SAMPLE SYSTEM EFFECTS OF FTIR MEASURED NH_3 RESPONSE

2013 DOE Crosscut Workshop
on Lean Emissions Reduction Simulation

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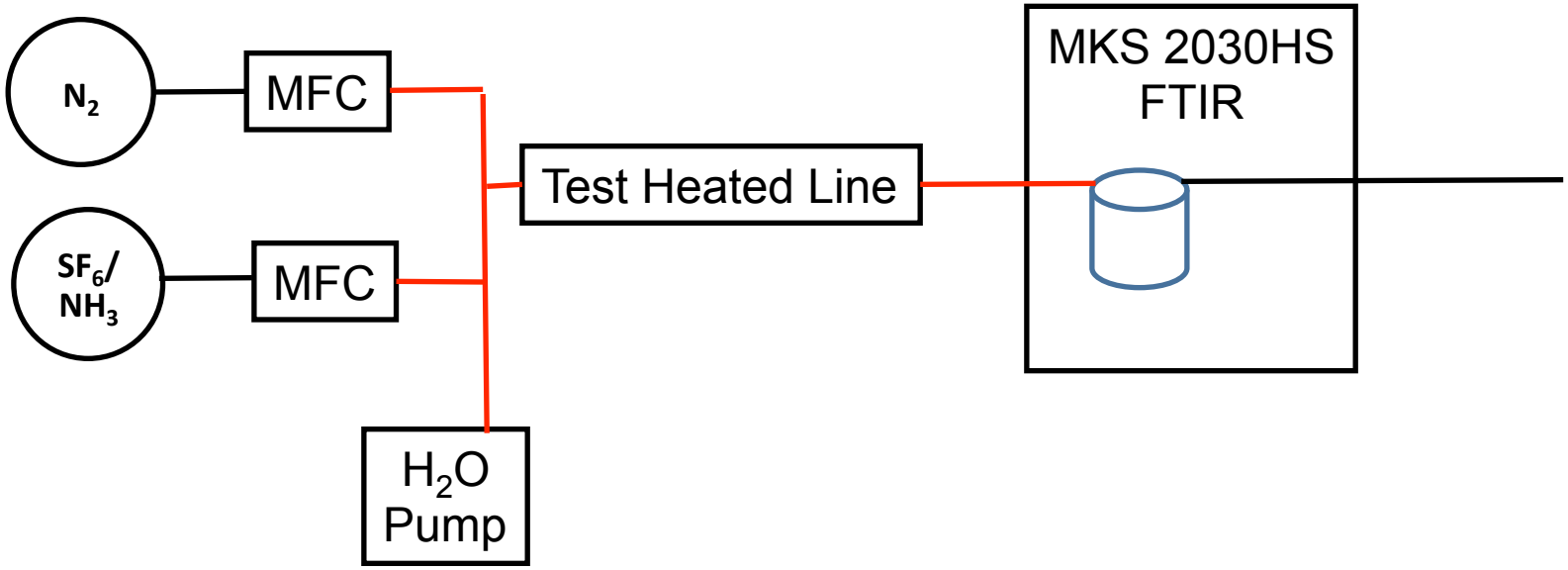
University of Michigan:
John Hoard
Nanda Gopalan Venkata Ramanan

MKS Instruments
Barbara Marshik

Introduction

- NH_3 is known to "stick" on walls
- Causes slower response than other gases
- Experiment to quantify this effect
- Ran step transient tests
  - SF_6/NH_3 gas used, 1/25 ratio
  - SF_6 does not stick, has good FTIR response
  - Compare SF_6 to NH_3 response to measure wall sticking

Test Schematic



Test Variables

- Heated line length
  - 20 or 35 feet (6.1 or 10.7 meter)
- Heated line diameter (nominal)
  - 1/4 or 3/8 inch (6.35 or 9.52 mm)
- Heated line type
  - SS, SS corrugated, Silico corrugated, Per-Fluro Alkoxy (PFA)
- Temperature (line and FTIR cell)
  - 113° or 191°C
- Water
  - Dry or ~5%
- Flow rate
  - 5, 10, 15, and 20 SLPM

