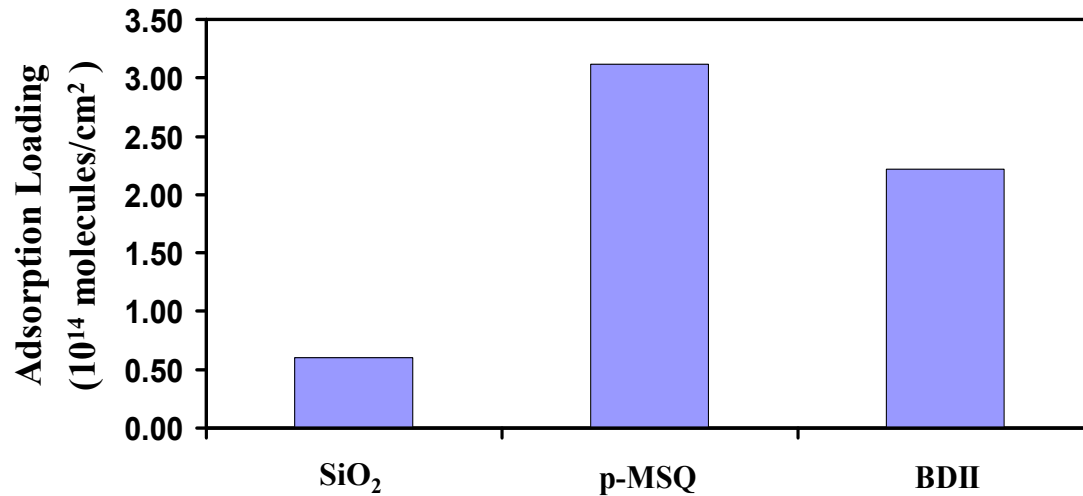
Temporal profile

Exposure to 110 ppb moisture; followed by temperature-programmed desorption
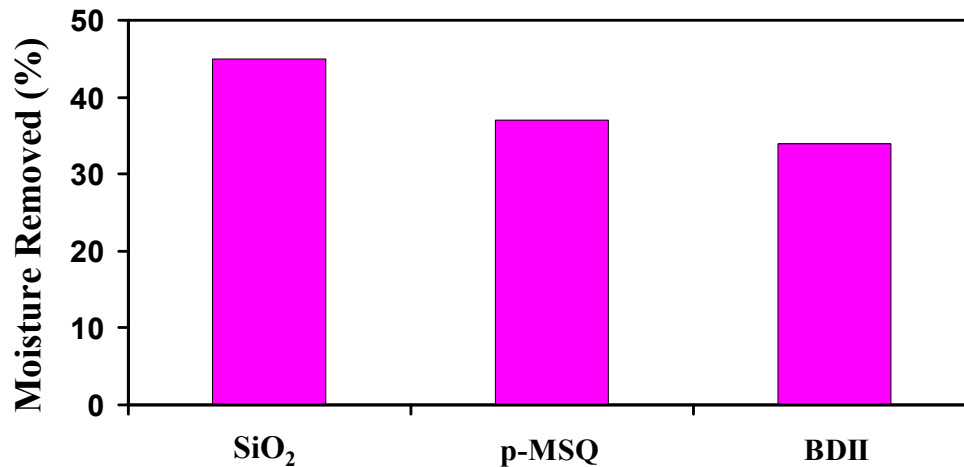
Moisture Loading and Retention Comparison

Challenge Concentration: 56 ppb; Purge Time: 10 hr

Porous low-k films have much higher sorption loading than SiO_2

Moisture removal is a very slow process
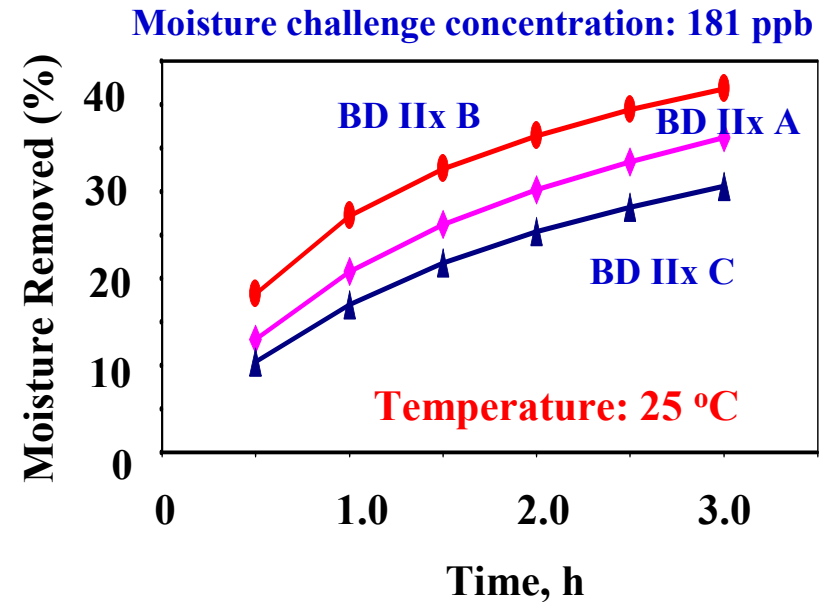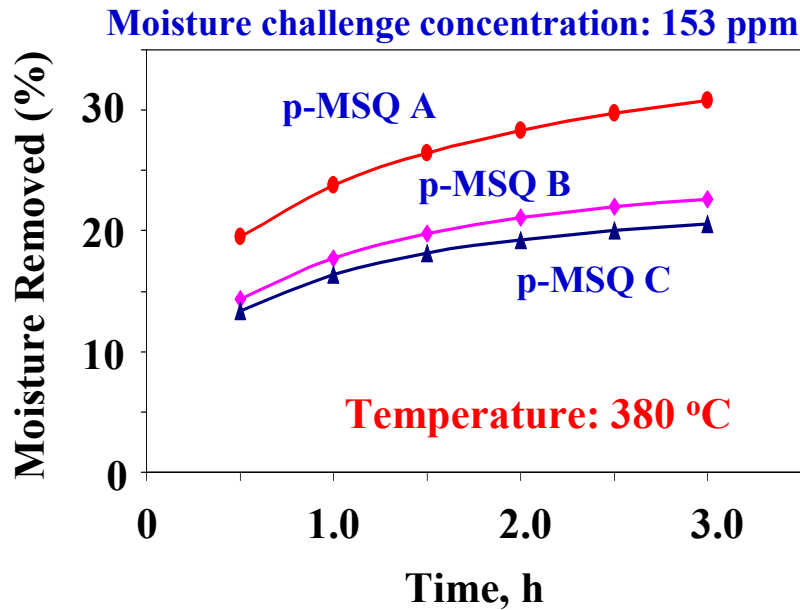
13

Dynamics of Moisture Removal

Purge gas purity: 1 ppb

<u>p-MSQ samples:</u>
A: 10s etch in N_2H_2, 20s ash
B: 10s etch in HeO_2, 20s ash
C: 10s etch in H_2, 20s ash

<u>BD IIx samples:</u>
A: Blanket
B: NH_3-plasma treated
C: NH_3He-plasma treated

Moisture challenge concentration: 153 ppm

Moisture challenge concentration: 181 ppb

Moisture removal is a very slow process

Moisture Transport Pathways in Porous Low-*k* Film

Gas flow

Desorption from matrix

Transport in pores

Permeation in matrix

Exchange between matrix and pores
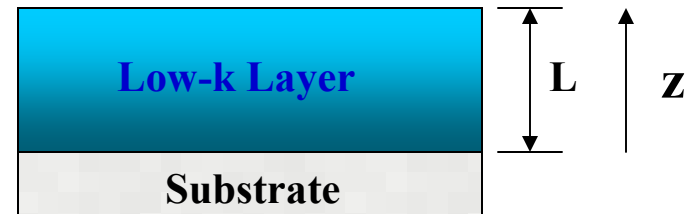
Substrate
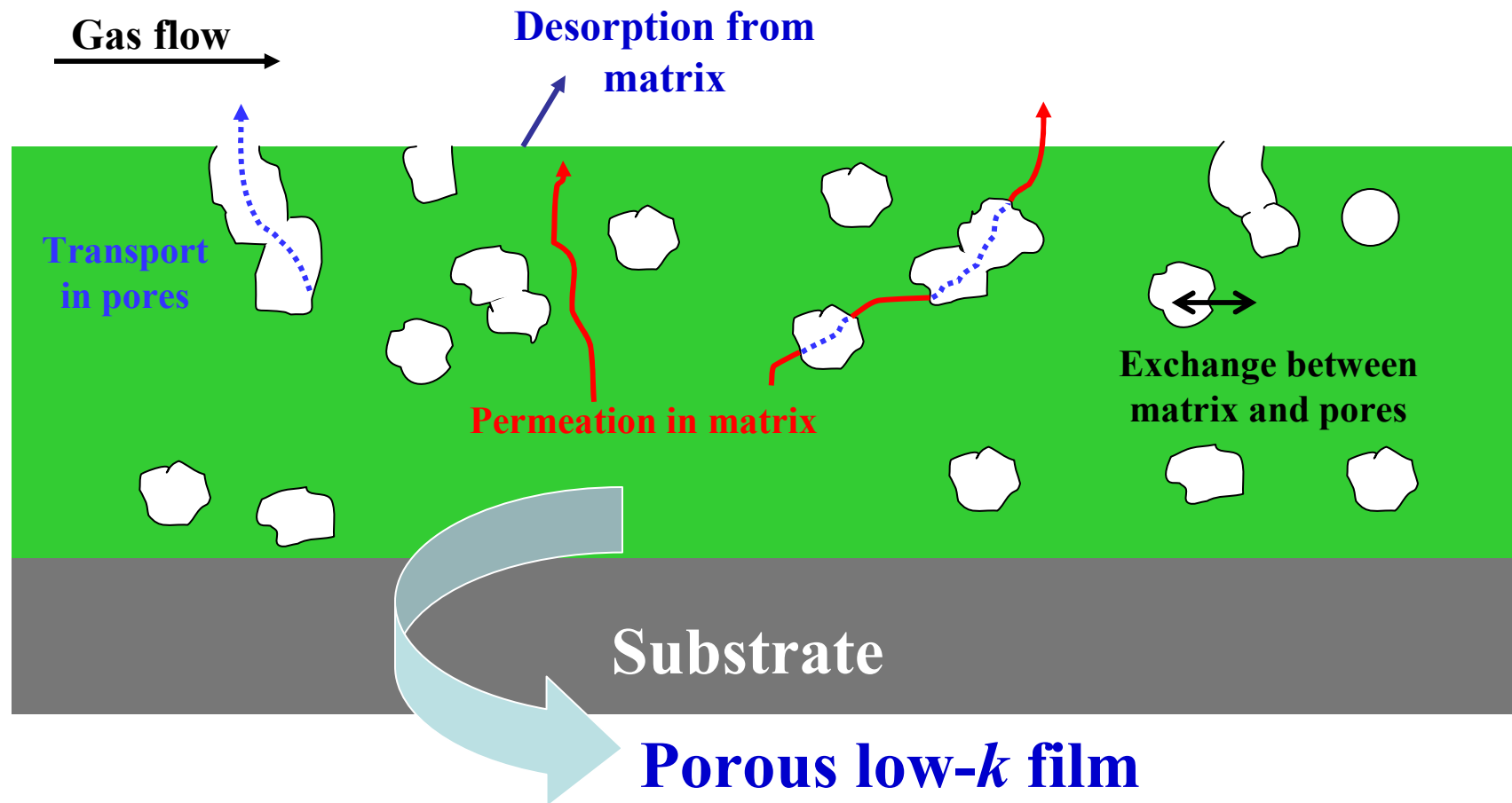
Porous low-*k* film

