40 YEAR ANNIVERSARY

IT^3 HWC

INTERNATIONAL CONFERENCE ON THERMAL TREATMENT TECHNOLOGIES & HAZARDOUS WASTE COMBUSTORS

September 13-14, 2023 • Charlotte, NC

SESSION 1

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Charlotte
2023

Revisions to the Hazardous Waste Combustor MACT regulations

Melvin Keener

Introduction

- History
- Deadline suit
- RTR process
- LEAN decision
- ICR
- What EPA is likely to do in the next rulemaking

History – part 1

- 1999 Phase 1 final rule
  - Incinerators
  - Cement kilns
  - LWAKs
- Vacated in 2001
- Industry asked for remand
  - Concern for case-by-case MACT
- Interim standards in 2002

History – part 2

- 2005 Replacement standards for Phase 1 sources
- Initial standards for Phase 2
  - Liquid fired boilers
  - Solid fired boilers
  - Halogen acid furnaces
- Litigated
- Brick MACT decision
  - Required EPA to consider all methods to control emissions
  - About half the 2005 emission limit failed to meet this criterion
- EPA took a full remand in 2009

Deadline suit – part 1

- Environmental groups informed EPA in August 2022
- Filed the suit in October 2022
  - Failure of EPA’s non-discretionary duty to develop an RTR rule within 8 years after promulgation of MACT standards
- Plaintiff’s brief
  - 9 months to propose a rule
  - Another 9 months to finalize
- EPA’s brief
  - August 14, 2025 to sign a proposed rule
  - August 14, 2026 to sign a final rule

Deadline suit – part 2

- Both parties agree that EPA has missed the deadline – arguing over the date
- Plaintiffs reply
  - Reiterated the 9 and 18 month schedule
- EPA reply
  - Due September 15
- Goes to judge for decision
- Bottom line
  - If judge finds for plaintiff on September 15
    - Proposed rule – June 2024
    - Final rule – March 2025
  - If judge finds for EPA
    - Proposed rule – August 2025
    - Final rule – August 2026

RTR process

- Two part process
- Risk review
- Technology review

Risk review process

- Develop a spreadsheet
    - Contain either actual or estimated emissions from every source for every HAP
    - Location data for every emission source
- Send emissions data to modeling group
    - Air modeling
    - Risk modeling
        - Calculate cancer risk and acute health risk for every facility
        - Calculate environmental risk for every facility
- Decisions on additional limits based on risk
    - If risks are less than 1 in a million – no additional restrictions required
    - If greater than 100 in a million – additional restrictions required
    - If in between, EPA has discretion

Technology review

- Clean Air Act section 112(d)(6)
  - Developments in practices, process, and control technologies
- Review process
  - Is there anything new since 2005
- Lead acid battery manufacturing RTR
  - Sued for failure to include fence line monitoring as a part of the technology review
  - Early in the process

LEAN decision

- 2020 decision
- Requires EPA to address unregulated emissions from a source category when conduction the technology review

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ICR

- Designed to
  - Support the RTR process
  - Determine if additional pollutants should be regulated
- Two part process
  - 18 page questionnaire
  - Testing

ICR – questionnaire

- Sent to nine companies on August 17, 2023
  - Ash Grove Cement
  - BASF
  - Blue Cube (Olin)
  - Clean Harbors El Dorado
  - Eastman
  - Holcim
  - INV Nylons
  - Norlite
  - Veolia
- 75 days to respond

Breakdown

- Incinerators
  - Solid
    - Rotary kilns – 9 (27)
    - Fixed hearths – 3 (3)
    - Fluidized bed – 1 (3)
  - Liquid – 11 (18)
- Liquid fired boilers – 20 (66)
- Solid fired boilers – 4 (7)
- Halogen acid furnaces – 3 (15)
- Cement kilns – 4 (13)
- LWAKs – 1 (1)

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Contents of questionnaire

- 76 questions
- 2020, 2021, and 2022
- All CEMs data
- Recent testing
- Feeds + fluorinated, brominated, PCB, asbestos
- Details for every startups, shutdown, malfunctions, ESV openings
- Supplemental fuel use
- Emissions data for unregulated HAPs

Test program

- Additional testing
- 9 companies
  - May not be the same as the first 9
- EPA will designate what pollutants to test for
  - Based on information gathered from the questionnaire
  - Fill in gaps in their emissions spreadsheet
  - 1-BP, HF, PAHs, PCBs, brominated dioxin-like, PFAS
- Designate the methods to be used
- Give 3-5 months to comply?
- Likely to come out late in 2023

Next rulemaking – part 1

- Require electronic reporting of all performance test data
- Remove the SSM provisions
  - Substitute work practices
- Revise some or all of the emissions limits
  - 100/10 ppm CO/HC threshold
  - What data to use?
    - 2002 database
    - CPT data from 2008
    - ICR data collection
  - Straight emissions approach
  - Subcategories
  - CO/HC issues
- CEMs requirements?

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Next rulemaking – part 2

- Conduct an RTR
    - Additional restrictions based on risk
    - Additional restrictions based on technology review
- LEAN
    - D/F for those sources with the one-time D/F test requirement
    - Additional metals (instead of using PM as a surrogate)
    - Additional organic HAPs (instead of CO as a surrogate)
    - HF, 1-BP
- Conduct a demographic analysis
- Earliest – June 2025
- Latest – August 2026

Questions?

Melvin Keener

mel@crwi.org

703-431-7343

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Enhanced Thermal Treatment of PFAS-Laden GAC with Additives

Charbel Abou-Khalil, **Liliya Chernysheva**, and Kyle Doudrick

September 13, 2023

University of Notre Dame

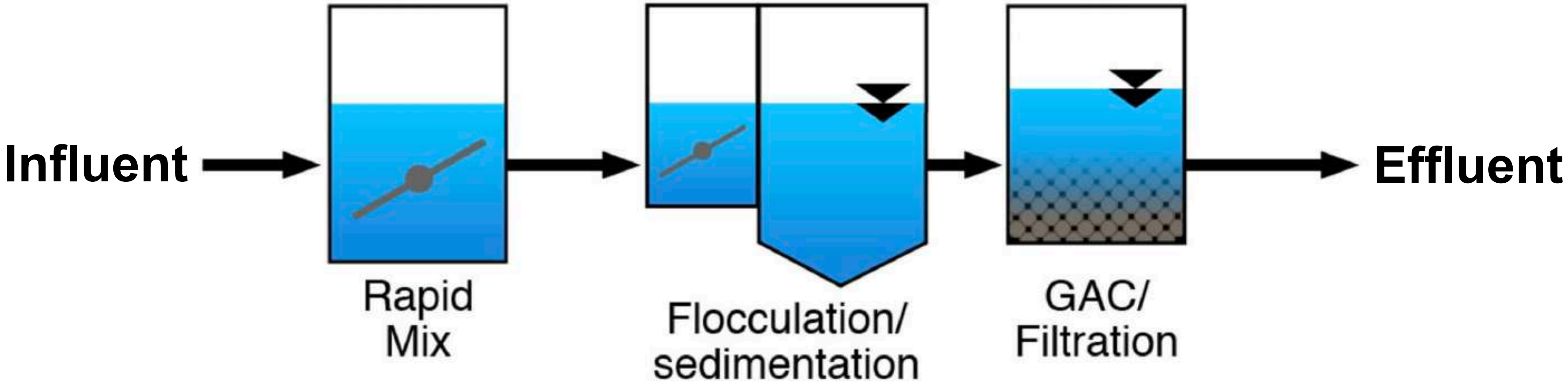
https://www.doudrick.info

Background

- Many commercial **water treatment** systems rely on removing **PFAS** from the contaminated water by **adsorption**

GAC

IX-RESIN



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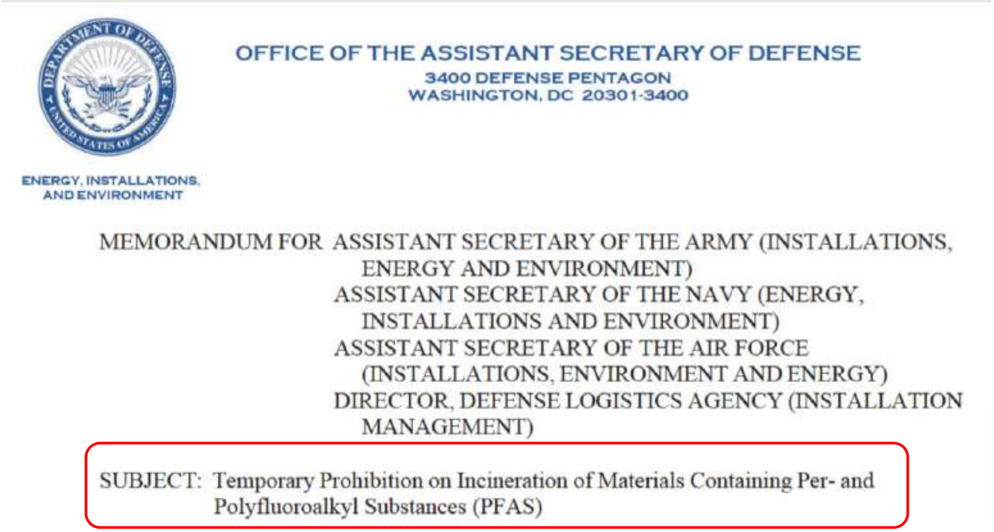
AFFF

NEWS

Study finds PFAS contamination in Cohoes around Norlite incinerator

Details emerge as city considers moratorium on burning controversial waste product

NY bans incineration disposal of toxic firefighting foam



OFFICE OF THE ASSISTANT SECRETARY OF DEFENSE
3400 DEFENSE PENTAGON
WASHINGTON, DC 20301-3400

ENERGY, INSTALLATIONS, AND ENVIRONMENT

MEMORANDUM FOR ASSISTANT SECRETARY OF THE ARMY (INSTALLATIONS, ENERGY AND ENVIRONMENT)
ASSISTANT SECRETARY OF THE NAVY (ENERGY, INSTALLATIONS AND ENVIRONMENT)
ASSISTANT SECRETARY OF THE AIR FORCE (INSTALLATIONS, ENVIRONMENT AND ENERGY)
DIRECTOR, DEFENSE LOGISTICS AGENCY (INSTALLATION MANAGEMENT)

SUBJECT: Temporary Prohibition on Incineration of Materials Containing Per- and Polyfluoroalkyl Substances (PFAS)

Products of incomplete destruction (PFAS, VOF)

PROBLEM

1. Thermal treatment of PFAS-laden adsorbents requires temperatures **>1000°C** to achieve complete mineralization.

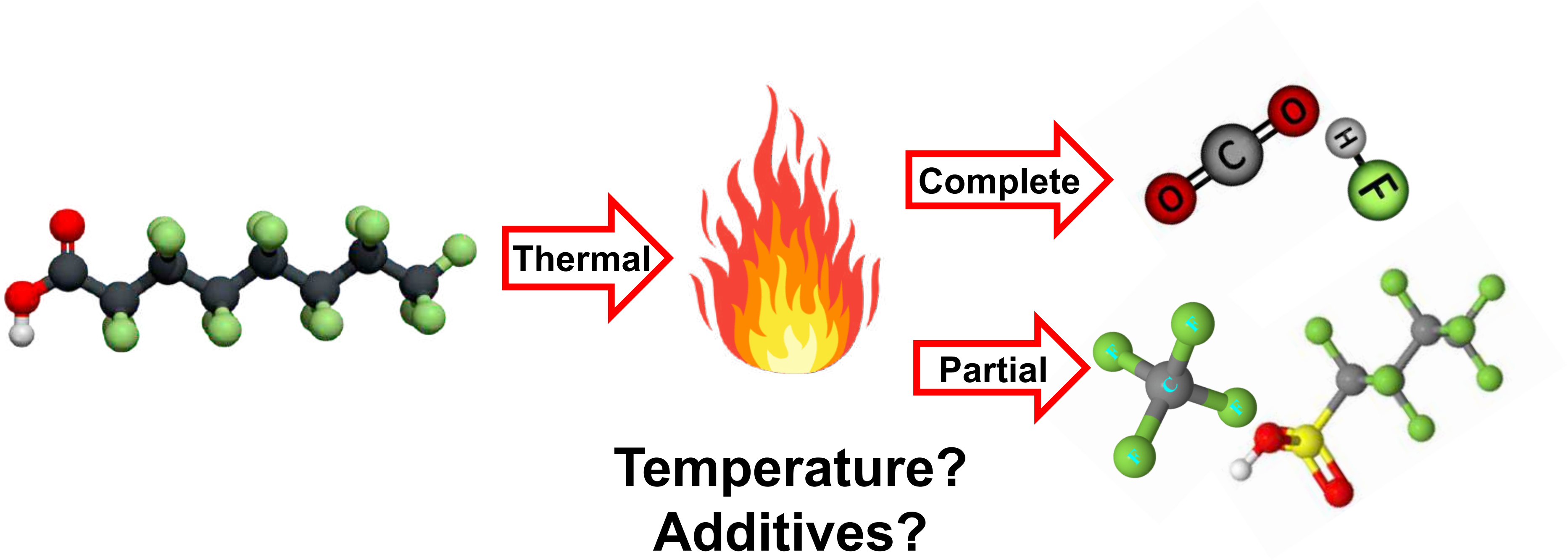
2. Thermal treatment of PFAS generates **undesirable products** of incomplete destruction such volatile organic fluorine compounds (VOFs).

1. Costly

2. Further treatment required

OBJECTIVE

- ➢Optimize the thermal treatment of PFOS-laden adsorbents with additives.



Temperature?
Additives?
Air Flow?
Time?

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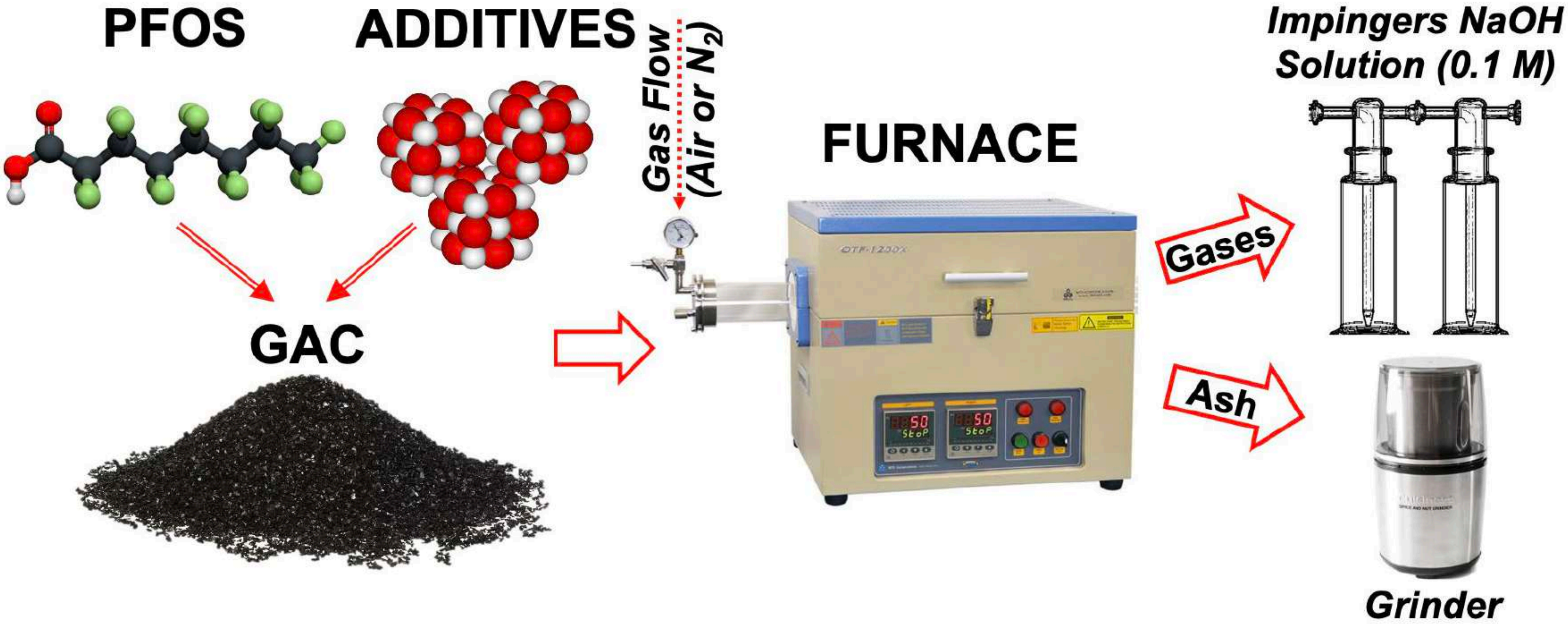
METHODS

Experimental Setup



PFOS

ADDITIVES

GAC

Gas Flow (Air or N_2)

FURNACE

Gases

Ash

Impingers NaOH Solution (0.1 M)

Grinder

METHODS
Analyses

Solids
(Ash)

Total F

Particle-induced Gamma Ray Emission (PIGE) for measuring total fluorine

Organic F

LC-MS/MS for measuring PFOS remaining on ash after treatment

Aqueous
(Impinger liquid)

HF in NaOH

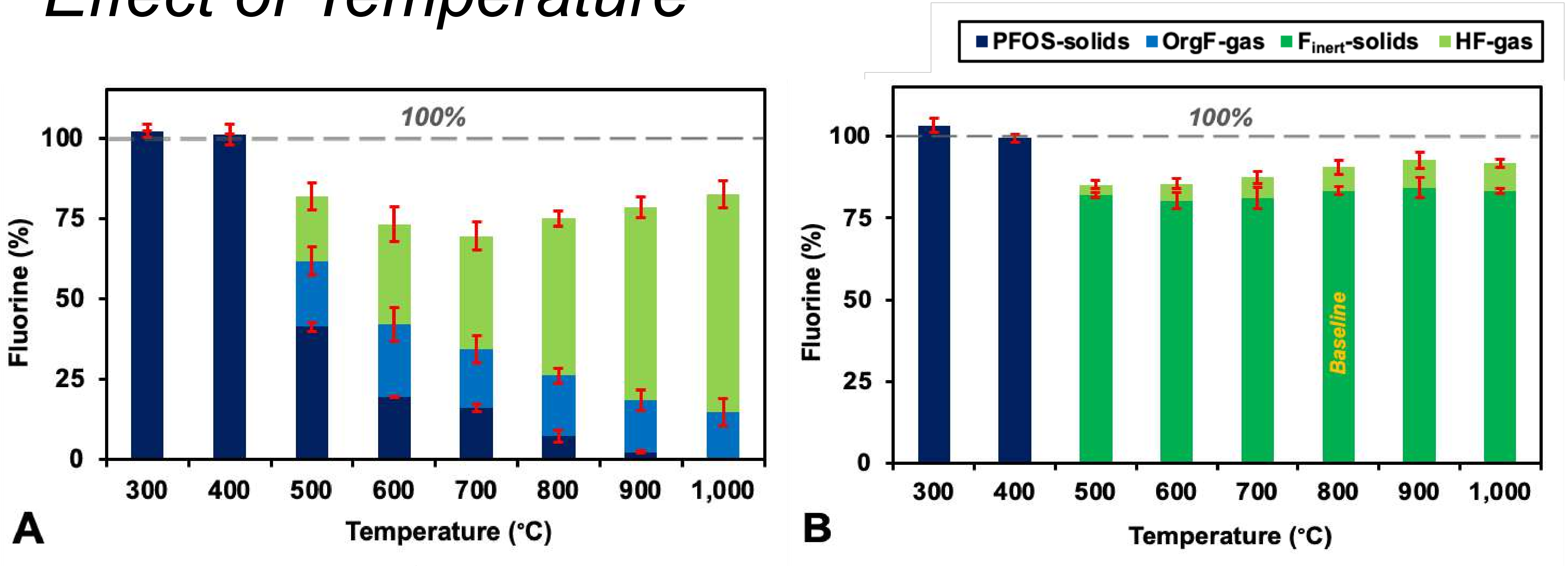
Total F
Combustion

Ion Chromatography (IC) for measuring soluble fluoride (from HF) captured in impingers

RESULTS

Effect of Temperature

*Charbel Abou Khalil, 2023 (in preparation)**

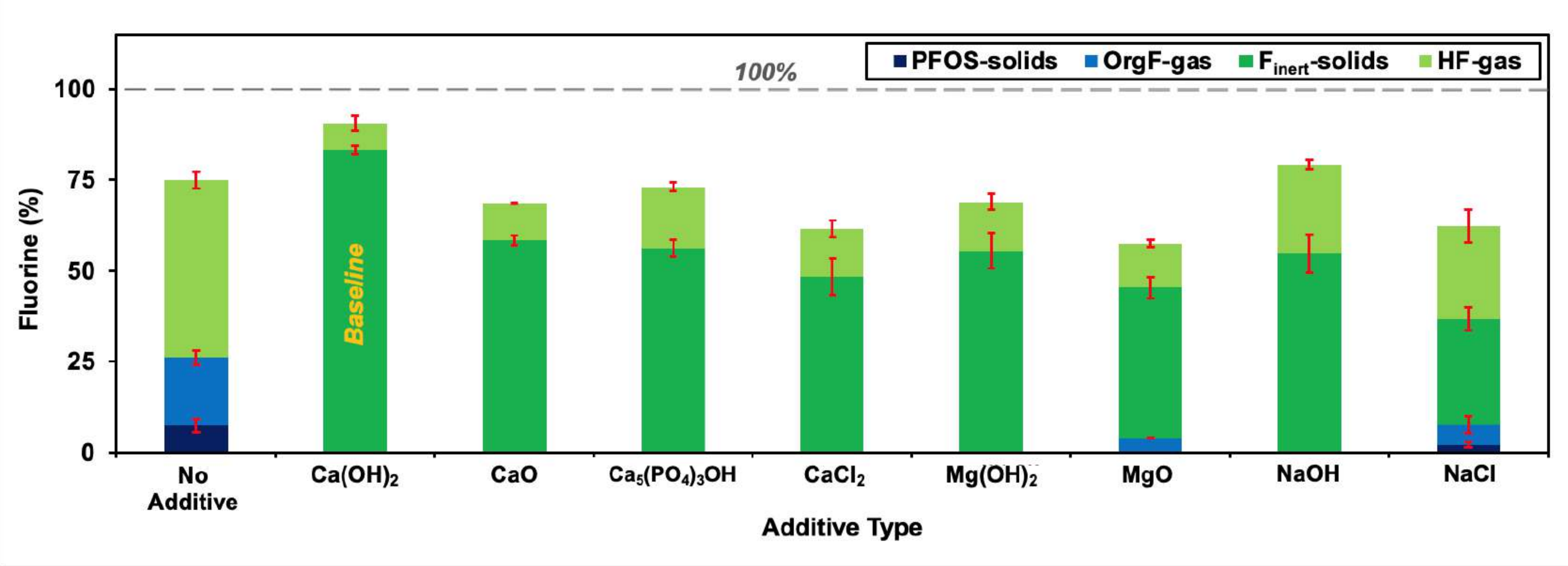


PFOS w/o $Ca(OH)_2$ PFOS w/ $Ca(OH)_2$

Fluorine recovered at different temperatures during thermal treatment of GAC contaminated with PFOS.