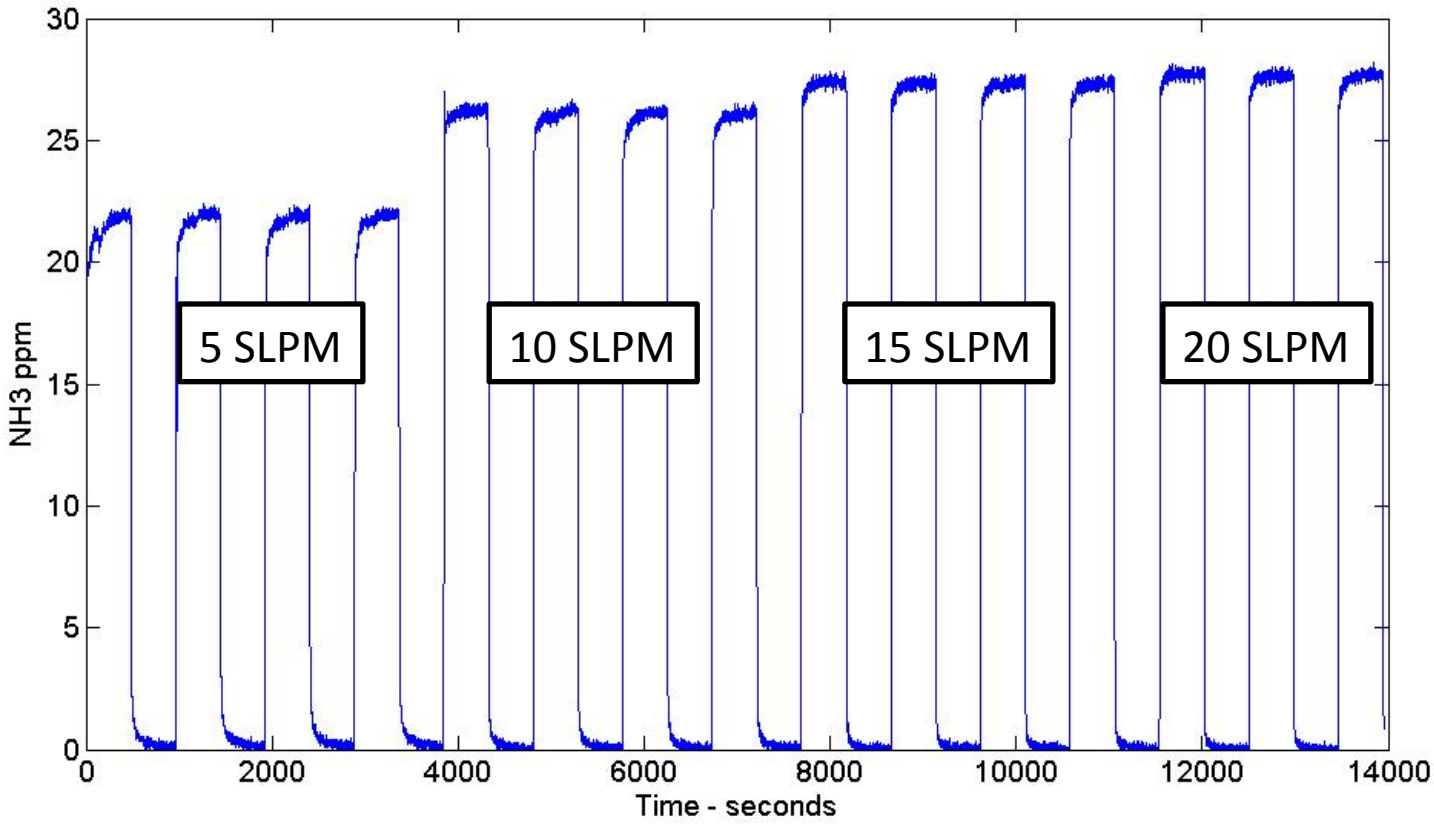
Test Lines

	Sample Lines	
1/4th inch lines	35 feet lines	
	Line 1	Stainless Steel Straight
	Line 2	Stainless Steel Silico Corrugated
	Line 3	Stainless Steel Corrugated
	Line 4	Per-Fluro Alkoxy (PFA) tubing
	20 feet lines	
	Line 5	Stainless Steel Straight
	Line 6	Stainless Steel Silico Corrugated
	Line 7	Stainless Steel Corrugated
3/8th inch lines	35 feet lines	
	Line 8	Stainless Steel Corrugated
	Line 9	Per-Fluro Alkoxy (PFA) tubing
	20 feet lines	
	Line 10	Stainless Steel Silico Corrugated

Experimental

- Partial factorial with three replicates
- Procedure:
  - Set line and cell temperature
  - Program to run:
    - Dry
      - 5 then 10, 15, 20 SLPM four on/off cycles each
    - Wet
      - Same as dry
  - Change set temperature and repeat
  - Change line and repeat

Raw data

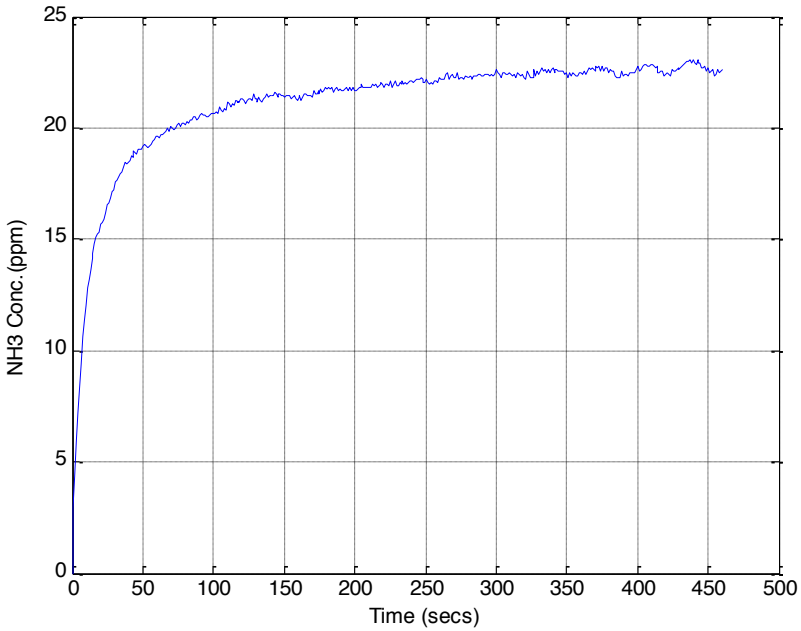


- All first peaks removed from data set
- Thus, three conditioned replicates

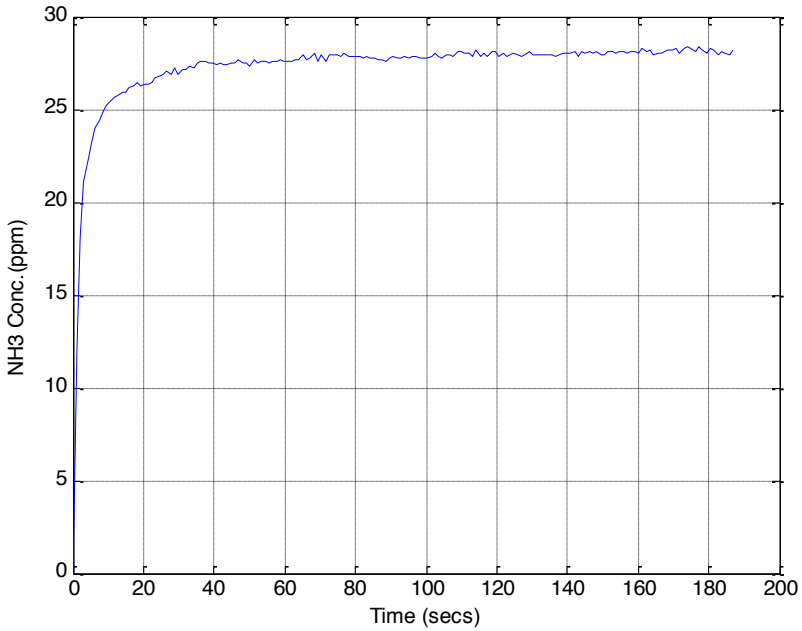
Data Reduction

- For each “up” transient:
- Fit curve
- Use fitted equation to estimate NH_3 storage
- Perform General Linear Model (ANOVA) on result using Minitab®

Typical "up" Response (NH_3)