Process Model for Predicting Impurity Concentration in Porous Low-k Film

Transport of moisture in matrix:

$$\frac{\partial C_S}{\partial t} = \frac{1}{1-\varepsilon}\frac{\partial}{\partial z}[(1-\varepsilon)D_S\frac{\partial C_S}{\partial z}] - \frac{\varepsilon}{1-\varepsilon}k_m S_p(\frac{C_S}{S} - C_g)$$

Low-k Layer

Substrate

L   z

Transport of moisture in pore:

$$\frac{\partial C_g}{\partial t} = \frac{1}{\varepsilon}\frac{\partial}{\partial z}[\varepsilon D_g\frac{\partial C_S}{\partial z}] + k_m S_p(\frac{C_S}{S} - C_g)$$

C_S / C_g: Moisture concentration in matrix / pore;

D_S / D_g: Moisture diffusivity in matrix / pore;

ε: Film porosity;

S_p: Specific surface area;

S: Moisture solubility in matrix;

k_m: Interphase transport coefficient between pore and matrix;

SRC/Sematech Engineering Research Center for Environmentally Benign Semiconductor Manufacturing

Validation of Model

Sample: p-MSQ A, partial etch for 10s in N_2H_2 and 20s ash; Moisture challenge concentration: 1500 ppm; Temperature: 25 ºC

Two smooth curves are model predictions

Outlet Gas Concentration (ppm) vs **Time (min)**
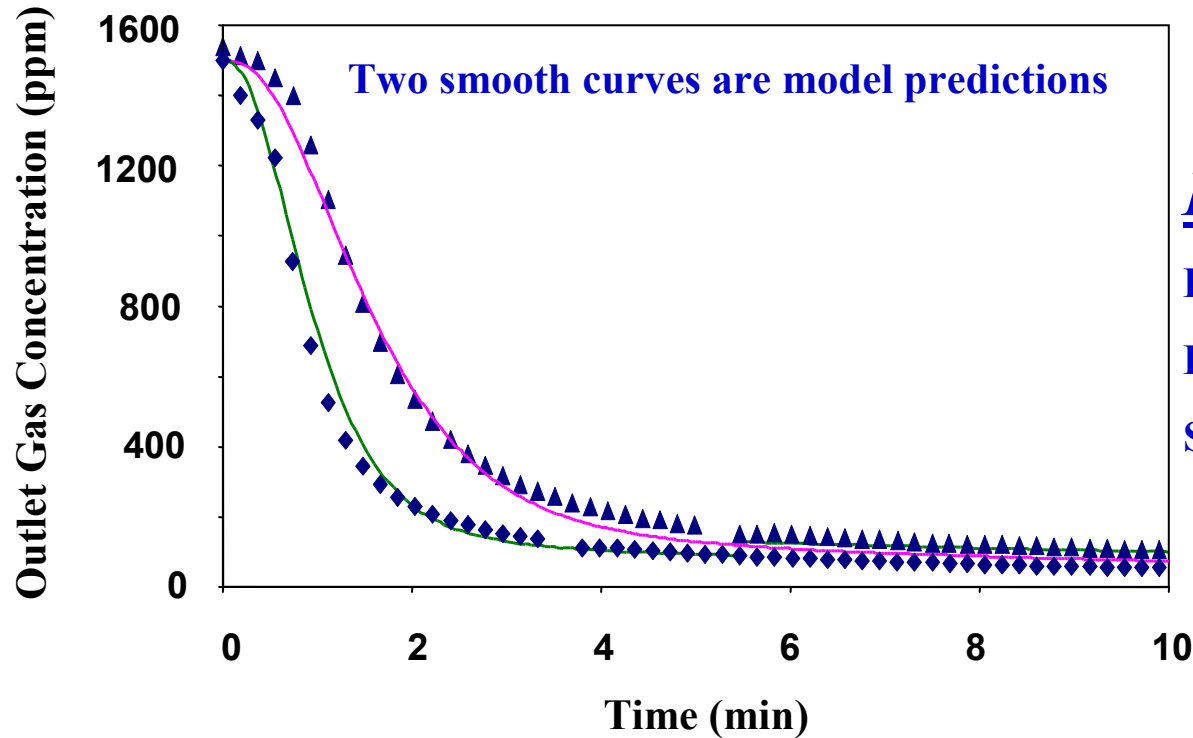
Estimated parameters:

D_S: $1 \times 10^{-15} \sim 1 \times 10^{-12}$ cm²/s

D_g: $1 \times 10^{-10} \sim 1 \times 10^{-8}$ cm²/s

S: $1 \times 10^3 \sim 1 \times 10^5$ cm³(gas)/cm³(solid)

Good agreement between the model and the experimental data

Cell Design

SIDE VIEW

CAUTION

Purge Dynamics of IPA in Empty Cell

Peak Area: 2950 – 3000 Wave number
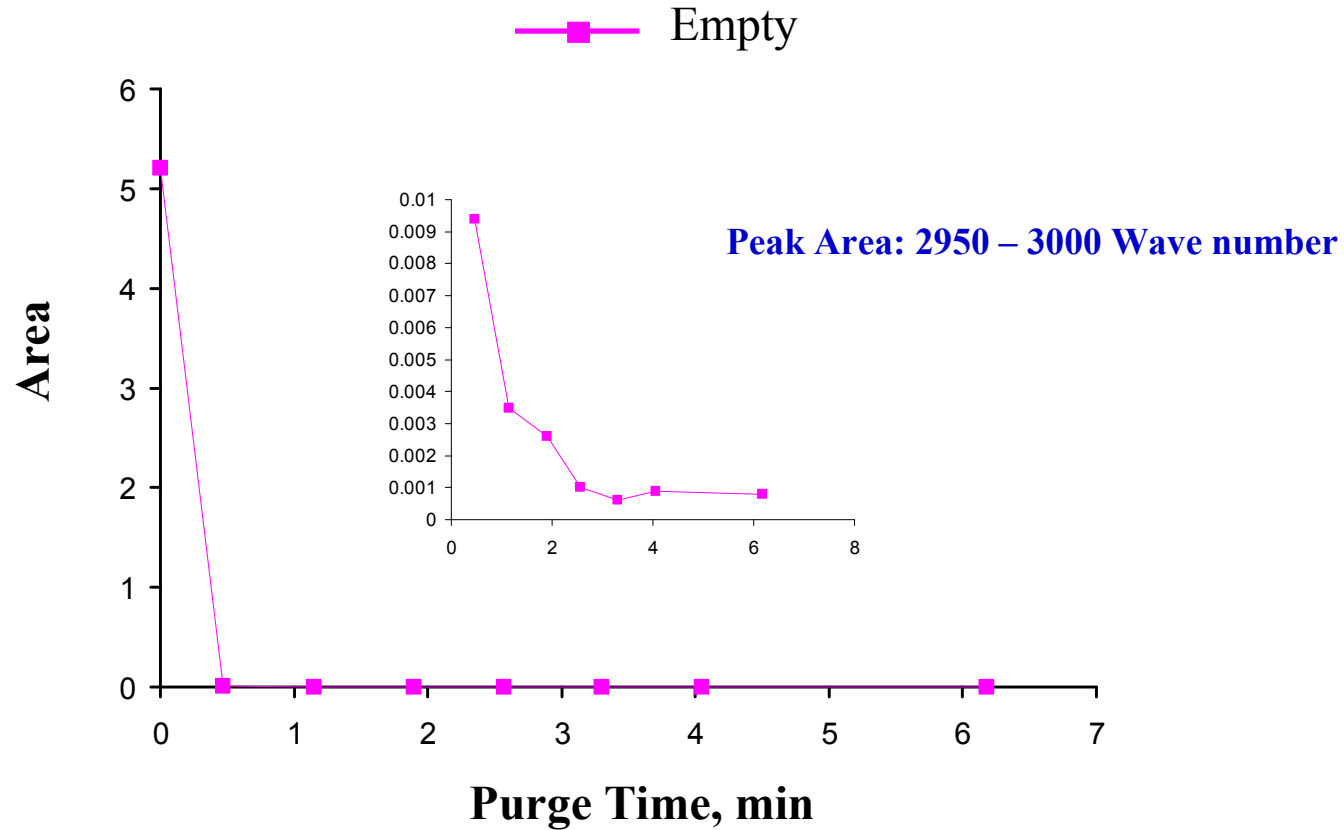
The cell is well purged, no accumulation

SRC/Sematech Engineering Research Center for Environmentally Benign Semiconductor Manufacturing