RESULTS

Effect of Additive Type



No PFOS remained for all the additive types used

Calcium compounds were more effective in enhancing mineralization

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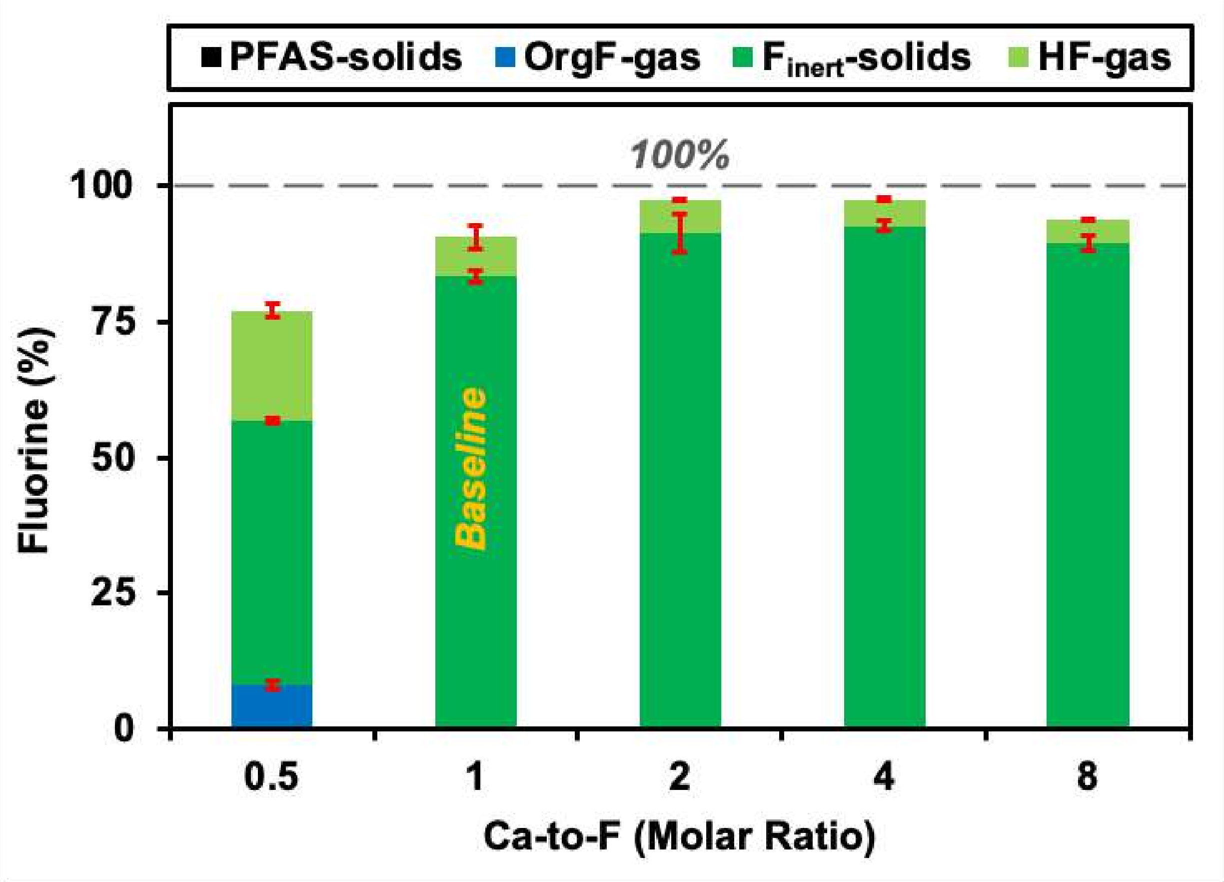
RESULTS

Effect of Ca:F Ratio



Fluorine recovered at different Ca:F ratios

<u>Optimal Ca:F ratio was 2:1</u>, which is 4x the amount of Ca required to transform all F to CaF_2

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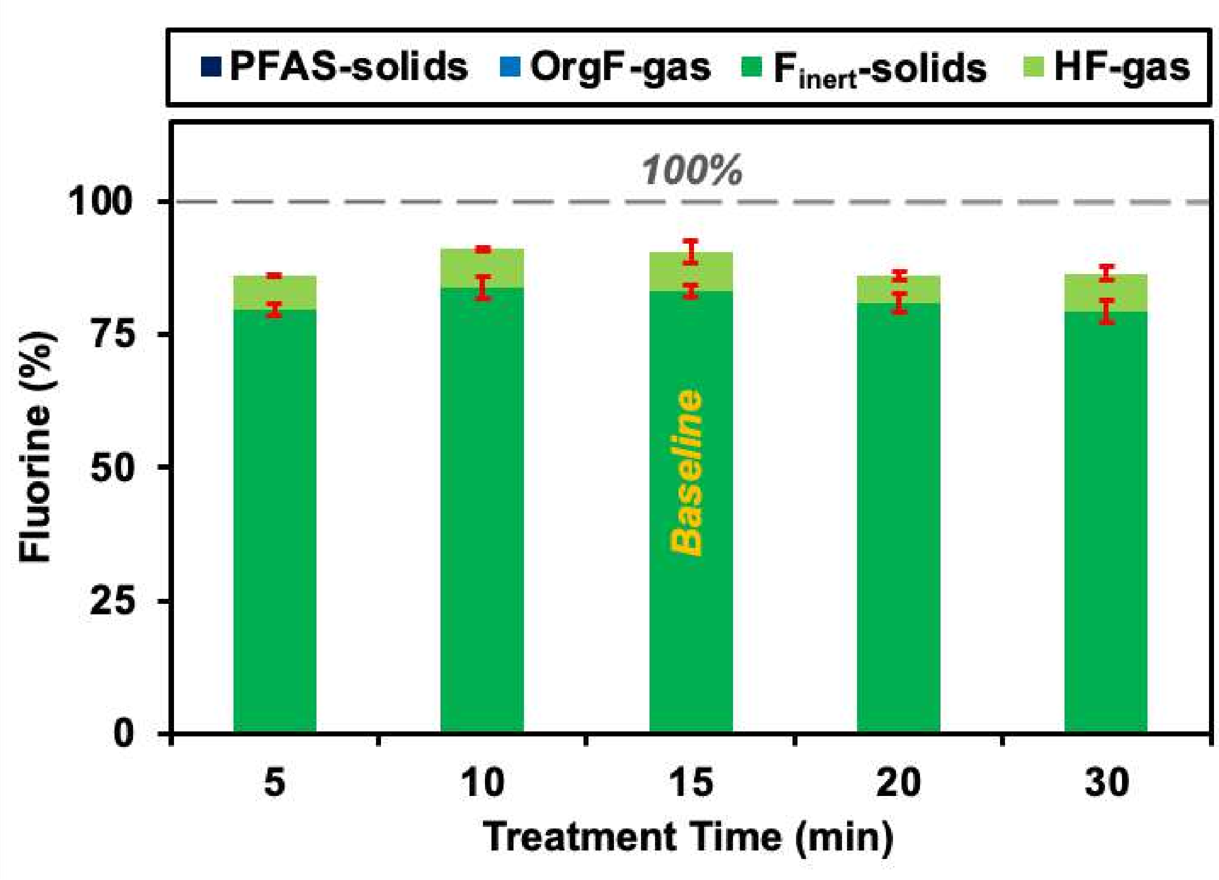
RESULTS

Effect of Treatment Time

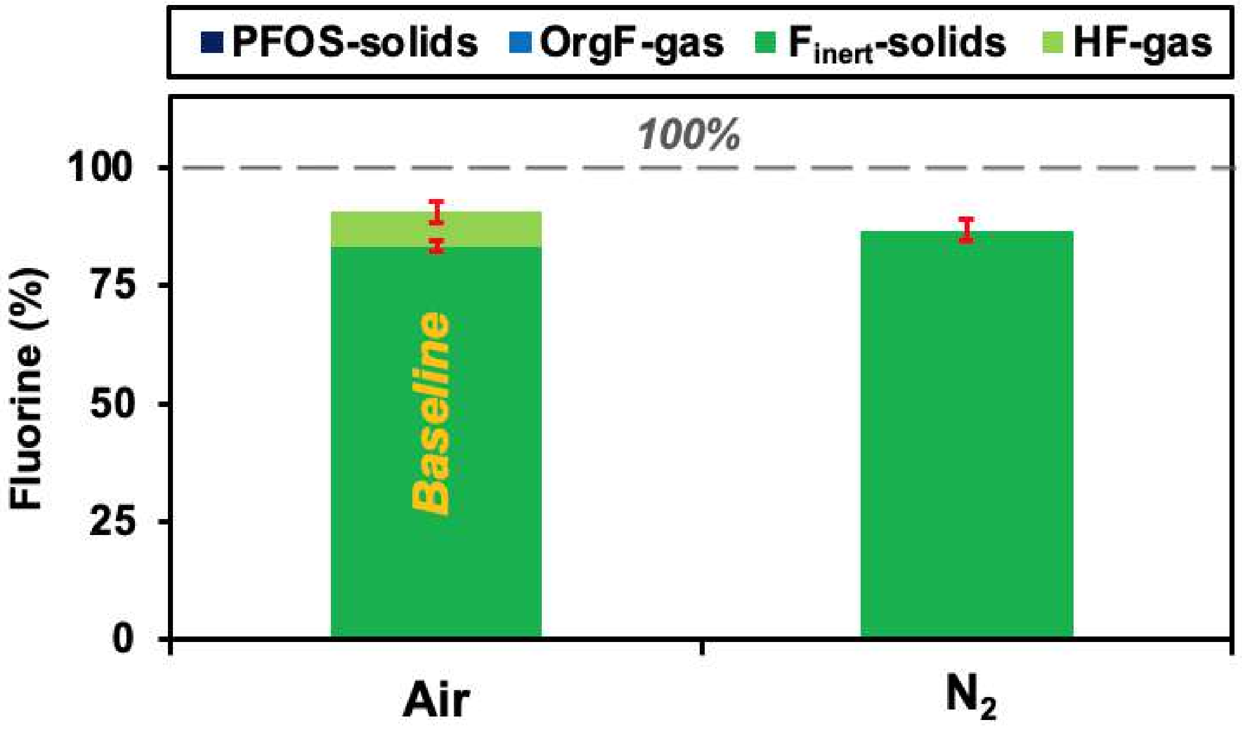


Fluorine recovered at different treatment times

All PFOS was removed after 5 min with 85% converted to inorganic fluorine compounds.

RESULTS

Effect of Carrier Gas



Fluorine recovered at different gas conditions

- Incineration and pyrolysis both produced >80% mineralization of F.
- Pyrolysis diminished HF formation but had a larger missing TOTF fraction.

CONCLUSIONS

Experiment	Optimal Condition	HF-gas (%F)	PFOS-solids (%F)	CaF_2-solids (%F)	Fluorine Recovered (%)
Baseline	N/A	7.2 ± 2.11	<LOQ	83.3 ± 1.17	90.6
Temp. (No $Ca(OH)_2$)	1000°C	68.1 ± 4.21	<LOQ	<LOQ	68.1
Temp. (With $Ca(OH)_2$)	500°C	3.21 ± 1.34	<LOQ	82.0 ± 0.80	85.2
Additive Type	$Ca(OH)_2$	7.23 ± 2.11	<LOQ	83.3 ± 1.17	90.6
Ca:F Ratio	2-to-1	6.12 ± 0.23	<LOQ	91.3 ± 3.49	97.4
Additive Size	Nano Form	4.23 ± 0.12	<LOQ	89.12 ± 2.01	93.6
Time	5 min	6.22 ± 0.24	<LOQ	79.9 ± 1.15	86.1
Gas Phase	Pyrolytic (N_2)	<LOQ	<LOQ	86.8 ± 2.17	86.8

Next Step?

Test if the optimized method and use of additives amends to other matrices and can be used to efficiently treat AFFF-contaminated adsorbents and soils.

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- Dr. Charbel Abou Khalil
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- CEST

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and Technology

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2023

Questions?