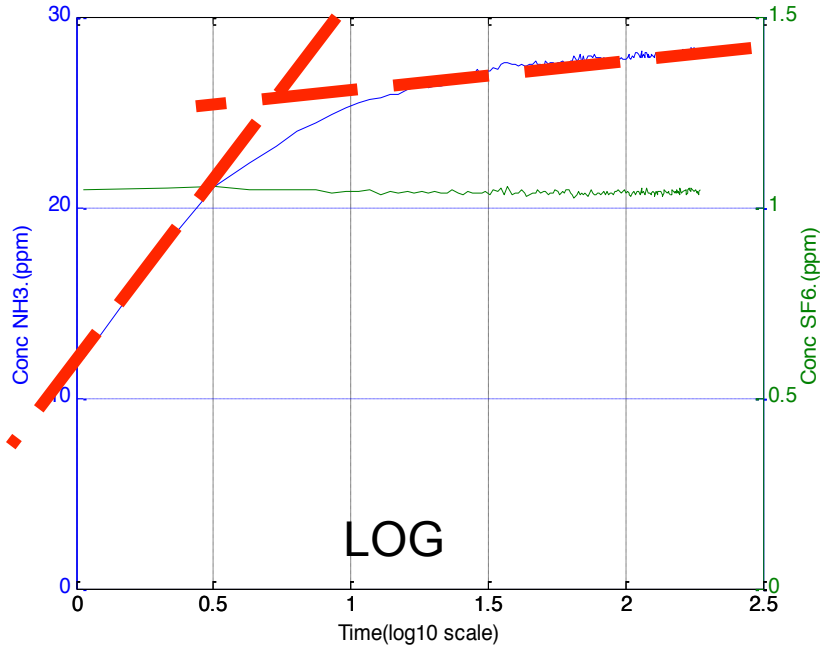


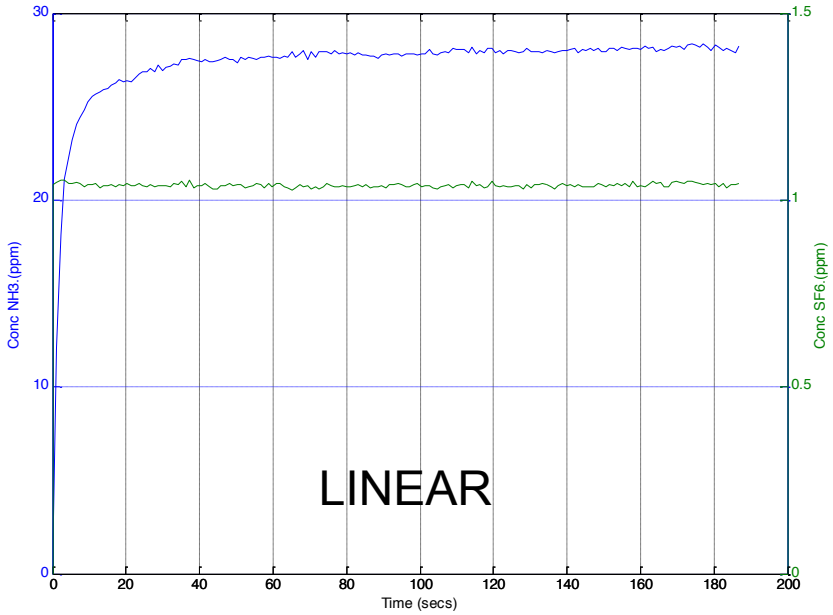
NH_3 response of SS Straight line at 113 C 5lpm



NH_3 response of SS Straight line at 113 C 20lpm

Typical "up" Response (NH_3 and SF_6)





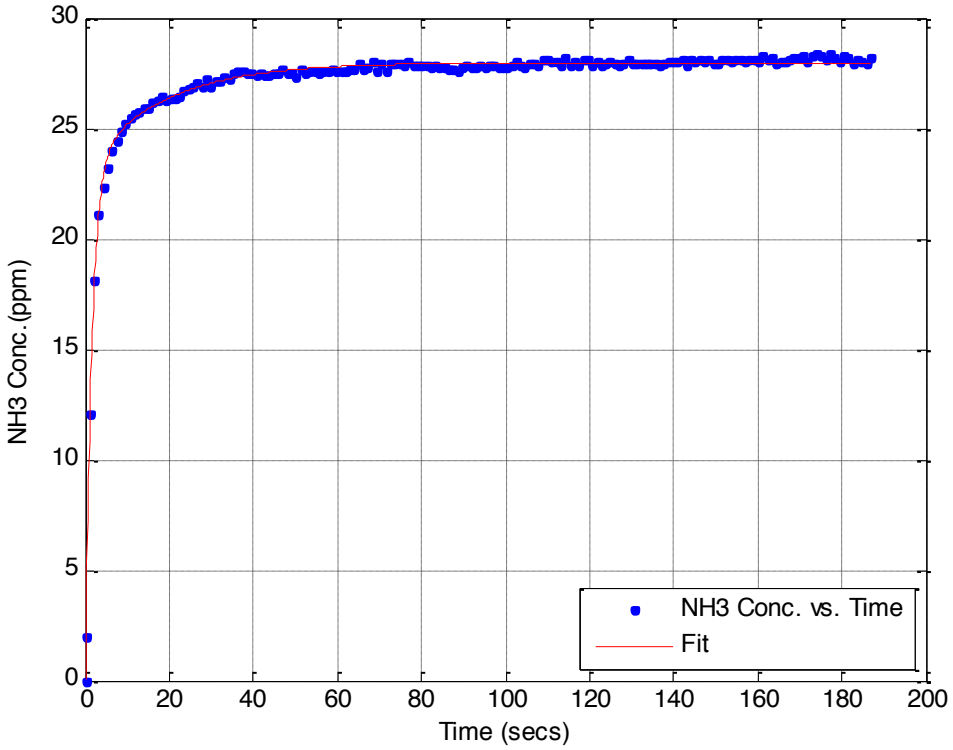
- NH_3/SF_6 response of SS Straight line at 113 C 20lpm
- log_{10} scale – note it is not linear!

NH_3/SF_6 response of SS Straight line at 113 C 20lpm

Analysis – Time Constants

- Expected response to be rounded
  - Mixing and diffusion during transport
  - Wall sticking
- MATLAB curve fit
  - Single exponential fits SF_6
  - Two terms needed for NH_3
  - Separate fits for each rise transient
    - Total of 307 transients after flyers removed

Curve fit to rise data



r^2= 0.999895

$$CNH3 = CNH3\_\text{final} \times \left(a0 \times \left(1 - e^{(-t-b)/T1}\right) + \left((1 - a0) \times \left(1 - e^{(-t-b)/T2}\right)\right)\right)$$

T1 sec	T2 sec	a0	b sec	CNH3_final ppm
1.5	18.3	0.829	0.000515	27.9

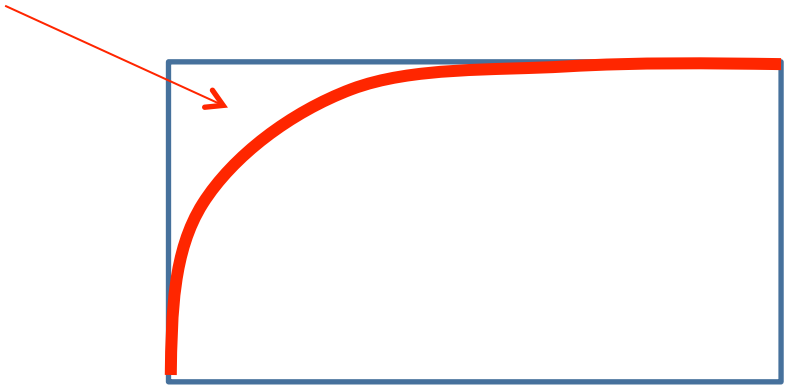
Fit Results

Value	Minimum	Maximum
Tau_1	1.0 sec	6.0
Tau_2	11 sec	199
a_0	0.76	0.999
r^2 fit quality	0.988	0.999

