

# Pilot Plant Testing of Piperazine (PZ) with High T Regeneration

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# Budget Period 1

\$ 1.65 M Federal Share

\$ 0.92 M Cost Share

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\$ 2.57 M Total BP1

## Cost share by CO<sub>2</sub> Capture Pilot Plant Project (C2P3)



# Objective is to develop PZ with advanced regeneration at 150°C

PZ

- Optimize solvent (8m vs 5m)
- Demonstrate solvent robustness

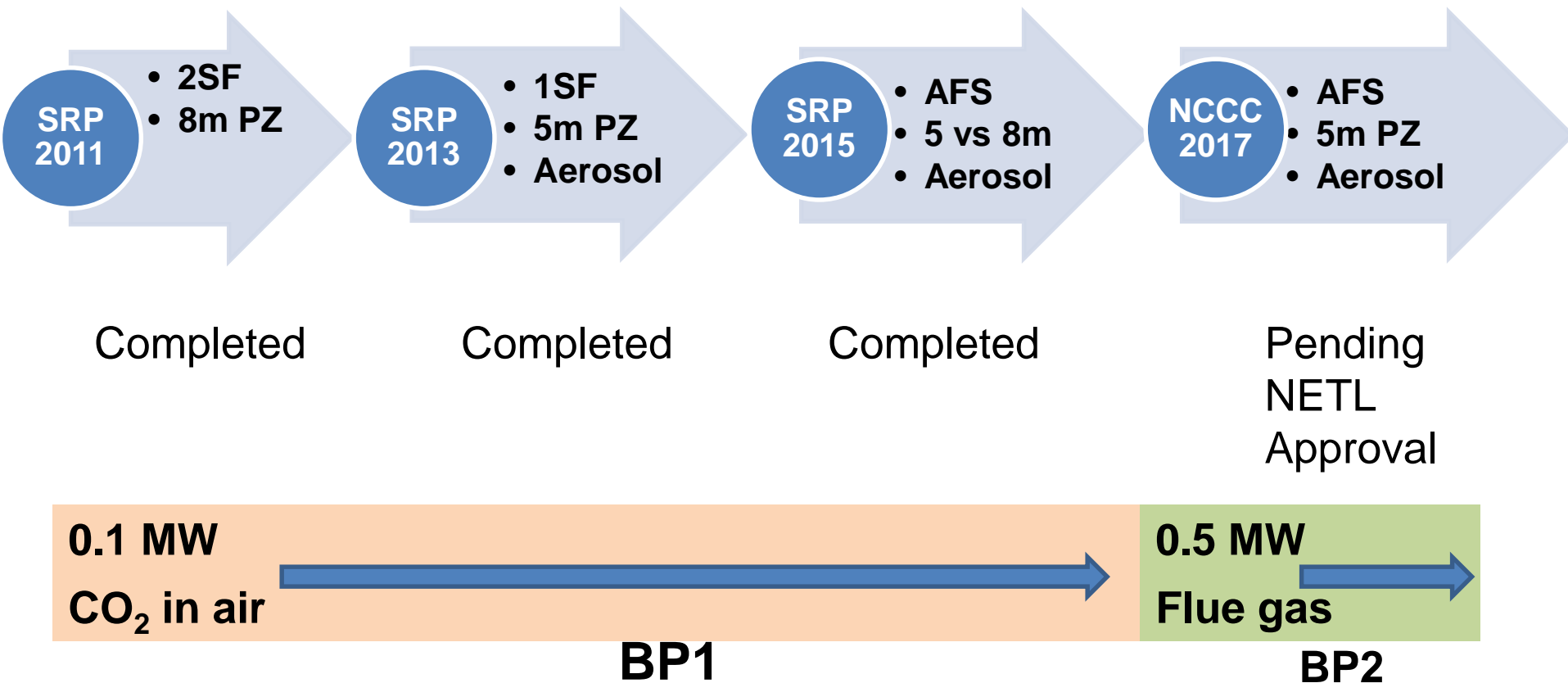
Regeneration

- Two stage flash (2SF)
- Advanced flash stripper (AFS)

Aerosols

- Formation and control
- Characterization

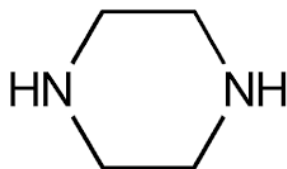
# Phased testing at UT SRP and NCCC to optimize PZ absorption/regeneration



# The Lessons

- 5m PZ is a superior solvent
- AFS minimizes energy use for regeneration
- 5m PZ + AFS decreases cost of CO<sub>2</sub> capture
- Amine aerosols can be measured with FTIR and PDI

**5m Piperazine**  
**is a superior solvent**



# PZ solvent properties

- Fast kinetics
- High capacity
- Low volatility
- Resistant to Degradation
  - Thermal (stable to 150°C)
  - Oxidation (4x more stable than MEA)
  - Nitrosation (MNPZ decomposes at 150°C)
- **Solid solubility** limits its application

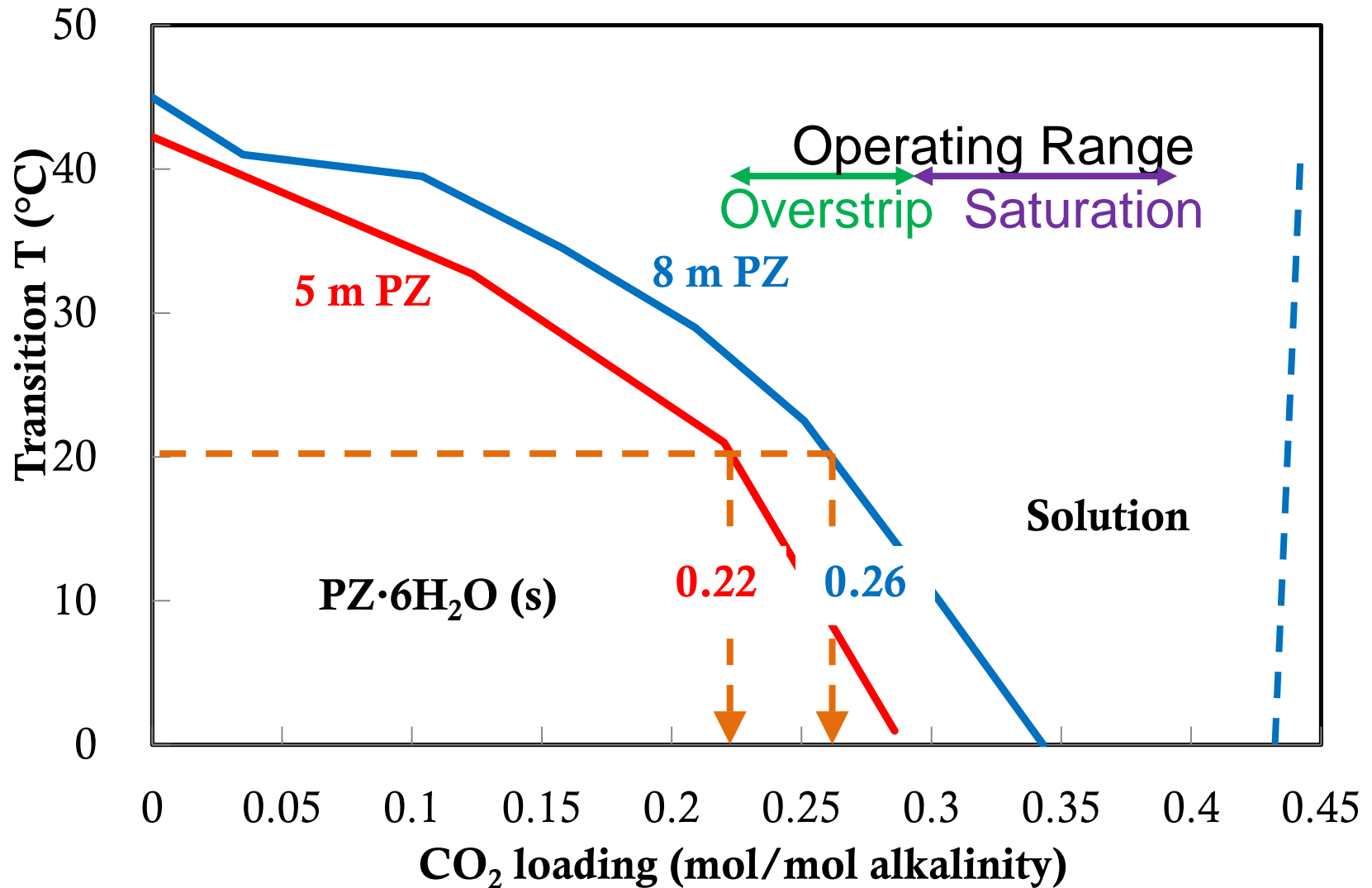
# 5m PZ: optimizes advantages of PZ

## Wider solubility

- Can be used at lower lean loading without solids ppt
- No solids precipitation at rich loading



# 5m PZ has a wider solubility window



# 5m PZ: optimizes advantages of PZ

## Wider solubility

- Can be used at lower lean loading without solids ppt
- No solids precipitation at rich loading

## Faster kinetics

- 33% faster absorption kinetics vs. 8m PZ

Amine	m	$k'_{g\text{ avg}} * 1e7$ mol/s·Pa·m <sup>2</sup>	$\mu$ cP	$\Delta C_{\mu}$ mol/kg	$T_{\text{max}}$ C
<b>PZ</b>	<b>8</b>	<b>8.5</b>	<b>11</b>	<b>0.84</b>	<b>163</b>
	<b>5</b>	<b>11.3</b>	<b>4</b>	<b>0.81</b>	<b>163</b>