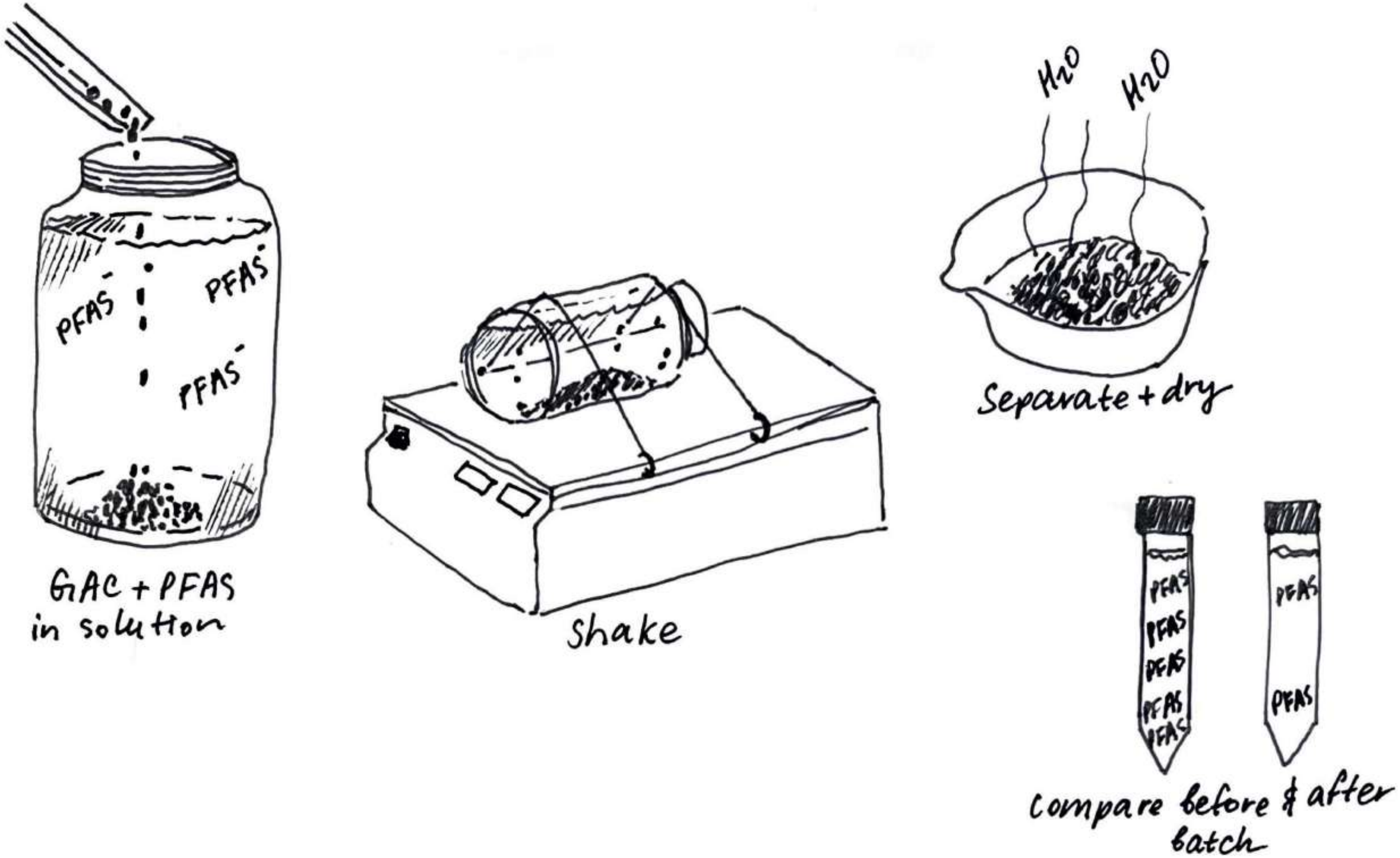
lchernys@nd.edu

caboukh4@nd.edu

kdoudrick@nd.edu

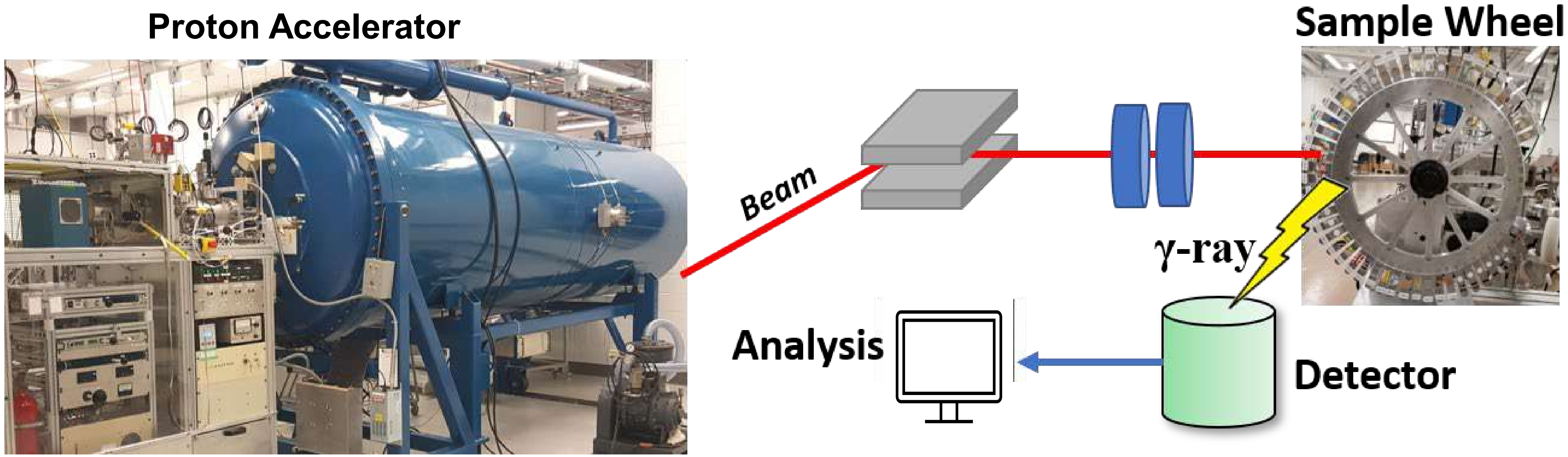
https://www.doudrick.info

Sample Preparation



The batch method

Particle-Induced Gamma Ray Emission (PIGE) Spectroscopy – TOTF Analysis



Overview of PIGE

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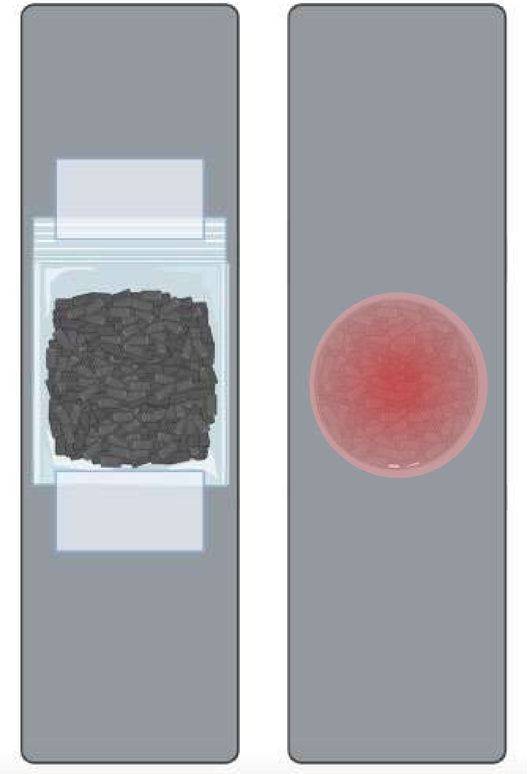
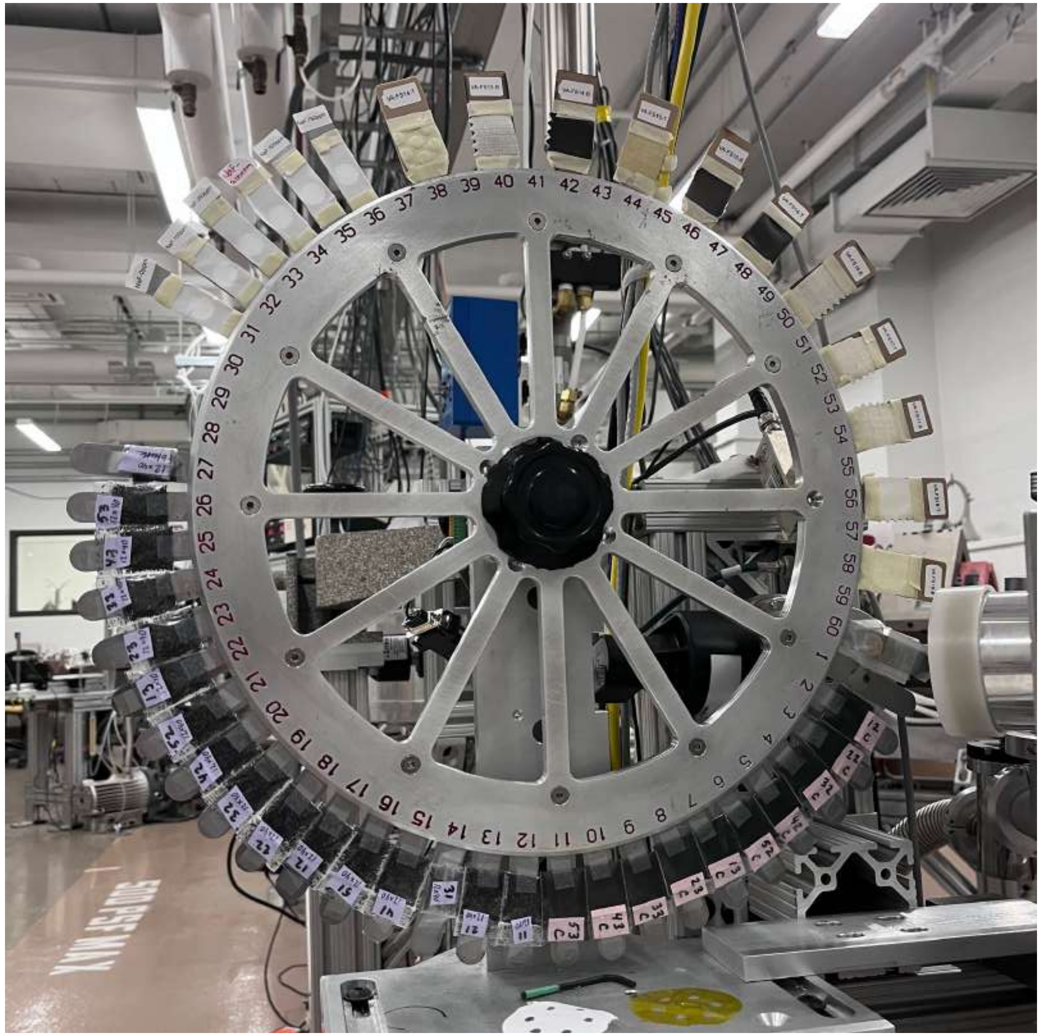
Particle-Induced Gamma Ray Emission (PIGE) Spectroscopy – TOTF Analysis



Front

Back
γ-rays



A closeup of the sample wheel

Pilot-scale Incineration of Fluoropolymers: Evaluation of the Potential Formation of PFAS in Flue Gases

Phil Taylor, P Taylor & Associates
H-J Gehrmann, KIT
K. Aleksandrov, KIT
S. Herremans, SGS Belgium NV
Deepak Kapoor, GFL
Pyrianga Gunasekar GFL

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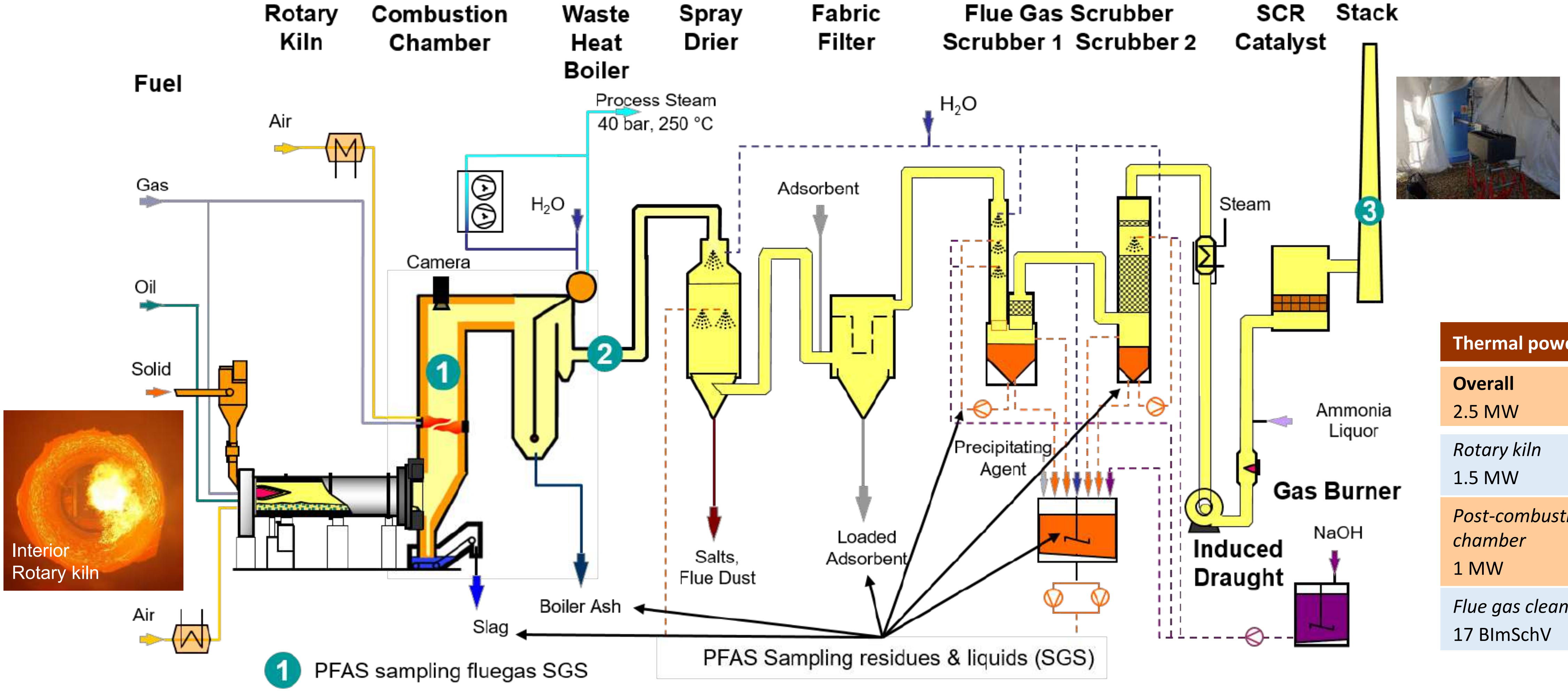
Incineration of fluoropolymers:
PFAS analysis along the flue gas pathway

A pilot scale trial at conditions similar to household and industrial waste-to-energy incineration plants that typically burn products containing fluoropolymers was conducted to assess the potential generation of any statistically significant uncontrolled emissions of Per- and Polyfluorinated Alkyl Substances (PFAS) at levels that might present a risk

Project partners

Research partner	Institute for Technical Chemistry (ITC) at Karlsruhe Institute of Technology (KIT)
Sampling partner	SGS Institut Fresenius GmbH, Industries & Environment
Laboratory partner	SGS Belgium NV, Institute for Applied Chromatography
Feed sampling	Pro-K, Fluoropolymer processing and downstream user association, Germany
Incineration Advisor	P Taylor & Associates, LLC, USA
Data quality review	Environmental Standards Inc., USA
Observer	UBA, Umweltbundesamt (German Federal Environment Agency)

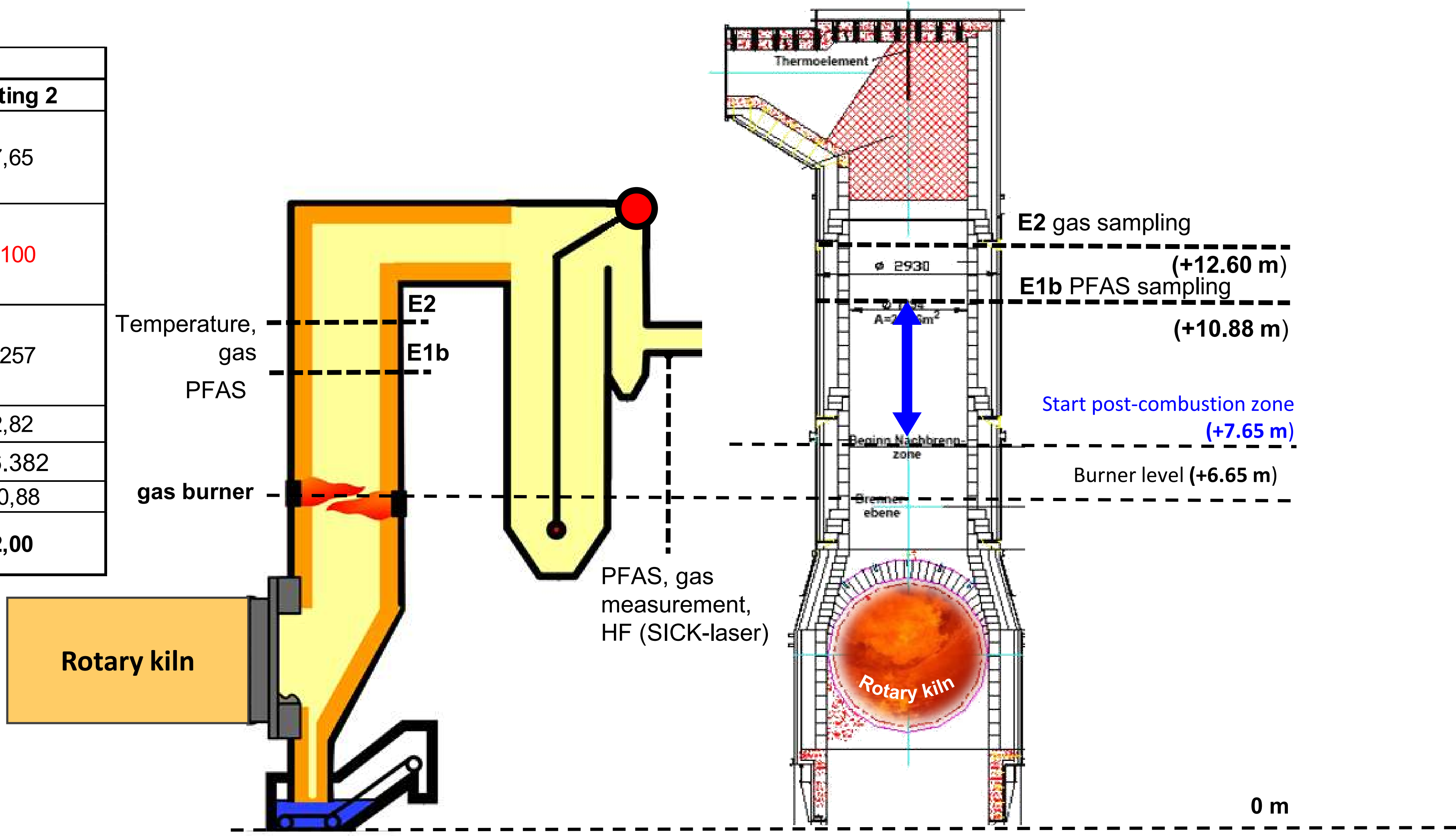
Test facility BRENDA / sampling locations



Thermal power
Overall 2.5 MW
Rotary kiln 1.5 MW
Post-combustion chamber 1 MW
Flue gas cleaning 17 BImSchV

Test facility BRENDA / post-combustion chamber-triple T

PFAS Project, Level E1b		
	setting 1	**setting 2**
Start post combustion zone [m] 1 meter above the burners	7,65	7,65
Temperature in the post combustion chamber (PCC) [°C]	860	1100
Volume flow V_{PCC} [m_N^3/h wet] after boiler	3947	3257
Cross section PCC [m^2]	2,82	2,82
Volume flow V_{PCC} [m^3/h]	16.382	16.382
Height h [m] level E1b	10,88	10,88
Residence time from start PCC zone to level E1b [s]	**2,00**	**2,00**



Experimental setup

test	parameters	number of HF and PFAS sampling	locations	duration [hrs]	RUN	date / remarks		day
start-up with natural gas and oil				24		25.2.23; 10 a.m.	day 1 and 2	
starting solid feeding (wood chips)				24		26.2.23; 10 a.m.		
background of rotary kiln / combustion chamber with oil, natural gas and 100 kg/h wood chips	T_{PCC}: 860 °C; 2.0 s	3	Top of post-combustion chamber (E1b), after boiler, stack	11	1	27.2.2023; 9 am	day 3	Monday
solid fuel: woodchip (100 kg/h) + 320 g/h FP together with oil and natural gas		no		9		feeding of fluoropolymers over night		
		3		11	2	28.2.2023; 9 am	day 4	Tuesday
background of rotary kiln / combustion chamber with oil, natural gas and 100 kg/h wood chips		no		13		stop feeding flouropolymers in the evening		
		3		11	3	01.03.2023; 9 am	day 5	Wednesday
Change of temperature post combustion chamber				12		over night		
background of rotary kiln / combustion chamber with oil, natural gas and wood chips	T_{PCC}: 1100 °C; 2.0 s	3	Top of post-combustion chamber (E1b), after boiler, stack	11	4	02.03.2023; 9 am	day 6	Thursday
solid fuel: woodchip (100 kg/h) + 320 g/h FP together with oil and natural gas		no		9		feeding of fluoropolymers over night		
		3		11	5	03.03.2023; 9 am	day 7	Friday
background of rotary kiln / combustion chamber with oil, natural gas and 100 kg/h wood chips		no		13		stop feeding flouropolymers in the evening		
		3		11	6	04.03.2023; 9 am	day 8	Saturday
shut down				24			day 9	

Material	Mass fraction [wt.-%]
PTFE tubes	63,00
PTFE tape	7,00
PVDF	18,00
PFA	6,00
FKM rubber	6,00

mass flow = 320 g/h

Basis of fluoropolymer feed mixture:

1. Feed mixture comprises of 4 largest volume fluoropolymers - PTFE, PVDF, PFA, FKM. Together these represent 80% of commercial fluoropolymer production
2. Pro-K supplied fluoropolymer samples of major applications that were grinded and mixed

Main operational parameters, setting 1 and 2

			setting S1	setting S2
		unit	RUN 1, 2, 3	RUN 4, 5, 6
Rotary kiln	mass flow wood chips	kg/h	98	98
	main air	m_N^3/h	418	423
	mass flow heating oil	kg/h	61	46
	volume flow natural gas	m_N^3/h	4	4
	volume flow combustion air	m_N^3/h	872	753
	inclination	°	2	
	rotation speed	rev p.m.	0.2	0.4
	temperature flue gas outlet	°C	800 - 900	
	thermal power	MW	1.1	0.9
combustion chamber	volume flow natural gas to burner D4.1	m_N^3/h	22	35
	sum of volume flow combustion air to burner D4.1	m_N^3/h	671	429
	volume flow natural gas to burner D4.2	m_N^3/h	22	35
	sum of volume flow combustion air to burner D4.2	m_N^3/h	671	428
	residence time	s	2	
	temperature flue gas post-combustion chamber outlet (with control)	°C	860	1095
	CO (level E2)	mg/m^3	0.2	1.2
	O_2 (level E2)	Vol.-% dry	11.2	7.0
	thermal power	MW	0.46	0.72
	total thermal power rotary kiln and post combustion chamber	MW	1.59	1.67
boiler / fluegas	volume flow	m_N^3/h	3958	3238
	O_2	Vol.-% dry	11.9	9.0
	CO	mg/m^3	1.35	1.64
	water vapour	Vol.-% wet	6.20	8.49

Increase of rotation speed to avoid slagging

- 200 kW, shift thermal power to the PCC

Increase of temperature by reduction of stoichiometric air/fuel ratio

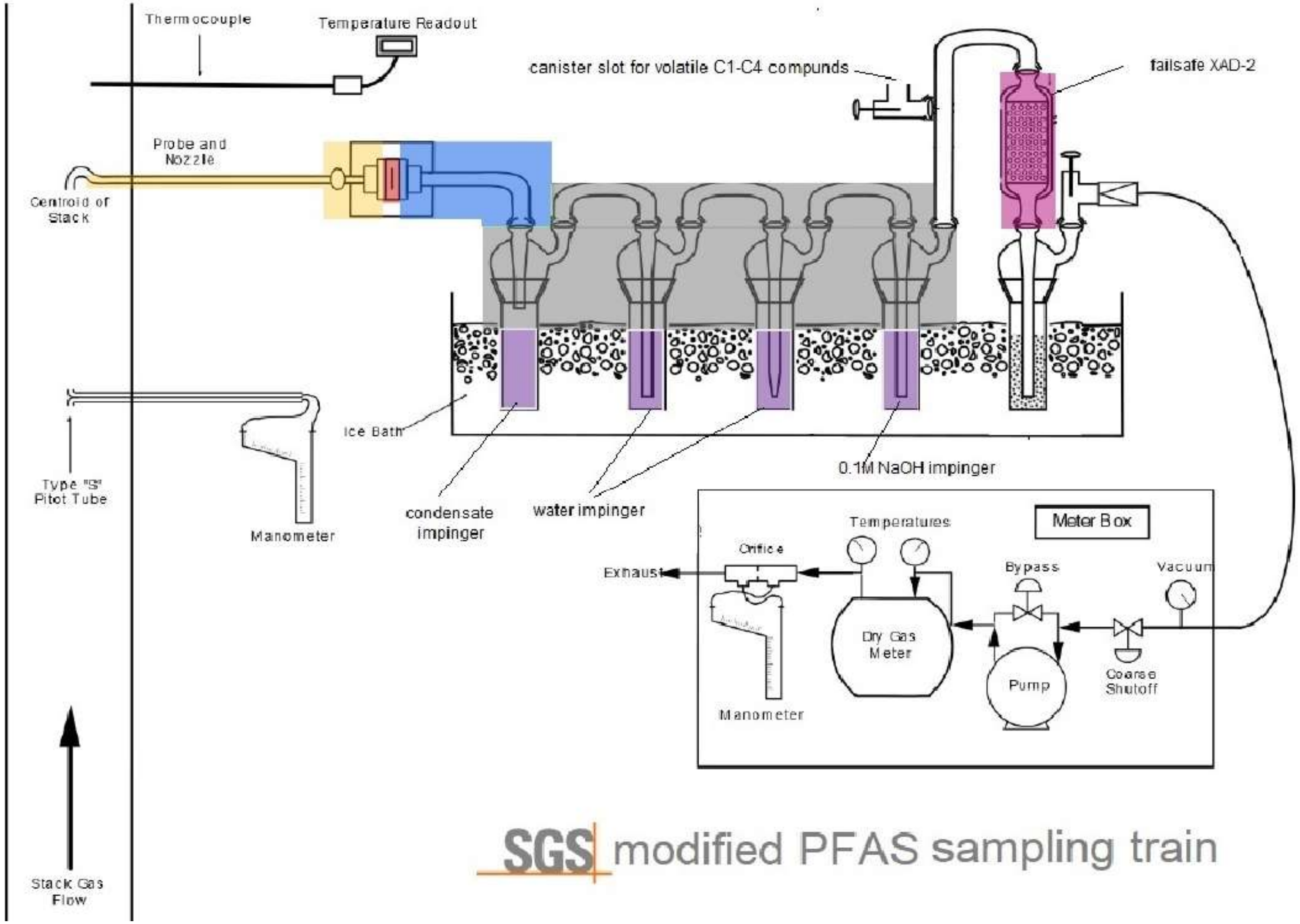
+ 260 kW
≈ constant

Setting 1:
Konz. CO = 1,35 [mg/m³] = **4,5 ppm**
Setting 2:
Konz. CO = 1,64 [mg/m³] = **6,58 ppm**

Sampling and Analysis

1. Modified OTM-45 sampling train
2. Combustion Ion Chromatography (CIC) for Adsorbable Organic Fluorine (AOF)
3. Ultrahigh-Performance Liquid Chromatography coupled to tandem Mass Spectrometer (UPLC-MS/MS) for targeted long chain PFAS
4. Gas chromatography coupled to mass spectrometry (GC-MS) for volatile Fluorocarbons
5. Ion chromatography (IC) for Trifluoroacetic Acid (TFA)
6. Ion Selective Electrode (ISE) for Inorganic Fluoride
7. Tunable Diode laser for Hydrogen fluoride