•Short time constant (transport/mixing) is similar to SF_6

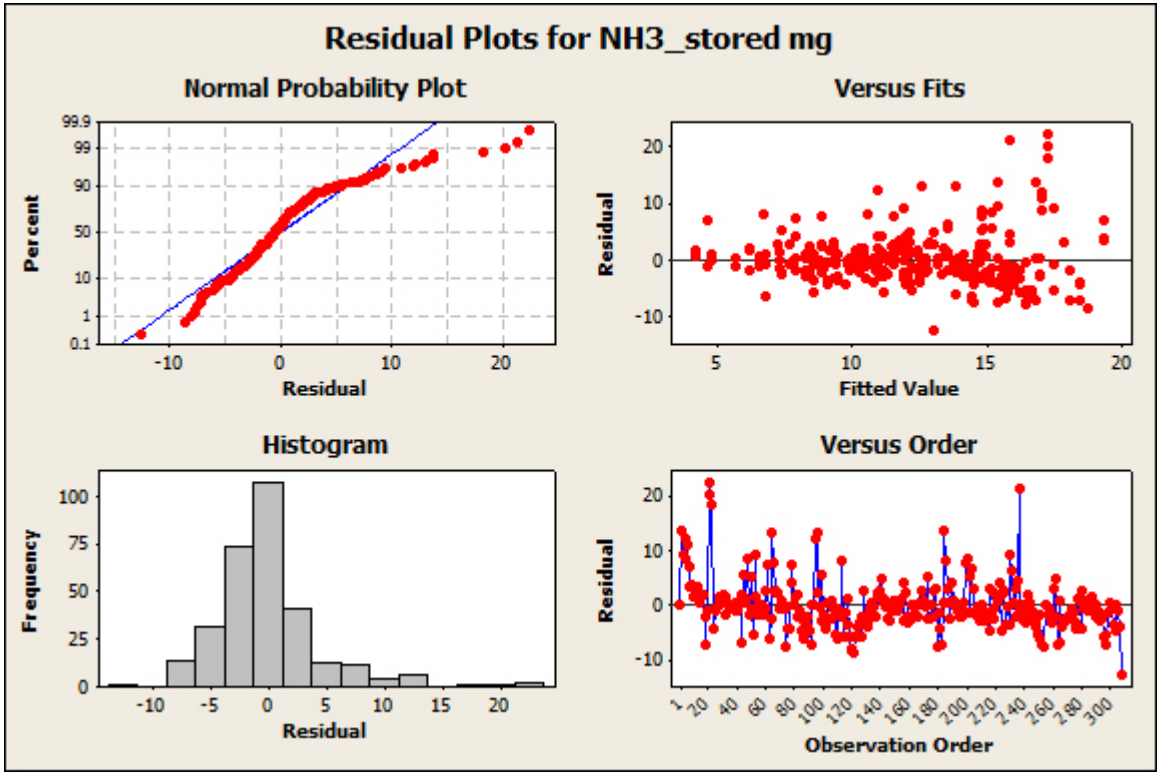
Further Analysis

- Estimate the NH_3 storage on walls from second term
- $Area=Y_f*(1-a_0)*(2Tau_2 + 2Tau_2*exp^{(-3)})$ *ppm-sec*



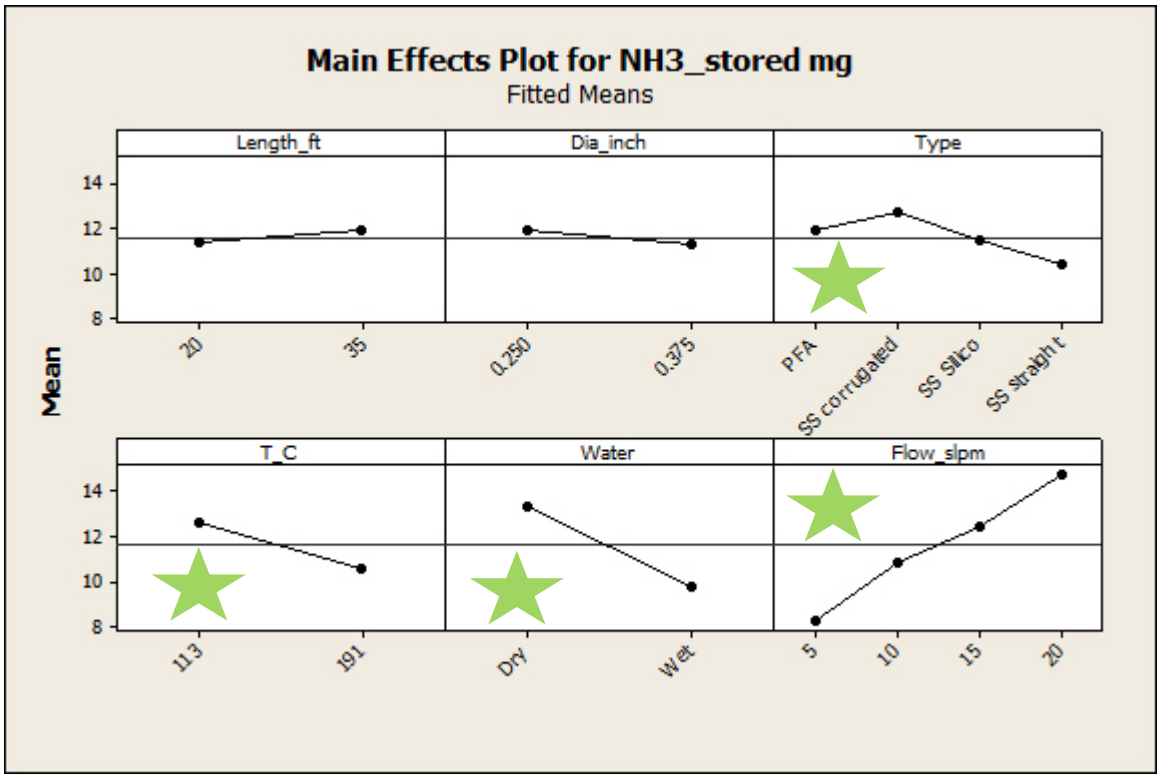
- NH_3 stored = Area * flow *22.4/60 *μmol*
- NH_3 stored = μmol * (17 gm/mol) / 1000 *mg*
- General Linear Model analysis in Minitab®