# 5m PZ improved CO<sub>2</sub> removal at SRP

	Run	Solvent	Solvent Rate GPM	Gas Rate ACFM	Titration LLDG mol CO <sub>2</sub> /mol alk	Measured Removal
<b>Test 1</b>	9	5 m	14	500	0.24	80%
	14	8 m				75%
<b>Test 2</b>	8	5 m	14	350	0.24	96%
	15	8 m				93%
<b>Test 3</b>	3	5 m	10.2	350	0.22	94%
	16	8 m				91%

# 5m PZ: optimizes advantages of PZ

## Wider solubility

- Can be used at lower lean loading without solids ppt
- No solids precipitation at rich loading

## Faster kinetics

- 33% faster absorption kinetics vs. 8m PZ

## Lower viscosity

- Higher heat transfer coefficients for cross exchangers, trim cooler, absorber intercooler

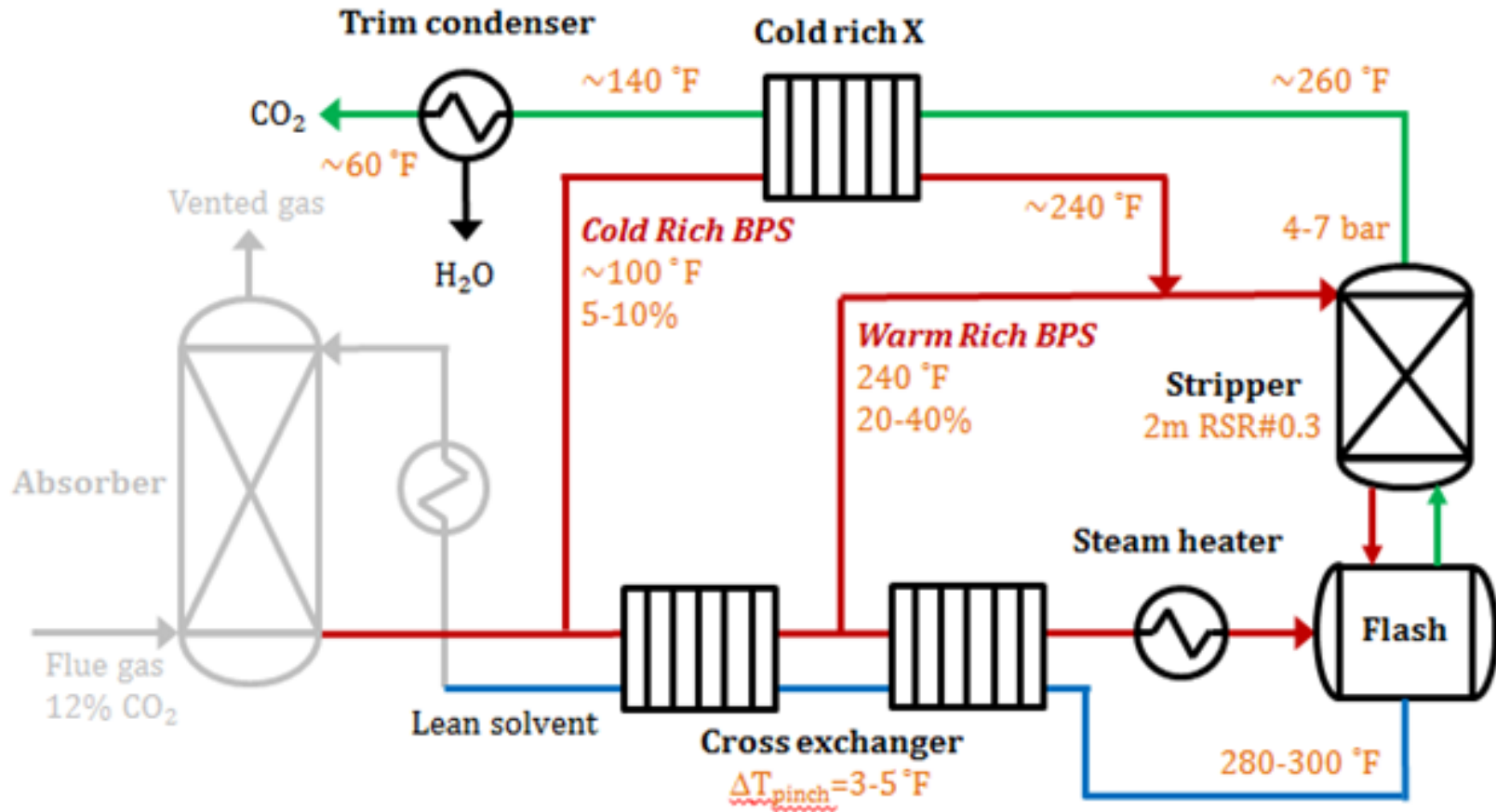
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# 5m PZ improved cross exchanger performance and reduced heat duty

	Comparison 1 (293°F 0.24 ldg)		Comparison 2 (293°F 0.24 ldg)	
Run	8	15	9	14
PZ concentration (m)	5	8	5	8
Solvent capacity (lb CO <sub>2</sub> /lb solution)	0.036	0.037	0.041	0.042
Total BPS ratio	25%	24%	26%	24%
Heat duty (GJ/tonne CO <sub>2</sub> )	2.36	2.51	2.21	2.41
Cross X cold side $\Delta T$ (°F)	11.7	15.2	11.5	15.7