Modified OTM-45 sampling train

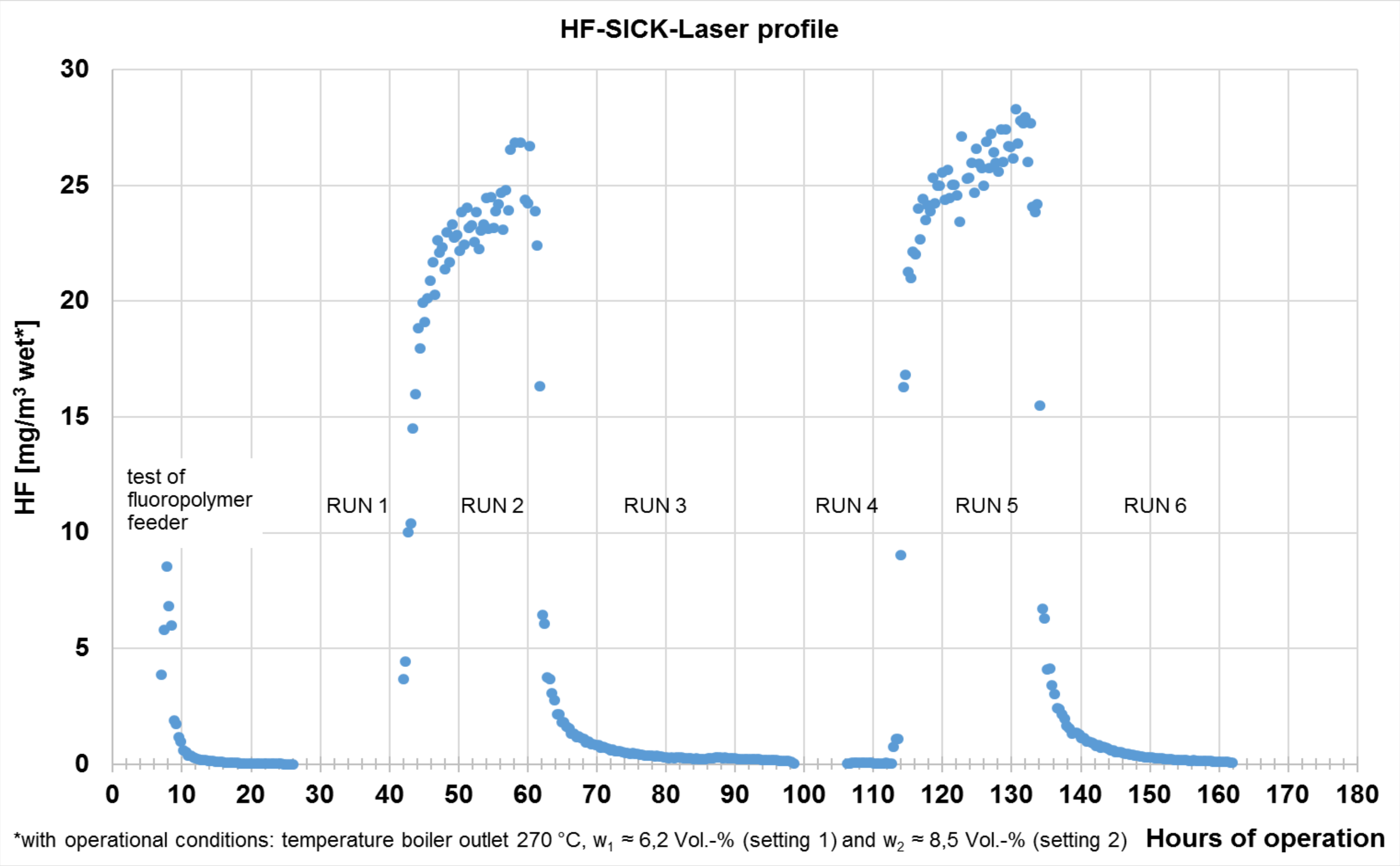


SGS modified PFAS sampling train

Testing methodology

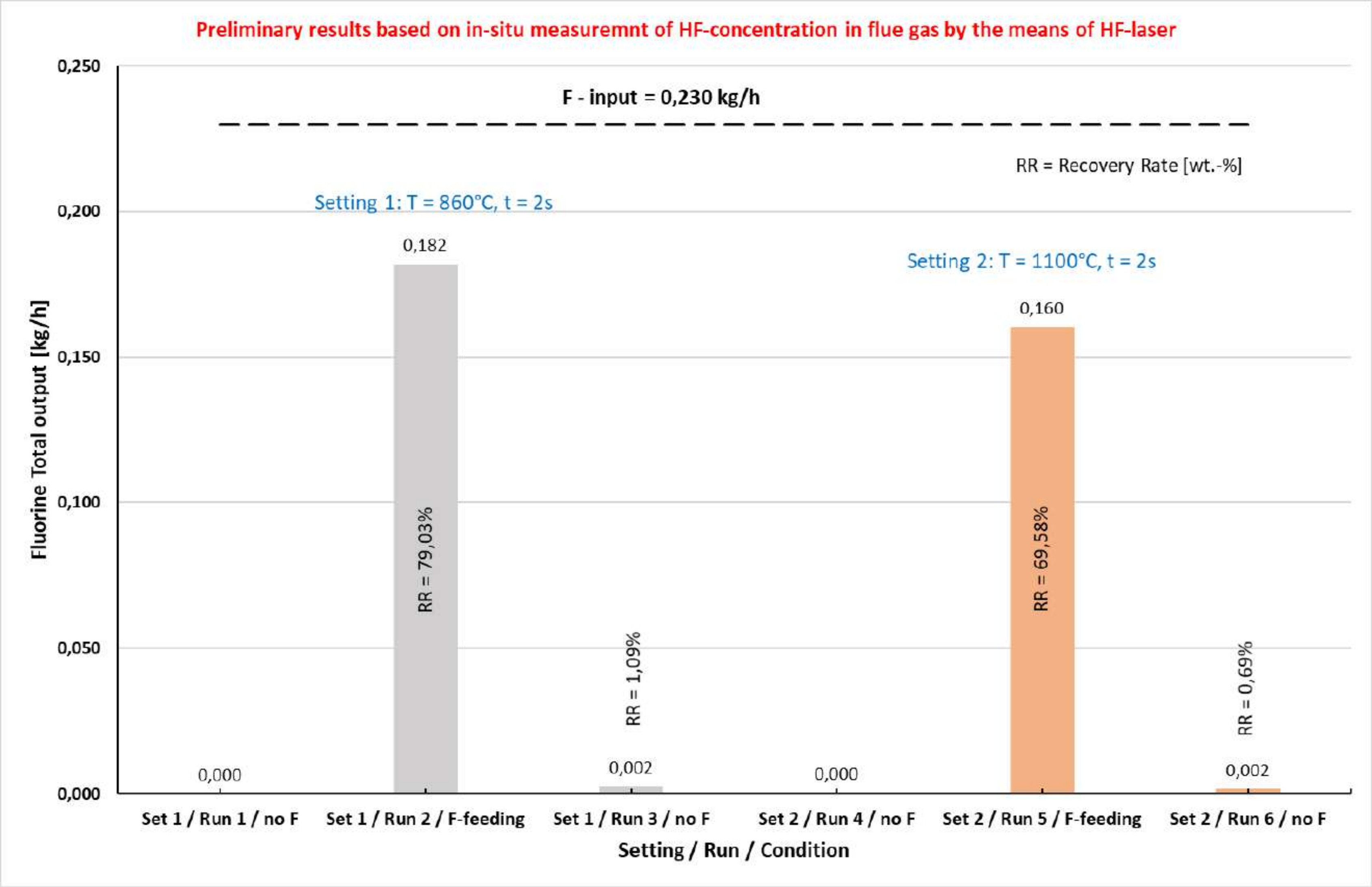
- 27 samples analyzed per setting
- 3 samples were collected and analyzed at each sampling point per setting (triplicate sampling)
- PFAS analyzed at Pre-run, Run and Post-run conditions
- Ash samples were analyzed for target PFAS content
- Blank media and solutions were analyzed for their respective parameters
- Blank sample train were analyzed at relevant sample locations

HF measurement at boiler exit (Tunable Diode Laser)



*with operational conditions: temperature boiler outlet 270 °C, $w_1 \approx 6{,}2$ Vol.-% (setting 1) and $w_2 \approx 8{,}5$ Vol.-% (setting 2)

Fluorine balance (HF Tunable Diode Laser)



Summary of Analytical Results - Combustion Runs

no. of analysis	RUN 2, 860 °C	average value AOF (LOQ - 27 µg/m^3)	total fluorine (gas and particle) (mg/m^3)	Sum of PFAS* (ng/m^3) from each single measurement	TFA (LOQ – 14 µg/m^3)
1st	**Post combustion**	< 27	31.4	1.42	not detectable
2nd		30.71	41.6	0.00	
3rd		32.27	36.5	0.00	
1st	**after boiler**	not detectable	17.2	0.29	not detectable
2nd			17.3	0.00	
3rd			17.3	0.00	
	stack	not detectable	0.0028	5.12	not detectable
				0.00	
				0.00	

* assumed < LOQ : = 0

no. of analysis	RUN 5, 1100 °C	average value AOF (LOQ - 27 µg/m^3)	total fluorine (gas and particle) (mg/m^3)	Sum of PFAS* (ng/m^3) from each single measurement	TFA (LOQ – 14 µg/m^3)
1st	**Post combustion**	27.79	36.6	11.76	not detectable
2nd		30.23	48.9	0.00	
3rd		< 27	47.5	3.67	
1st	**after boiler**	not detectable	14.2	0.64	not detectable
2nd			32.2	0.00	
3rd			17.2	21.52	
	stack	not detectable	0.0023	2.25	not detectable
				0.00	
				11.01	

Partial Re-Analysis of PFAS (Combustion Runs)

Sum of PFAS: 860 C (ng/m^3 $_{N, dry}$)		Sum of PFAS: 1100 C (ng/m^3 $_{N, dry}$)	
Initial Analysis of all three samples	Re-Analysis of Sample 2 and 3	Initial Analysis of all three samples	Re-Analysis of Sample 2
105	ND	96.4	ND

Results from GC-MS analysis (14 samples)

Fluorocarbon	LOQ (µg/m³)	Results (Stack)
Tetrafluoromethane	20	ND except 5 values at or just above detection limits (20 (2), 27, 29, 34 µg/m³) – 4 of 5 detects were from 850 C tests
Hexafluoroethane	30	ND
Trifluoromethane	20	ND
Hexafluoropropylene	5	ND
Pentafluoroethane	25	ND
Octafluorocyclobutane	25	ND

Total Expected PFAS Emissions from EU Incineration Plants

In the EU: 62 million tons of waste incinerated per year*

Sum of PFAS released (stack) at 860°C and 1100°C = 18.4 $ng/m^3_{N,\ dry}$ assuming PFAS < LOQ = 0

Specific flue gas amount released per ton of waste** = 4060 $m^3_{N,\ dry}$

Total load of PFAS emitted in the EU = 4.63 kilograms per year

*https://ec.europa.eu/eurostat/statistics-explained/index.php?title=Municipal_waste_statistics#Municipal_waste_generation
**VDI guideline 3925 "Methods for evaluation of waste treatment processes"

Results

Fluorine Recovery: Fluorine recoveries ranged from 69 to 84% using Tunable Diode Laser - provides strong evidence for mineralization of the fluoropolymer feed mixture.

Trifluoroacetic acid: TFA was not detected for all samples at a reporting limit of 14 µg/m^3.

Targeted PFAS analysis: Long-chain PFAS detected at trace levels in incineration tests (< 10 ng/m3, N, dry). Re-analysis of 3 of the 6 samples (two at 860 C and 1 at 1100 C) were negative for PFAS suggesting contamination external to the incineration system is a likely source of the PFAS detected. 3rd party data validation is continuing.

PFAS analysis of wastewater and ash residue: A large majority of the samples were non-detectable with reporting limits of 0.02 µg/L

GC-MS analysis for short chain fluorocarbons: Excluding CF_4, short chain fluorocarbons were non-detectable at a reporting limit of 5-30 µg/m^3; CF_4 detected in 5 samples at levels just above reporting limit

Conclusions

- 69-85% fluorine recoveries (as HF) is evidence for complete mineralization of fluoropolymers
- Incineration of fluoropolymers do not generate TFA or C_2-C_4 FCs as PICs
- Trace-level PFAS detection capability demonstrate the significance of external contamination sources on the interpretation of the results
- Standard waste-to-energy incineration operating conditions are sufficient for mineralization of fluoropolymers
- Fluoropolymers pose low risk to human health and the environment at their end of life when incinerated

Unresolved Questions:

- What is the speciation of the unrecovered fluorine?

- What is the detected long-chain PFAS attributable to?

- Is CF_4 actually produced as a PIC?

Acknowledgements

This study was funded by Gujarat Fluorochemicals GmbH

For further information, contact:

Deepak Kapoor: dkapoor@gfl.co.in

Phil Taylor: Taylorphd6397@gmail.com

Hans-Joachim Gehrmann: Hans-Joachim.Gehrmann@kit.edu

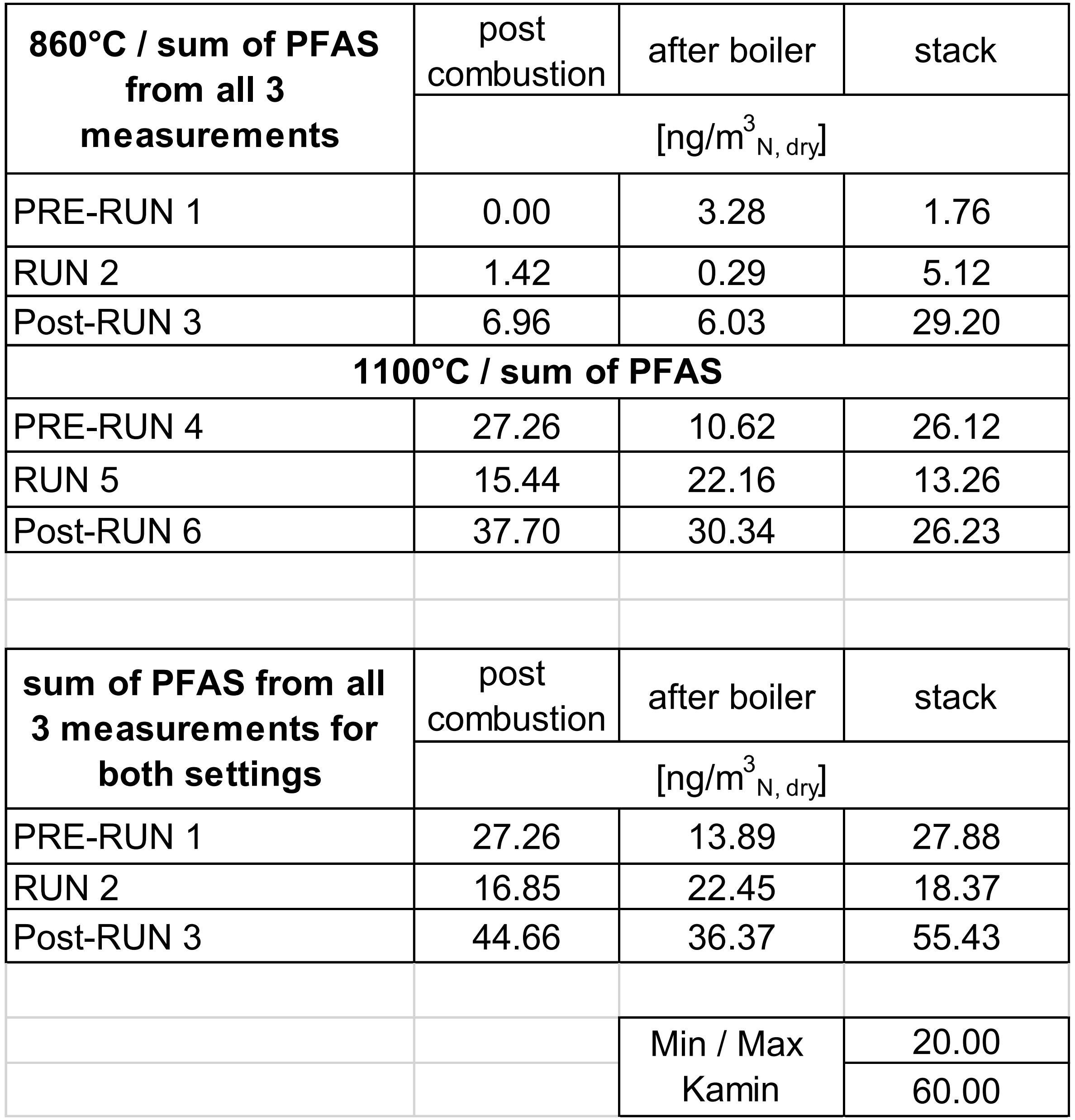
Questions?

Summary of Analytical Results (860 C)

	Avg. Total Fluoride (mg/m^3) (LOQ (gas) - 27 $\mu g/m^3$) (LOQ (part) – 1.7 $\mu g/m^3$)	Avg. AOF ($\mu g/m^3$) (LOQ - 27 $\mu g/m^3$)	TFA (LOQ – 14 $\mu g/m^3$)
Post combustion	36.5	21.0	ND
After Boiler	17.2	ND	ND
Stack	<0.001	ND	ND

Summary of Analytical Results (1100 C)

	Avg. Total Fluoride (mg/m^3) (LOQ (gas) - 27 $\mu g/m^3$) (LOQ (part) – 1.7 $\mu g/m^3$)	Avg. AOF ($\mu g/m^3$) (LOQ - 27 $\mu g/m^3$)	TFA (LOQ – 14 $\mu g/m^3$)
Post combustion	44.3	19.3	ND
After Boiler	21.2	ND	ND
Stack	<0.001	ND	ND

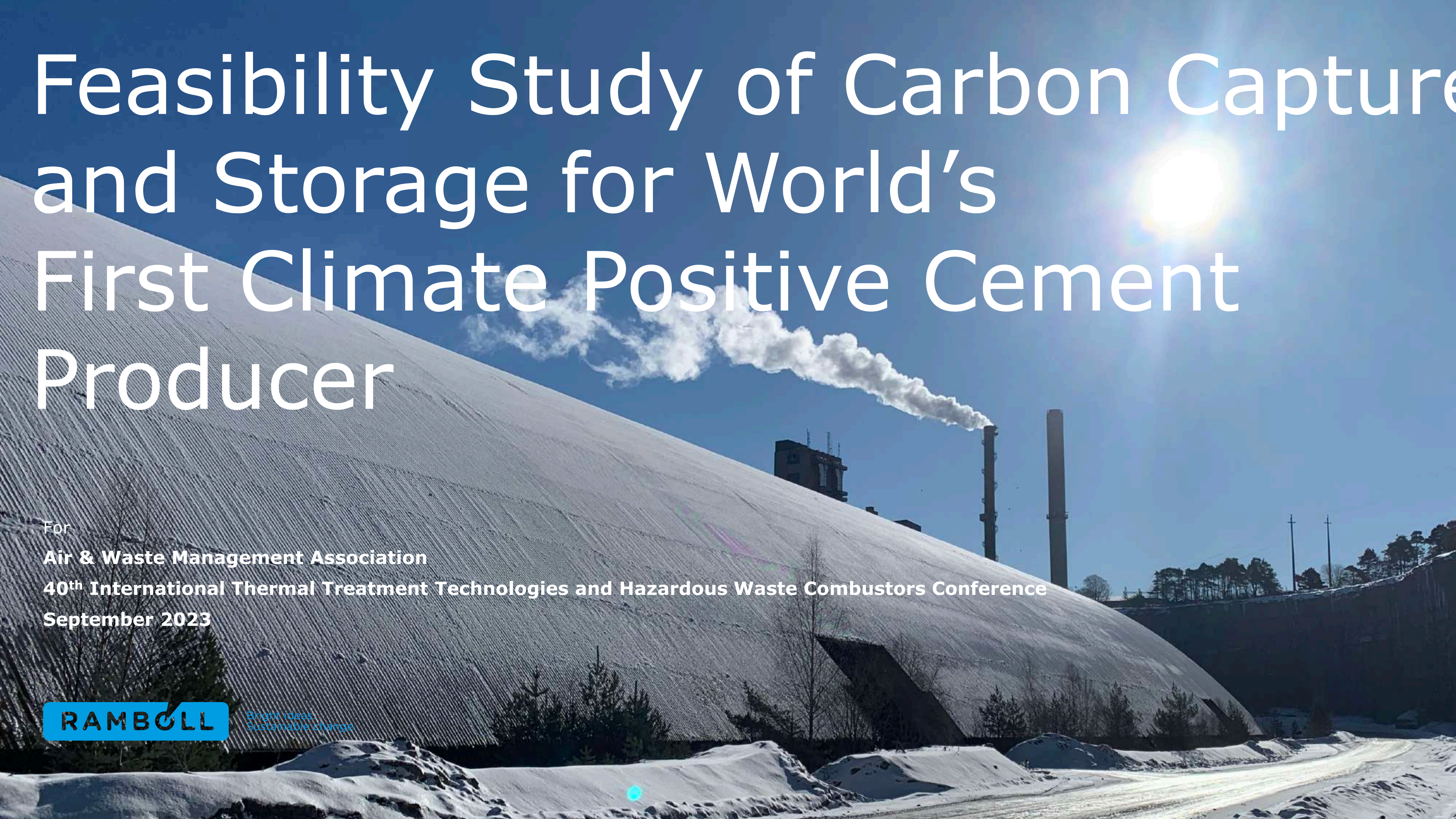


860°C / sum of PFAS from all 3 measurements	post combustion	after boiler	stack
	$[ng/m^3_{N, dry}]$		
PRE-RUN 1	0.00	3.28	1.76
RUN 2	1.42	0.29	5.12
Post-RUN 3	6.96	6.03	29.20
1100°C / sum of PFAS			
PRE-RUN 4	27.26	10.62	26.12
RUN 5	15.44	22.16	13.26
Post-RUN 6	37.70	30.34	26.23

sum of PFAS from all 3 measurements for both settings	post combustion	after boiler	stack
	$[ng/m^3_{N, dry}]$		
PRE-RUN 1	27.26	13.89	27.88
RUN 2	16.85	22.45	18.37
Post-RUN 3	44.66	36.37	55.43

Min / Max Kamin	20.00
	60.00

SESSION 2



Feasibility Study of Carbon Capture and Storage for World’s First Climate Positive Cement Producer

For

Air & Waste Management Association

40th International Thermal Treatment Technologies and Hazardous Waste Combustors Conference

September 2023

Bright ideas.
Sustainable change.