Fit Quality



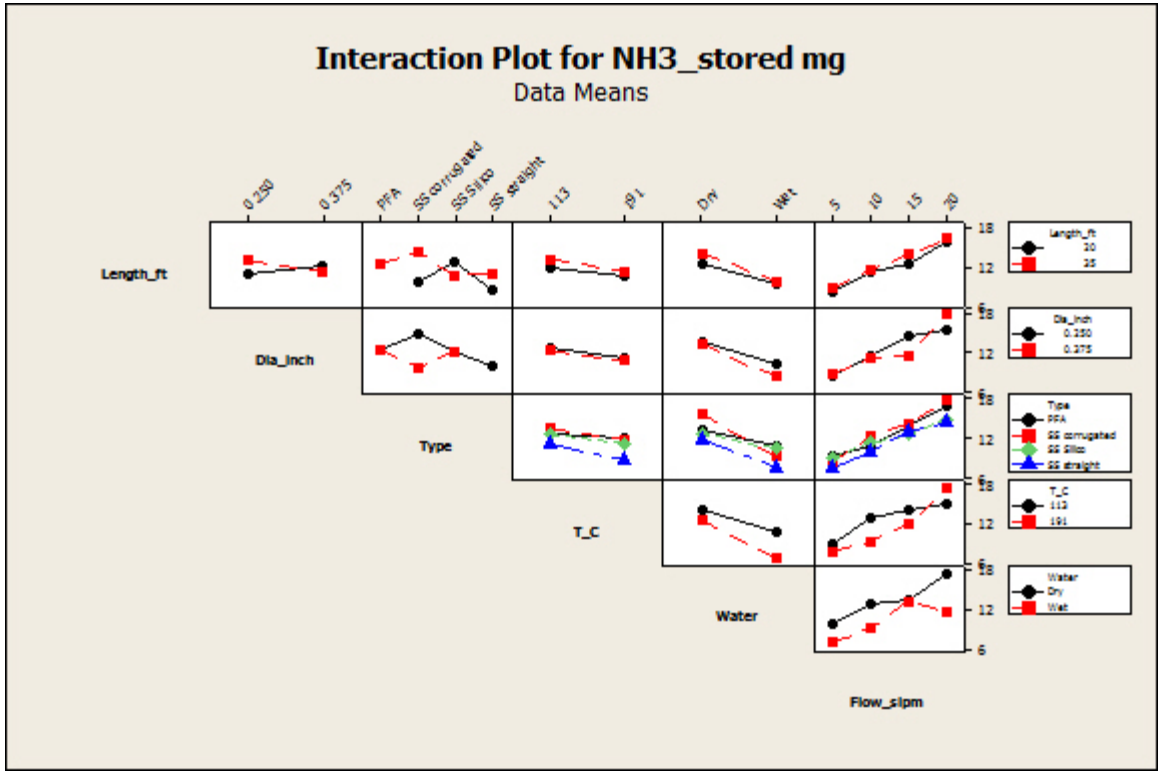
- This is a linear model
- Required with categorical variables and two-value variables
- Real responses might be curved

NH_3 Stored Main Effect



•Significant at 95% confidence

Interaction NH_3



- Some significant interactions:
- Type by length, diameter, and temperature
- Water by all others

Relative Importance

- Test a brick of SCR catalyst, 0.75 x 0.83”
- 0.006 liter catalyst volume
- Typical SCR 200-1500 mg/L NH_3 capacity
- Thus, catalyst stores 1.2-9.0 mg NH_3
- In this experiment, NH_3 storage is minimum 0.224, maximum 39 mg
- Can be large with respect to catalyst!
- Check against catalyst before fitting kinetics

Conclusions

- As expected, NH_3 responds more slowly than SF_6
- Mixing/transport time constant ranged ~1-6 sec, median 1.6
- NH_3 wall storage time constant ranged ~11-199 sec, median 55 seconds
- a_0, fraction of transient due to transport and mixing, ~0.76-0.999, median 0.94
- NH_3 wall storage quantity is significant compared to small SCR samples

Recommendations

- For transport and mixing:
  - Flow > 5 SLPM; 10-15 seems a good range
  - Line length and diameter had little effect in this range
  - The sample line type of material: corrugated is slower
- With respect to NH_3 retention effects:
  - Length and diameter not very critical in this range
  - Corrugated line stores most NH_3 (but Silco offsets), straight line least
  - Presence of water reduces NH_3 storage
  - Higher temperature reduces storage
  - Higher flow increases NH_3 storage (but lower as a percent of NH_3 flow)

Acknowledgments

- This work was done at the University of Michigan's Walter E. Lay Automotive Laboratory for MKS Instruments
- All test data were taken by Nanda
- Thanks to Bill Murphy and Tim Martin at MKS for their invaluable assistance in arranging the test lines and gases

Backup

Analysis of Time Constants

- Are the time constants related to the test variables?
- General Linear Model in Minitab®
  - 307 samples after flyers removed
  - Analyzed Tau_1, Tau_2, a_0

ANOVA Result

Significant at 95% Confidence?

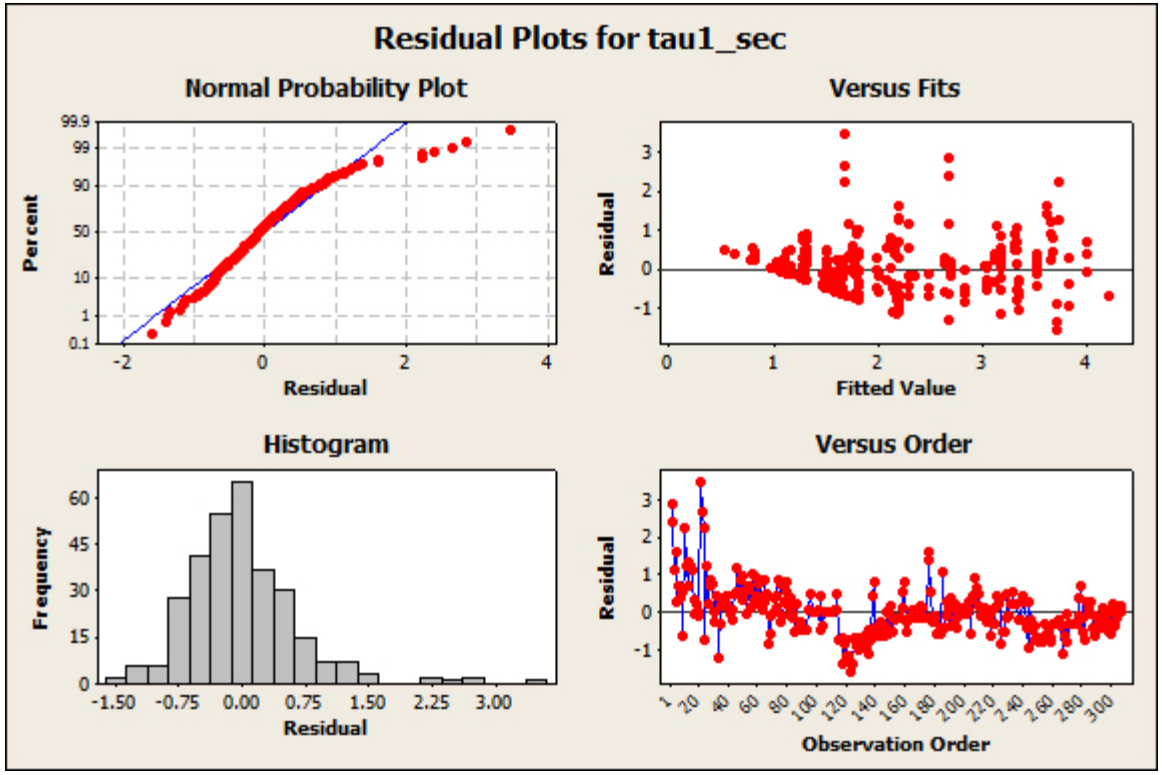
Test Factor	Tau_1	Tau_2	a_0
Length	No	Yes	Yes
Diameter	Yes	Yes	Yes
Material	Yes	Yes	Yes
Temperature	Yes	Yes	Yes
Water	Yes	Yes	Yes
Flow	Yes	No	Yes