**The Advanced Flash Stripper (AFS)**  
**minimizes energy use**

# Advanced Flash Stripper with 5m PZ

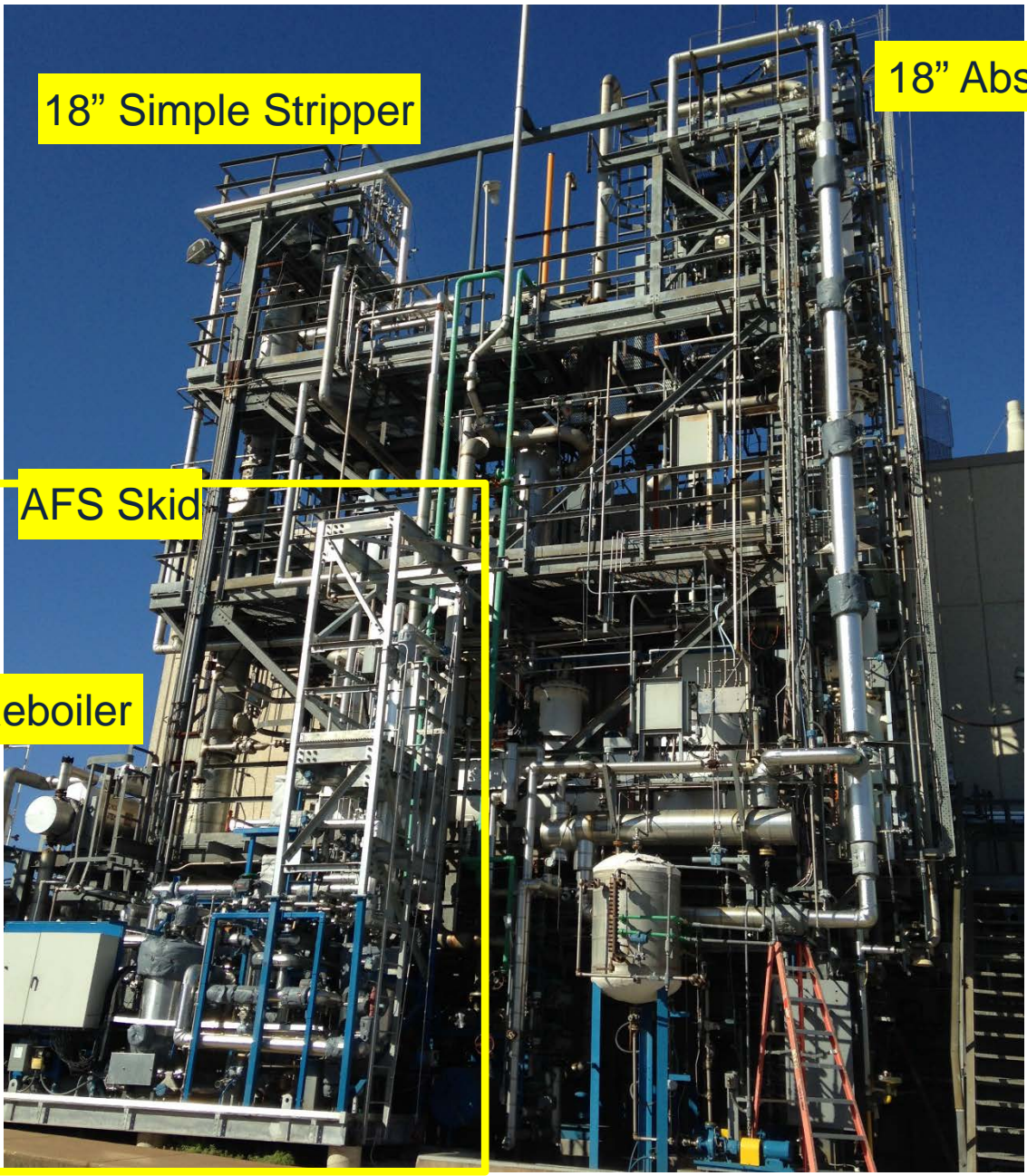


18" Simple Stripper

18" Absorber

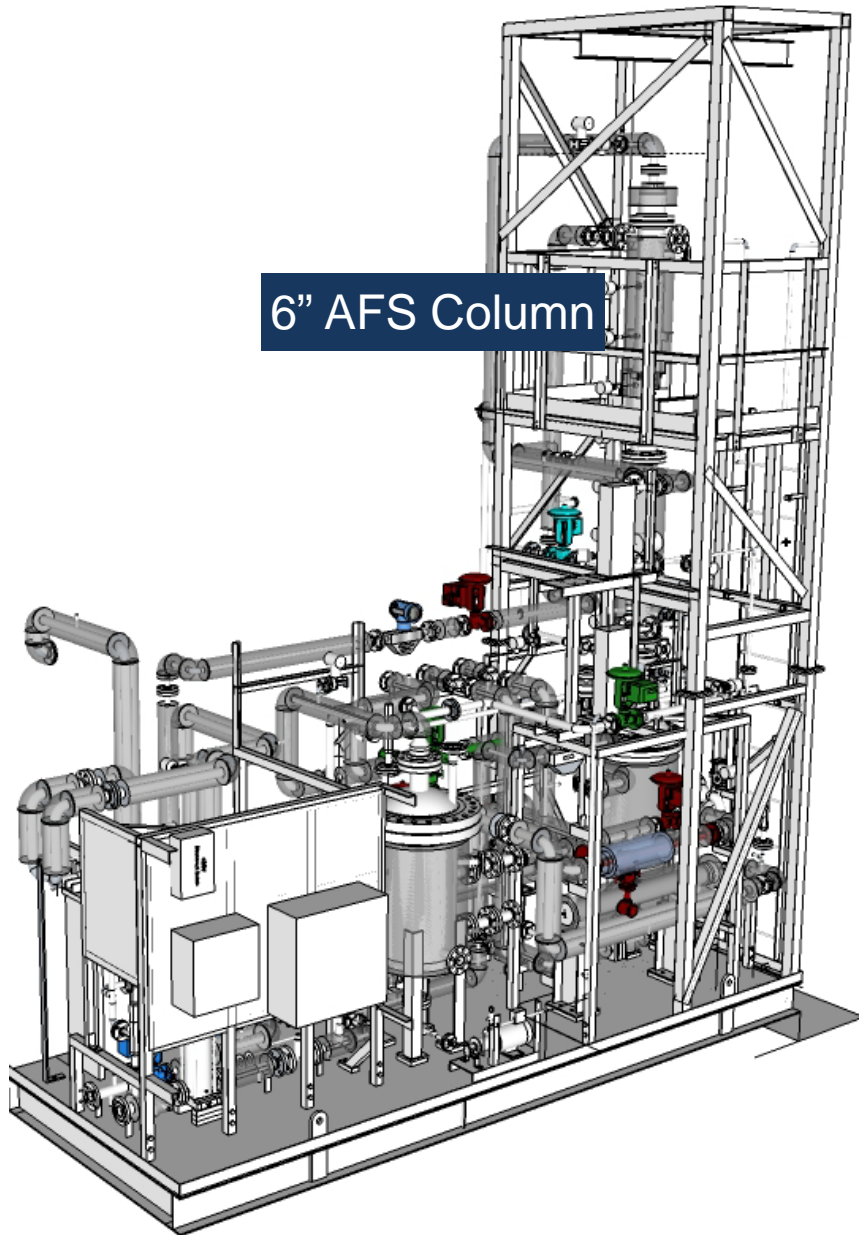
AFS Skid

Reboiler

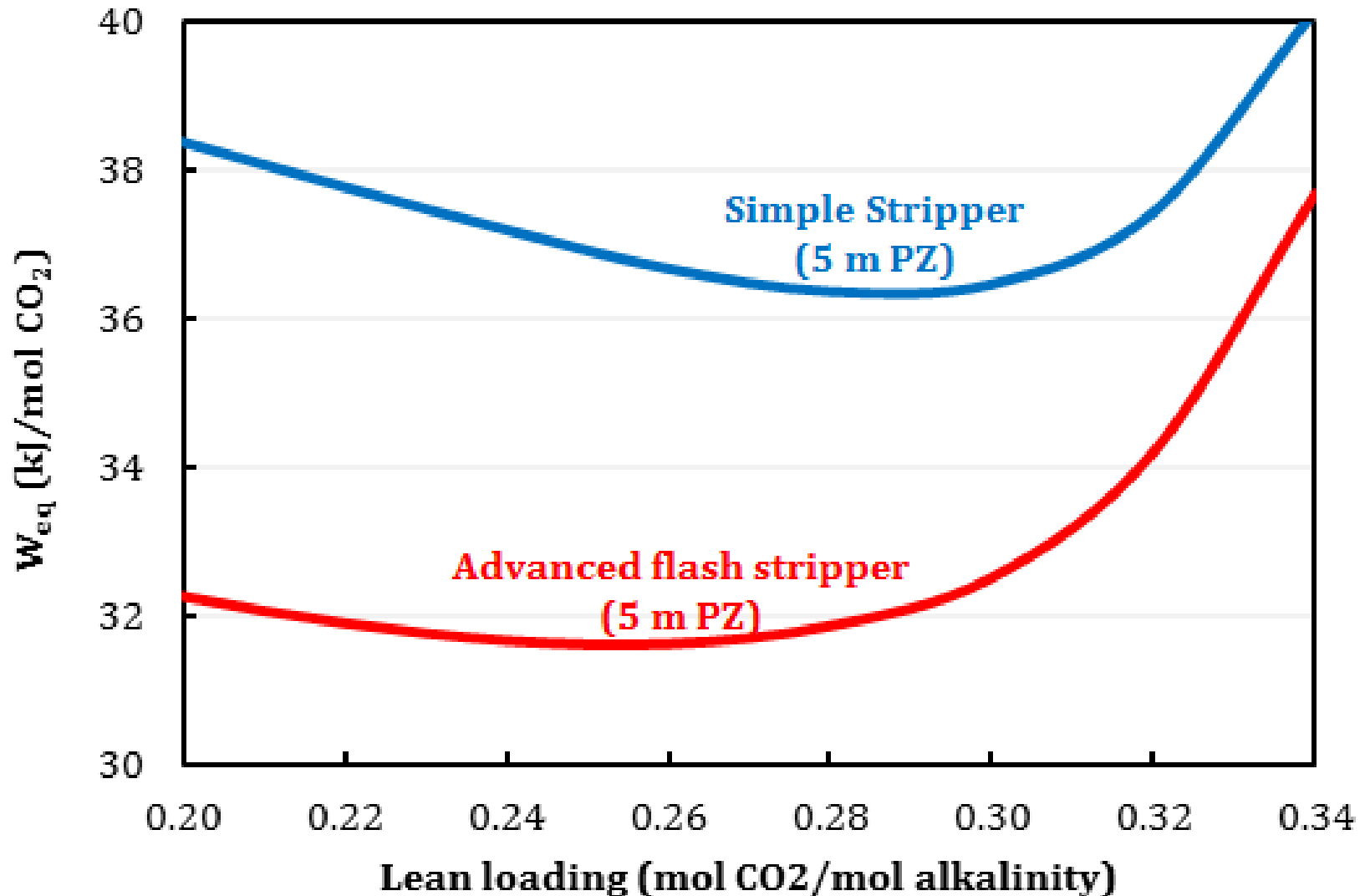




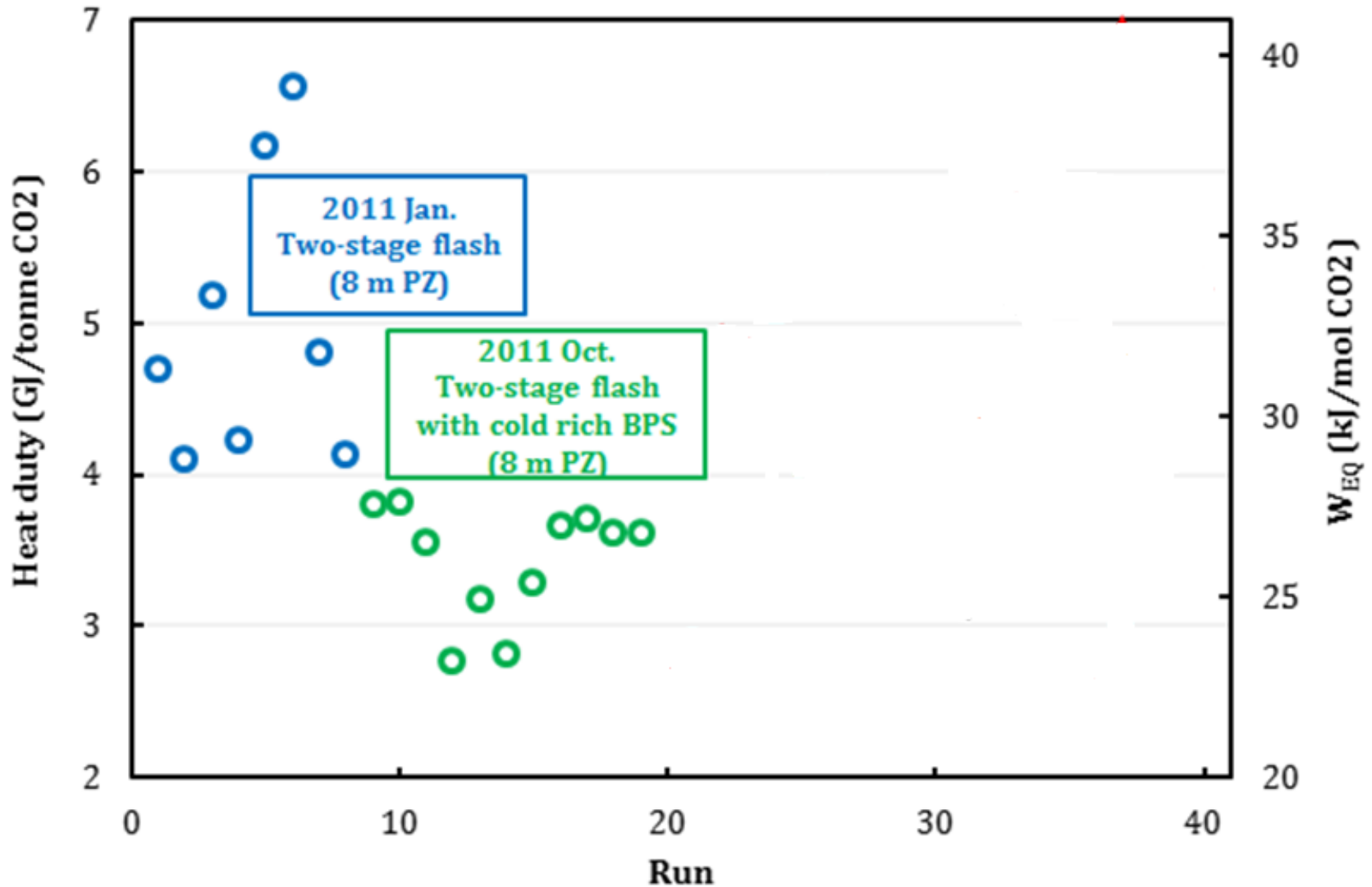
6" AFS Column



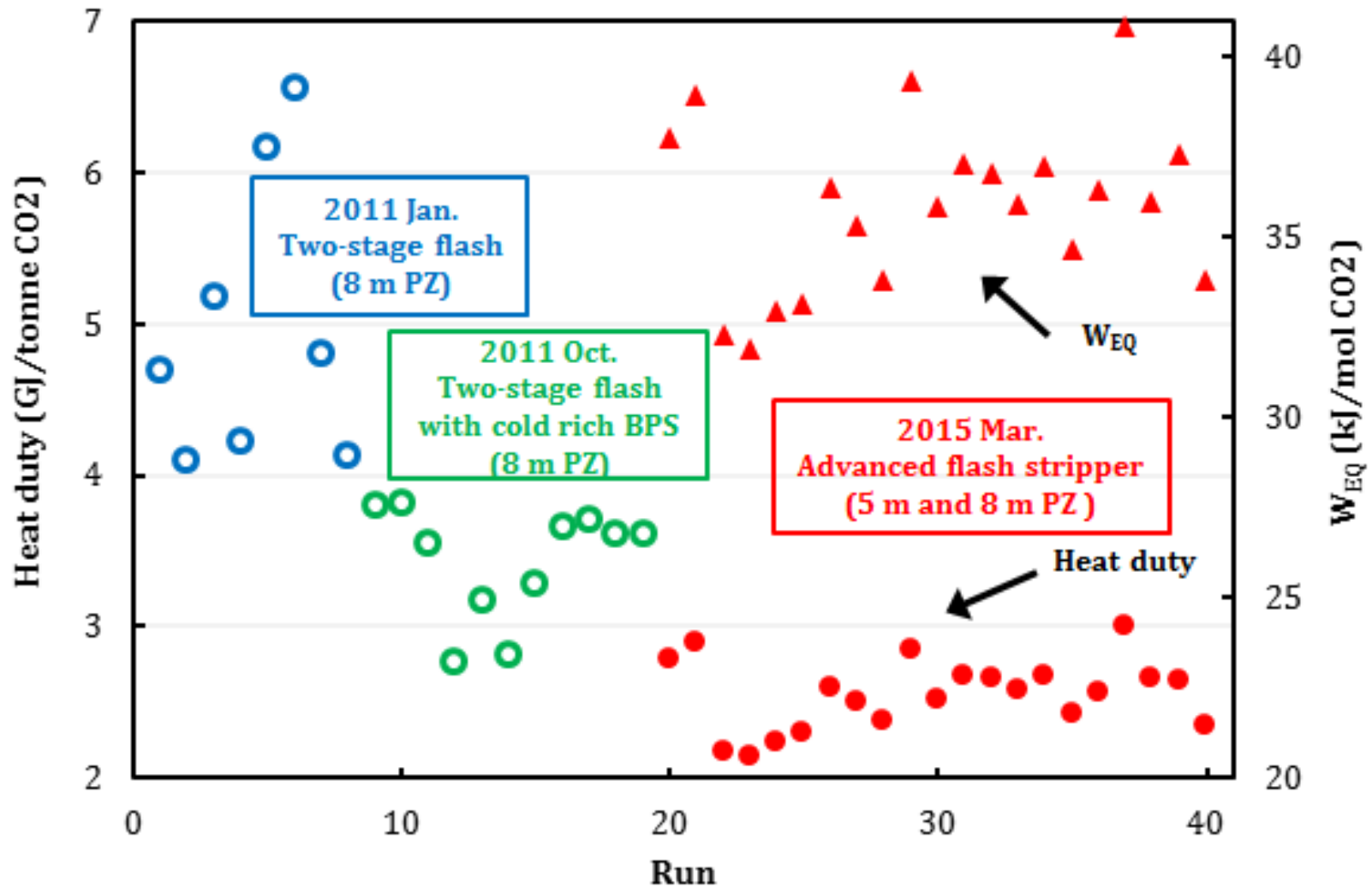
# AFS has lower $W_{eq}$ than SS



# Cold-rich bypass reduced energy requirement of 2SF



# AFS reduced energy requirement by 25%



5m PZ + AFS

decreases cost of CO<sub>2</sub> capture