Carbon Capture, Utilization & Storage at Ramboll

- Ramboll is an internationally recognised consultancy at the forefront of the CCUS development
- World-class experience in CC and PTX across all technologies
- 40+ project managers and specialists serving the CC market through our centre of excellence in Copenhagen.
- 100+ project managers and specialists offering transport, interim storage, shipping, geological storage and PtX services in connection with CC.
- Ramboll has worked on more than 100 Carbon Capture and more than 60 successful hydrogen projects studies.
- Strong legacy competencies within Energy-from-Waste, Power, Oil & Gas, Biomass, Pulp & Paper
- Currently high level of activity and many ongoing projects in Northern Europe with new opportunities developing in the Americas market

Ramboll authors

Christian Riber
Chief Project Manager
Copenhagen, Denmark

Jimmy Andersen
Lead Carbon Capture
Consultant
Copenhagen, Denmark

Burcin Temel McKenna
Head of Carbon Capture
Competency Department
Copenhagen, Denmark

Presenter:
William Norris
Sr. Technical Manager
Hunt Valley, MD

Carbon capture, transport and storage feasibility for Heidelberg Materials Cementa plant in Sweden

The challenge

Design a facility to achieve ~95% carbon capture from one of Europe's largest cement producers.

Our approach

Carrying out feasibility work to concept freeze phase / from capture to off-loading point. Ramboll is performing design work, risk profile and CAPEX/OPEX estimates to enable the identification of best technology within capture process, heating and cooling integration of the primary process facility, electricity supply, piping, liquefaction and intermediate storage as well as harbour and off-shore development.

The result

Cementa will have a sound basis to take the project forward into FEED phase and ultimately become carbon neutral by 2030. The project aims to eliminate approximately 1.8 million tonnes of CO2 annually.

Cementa CCS project development

2022 →
Pre-feasibility study
Completed

2022-2023 →
Feasibility study
In progress

2024-2026/27 →
FEED

2027-2030 →
EPC

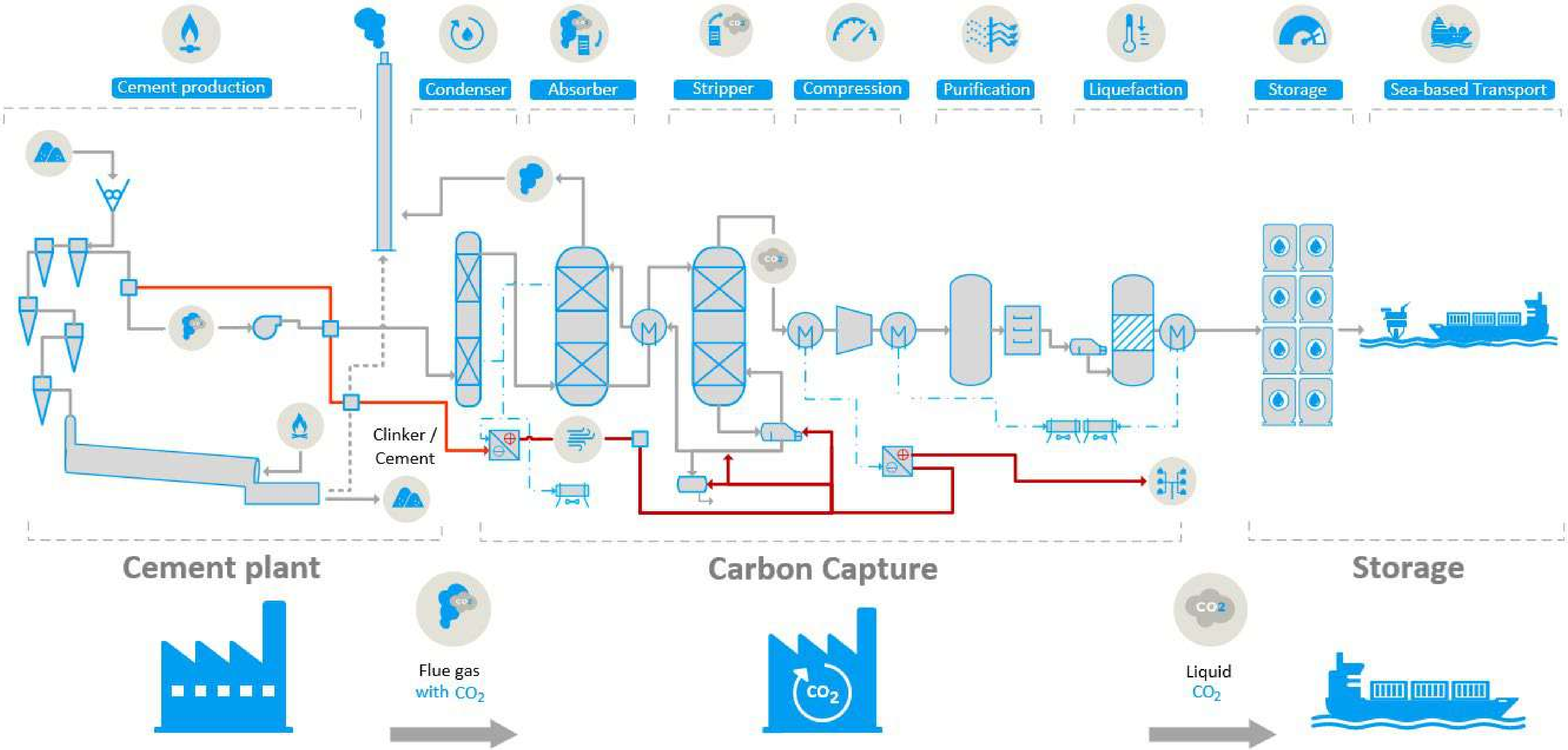
2030 →
Climate-positive cement production

Feasibility

- Carbon Capture
  - Flue gas treatment
  - Process, H&MB
  - Heat and cooling
  - Amines and solvents
  - Emissions and water treatment
  - Compression and liquefaction
- Transport
  - Port development
  - Floating CO2 facility
  - Intermediate storage and pipeline
- Auxiliaries
  - Civil studies
  - Electrical and automation
  - Layout/3D design

- Capex/opex
- Risk management
- Transport and storage
- HSE
- Environmental permitting guidance

Amine-based CO_2 capture at a cement plant



Amine-based CO_2 capture

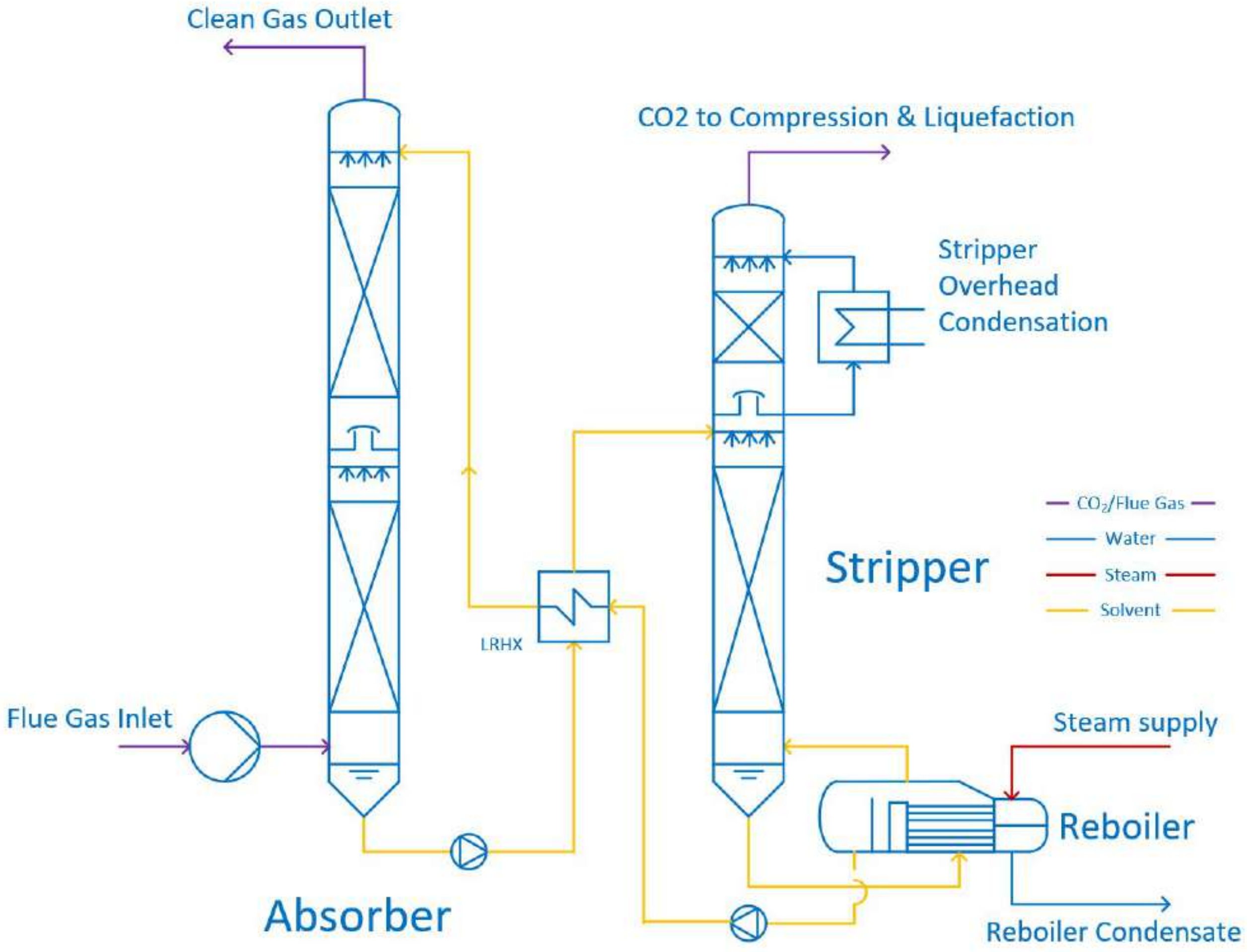
CO_2 containing flue gas enters the absorber at the lower left and contacts the solvent, which enters at the top right, in a counter-current flow.

The absorption reaction is **exothermal** which increases the temperature of the gas and solvent

Higher temp. counteracts solvent performance -> lowers CO_2 solubility:

In the stripper column, the solvent is sprayed over a packing material and heated with steam in a counter-current flow, which causes the CO_2 to desorb from the liquid.

The stripping steam is generated in the reboiler by heating the solvent, with an external heat source (usually steam).



Amine-based CO_2 capture – Absorption requirements

Clean and cold flue gas

- Clean to avoid solvent degradation

SO_2	< 30 ppm (depends on solvent)
NOx	< 50-100 ppm
Dust	< 20 mg/Nm^3

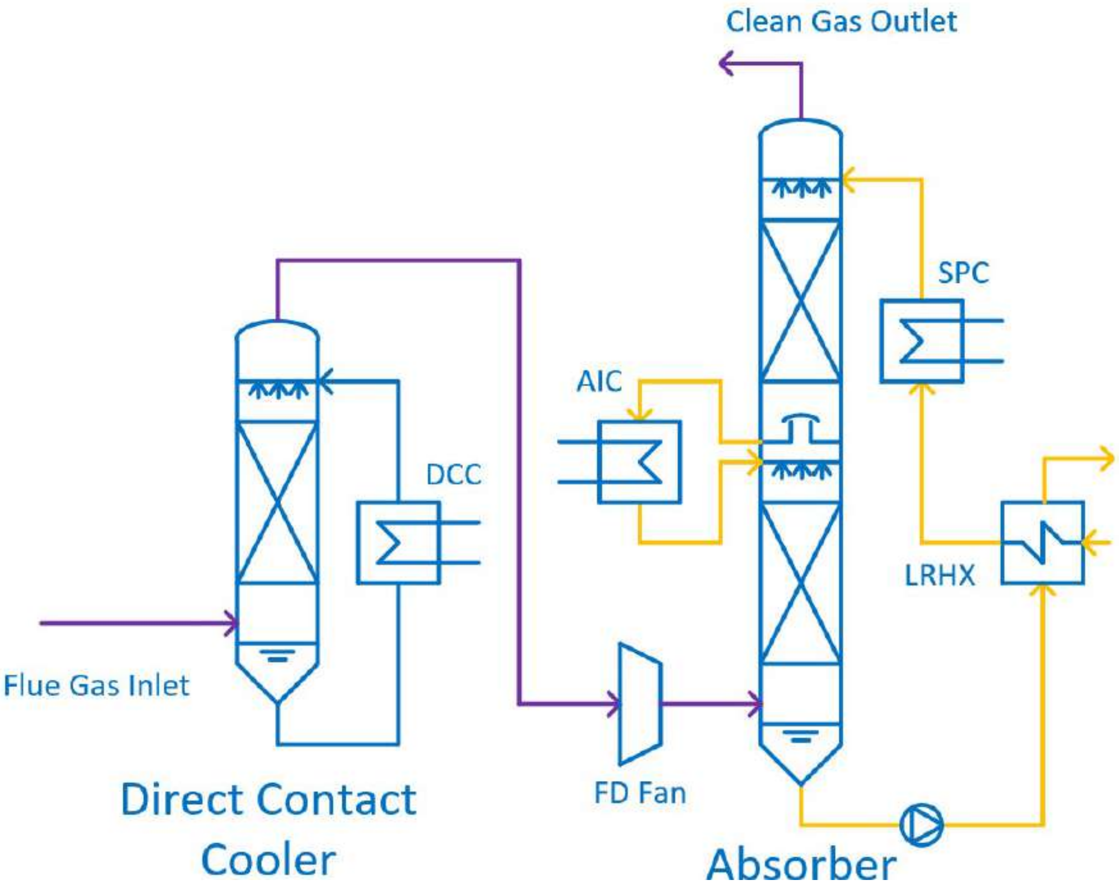
Extensive flue gas cleaning upstream the carbon capture plant a prerequisite

Cold flue gas into absorber to optimize absorption process (~30-45°C)

Solvent cooling

- Solvent Pre-Cooling (SPC)
- Absorber Intercooling (AIC)

Large cooling duty required!!



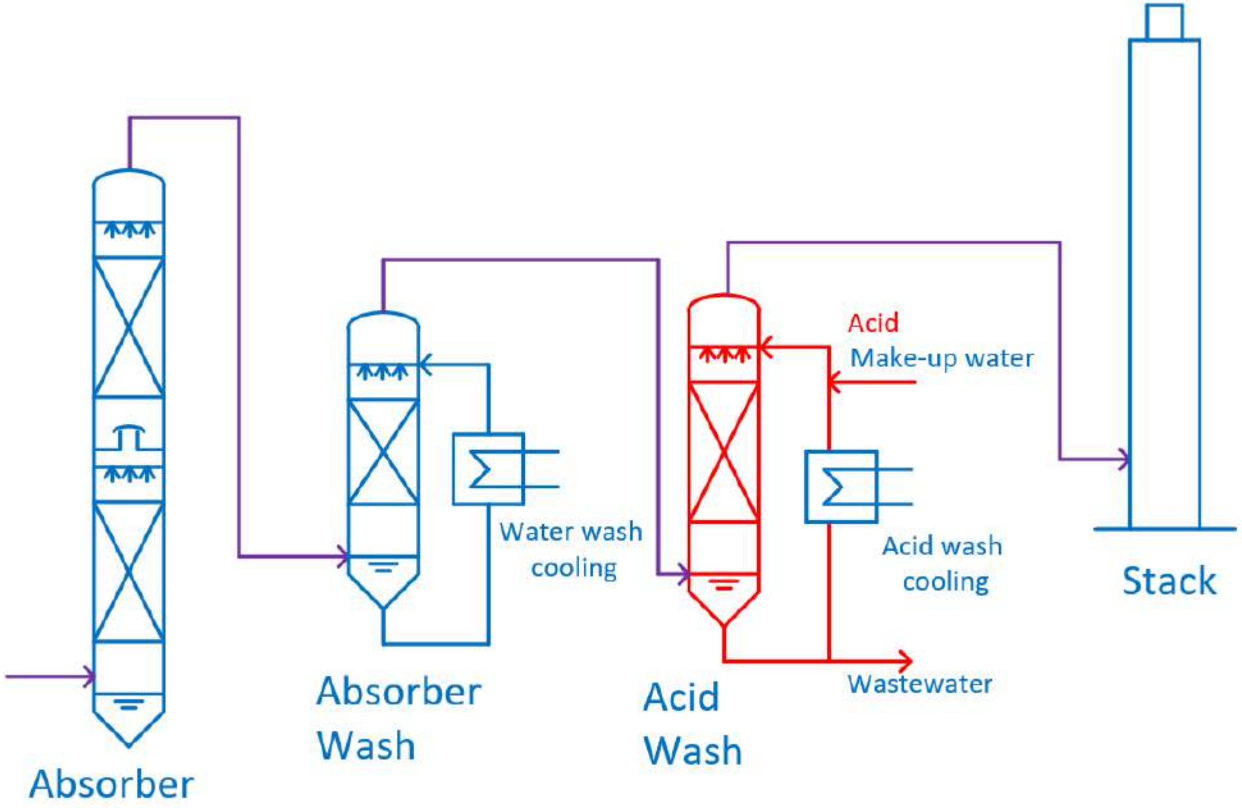
Purple: Flue gas Yellow: Solvent

Amine-based CO_2 capture – Solvent degradation and emissions

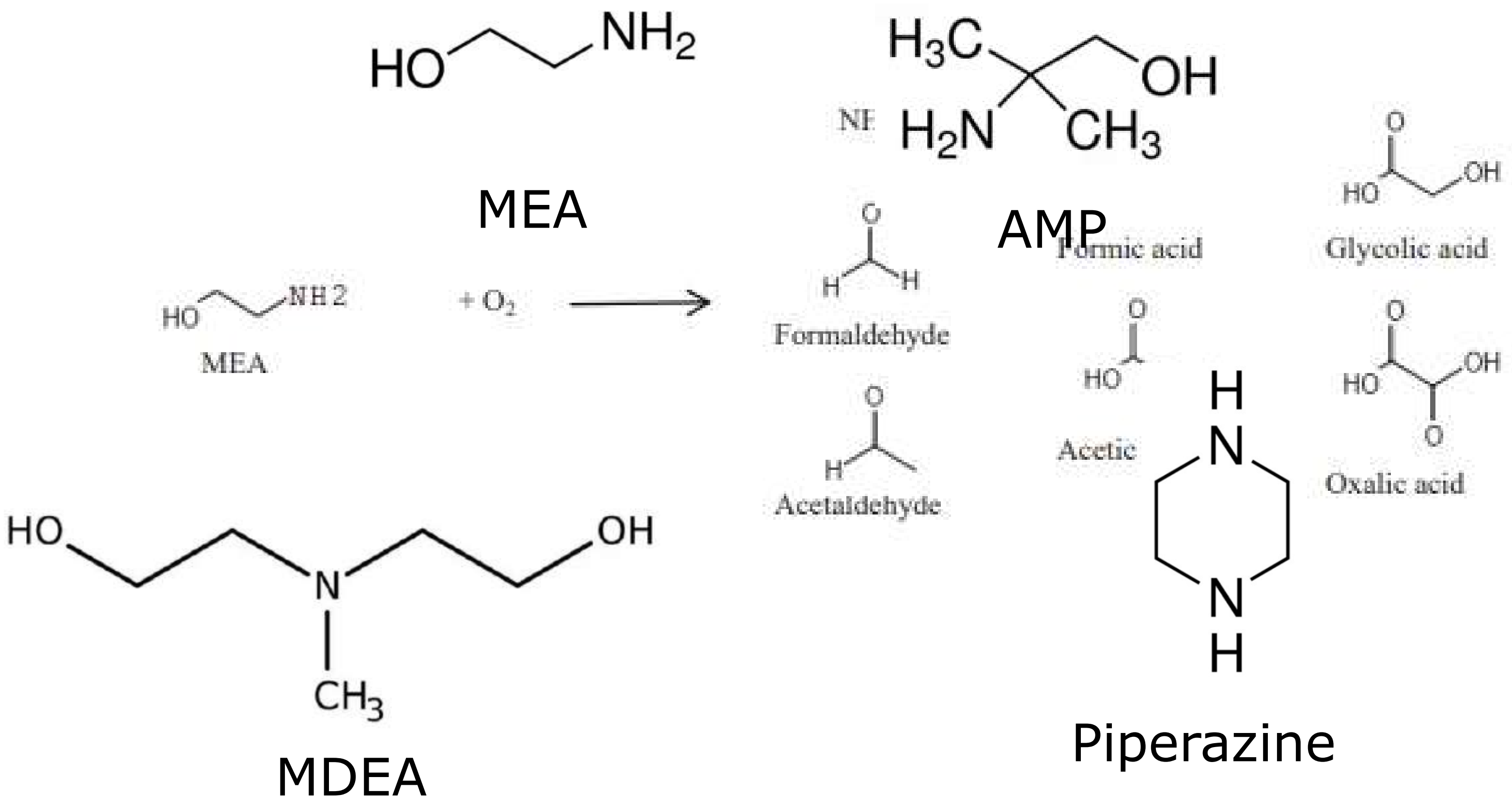
- **The amine solvents will degrade during operation**
  - Oxidative degradation (reaction with O_2 from flue gas)
  - Thermal degradation (due to stripper conditions, high T, P)
- **New emissions to be managed**
  - Solvent amines and degradation products (ammonia, aldehydes, nitrosamines, nitramines, etc.)