Tau_1:
Short, mixing and transport

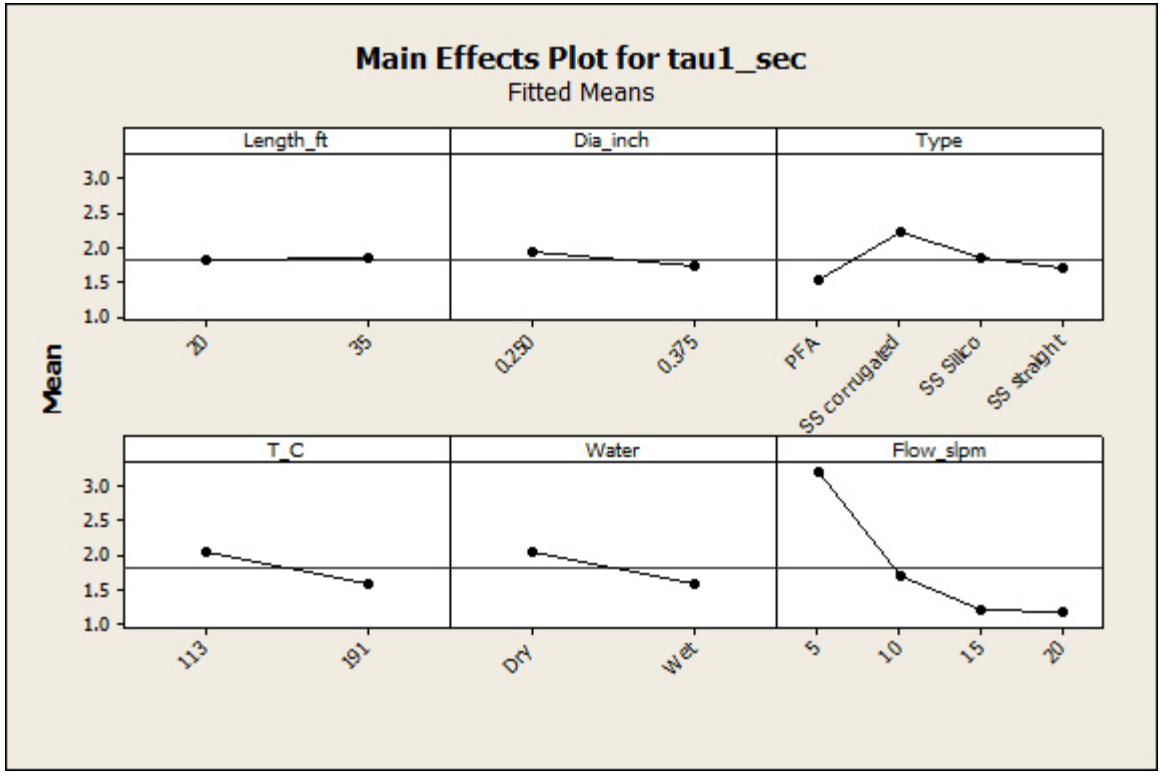
Tau_2:
Longer, wall sticking

a_0:
Fraction: 1 means all Tau_1, 0 means all tau_2

Tau_1 Fit Quality

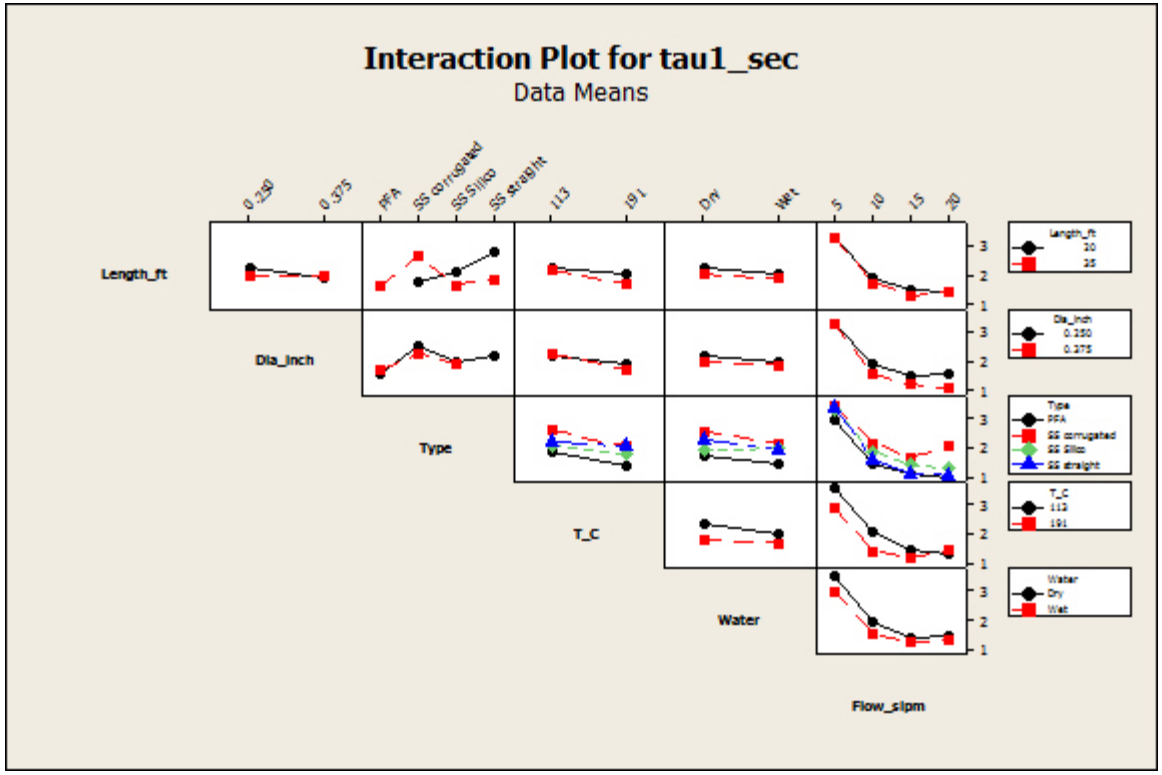


Main Effect – Tau_1



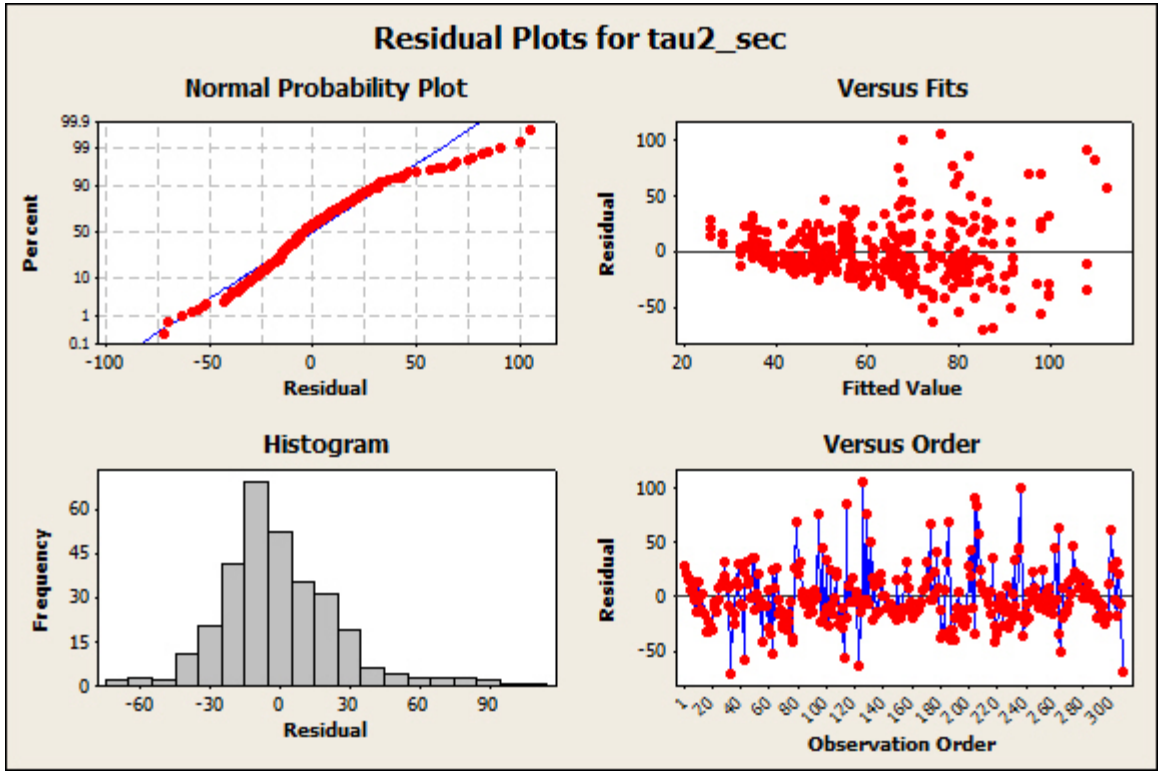
- Flow rate is the main effect
- Approximately 2 seconds mean time constant