Outgassing Dynamics of IPA using FTIR

BD IIx, NH$_3$He-plasma treated, k~2.6

Purge time ~27 hr

12 hr liquid IPA exposure

Unexposed sample

Absorbance

Wave number, cm^{-1}
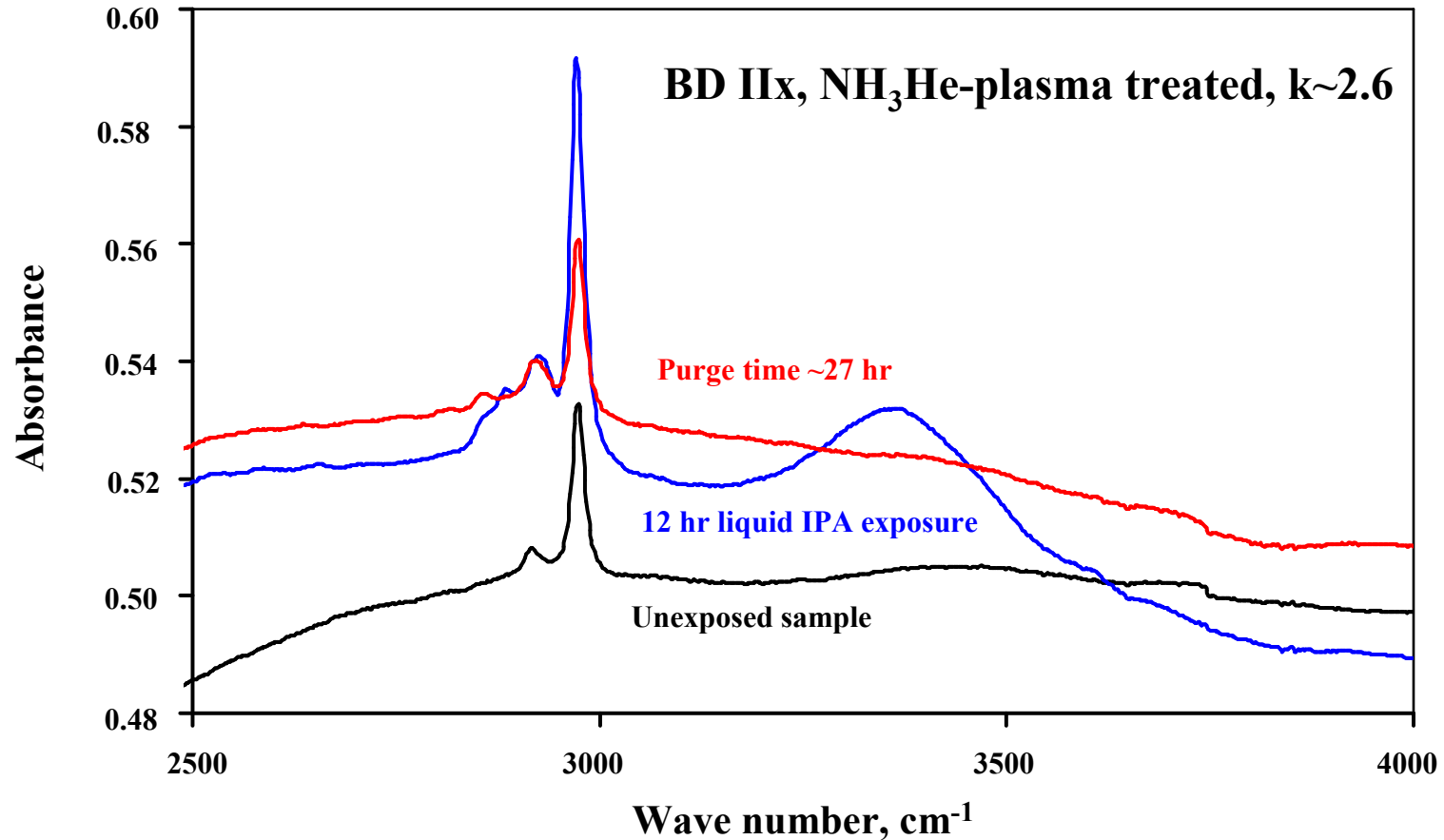
FTIR Spectra for IPA Exposure

Outgassing Dynamics of IPA using FTIR

Desorption

BD IIx, NH$_3$He-plasma treated, k~2.6

Peak Area: 2950 – 3000 Wave number

(chart: Area vs Time, min)

Y-axis: Area (0.4 to 1.2)
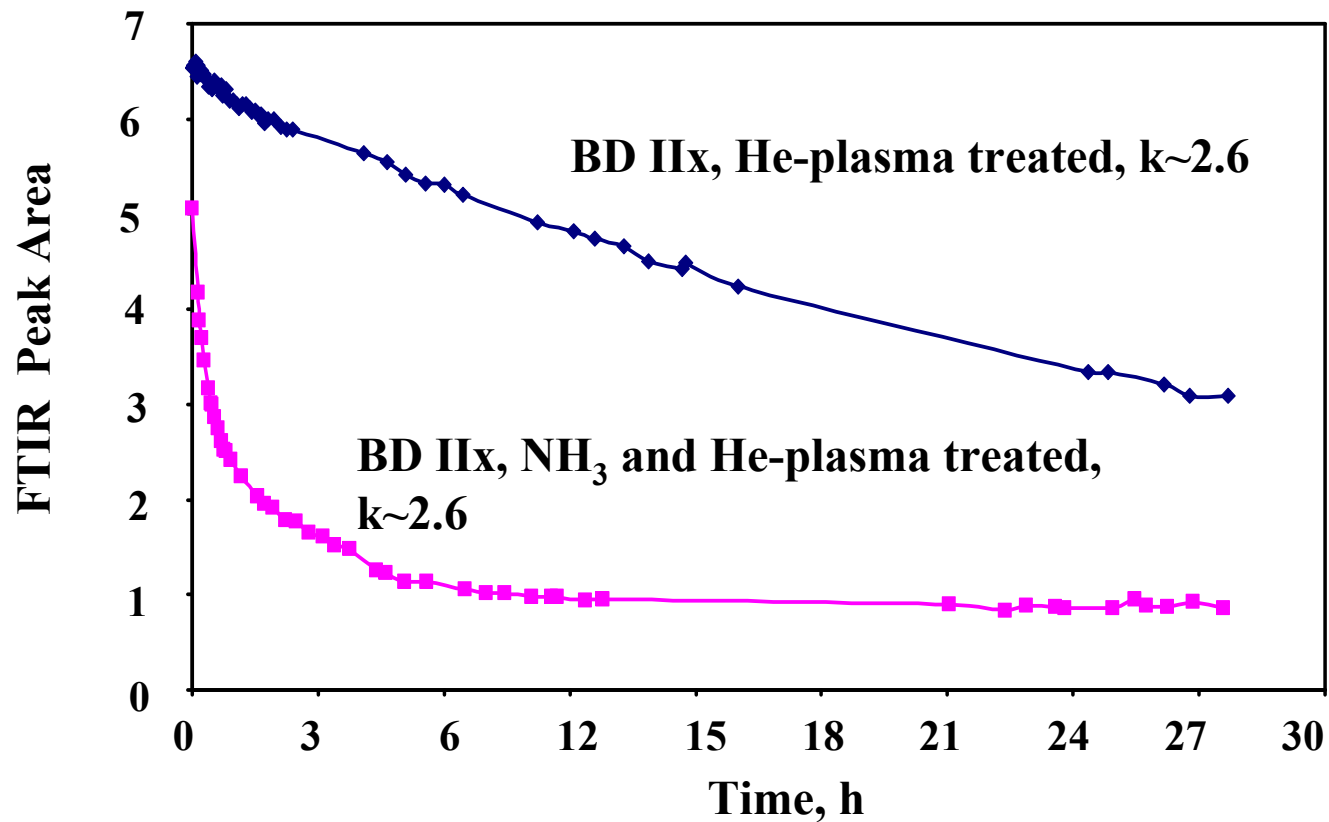X-axis: Time, min (0 to 1600)
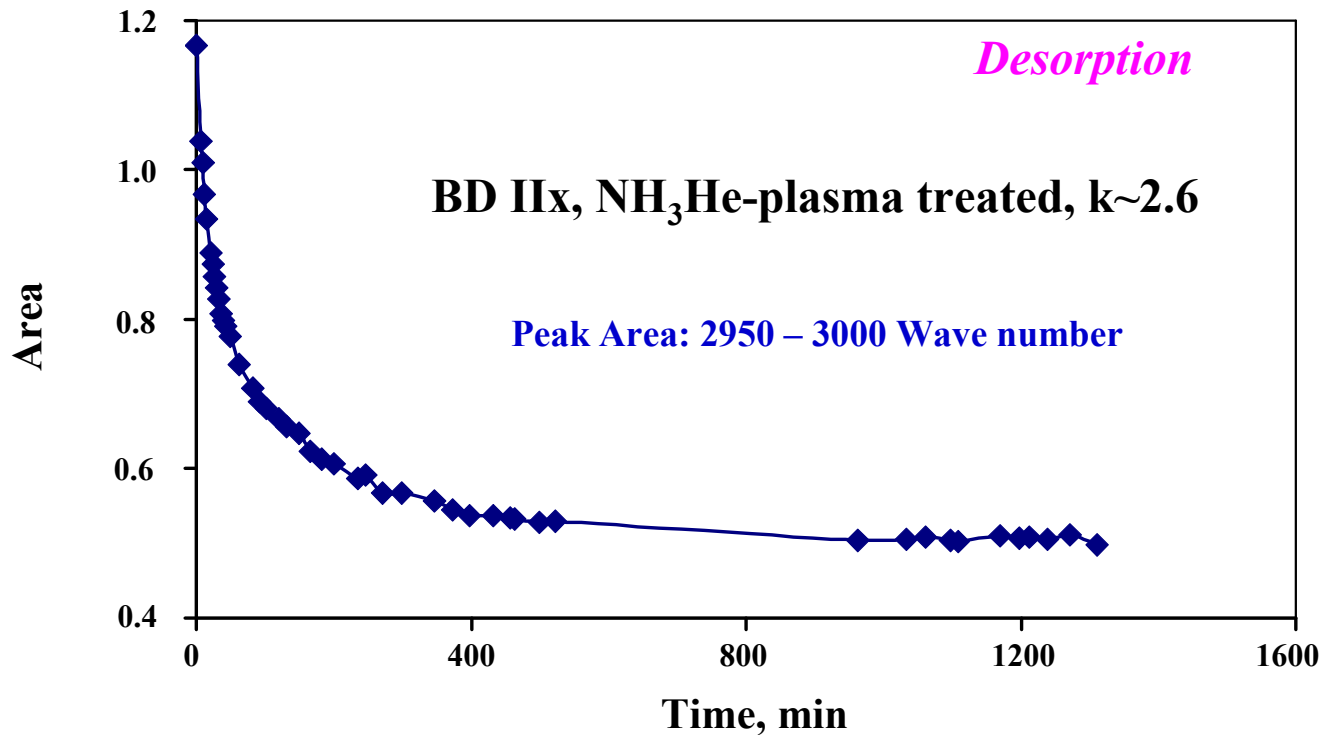
IPA removal is a slow process

IPA Outgassing Comparison

Initially the samples were saturated with liquid IPA; Purge gas: UHP N_2;
FTIR peak at 2950-3000 cm^{-1} (-CH_3 stretching)

BD IIx, He-plasma treated, k~2.6

BD IIx, NH_3 and He-plasma treated, k~2.6

FTIR Peak Area (y-axis)

Time, h (x-axis)

Conclusion

❑ **FTIR looks a promising technique to study dynamics of impurity interaction with thin films.**