- **Emission abatement strategies**
  - Flue gas pre-treatment (previous slide)
  - Solvent selection
  - Absorber washing (acid wash)
  - Thermal reclaiming (a distillation process to remove degradation products and impurities)

- **Other new challenges:**
  - Flue gas monitoring
  - Dispersion modelling
  - Stack design



Amine-based CO_2 capture – Solvents degradation and emissions



- Solvent ~30% wt concentration
- Typical solvents

MEA – Mono-Ethanol-Amine

AMP – 2-Amino-1-Methyl-Propanol

MDEA – MethylDiEthanolAmine

Pz - Piperazine

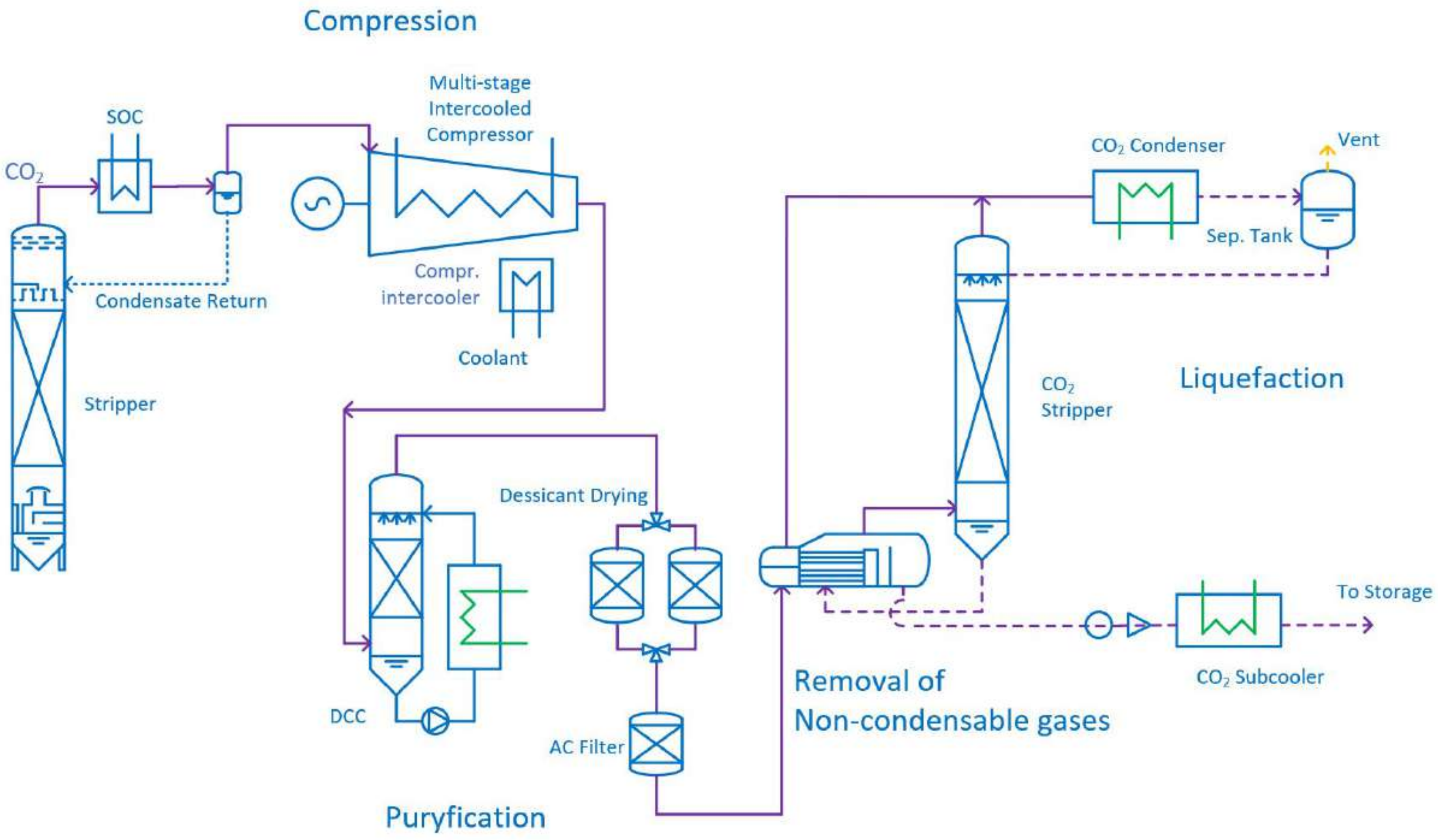
- Oxidative degradation of MEA
- New emissions:
  - Ammonia
  - Aldehydes
  - …

Amine-based CO_2 capture – CO_2 handling

- A very clean CO_2 stream exits the stripper

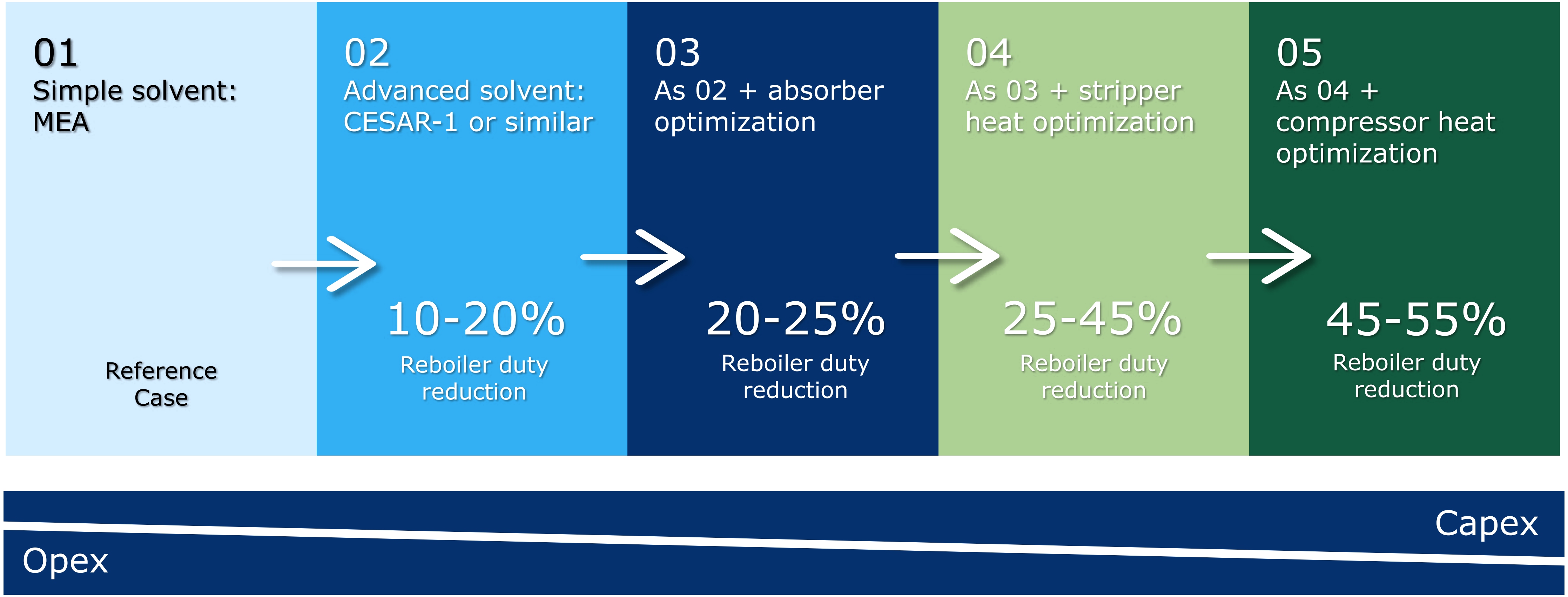
- It still needs further treatment to meet CO_2 quality specifications
  - Compression with intercooling
  - Drying, purification (carbon filter)
  - De-gassing (removal of non-condensables)
  - Liquefaction

- CO_2 handling depends on storage/use of CO_2



Amine-based CO_2 capture – Energy efficiency and optimization

Cement plants do not have the steam needed for the reboiler, hence electricity based steam generation needed in the design



01
Simple solvent: MEA

Reference Case

02
Advanced solvent: CESAR-1 or similar

10-20%
Reboiler duty reduction

03
As 02 + absorber optimization

20-25%
Reboiler duty reduction

04
As 03 + stripper heat optimization

25-45%
Reboiler duty reduction

05
As 04 + compressor heat optimization

45-55%
Reboiler duty reduction

Opex

Capex

Conclusion

- **Cement emits fossil CO2:** Carbon neutral cement design completed
- **Cement plants do not have enough waste heat for carbon capture:** Problem solved by innovative heat pump implementation
- **The risk is too high:** Proven technology and design used
- **Will it be anytime soon:** Timetable is for 2030
- **Does the scale matter**: Will remove 1,800,000 metric tonnes of CO2 annually from the atmosphere
- **What is the main challange**: Close integration needed, which means that experts on cement production, carbon capture, energy utilization, heat pumps, export terminals, high voltage power supply etc. must perform together.

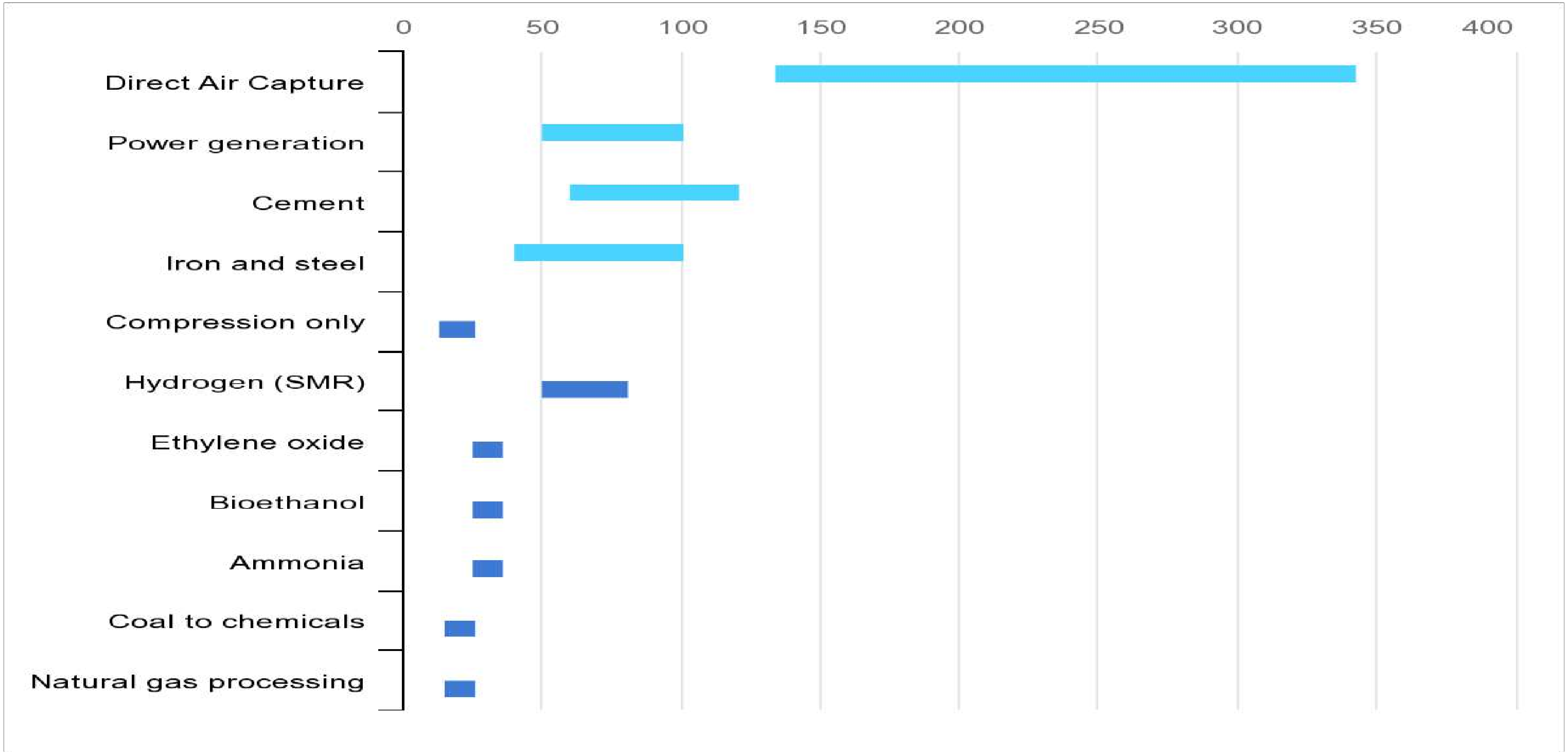
Bright ideas. Sustainable change.

▬ Low CO2 conc

▬ High CO2 conc

IEA LEVELISED COST

USD/tonne



IEA, Levelised cost of CO2 capture by sector and initial CO2 concentration, 2019, IEA, Paris https://www.iea.org/data-and-statistics/charts/levelised-cost-of-co2-capture-by-sector-and-initial-co2-concentration-2019, IEA. Licence: CC BY 4.0

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Small WTE Generation: Benefits to Industry and Communities

SCS ENGINEERS

Green Worldwide

A Renewable Energy Boom

- Multiplication of renewable generation
- More power than we can consume **when producing**
- Feasibly more **capacity** than traditional sources

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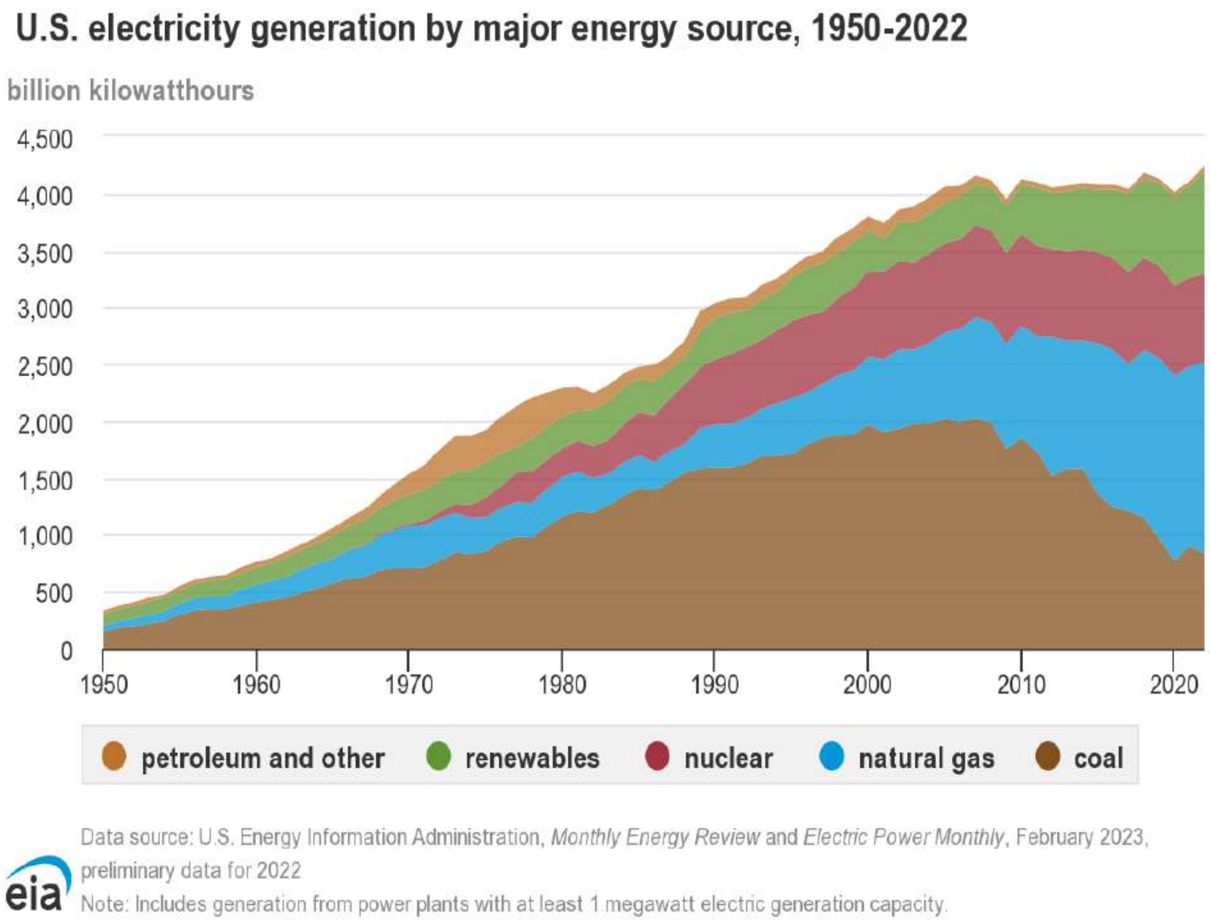
Renewables Statistics

- About 21.5% of all generation in 2022
- Wind and solar outstrip hydro production
- Relieving burden of fossil power on environment



U.S. electricity generation by major energy source, 1950-2022

Data source: U.S. Energy Information Administration, *Monthly Energy Review* and *Electric Power Monthly*, February 2023, preliminary data for 2022

Note: Includes generation from power plants with at least 1 megawatt electric generation capacity.

What could go wrong?

Growing Challenges in Power Transmission

- Aging power infrastructure
- Variable inputs puts adds risk
- Solar and wind limitations
- Impact of EVs

How does this impact development, new commercial and industrial siting, and rural economies?

You Need Power When You Need It

- Power demand peaks, as renewable supply wanes
- Manufacturing/Pubic Works/Emergent Care all require constant power supply
- Communities are threatened by power supply interruptions
- Communities tire quickly of rolling blackouts
- Insufficient DERs to meet energy emergencies

Industry and communities need renewable energy that's always there, fair weather and foul

Could We Use "Secondary Materials" as Fuel for Sustainable DER Power Generation?

- Fueled by "secondary materials" (40 CFR 241.2)
- Would not be considered "waste burning"
- Reduces landfilling for hard-to-recycle materials
- Reduces GHG and transport emissions

Back to the Future, Amblin Entertainment/Universal Pictures

Imagine minimal fuel costs, reduced landfilling fees, clean sustainable power, and short ROI period

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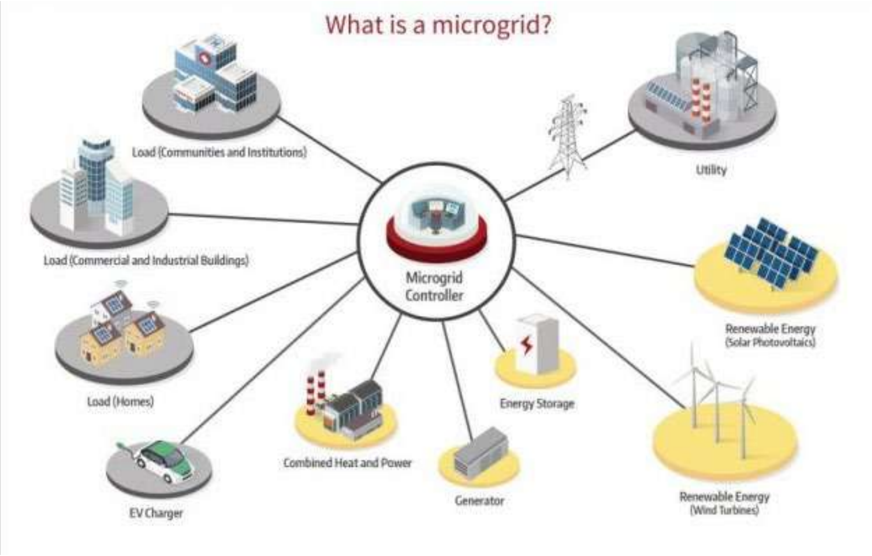
What if you could develop your own reliable, clean, and sustainable power?