# **5m PZ/AFS has lowest costs of configurations modeled by UT**

- PZ/AFS = \$39.03/tonne (no TS&M)
- Econamine = \$56.47/ton (no TS&M)

**Amine Aerosols can be measured  
by FTIR and  
Phase Doppler Interferometer (PDI)**

# Amine aerosols cause high amine emissions

Nucleation sites in flue gas

- $\text{SO}_3/\text{H}_2\text{SO}_4$
- Submicron fly ash
- $\text{SO}_2$ /amine

+ Amine condensation

- Amine/ $\text{CO}_2$ / $\text{H}_2\text{O}$  from solvent to aerosol

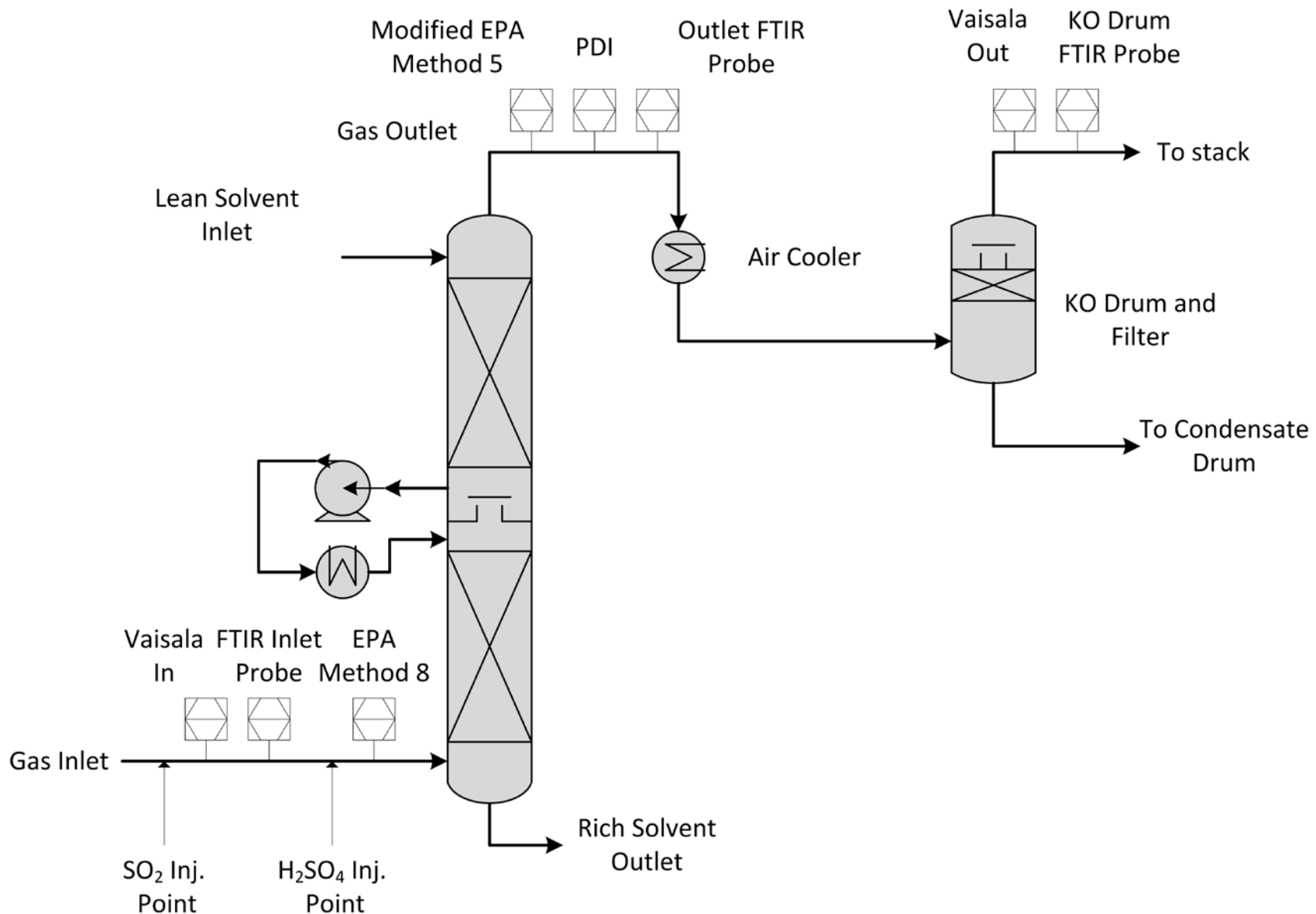
+ Poor collection of small drops in water wash