Interactions – Tau_1

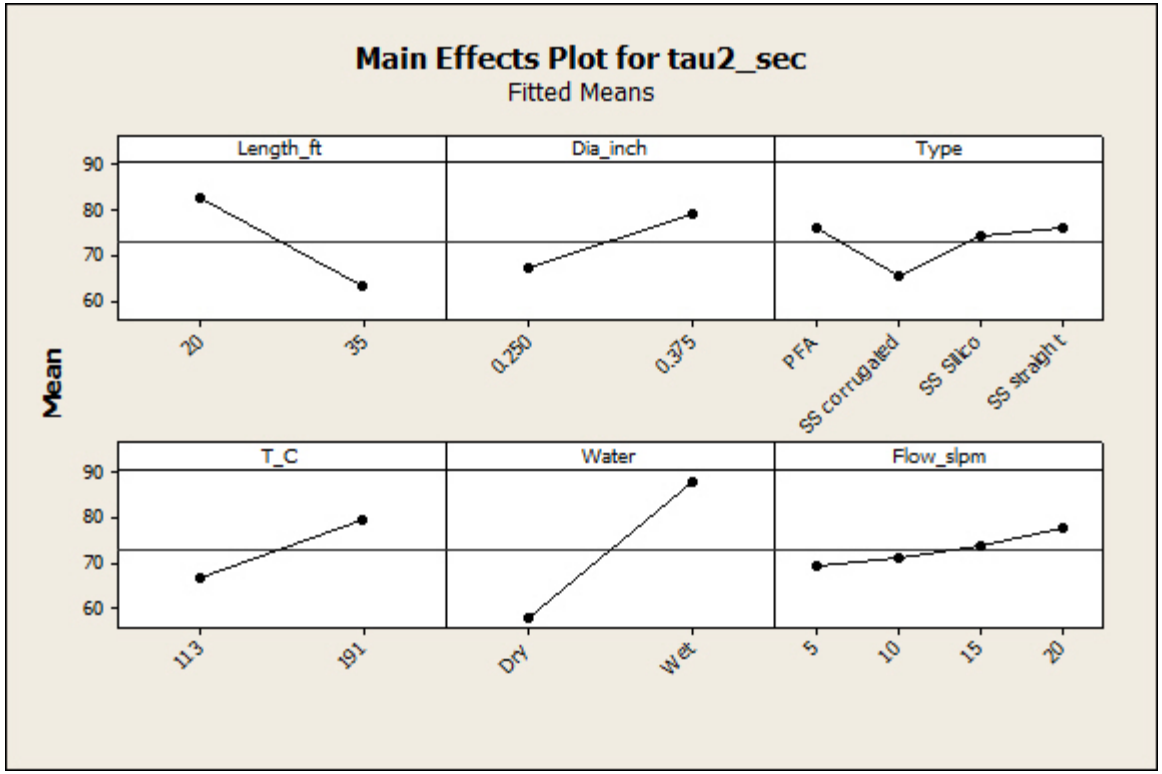


•Interaction of length, type

Tau_2 Fit Quality

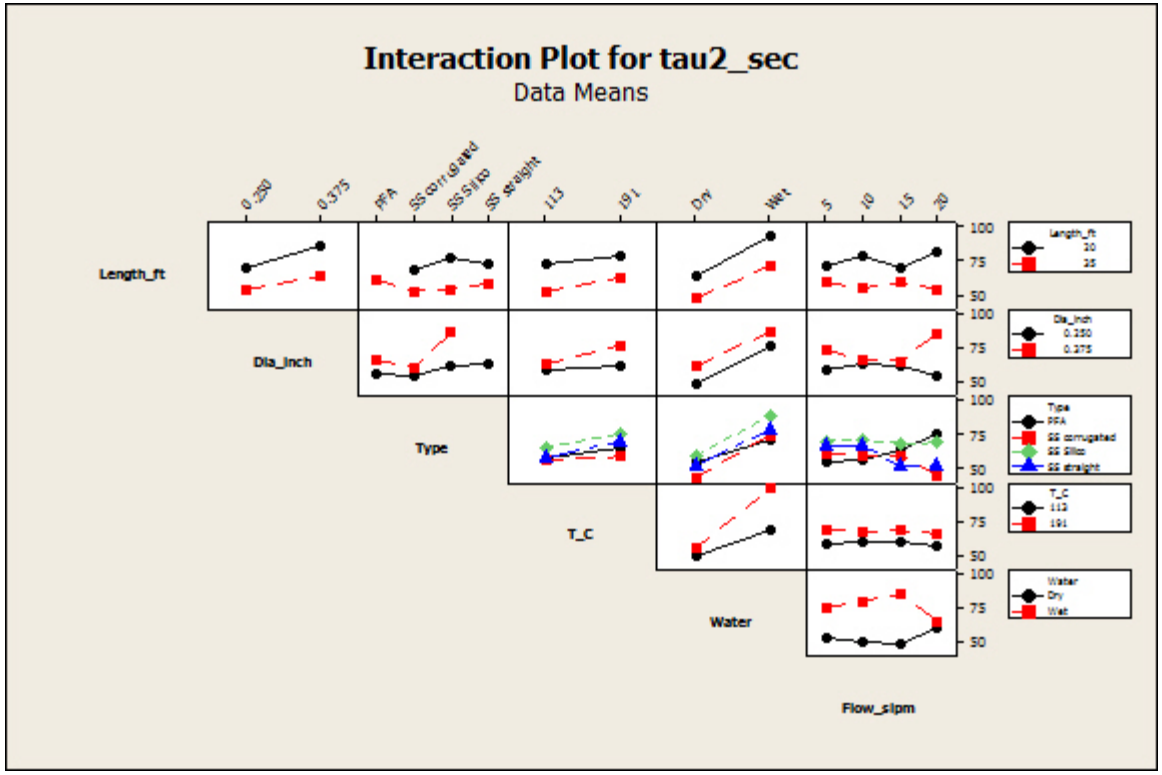


Main Effect – Tau_2



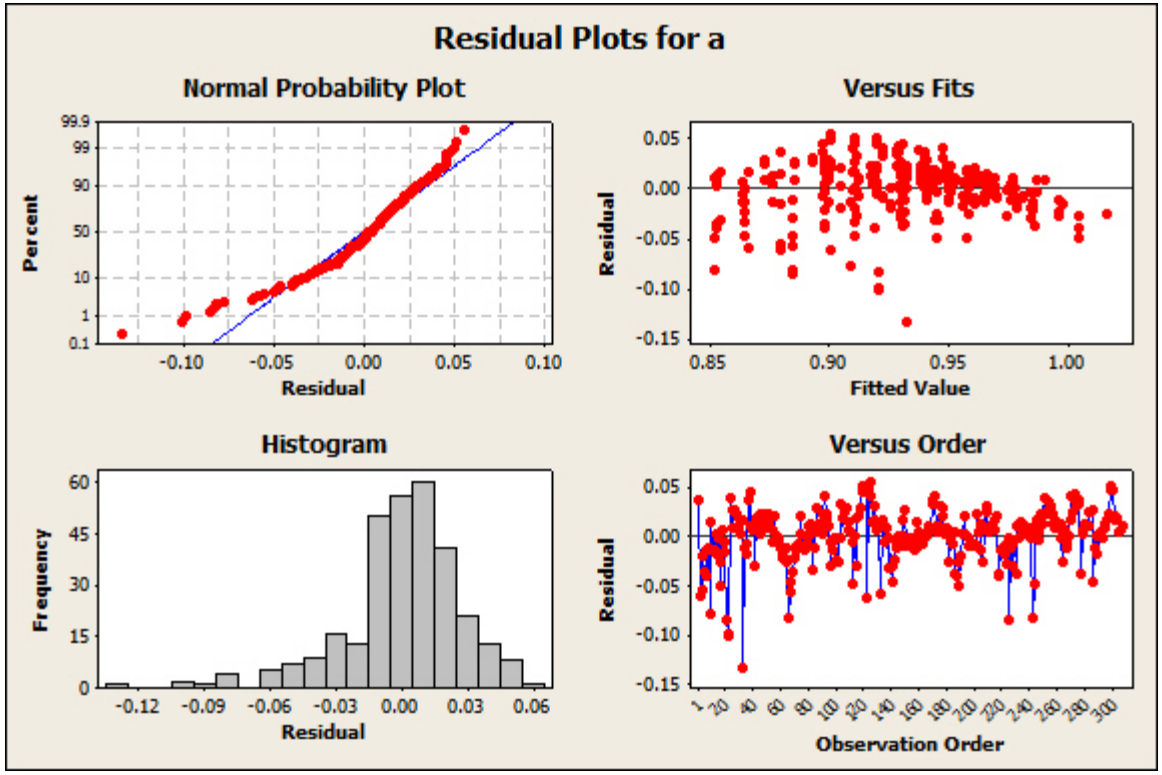
- All variables significant except flow rate
- Approximately 70 seconds mean time constant
- Relative importance of Tau_2 and Tau_1 depends on a_0
- Surprising direction of temperature effect – see a_0

Interactions – Tau_2