- Fueled by your own “secondary materials”
- Microgrid potential
- Reducing waste costs
- Reduce stress on the aging grid
- Avoiding dreaded curtailments and brownouts



What if this were clean baseline power, capable of operating in tandem with other DERs and maintaining continuous, sufficient, reliable power?

Reliable, Renewable, Small Generation

- Fueled by
  - Plastics
  - Rubber
  - Wood pallets and Packing
  - ASR
  - Other secondary materials
- Environmentally responsible
- Reduced wastes and environmental impact while generating clean energy.

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Reliable, Renewable, Small Generation

- Fueled by
  - Plastics
  - Rubber
  - Wood pallets and packing
  - ASR
  - Other secondary materials
- Environmentally responsible
- Reduced wastes and environmental impact while generating clean energy

Distributed Generation

- More economically attractive to small communities
- Affordable for Industries with "Secondary Materials"
- Allow for microgridding easing strain on grid

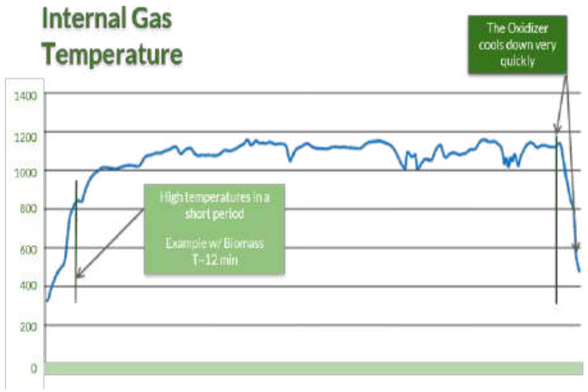
Case Study

6 ton/hr Suspension Burner Conversion System

- Fuel: 9k Btu/lb secondary materials (solid and/or liquid)
- Temp: 1000-1200°C (consistent profile)
- Ignition: Self sustaining (aux. fuel only on start up)
- Output: 27 MW (thermal)
  5.9 MW (electric)
- Annual: $3+M (revenue)

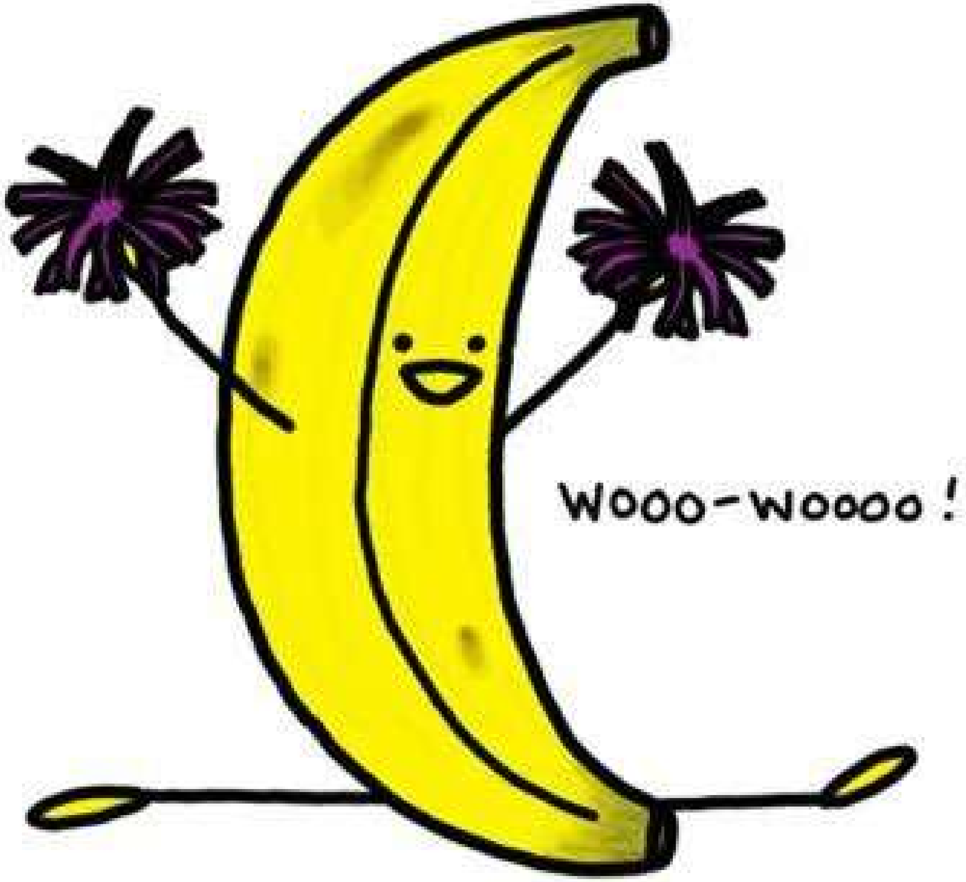
System Highlights

- Low thermal inertia
- Small footprint
- Highly efficient
- Multiple pollutant offsets
- 20+ yr. Operation
- Customizable end-of-pipe controls
- Not “waste burning”



System Challenges

- Secondary material qualities
- "Guinea pig" syndrome
- BANANA
- Faulty perceptions
- Rulemaking with limited field of view



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Reliable Power for Rural Communities

- Creates opportunity
- Enhances quality/availability of Public Services
- Improves feasibility of new commercial/industrial development
- Reduces strain on transmission lines
- Reduces emissions

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Small WTE Generation Beneficiaries

Industrial Complexes

- Disposal of Scrap Plastics
- Disposal of Packing Materials
- Disposal of Wood Pallets
- Disposal of Scrap Tires and Rubber
- Disposal of Auto-Fluff
- Thermal Energy for industrial processes
- Electrical Energy generation for electricity cost offsets/reductions
- Hot Water for Industrial or Manufacturing

Municipalities Local Government

- Recycling of Municipal Solid Waste
- Biogas Capture
- Sludge
- Electricity Generation
- Thermal Energy for Processes
- Building heating and cooling

Food Industry

- Disposal of Residues
- Dehydration and Drying of Consumer Goods

Oil Industry

- Disposal of Sludge, Rubber, Monomers, Burlap, Etc...
- Thermal Energy for Processes

Hotels and Buildings

- Disposal of Waste and Residues
- Thermal Energy, Heating, Steam

Chemical Industry

- Disposal of Toxic Waste
- Steam, Distilled Hot/Cold Water

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Small WTE Generation: Benefits to Industry and Communities

SCS
ENGINEERS

Dale J. Haase, PE
Project Manager
dhaase@scsengineers.com
864-313-9432

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Pilot-Scale Thermochemical Conversion of High Water Content Waste Biomass to Hydrochar: Mass and Energy Balance, Benefits, Challenges, and Scalability

Mukesh Kapila, P. Eng., Richard Bingham, C.Eng., Kieran Kapila, B.Eng.,
Enoverra Energy & Environment Inc.

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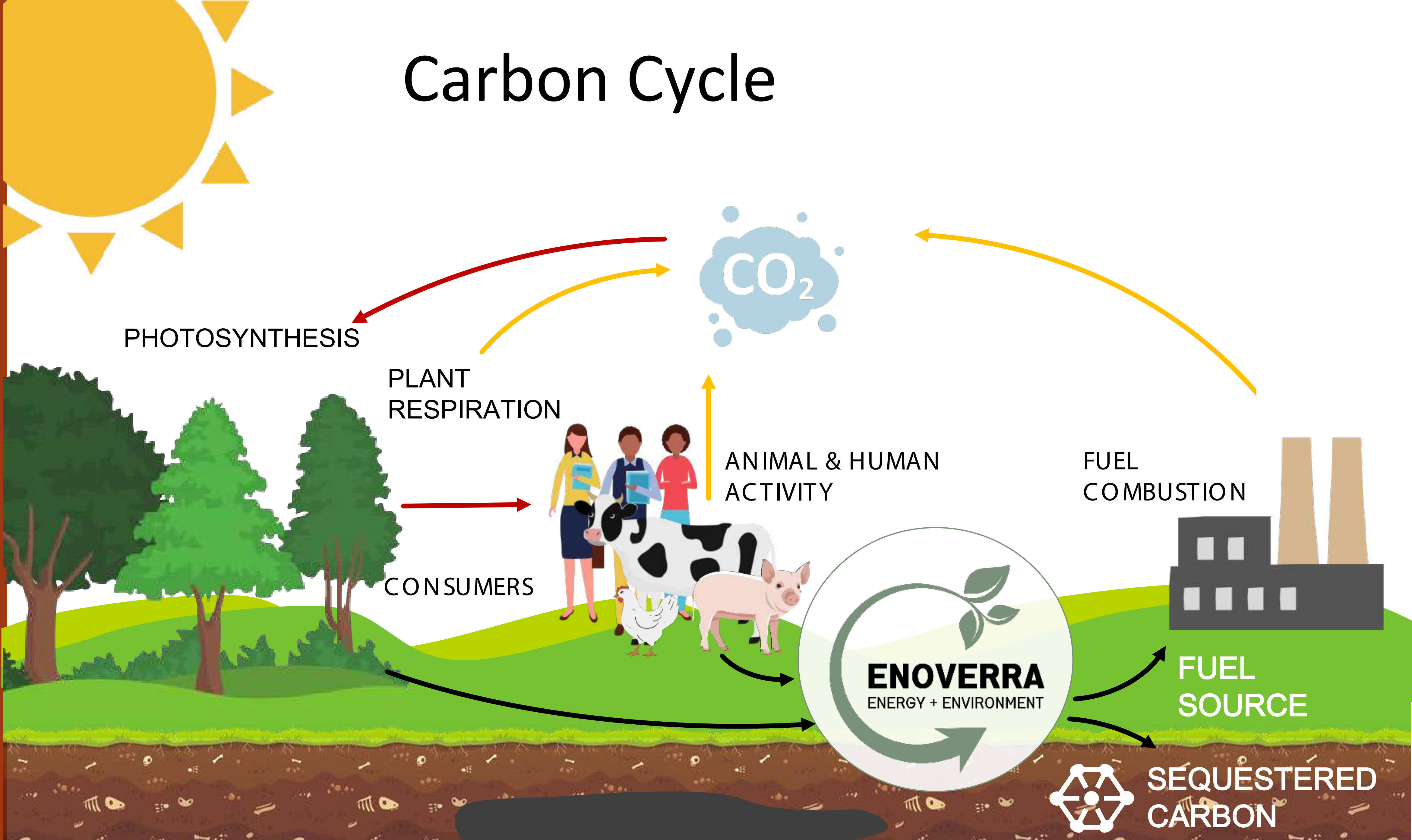
Carbon Cycle



PHOTOSYNTHESIS

PLANT
RESPIRATION

CO_2

ANIMAL & HUMAN
ACTIVITY

FUEL
COMBUSTION

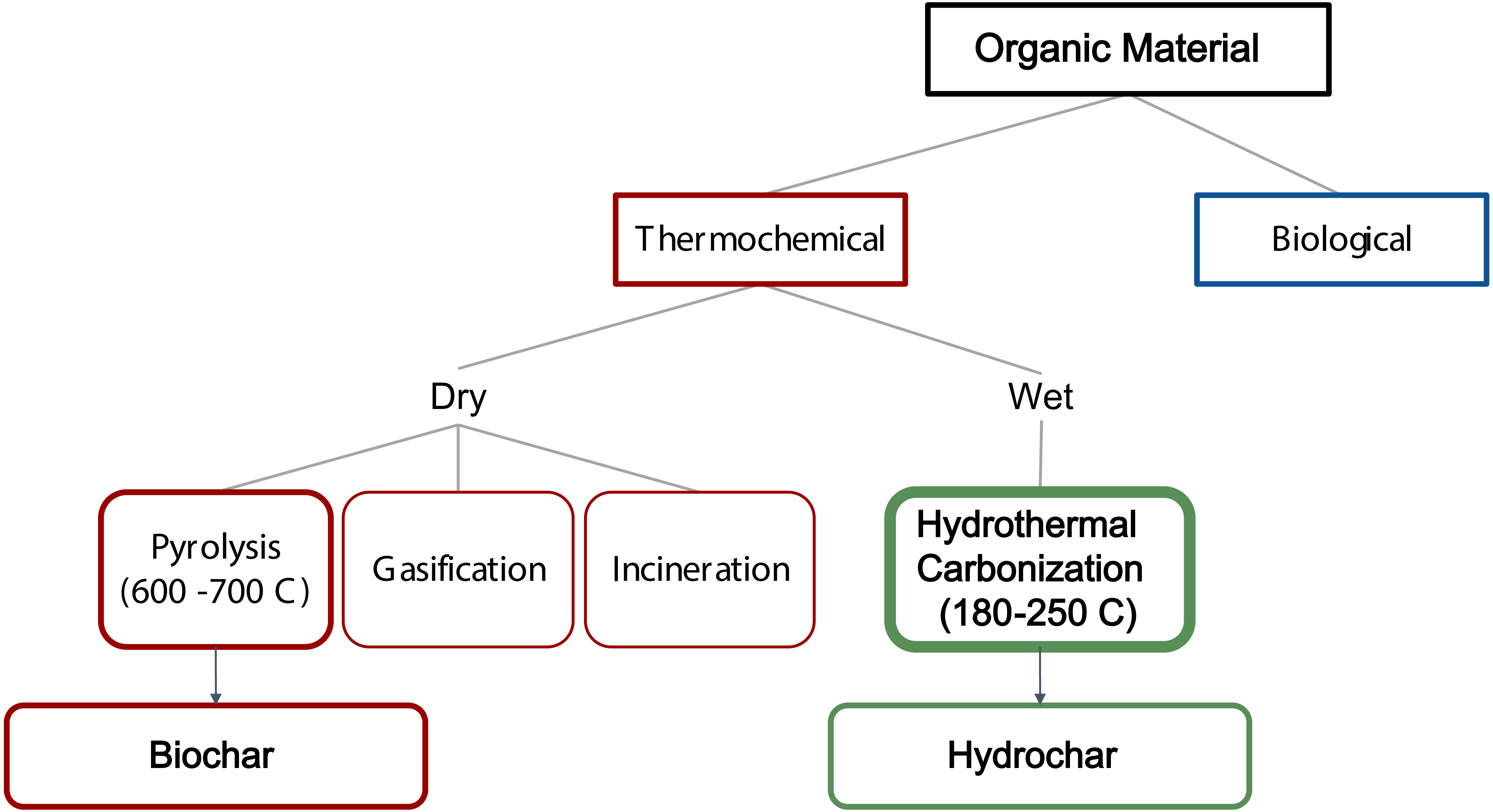
CONSUMERS

ENOVERRA
ENERGY + ENVIRONMENT

FUEL
SOURCE

SEQUESTERED
CARBON

Biomass Conversion Methods



Organic Material

Thermochemical

Biological

Dry

Wet

Pyrolysis
(600 -700 C)

Gasification

Incineration

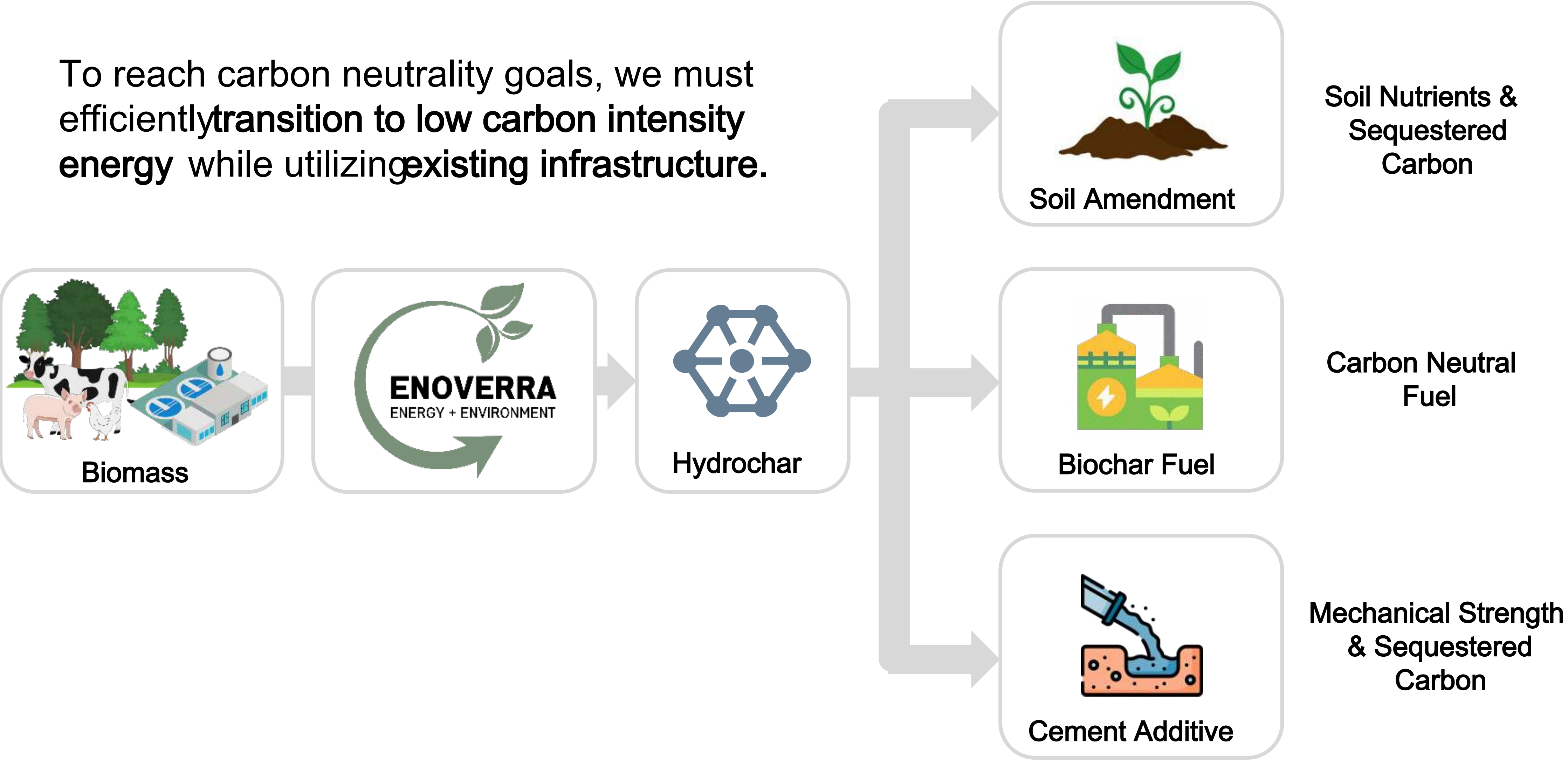
**Hydrothermal Carbonization
(180-250 C)**

Biochar

Hydrochar

Transition to low carbon intensity energy

To reach carbon neutrality goals, we must efficiently **transition to low carbon intensity energy** while utilizing **existing infrastructure.**