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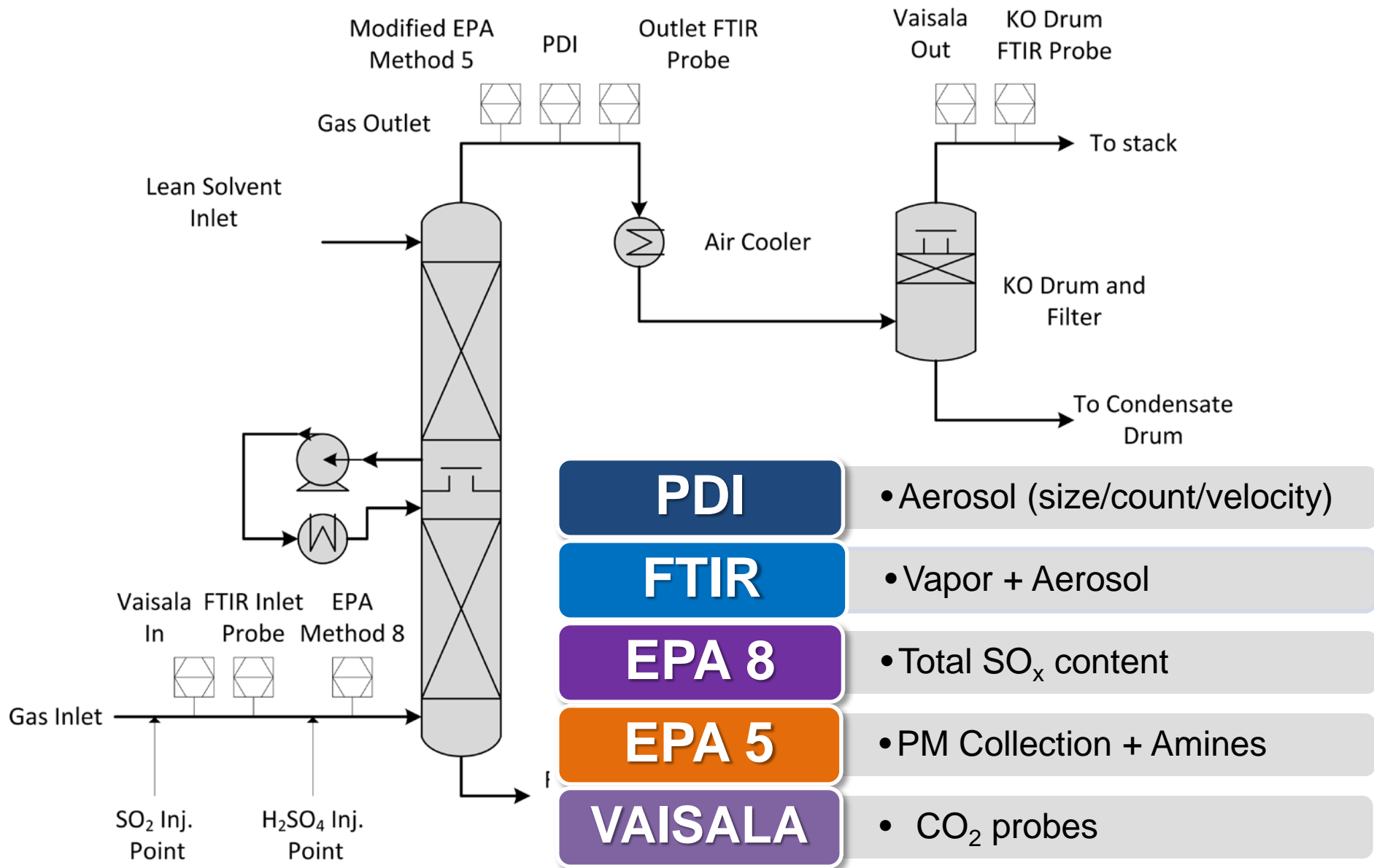
= Unacceptable amine emissions