❑ **A novel cell was designed to study outgassing dynamics.**

❑ **IPA removal depend on the low-k type and the processing conditions.**

❑ **Etching and ashing affects IPA interaction.**

Future Work

❑ **Extend this study for moisture interaction with low-k films.**
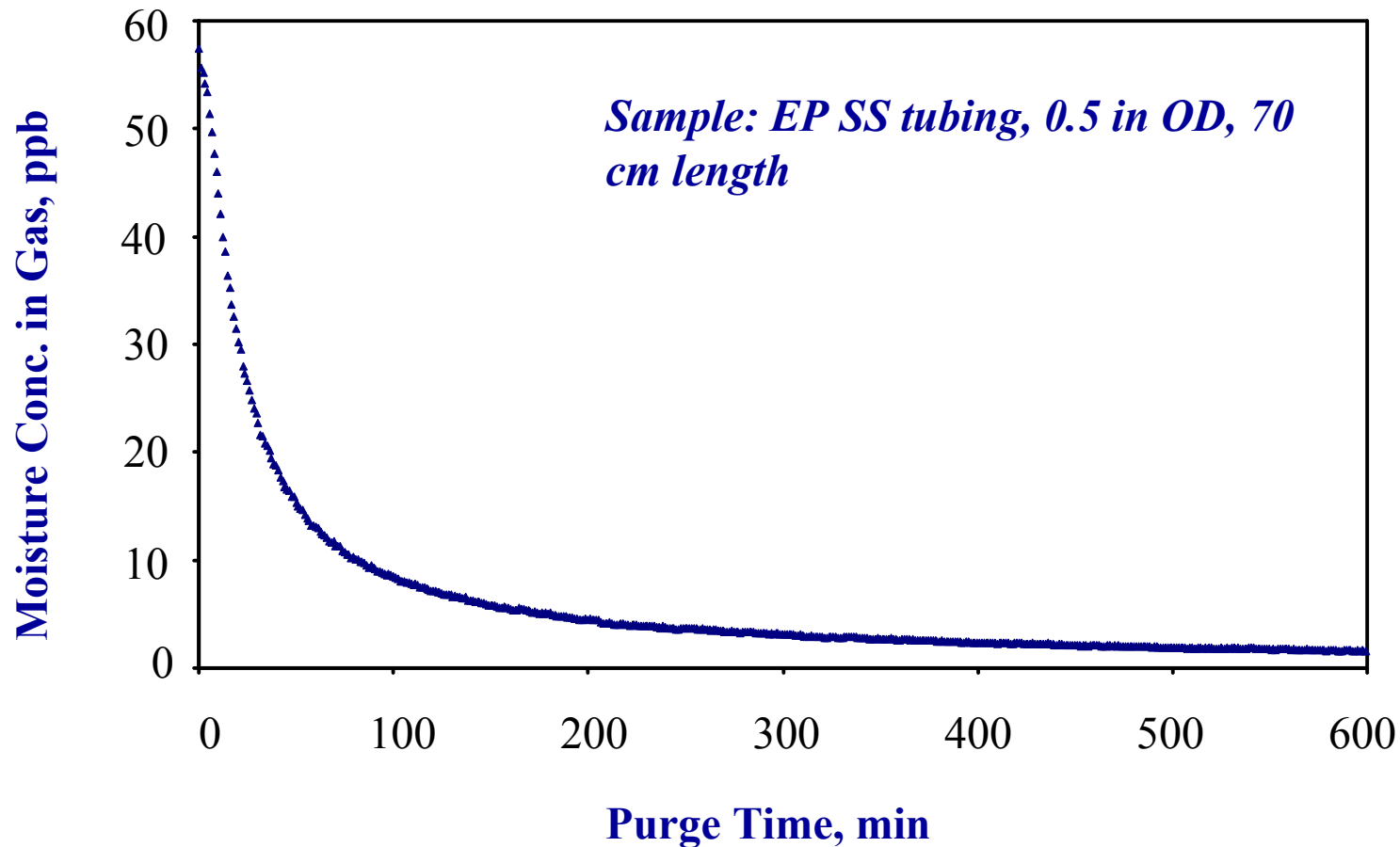
❑ **Study the effect of multicomponent on outgassing dynamics.**

Interaction of Molecular Contamination with EPSS Surface

Background

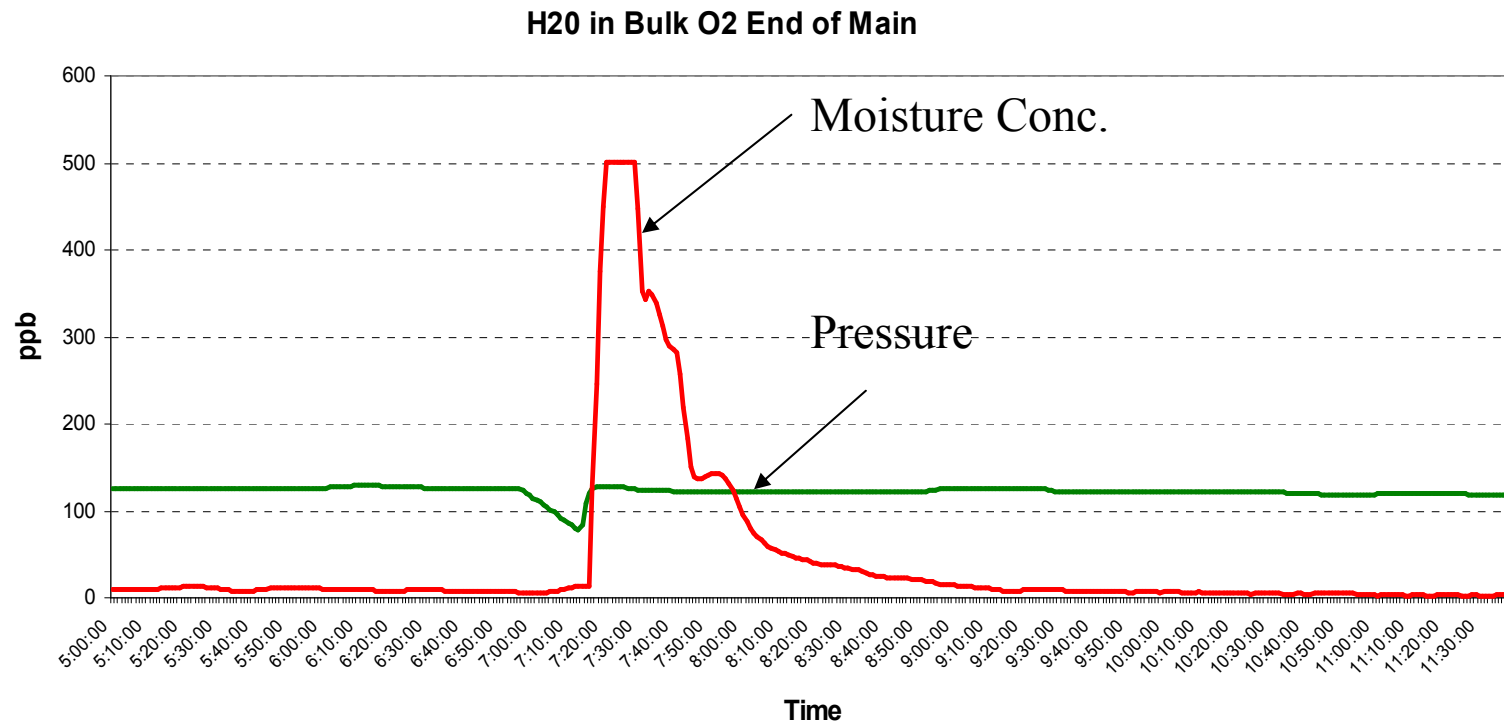**1. Moisture removal is a slow process in gas-distribution system.**

Sample: EP SS tubing, 0.5 in OD, 70 cm length

(Y-axis: Moisture Conc. in Gas, ppb; X-axis: Purge Time, min)

Background

2. Surface adsorption and desorption, back diffusion , dead legs, and pressure fluctuation can cause fluctuation of moisture concentration in gas distribution system.
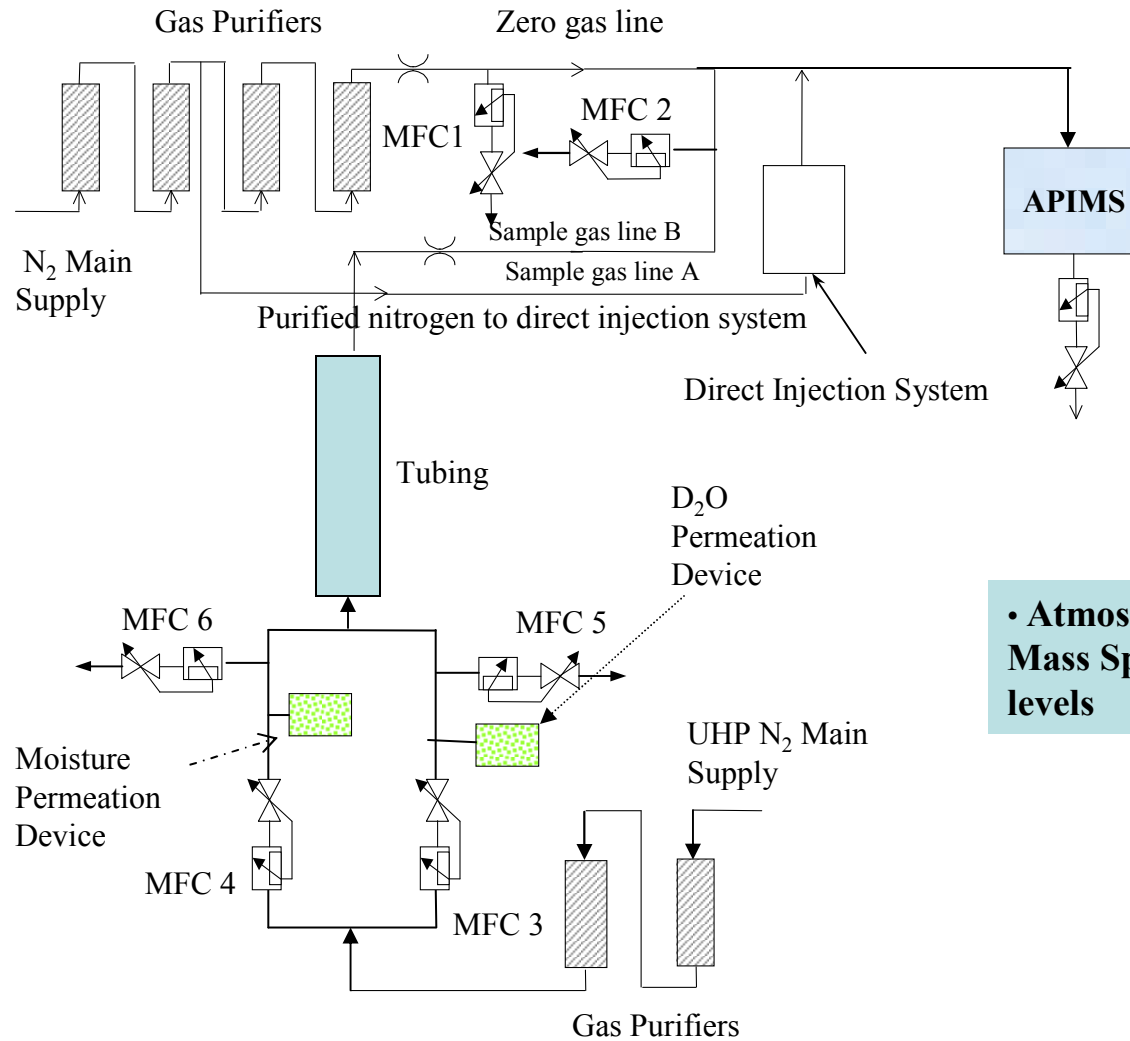
H20 in Bulk O2 End of Main

Research Objective

To develop a model that allows us to optimize the purge process for moisture contaminated gas distribution system, in other words, with shortest time and lowest chemical and energy cost.