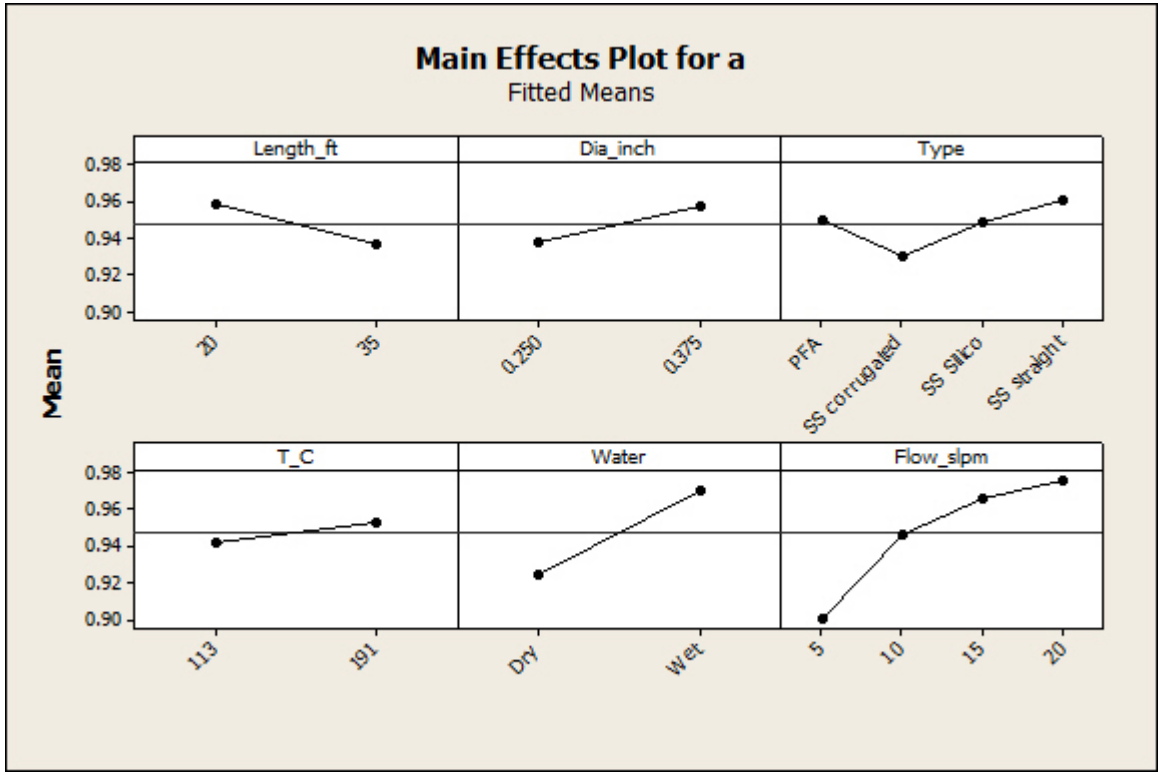


•Interaction of Water, temperature: temperature matters more when wet

a_0 Fit Quality



Main Effect – a_0



- Higher value means transport and mixing are more important
- All variables significant
- Approximately 0.95 of the transient is attributed to Tau_1
- More important at higher flow
- High temperature increases a0 ~0.94 to 0.96 – i.e., wall effect drops from 6% of the transient to 4%

Interactions – a_0