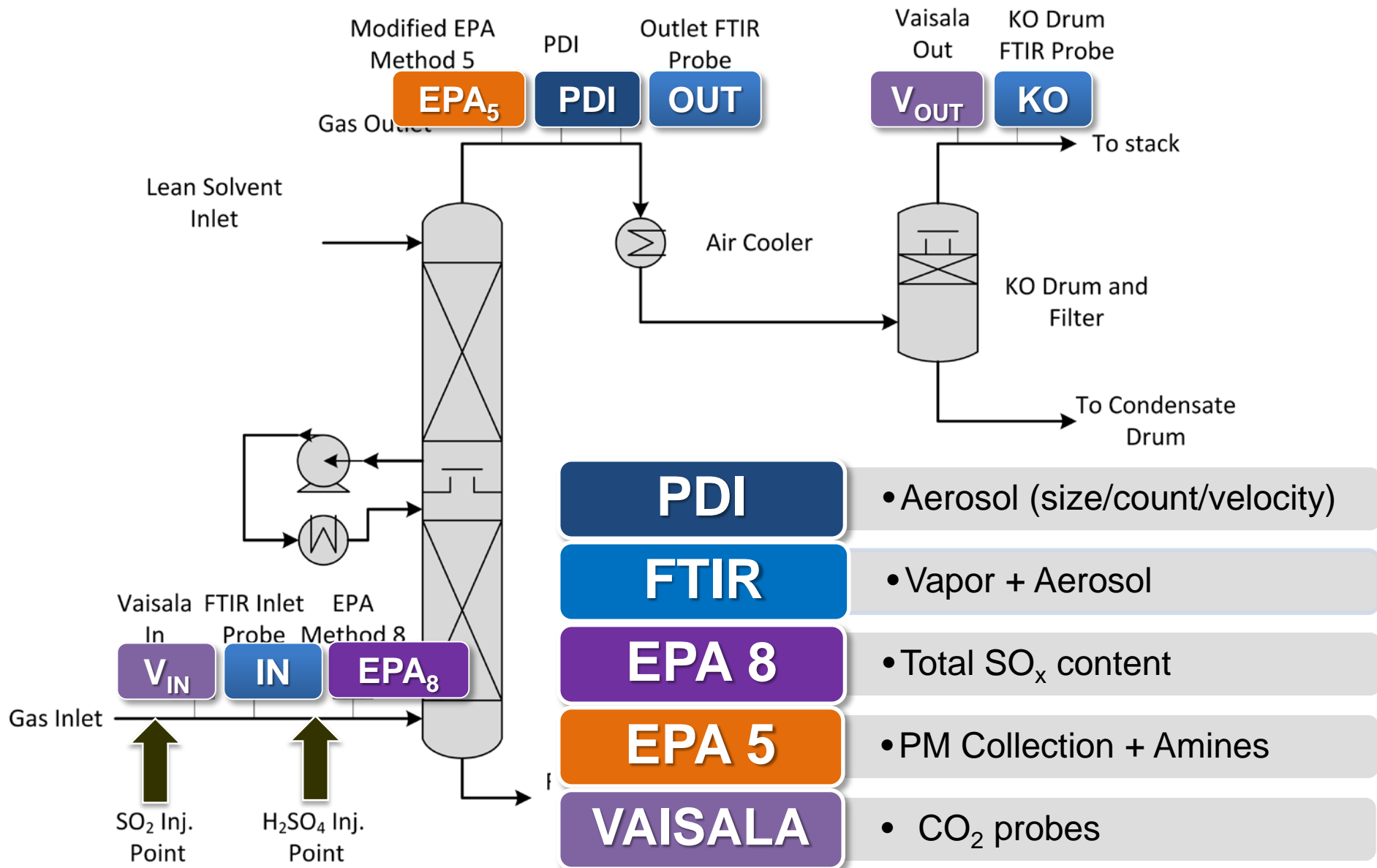
# PDI, FTIR measurements at SRP



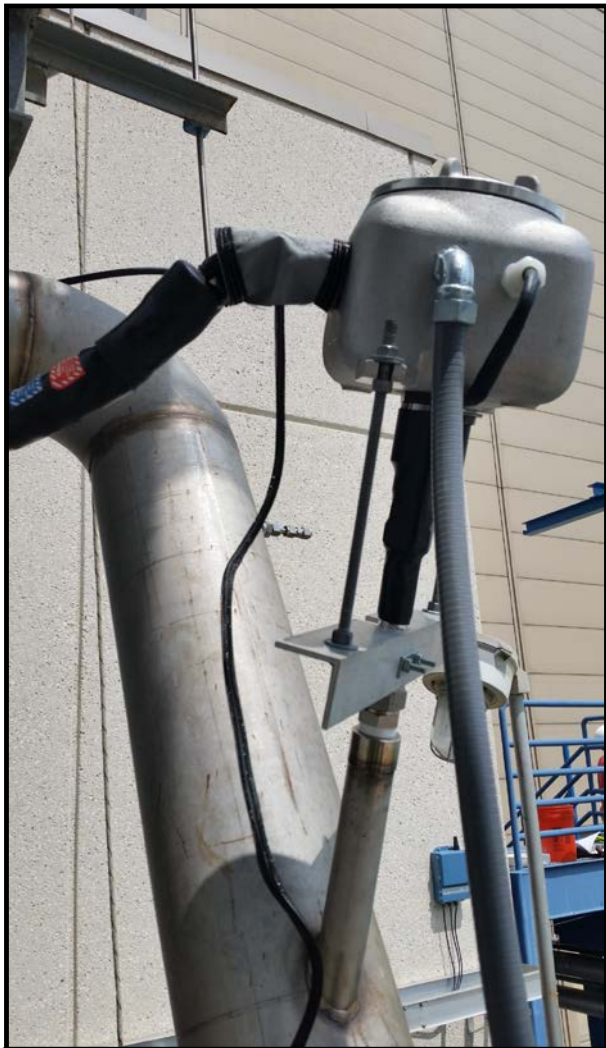
# PDI, FTIR measurements at SRP



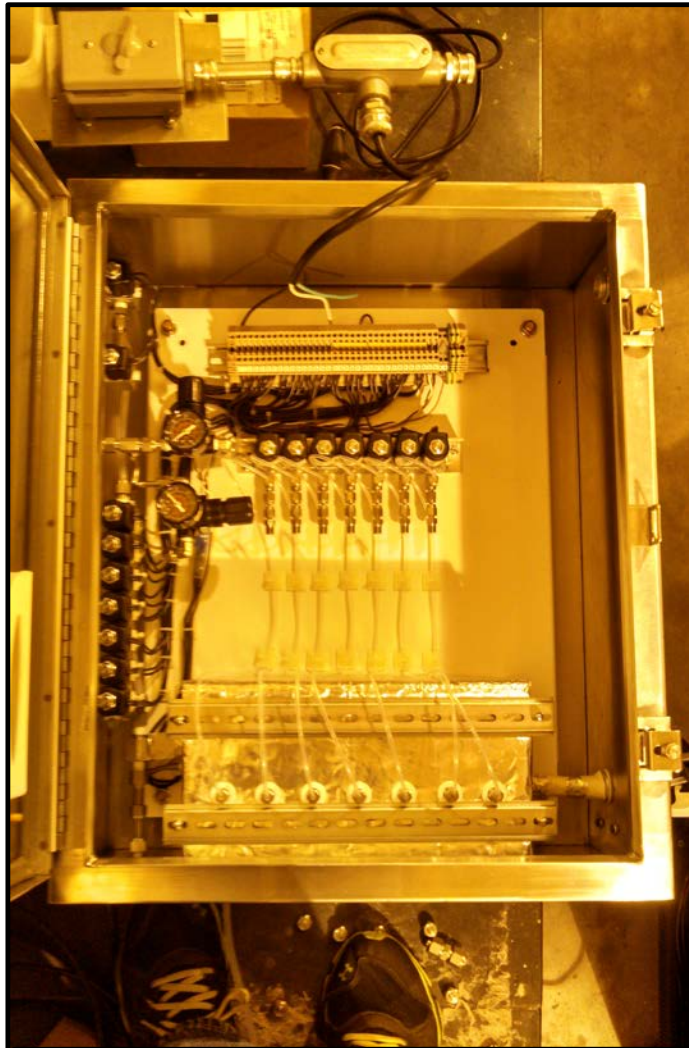
# PDI, FTIR measurements at SRP



# FTIR Sampling



**Field Sampling**



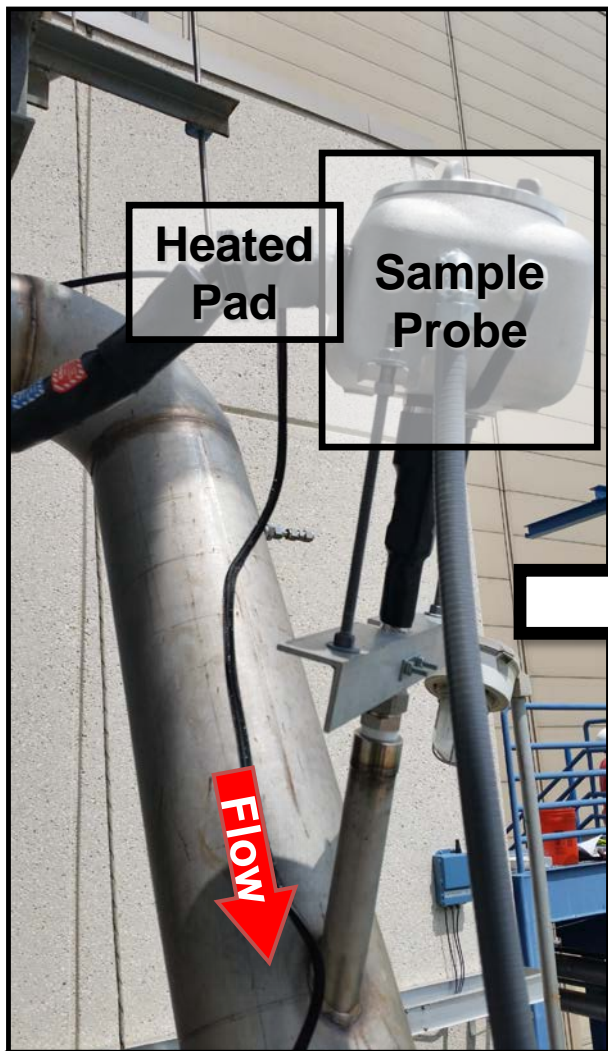
**Select Sample Point**



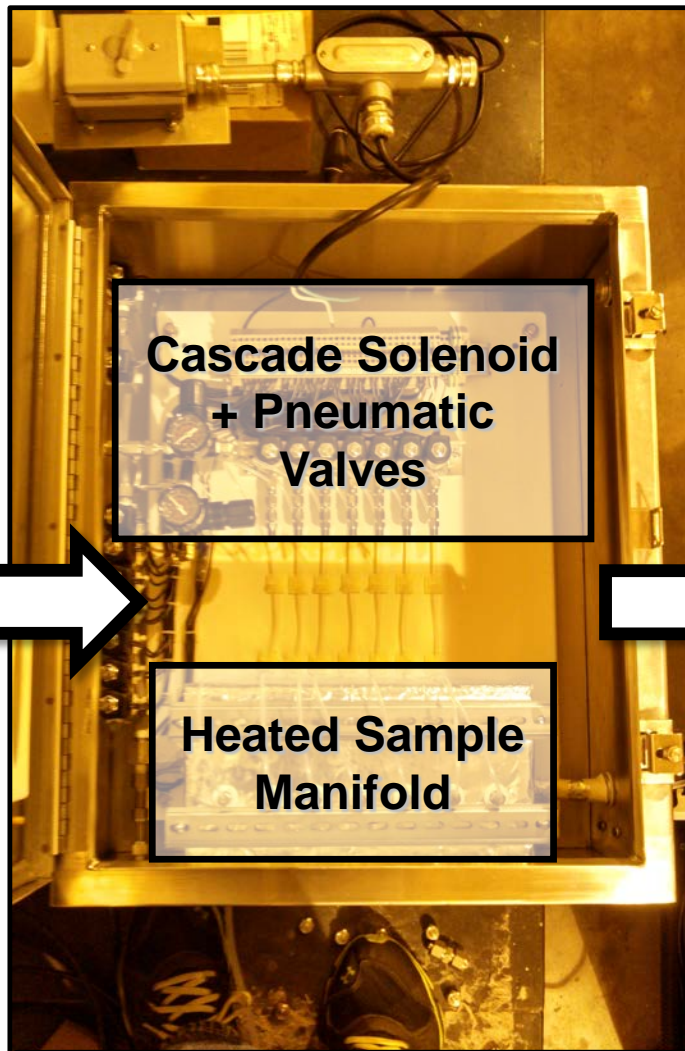
**FTIR Analysis**



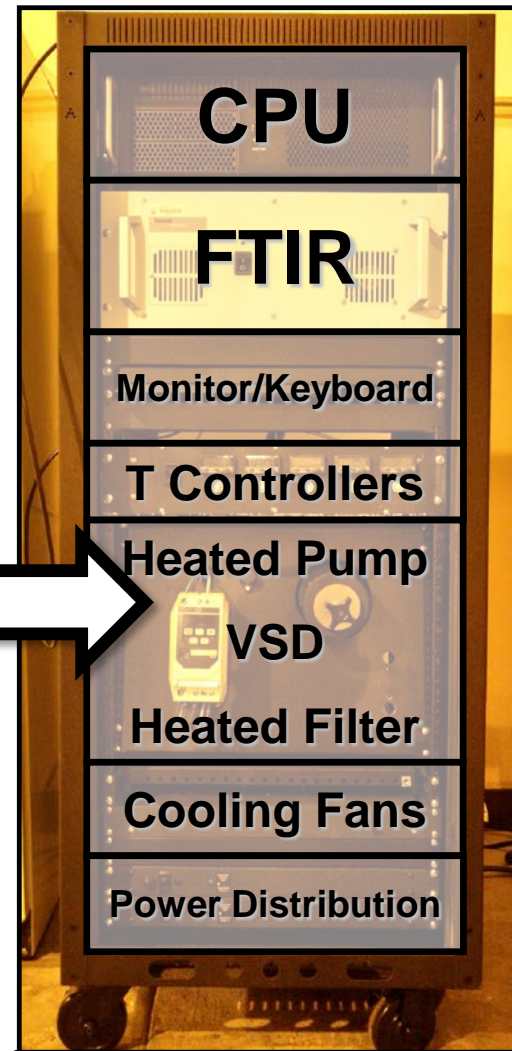
# FTIR Sampling



**Field Sampling**

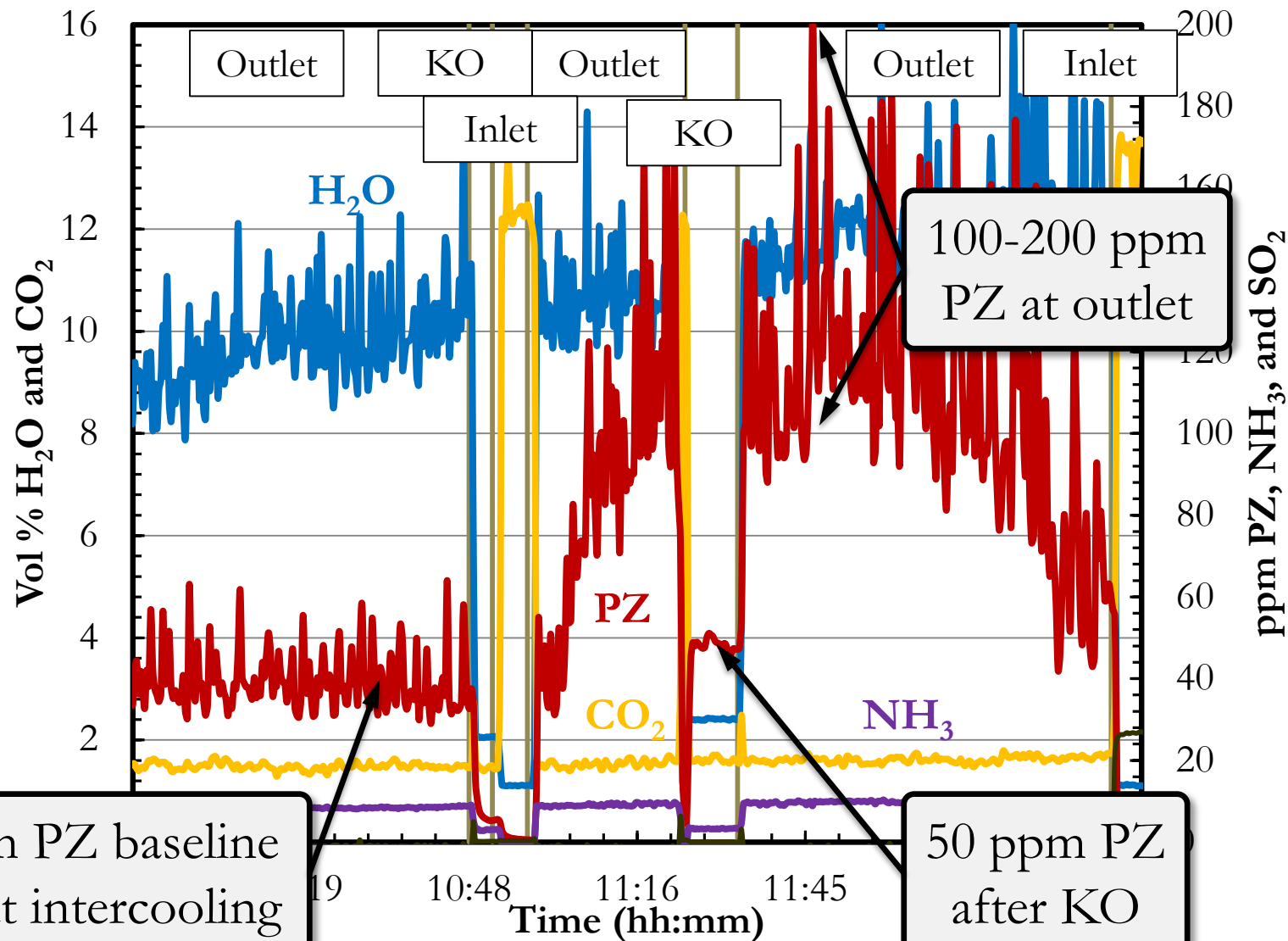


**Select Sample Point**



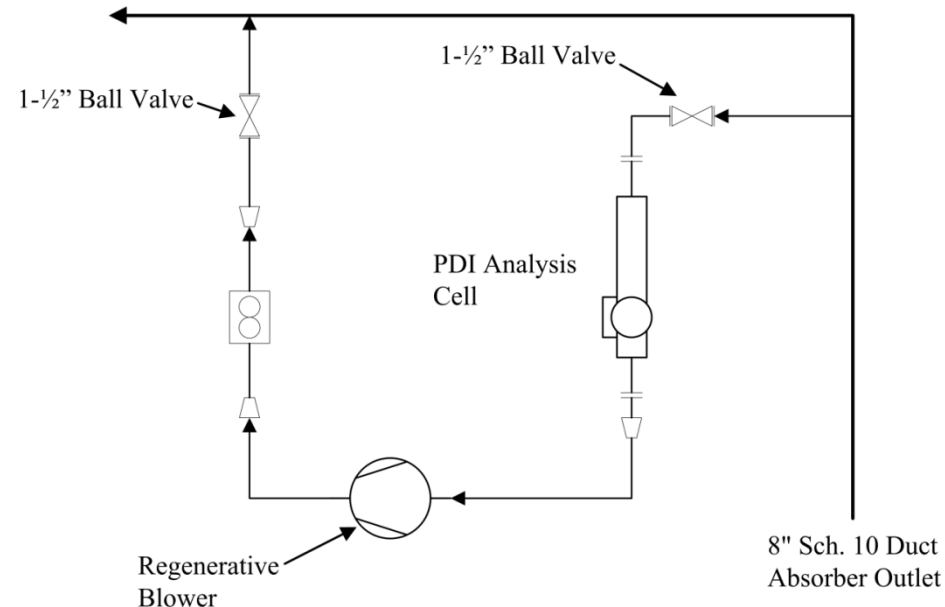