Experimental Setup

Gas Purifiers Zero gas line

MFC 2

MFC1

APIMS

N₂ Main
Supply

Sample gas line B
Sample gas line A

Purified nitrogen to direct injection system

Direct Injection System

Tubing

D₂O
Permeation
Device

MFC 6

MFC 5

Moisture
Permeation
Device

UHP N₂ Main
Supply

• **Atmospheric Pressure Ionization**
Mass Spectrometer (APIMS) – ppb
levels

MFC 4

MFC 3

Gas Purifiers

Experimental Procedure

Temporal profile of moisture absorption/desorption

Adsorption at 25 ºC;

Desorption at 25 ºC;
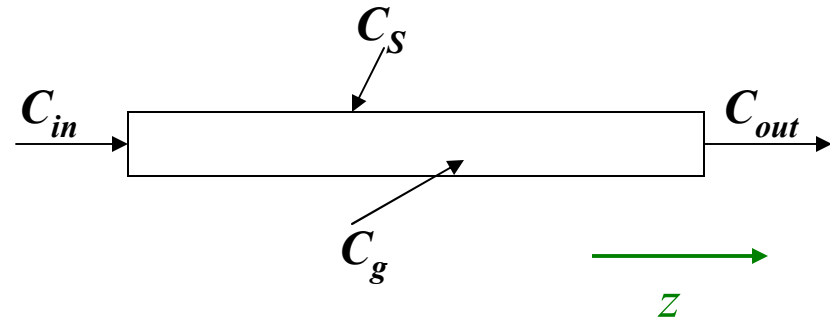
Challenge Conc.: 56 ppb
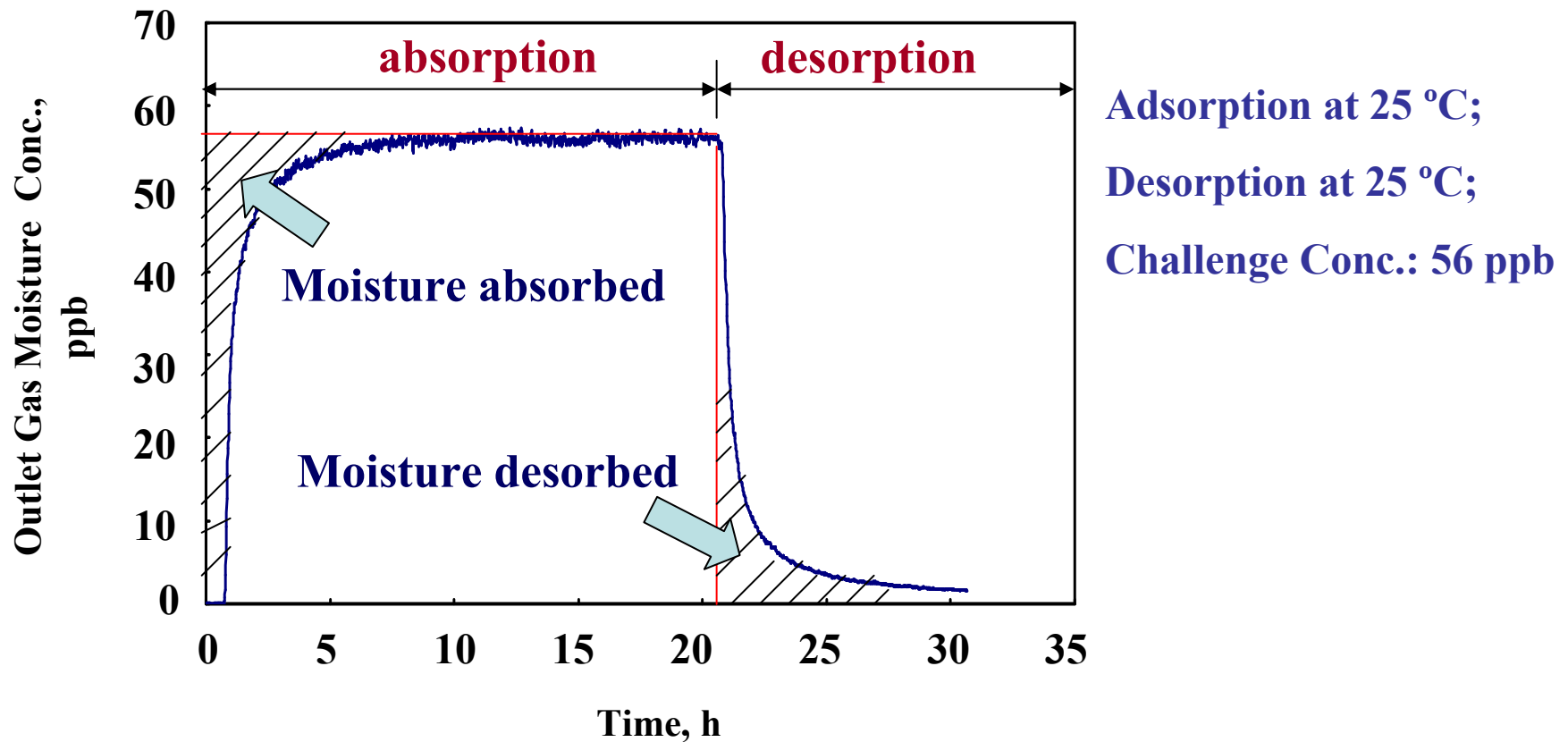
Model Development for Mass Transport in Cylindrical Tubing

Moisture sorption on tubing wall:

$$\frac{\partial C_S}{\partial t} = k_{ads} C_g (S_0 - C_S) - k_{des} C_S$$

Governing equation for gas phase:

$$\frac{\partial C_g}{\partial t} = D_L \frac{\partial^2 C_g}{\partial z^2} - u \frac{\partial C_g}{\partial z} + \frac{A_S}{V} (k_{des} C_S - k_{ads} C_g (S_0 - C_S))$$

C_S: Moisture concentration on wall, mol/cm^2;

C_g: Moisture concentration in gas, mol/cm^3;

k_{ads}: Adsorption rate constant, cm^3/mol/s

k_{des}: Desorption rate constant, 1/s
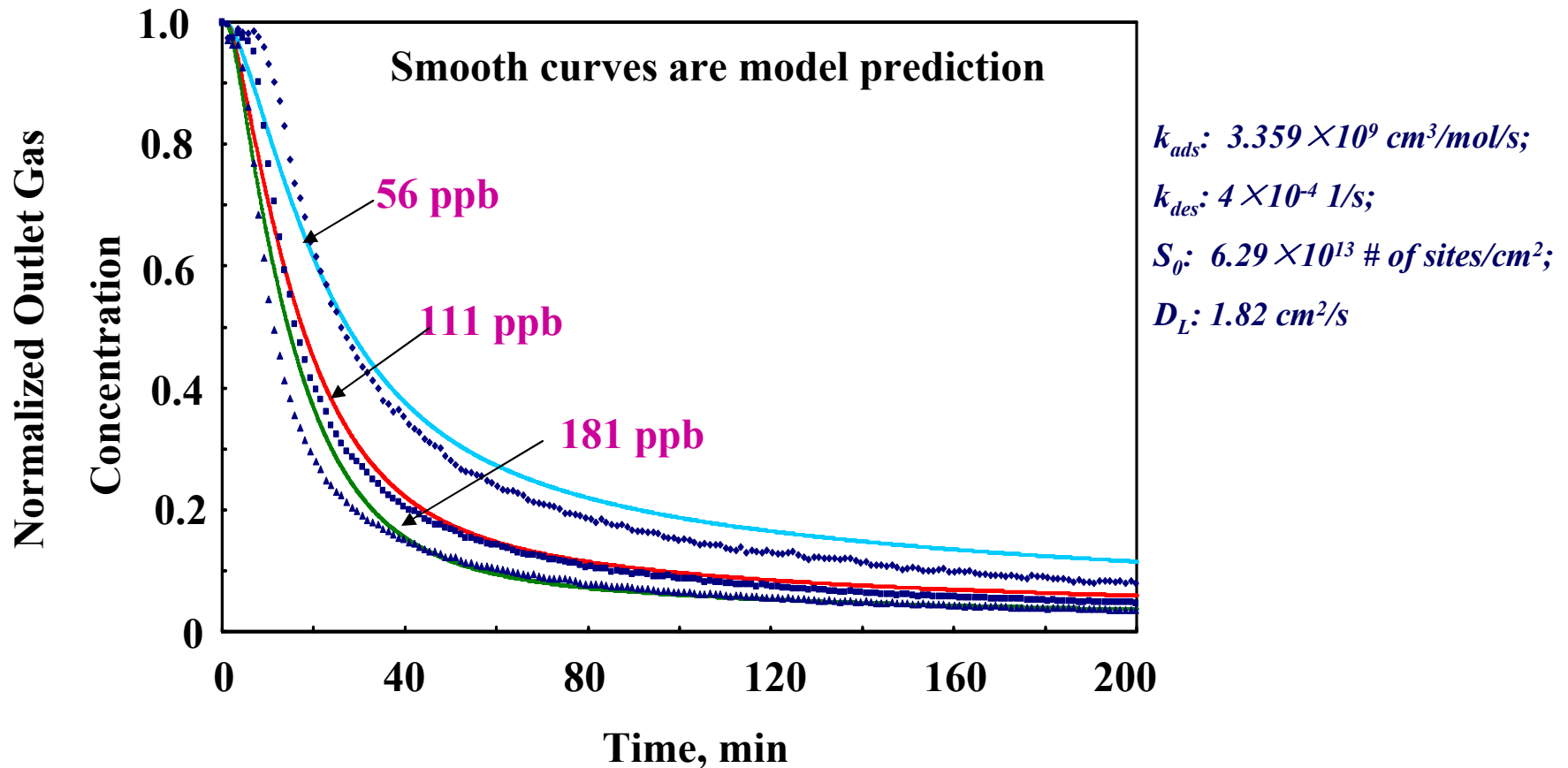
S_0: Site density of surface sorption, # of sites/cm^2;

D_L: Dispersion coefficient, cm^2/s;

u: Velocity, m/s; A_S: Surface area of wall, m^2; V: Volume of tubing, m^3

Model Validation at Different Concentrations

Purge gas flow rate: 350 sccm; Temperature: 25 ºC;
Purge gas purity: 1 ppb,

Smooth curves are model prediction

56 ppb

111 ppb

181 ppb

k_{ads}: *3.359 $\times$ 10⁹ cm³/mol/s;*

k_{des}: *4 $\times$ 10⁻⁴ 1/s;*

S_0: *6.29 $\times$ 10¹³ # of sites/cm²;*

D_L: *1.82 cm²/s*

Normalized Outlet Gas Concentration (y-axis)

Time, min (x-axis)

Effect of Purge Flow Rate

Challenge conc.: 181 ppb; Temperature: 25 ºC ;Purge gas purity: 1 ppb; Length: 0.9 m
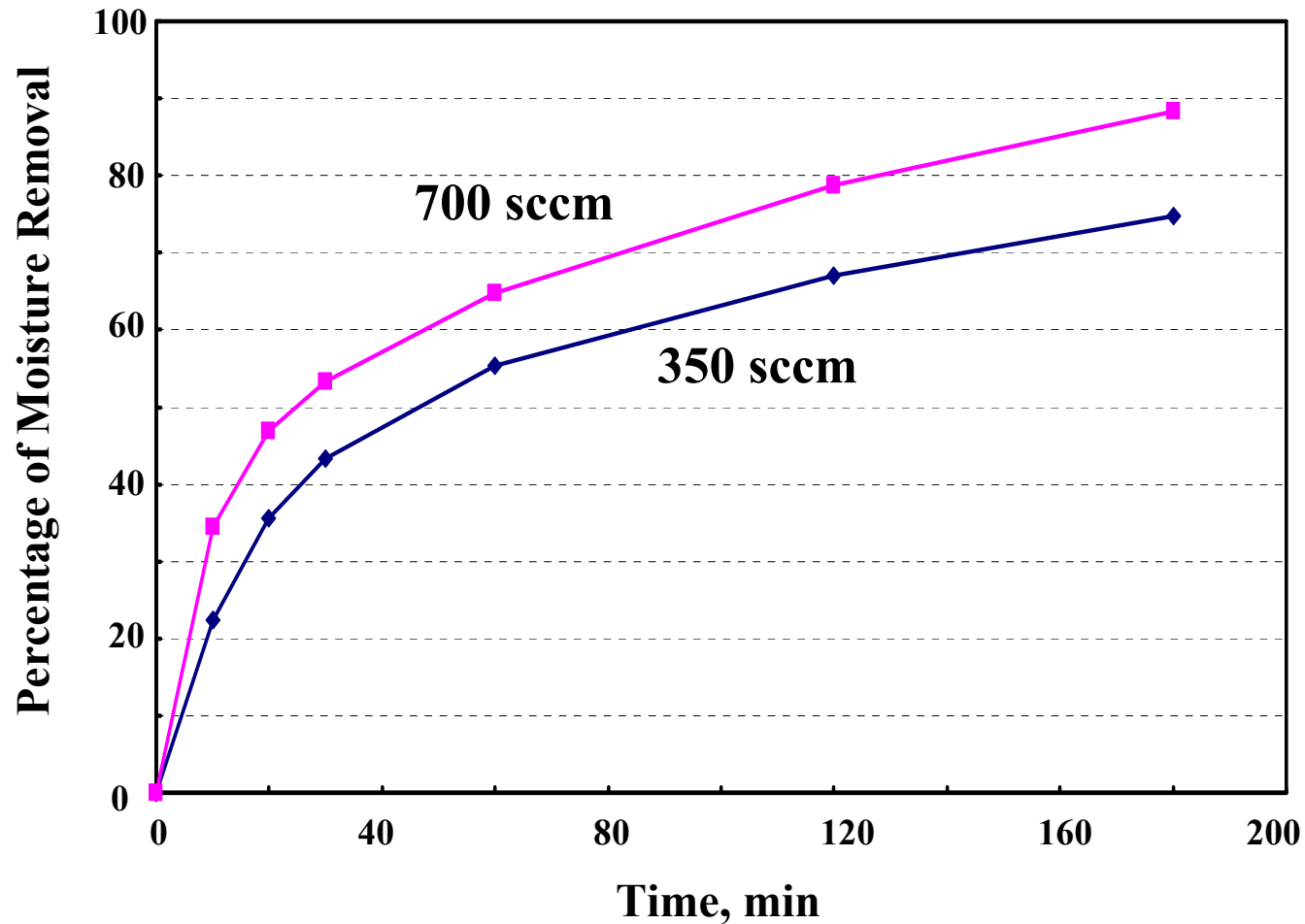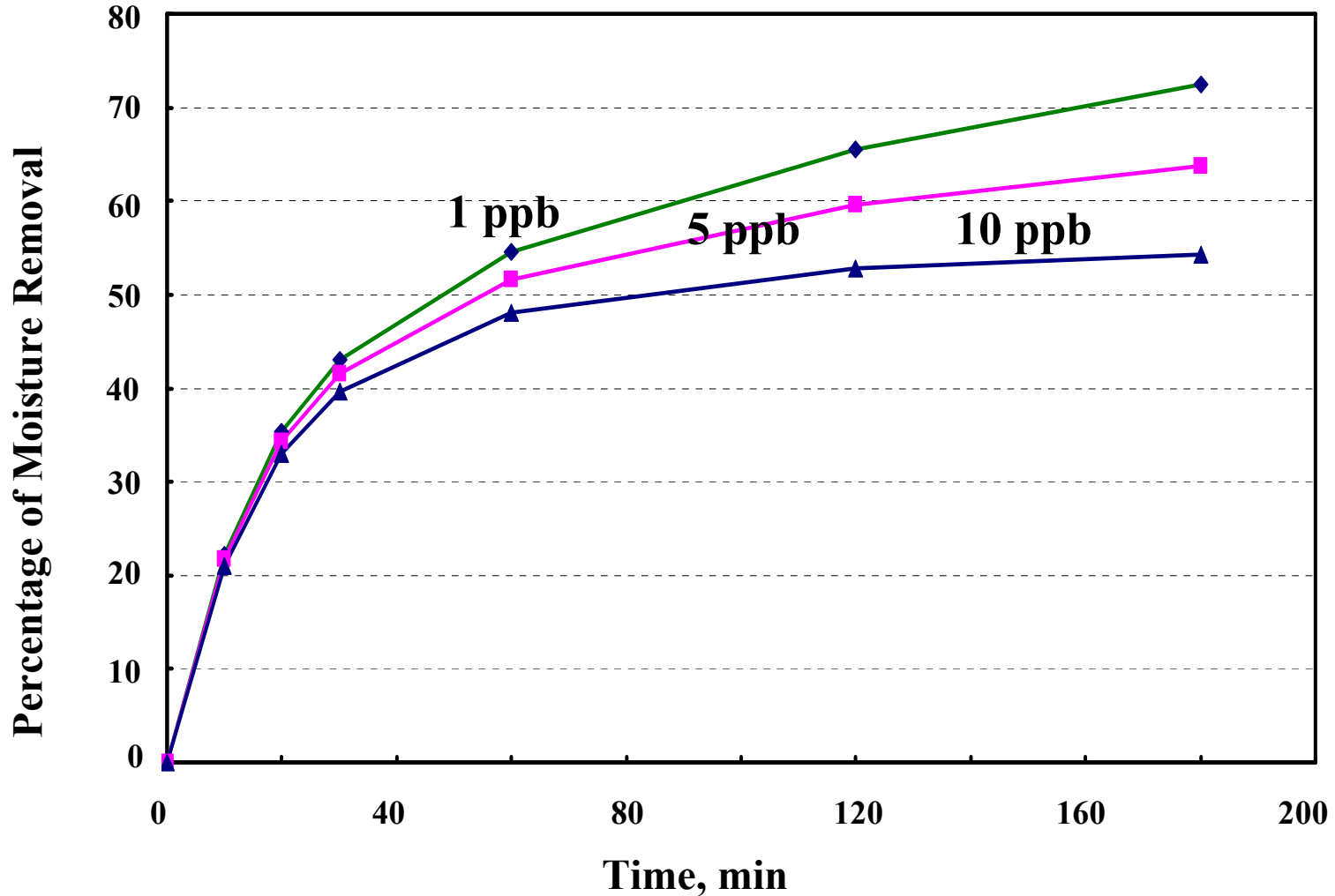
Effect of Purge Gas Purity