**FTIR Analysis**

# PZ emissions increase with 10 ppm H<sub>2</sub>SO<sub>4</sub>

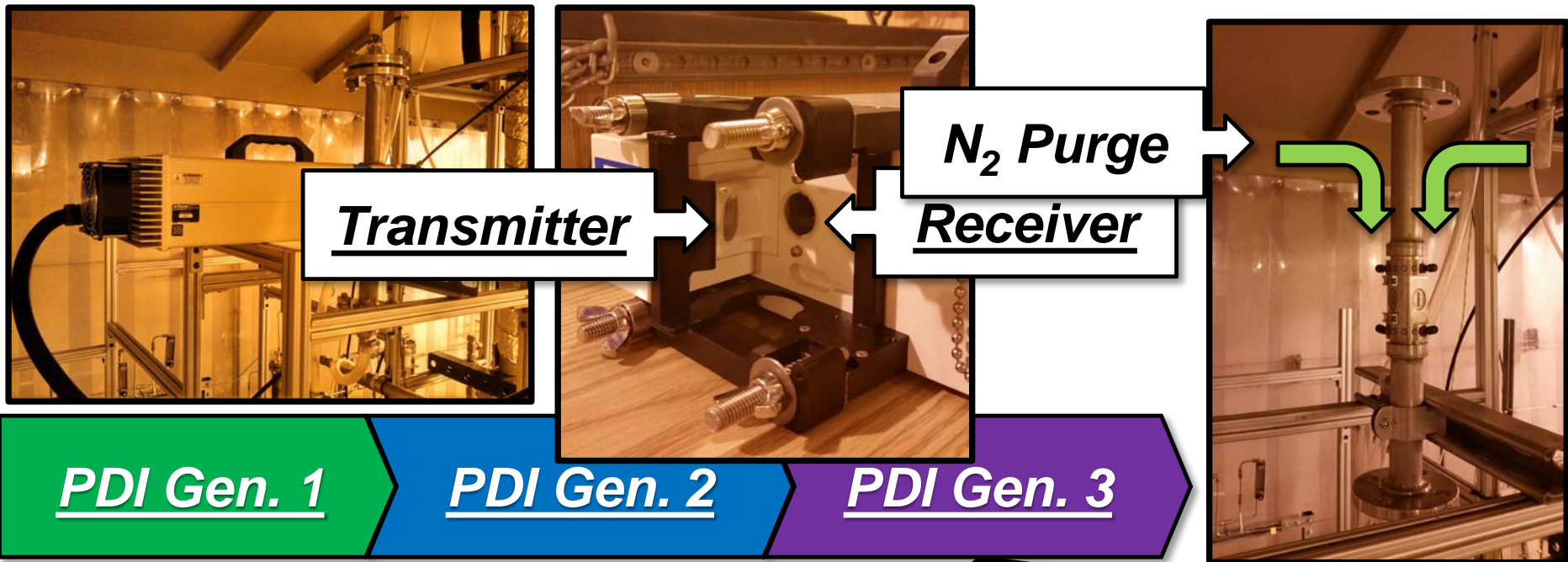


# PDI with bypass sampling provided high quality aerosol measurements

- In-situ analysis for aqueous aerosols
- Measure 0.1 – 10  $\mu\text{m}$  at high ( $10^6$  part/cm<sup>3</sup>) concentrations
- Eliminate extractive sampling errors
  - Sampling: isokinetic
  - Dilution: concentration limitations, RH
  - State: P/T – Condensation/Evaporation
  - Transmission: impingement, diffusion, settling, deposition