Challenge conc.: 181 ppb; Temperature: 25 ºC; Flow rate: 350 sccm; Length: 0.9m
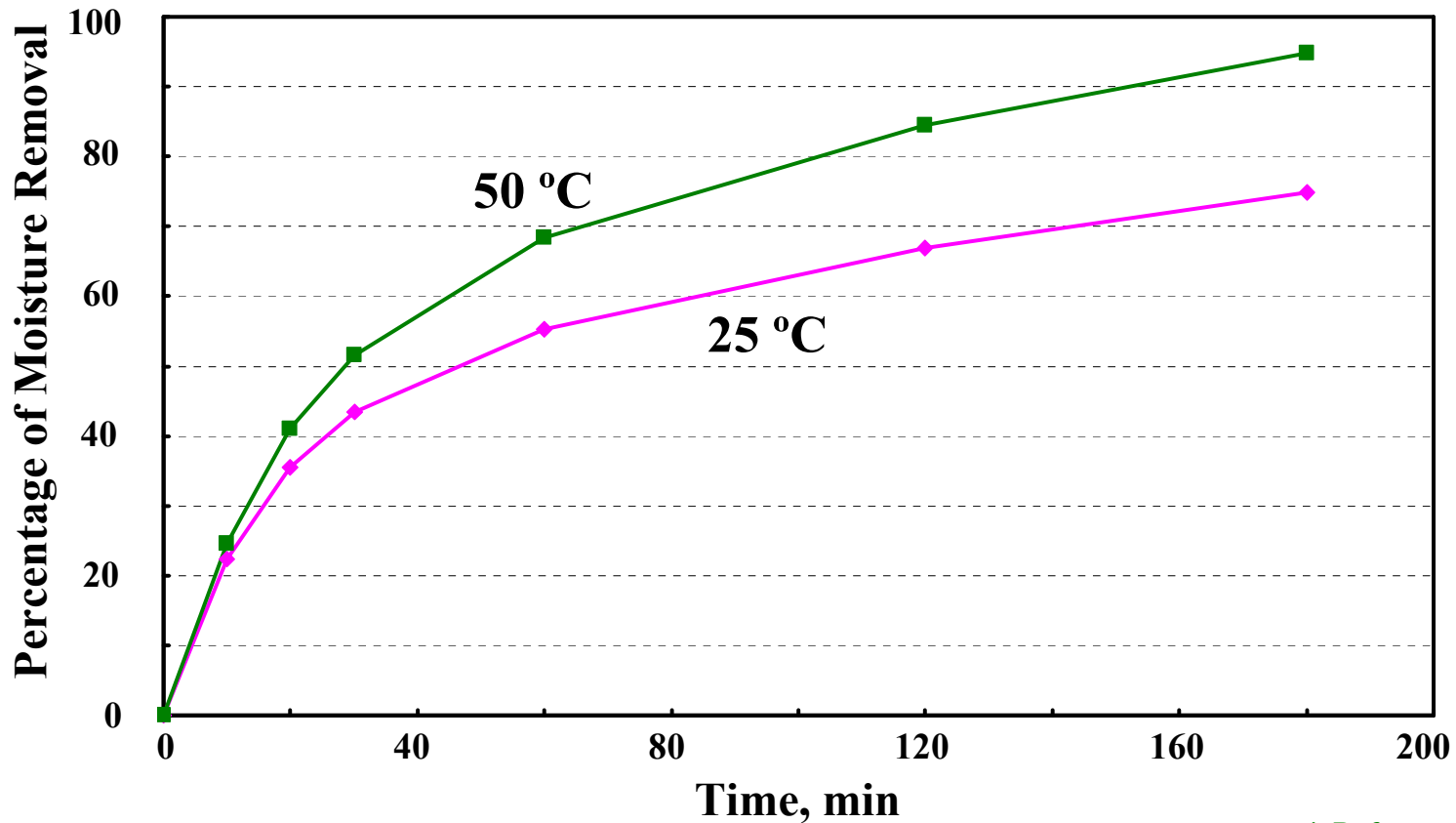
Effect of Purge Gas Temperature

Challenge conc.: 181 ppb; Temperature: 25 ºC;
Flow rate: 350 sccm; Purge gas purity: 1 ppb

E_{ads}: ~ 19 kJ/mol; E_{des}: ~ 47 kJ/mol*

50 ºC

25 ºC

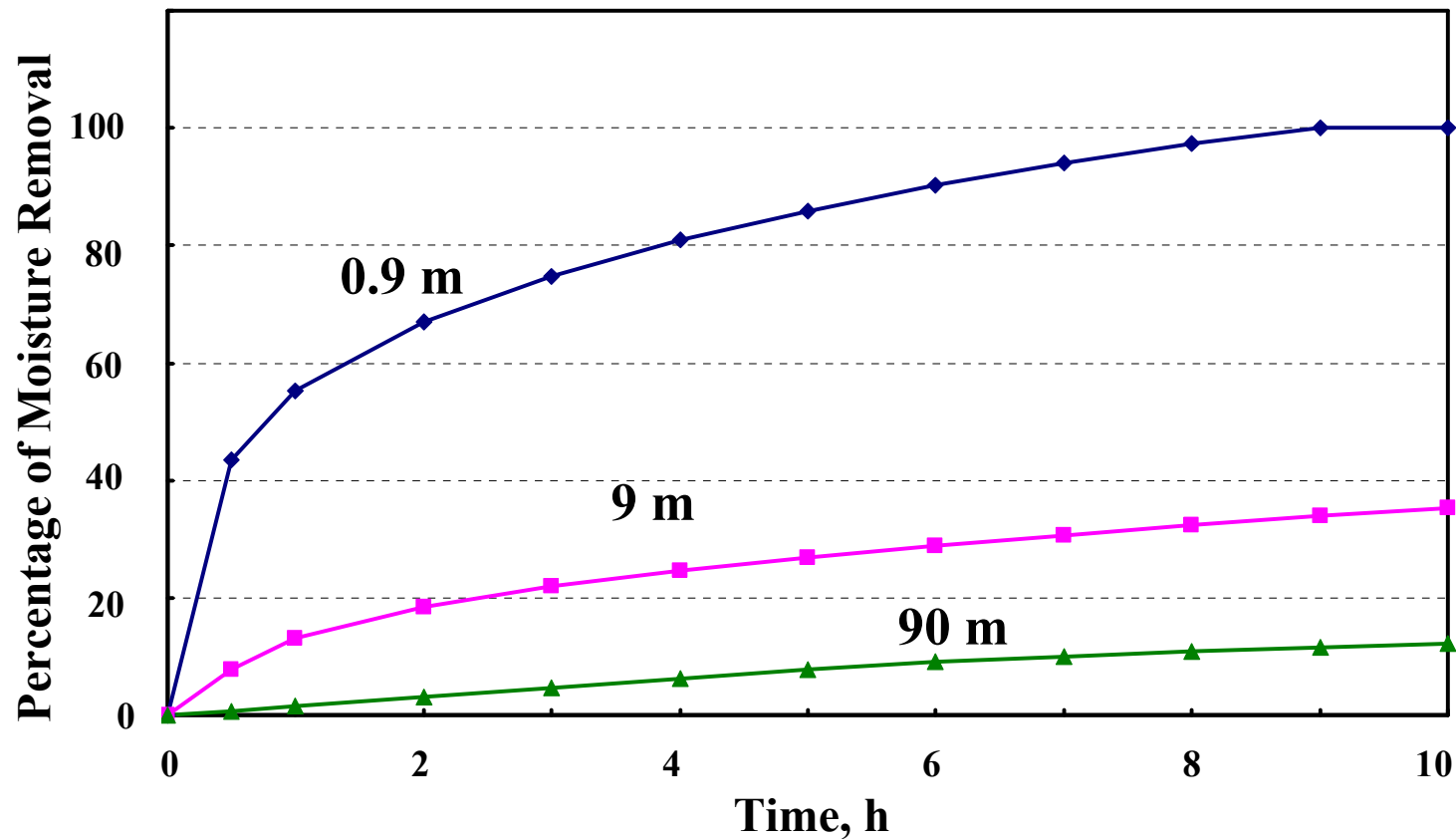*Percentage of Moisture Removal*

Time, min

* Reference data

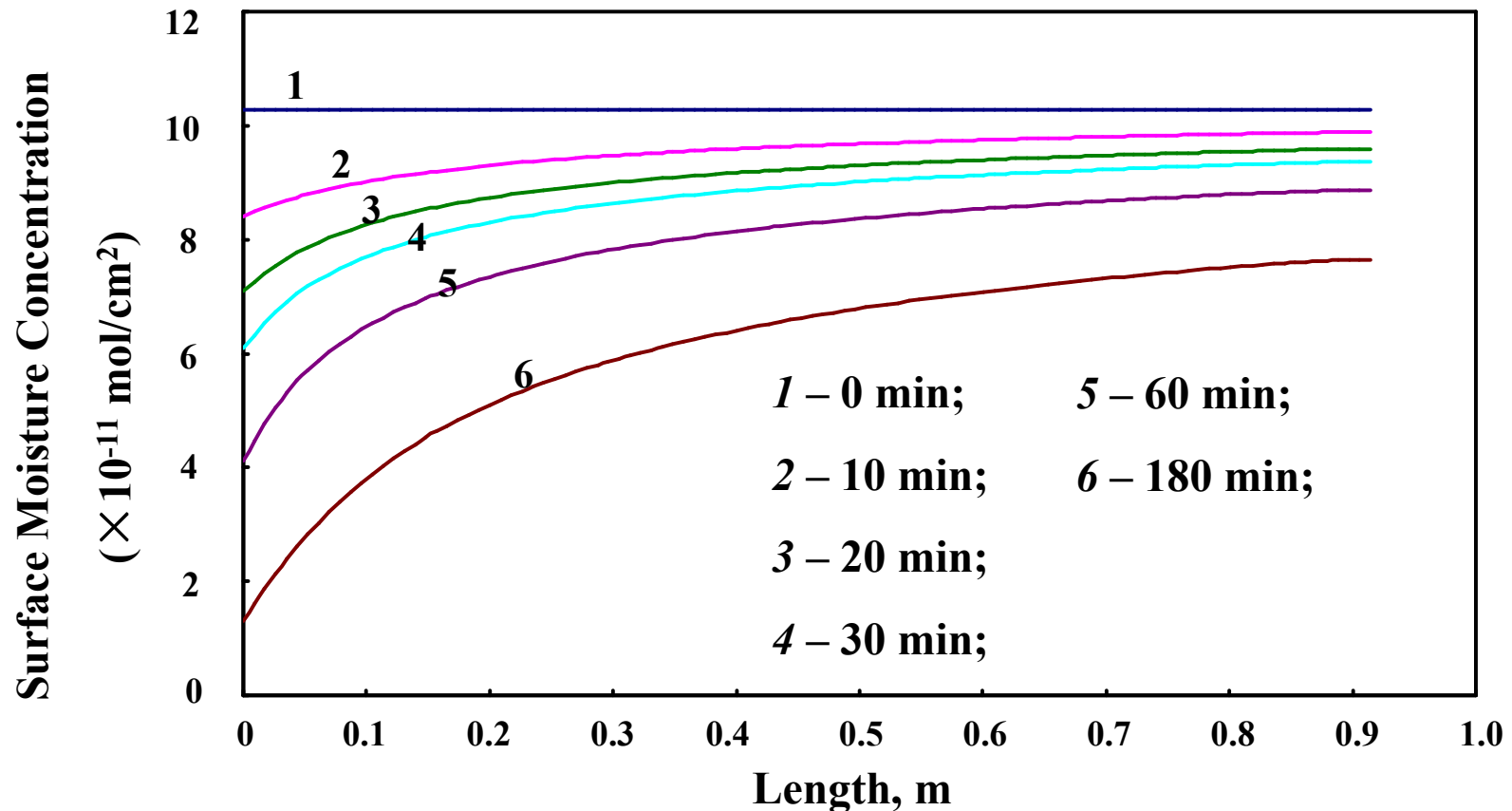# Model Application: Extension of Transfer Line

Challenge conc.: 181 ppb; Temperature: 25 °C;
Flow rate: 350 sccm; Purge gas purity: 1 ppb

Moisture Distribution along the Tubing at Different Purge Times

Challenge conc.: 181 ppb; Temperature: 25 °C;
Flow rate: 350 sccm; Purge gas purity: 1 ppb

- *1* – 0 min;
- *2* – 10 min;
- *3* – 20 min;
- *4* – 30 min;
- *5* – 60 min;
- *6* – 180 min;

Model Application: Back Diffusion at Laterals

Governing equation for bulk gas:

$$U = 2U_{avg}\left[1 - \left(\frac{r}{R}\right)^2\right] \quad [1]$$

$$2u_{avg}\left[1 - \left(\frac{r}{R}\right)^2\right]\frac{\partial C_g}{\partial z} + D_g\frac{\partial^2 C_g}{\partial z^2} + \frac{D_g}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C_g}{\partial r}\right) = 0 \quad [2]$$
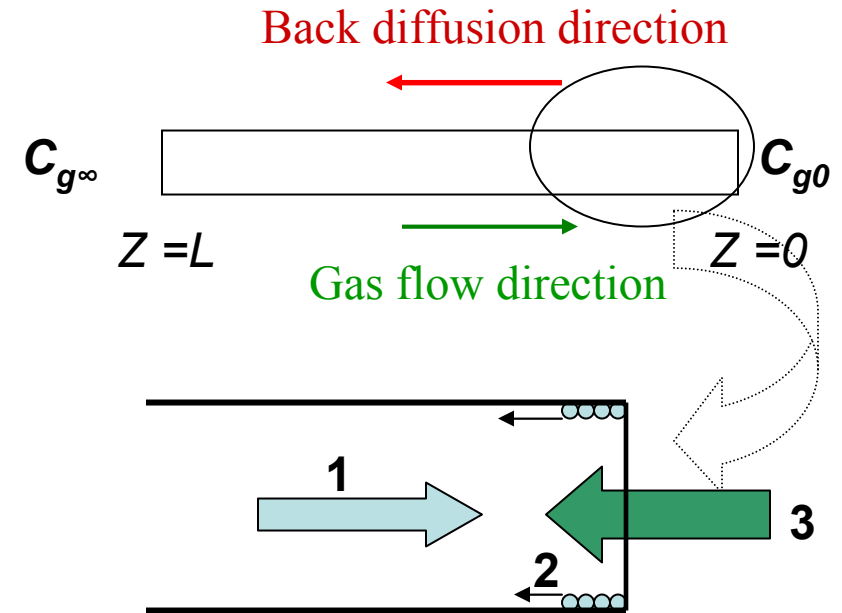
The boundary conditions used for Eq. 2 are

$$C_g = C_{go} \quad \text{at } z = 0, \quad 0 \le r \le R \quad [3]$$

$$C_g = C_{g-} \quad \text{at } z = L, \quad 0 \le r \le R \quad [4]$$

$$\frac{\partial C_g}{\partial r} = 0 \quad \text{at } r = 0, \quad 0 \le z \le L \quad [5]$$

$$-D_g\frac{\partial C_g}{\partial r} = k_a C_g - k_d C_s \quad \text{at } r = R, \quad 0 \le z \le L \quad [6]$$

Back diffusion direction

$C_{g\infty}$ C_{g0}

$Z = L$ $Z = 0$

Gas flow direction

1

3

2

Governing equation for surface diffusion:

$$k_a C_g\big|_{r=R} - k_d C_s + D_s\frac{d^2 C_s}{dz^2} = 0 \quad [7]$$

$$C_s = \frac{k_a}{k_d}C_g \quad \text{at } z = 0 \quad [8]$$

$$C_s = \frac{k_a}{k_d}C_{g-} \quad \text{at } z = L \quad [9]$$

1: Bulk Convection

2: Surface diffusion

3. Bulk diffusion

Back Diffusion at Laterals-Simplified model

Governing equation:

$$D_L \frac{\partial^2 C_g}{\partial z^2} - u \frac{\partial C_g}{\partial z} = 0$$
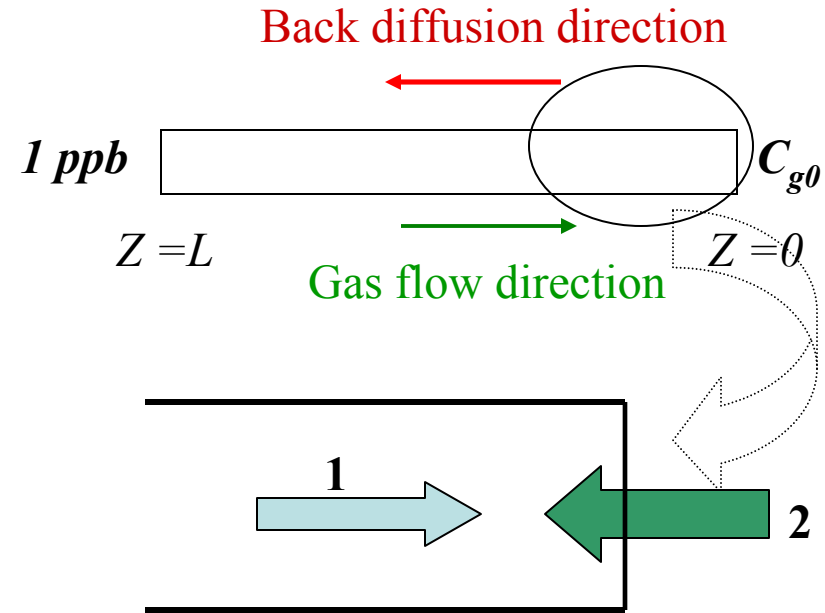
BC:

$$z = 0, \ C_g = C_{g0}$$

$$z = L, \ C_g = 1 ppb$$

C_g: *Moisture concentration in gas, mol/cm³;*

D_L: *Dispersion coefficient, cm²/s;*

u: Velocity, m/s;

C_{g0}: *Ambient moisture concentration*

Back diffusion direction

1 ppb C_{g0}

$Z = L$

Gas flow direction

$Z = 0$

1

2

1: Bulk Convection

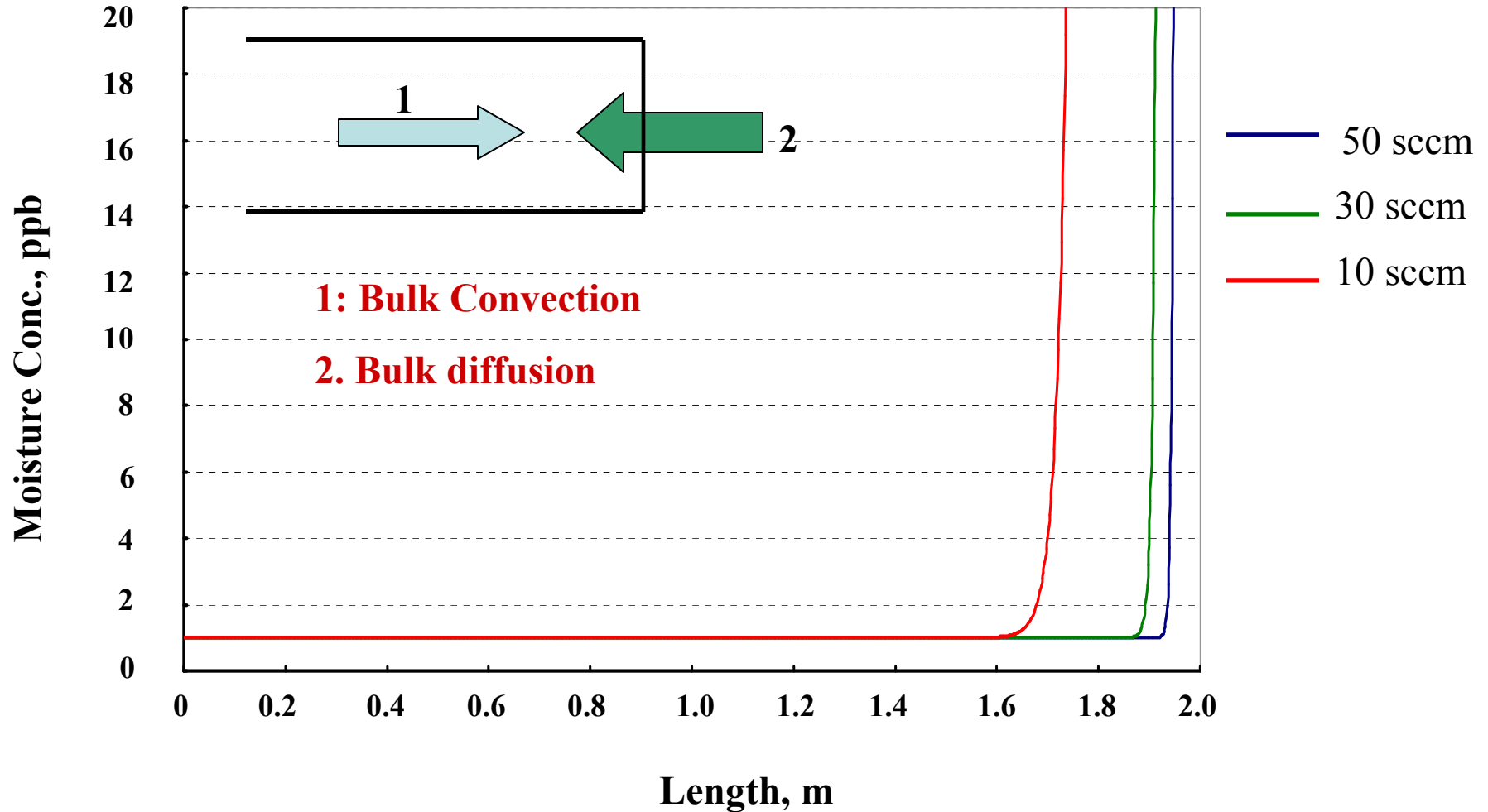**2. Bulk diffusion**

Back Diffusion at Laterals

----Contd.

Moisture profile along the lateral (Length: 2 m)

1: Bulk Convection

2. Bulk diffusion

Legend:
- 50 sccm
- 30 sccm
- 10 sccm

Y-axis: Moisture Conc., ppb

X-axis: Length, m

Conclusion

1. The combination of experiments and modeling we have developed helps in optimizing the dry-down time and lower the purge-gas and energy consumption during system start-up or recovery.

2. This technique can be used to minimize the back diffusion problem.

Future Work

1. Extend the application of the model

Single tubing ⟶ **one lateral** ⟶ **More laterals**

⟶ **Complex gas delivery system**

2. Effects of dead legs and pressure fluctuation

Acknowledgement

Dr. Farhang Shadman	**Advisor, Regents Professor in Chemical Engineering and Optical Sciences Department, U of Arizona**
Dr. Roger Sperline	**Professor in Chemistry Department, U of A for helping with FTIR Analysis**
Dr. Prashant Raghu	**Process Engineer, Micron**
Carl Geisert	**Az/FSM Sr. Principal Engineer, Intel Corporation**
Dr. Ting Tsui	**Assistant Professor, U of Waterloo, formerly at Texas Instruments**
Sematech (Interconnect Group)	**For partial support of this research**