# PDI Development

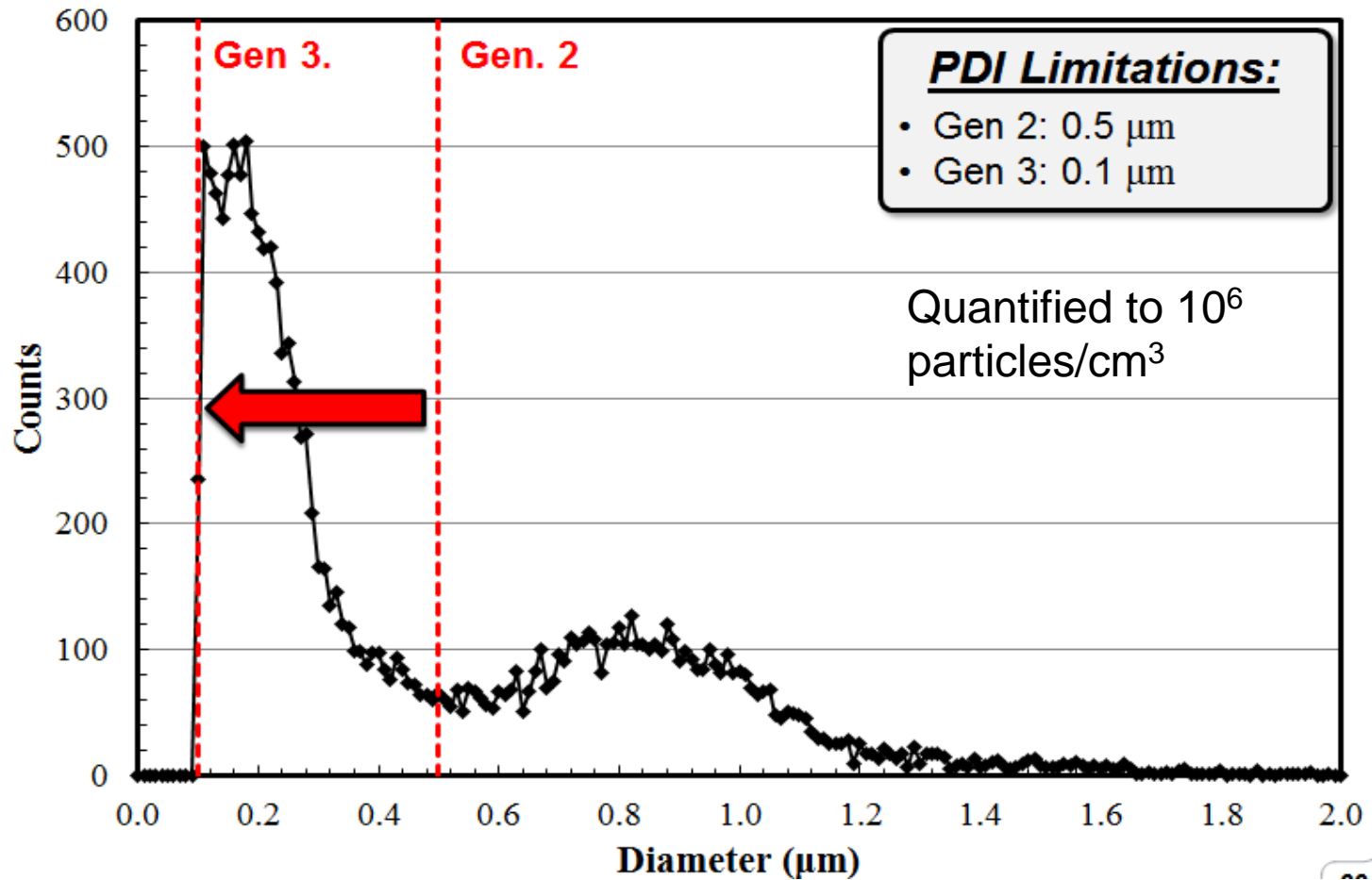


## **PDI Gen3:**

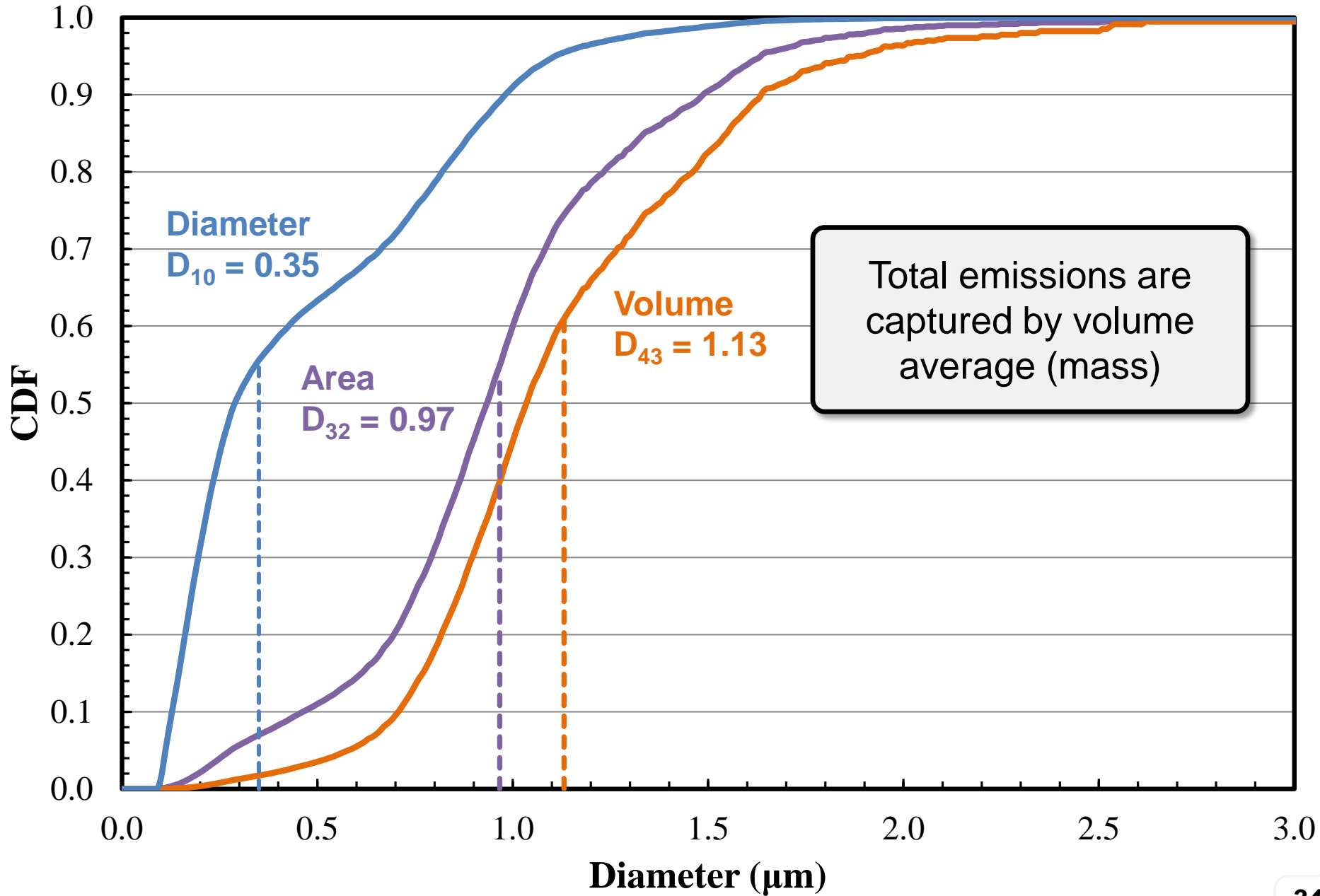
- Custom PDI on 1" Duct (25 mm TX, 39° Cross, 50 → 17.8 μm laser)
- 0.1 μm lower detection limit, 10<sup>6</sup> #/cm<sup>3</sup> estimate



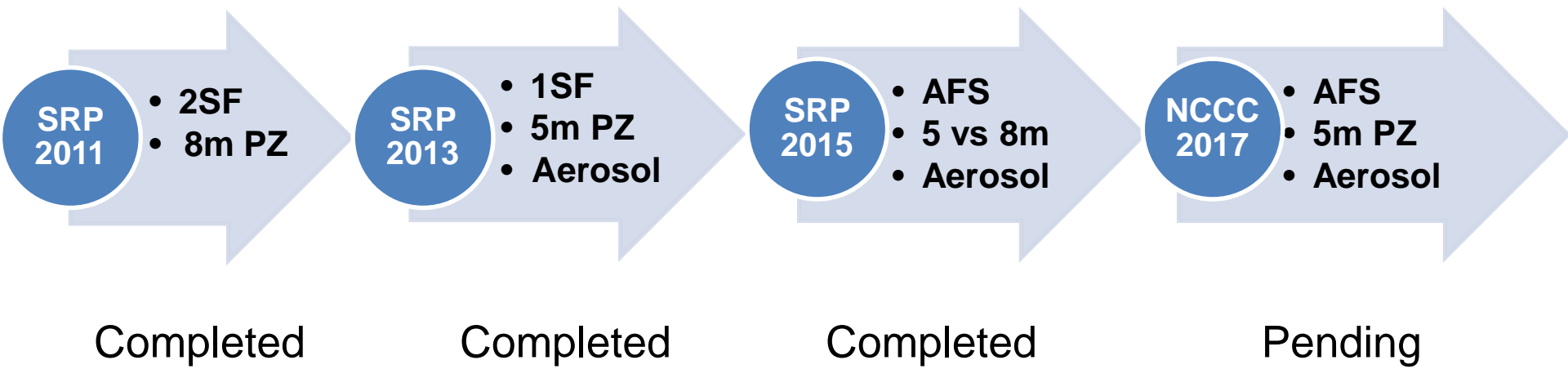
# Gen3 PDI detected 0.1 $\mu\text{m}$ particles



# Cumulative Distributions (CDF)



# BP2 test at NCCC pending NETL approval



# BP2 Test Objectives for NCCC

- Demonstrate energy performance & operability at 0.5-MW scale on coal-fired flue gas
  - 5 m PZ
  - AFS
- Confirm economic advantage of 5m PZ + AFS
- Continue study of aerosol formation and measurement

# BP2 Schedule

Date	Activity
October 2015	Authorization to begin BP2
January 2016	Process Design Package completed
April 2016	AFS Skid PO issued
November 2016	AFS Skid delivered to NCCC
May – August 2017	NCCC Test Program

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# 5m PZ has advantage at SRP with packing area is limited