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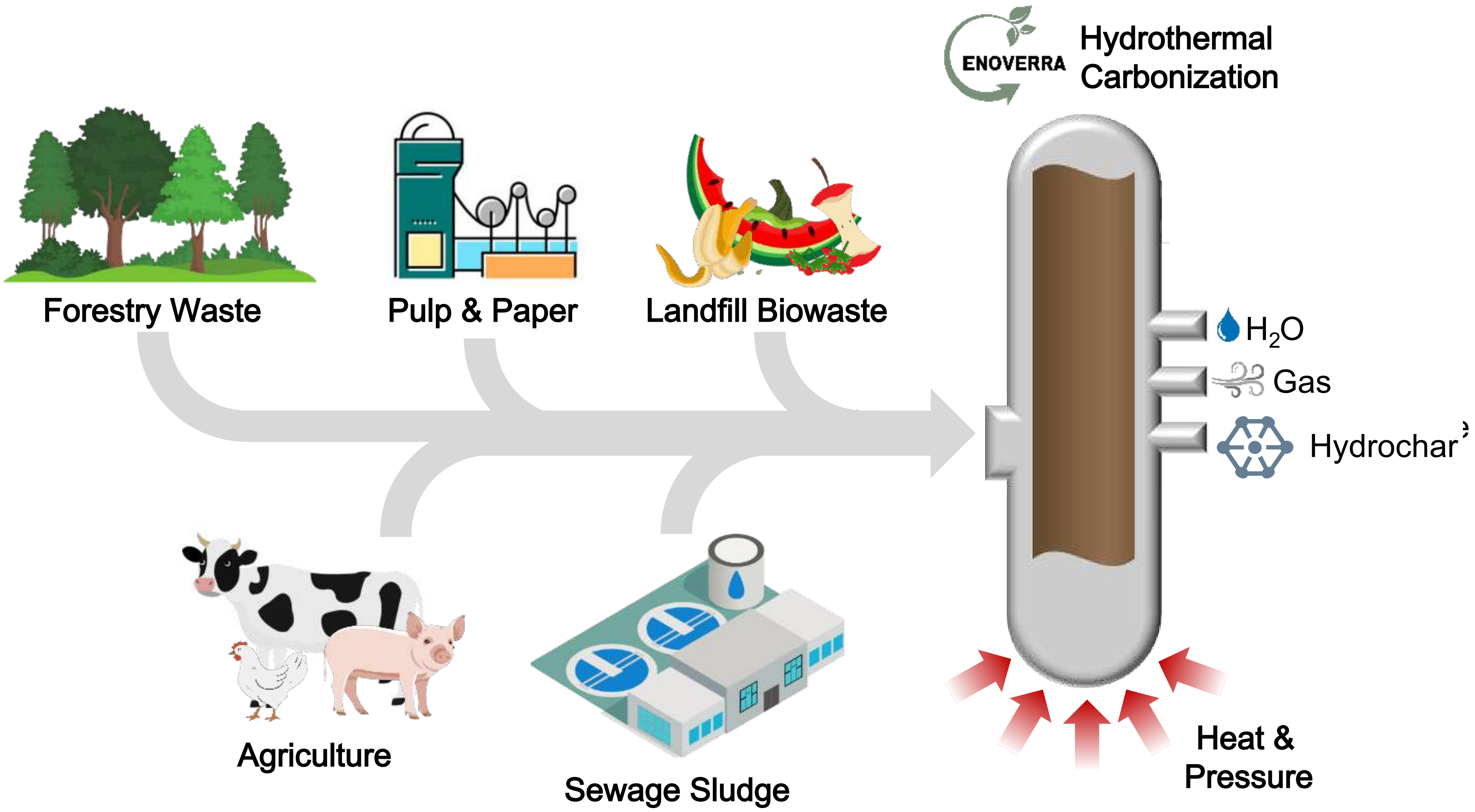
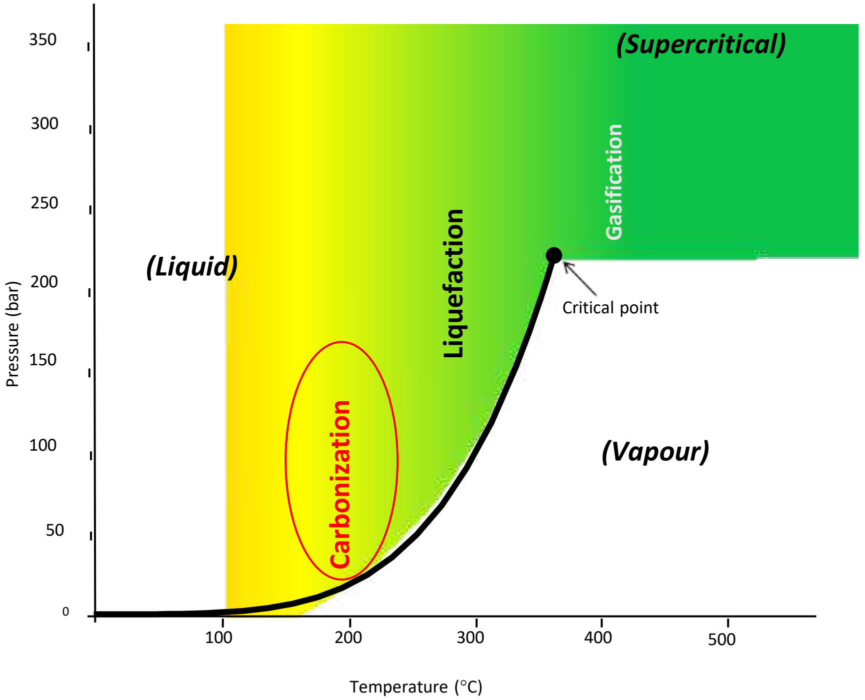
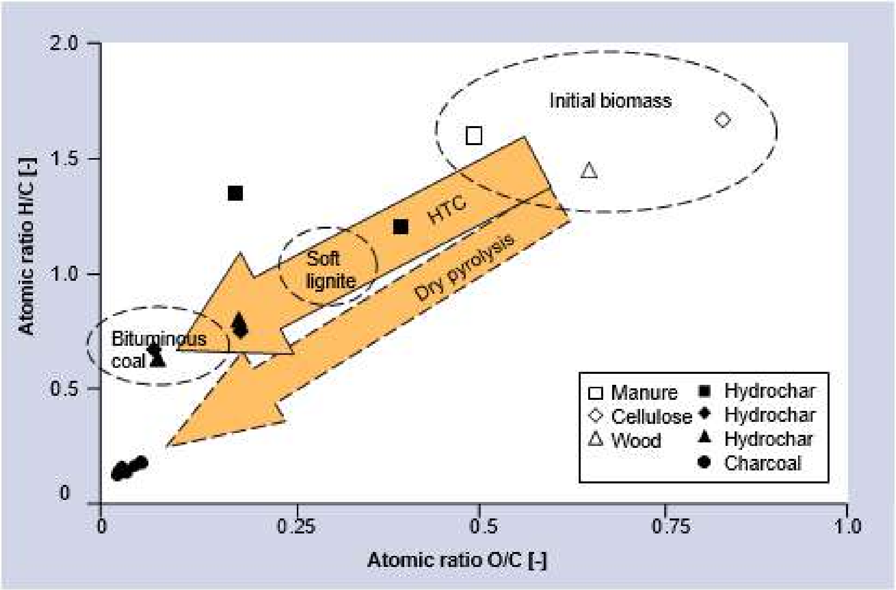
Hydrothermal Carbonization



Hydrothermal Carbonization



Water -phase Diagram



- 180 to 250°C at 0.5 to 8 hours.
- Major advantage of HTC - feedstocks to be converted without pre-drying.
- Reactions occur under high temperature and pressure and play a vital role in lowering the hydrogen to carbon (H/C) and oxygen to carbon (O/C) ratios to produce the carbon-rich hydrochar.

Hydrothermal Carbonization: Upgrading Waste Biomass to Char, Originally posted Jan 11, 2021
Shyam Sivaprasad, Graduate Research Associate, Dr. Ashish Manandhar, Postdoctoral Researcher, Dr. Ajay Shah, Associate Professor, Department of Food, Agricultural and Biological Engineering, The Ohio State University

J A Libra et al, Hydrothermal carbonization of biomass residuals: a comparative review of the chemistry, processes and applications of wet and dry pyrolysis, Biofuels (2011) 2(1), 71–106

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Comparison of Hydrochar and Biochar

Characteristic	Hydrochar	Biochar
Production Method	Hydrothermal carbonization process	Pyrolysis process
Feedstock	High moisture biomass (e.g., sludge)	Dry biomass (e.g., wood, agricultural residues)
Production Temperature	Moderate temperatures (180-250°C)	High temperatures (400-800°C)
Production Pressure	High pressure environment (up to 70 bar)	Atmospheric pressure
Moisture Content	Higher moisture content (typically 50-80%)	Lower moisture content (typically less than 20%)
Carbonization Time	Relatively shorter carbonization time	Longer carbonization time
Structure	Amorphous structure	Crystalline or semi-crystalline structure
Porosity	Higher porosity	Lower porosity
pH Level	Typically neutral or slightly acidic	Neutral to alkaline
Nutrient Content	Relatively higher nutrient content	Lower nutrient content
Carbon Sequestration	Potential carbon sequestration value	Considered as a method for carbon sequestration and climate change mitigation
Energy Intensity	Lower energy-intensive process	Higher energy-intensive process
Market Maturity	Emerging technology	Established technology

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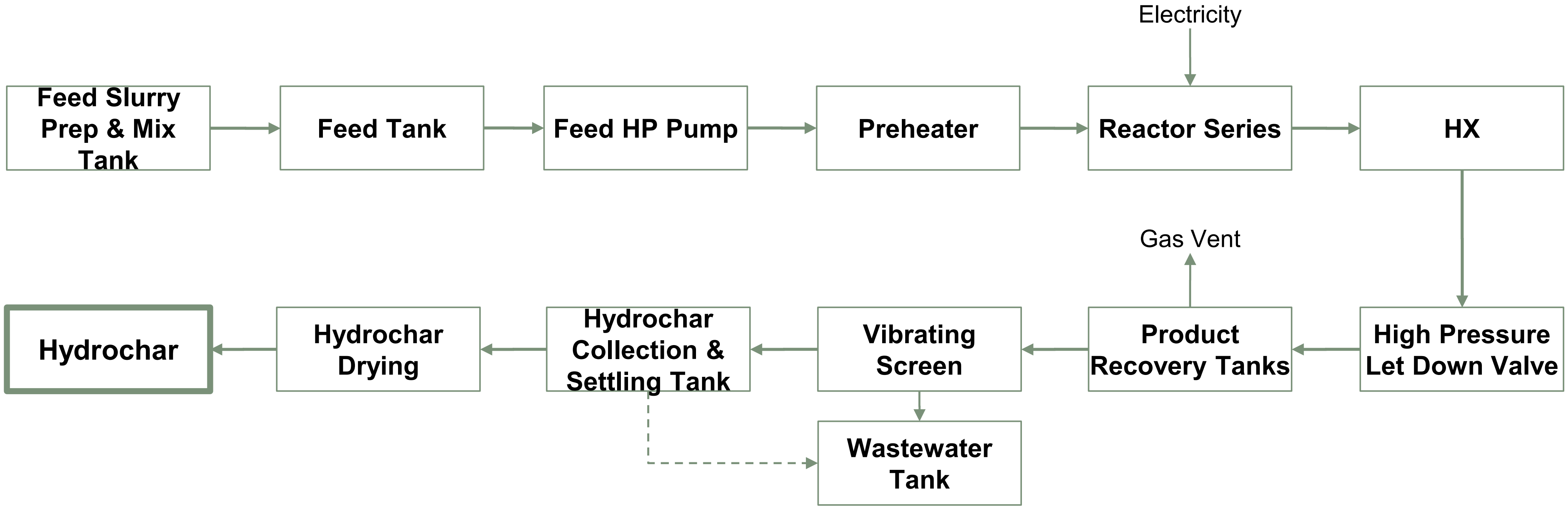
High Level Pilot PFD

30 - 50 kg/hr

Up to 300 C & 2,500 psi


Electricity

Feed Slurry Prep & Mix Tank → Feed Tank → Feed HP Pump → Preheater → Reactor Series → HX

Gas Vent

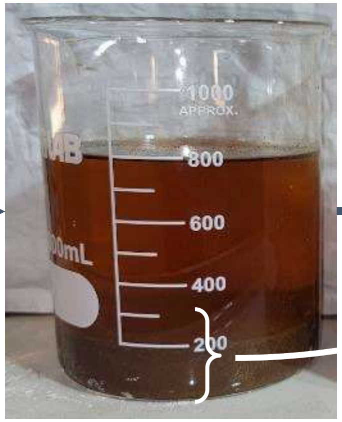
High Pressure Let Down Valve → Product Recovery Tanks → Vibrating Screen → Hydrochar Collection & Settling Tank → Hydrochar Drying → **Hydrochar**

Wastewater Tank

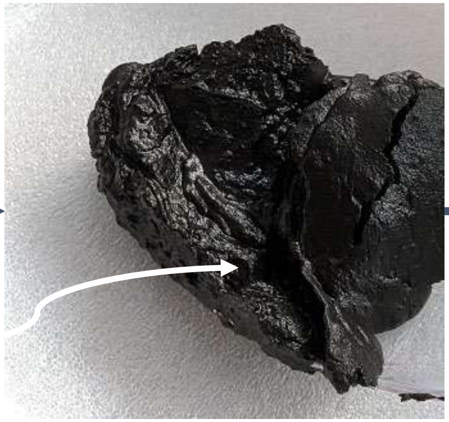
Enoverra Pilot Unit Hydrochar Process

10% wt% Woody Biomass Slurry 30 L/h

Hydrothermal Carbonization Reactor
200 C & 900 psi
@ 60 - 90 min



Gravity Settled Hydrochar & Aqueous Phase
50 - 70% wt% biomass conversion to hydrochar



Dewatered Hydrochar
50%- 60% wt% Solids
40%- 50% moisture

Dried Hydrochar
>90% solids & <10% moisture

- Carbon Negative Soil Amendment
- Carbon Neutral Biofuel ~ lignite
- Cement Additive
- Coke Alternative

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HTC Pilot Results

Component	Carbon	Hydrogen	Nitrogen	Oxygen	Sulfur	HHV (MJ/kg)	Volatile matter	Ash	Fixed carbon
Woody Biomass Feed	45.9	6.2	0	47.8	0	23.5[a]	77.5	1.02	12.1
Hydrochar	64.3	5.5	0	30	0	**28.5**[a]	53.7	0.17	46.1
Feedstock (Olive Plant)[b]	48.15	5.74	0.39	45.67	0.05	19.19			
Sample 220_9[b]	61.94	5.08	0.67	32.26	0.05	24.82			
Sample 220_3[b]	56.08	5.47	0.60	37.82	0.03	22.04			
Sample 280_9[b]	75.44	4.90	1.32	18.30	0.04	29.59			

a: Ayhan Demirbaş, Calculation of higher heating values of biomass fuels, Fuel, Volume 76, Issue 5, 1997, Pages 431-434, ISSN 0016-2361

b: Hydrothermal Carbonization of Olive Tree Pruning as a Sustainable Way for Improving Biomass Energy Potential: Effect of Reaction Parameters on Fuel Properties. Judith González-Arias, Marta Elena Sánchez, Elia Judith Martínez, Camila Covalski, Ana Alonso-Simón, Rubén González and Jorge Cara-Jiménez

Wet biomass waste has no calorific value.

Hydrochar analyzed for elemental content for Higher Heating Value (HHV).

Removal of oxygenated functional groups from feed increased HHV.

HHV similar to Sub-Bituminous Coal

[b]Comparative study performed on olive tree wastes shows similar HHV.

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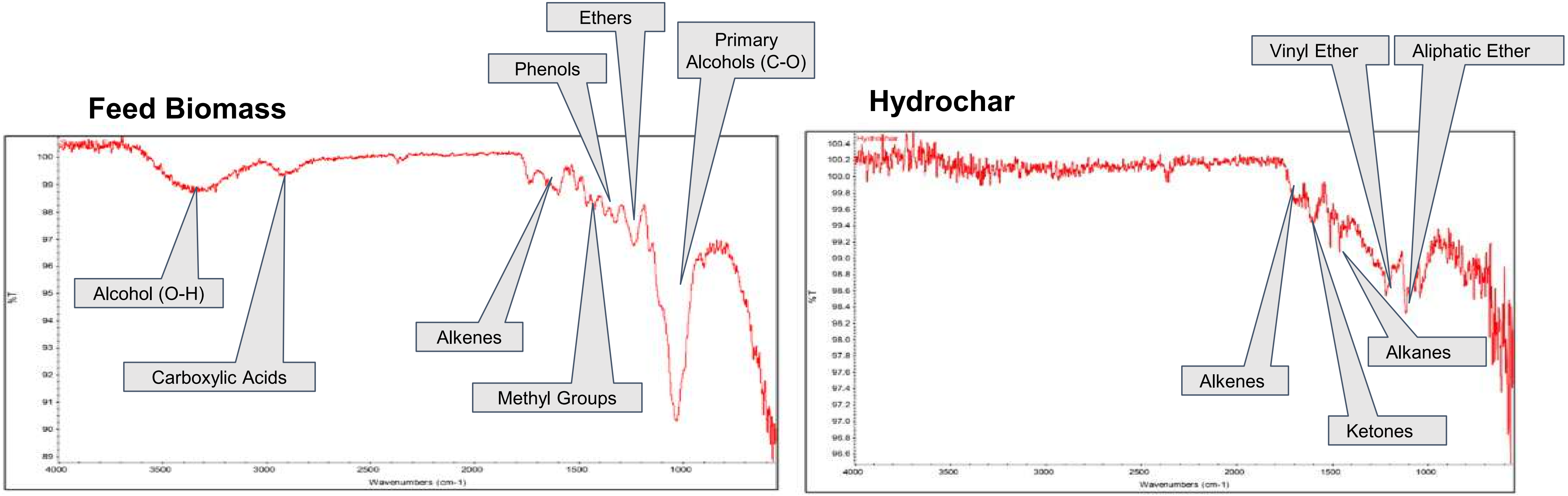
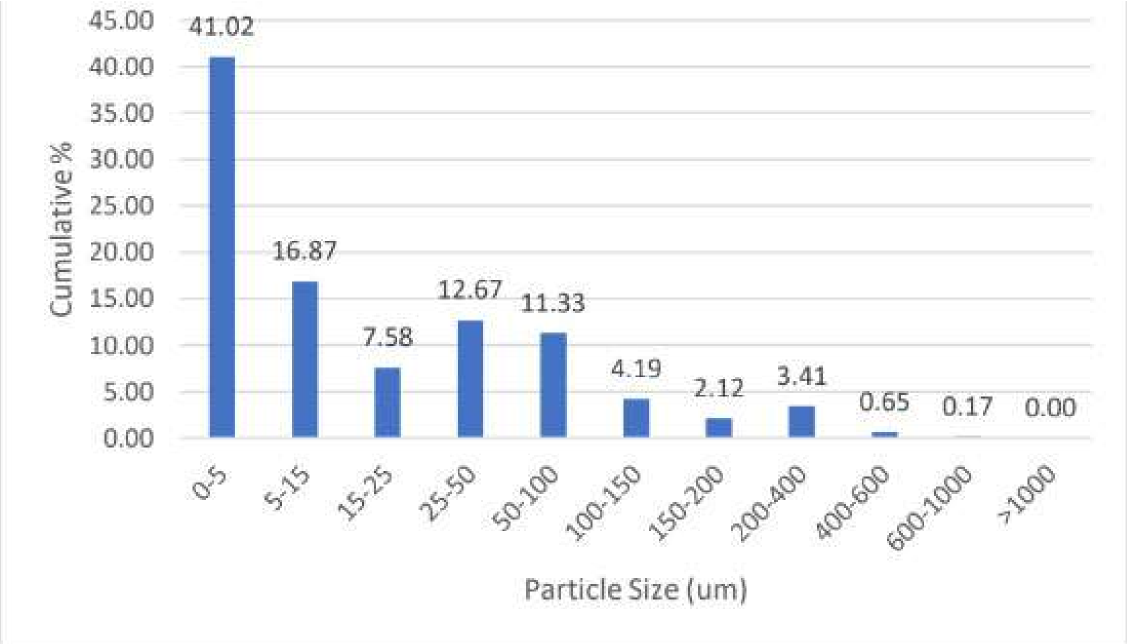
HTC Pilot Results



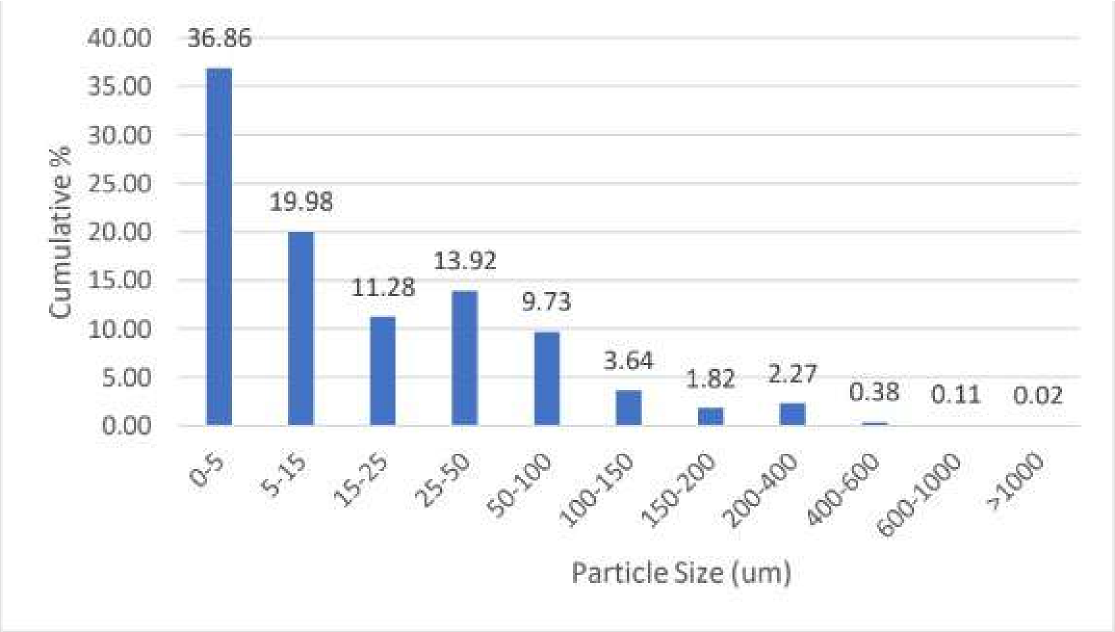
- Dehydration and decarboxylation reactions occurred during the carbonization process as shown by the absence or weakening of the free and intermolecular bonded hydroxyl groups (3600 to 3000 cm^{-1});
- Additionally, Aliphatic carbons, methylene, and methyl groups are preserved during HTC (1450 to 1200 cm^{-1});
- The weakened peaks surrounding esters, phenols, and aliphatic alcohols further indicate that dehydration and decarboxylation reaction took place in HTC (1200 to 1000 cm^{-1})

HTC Pilot Results

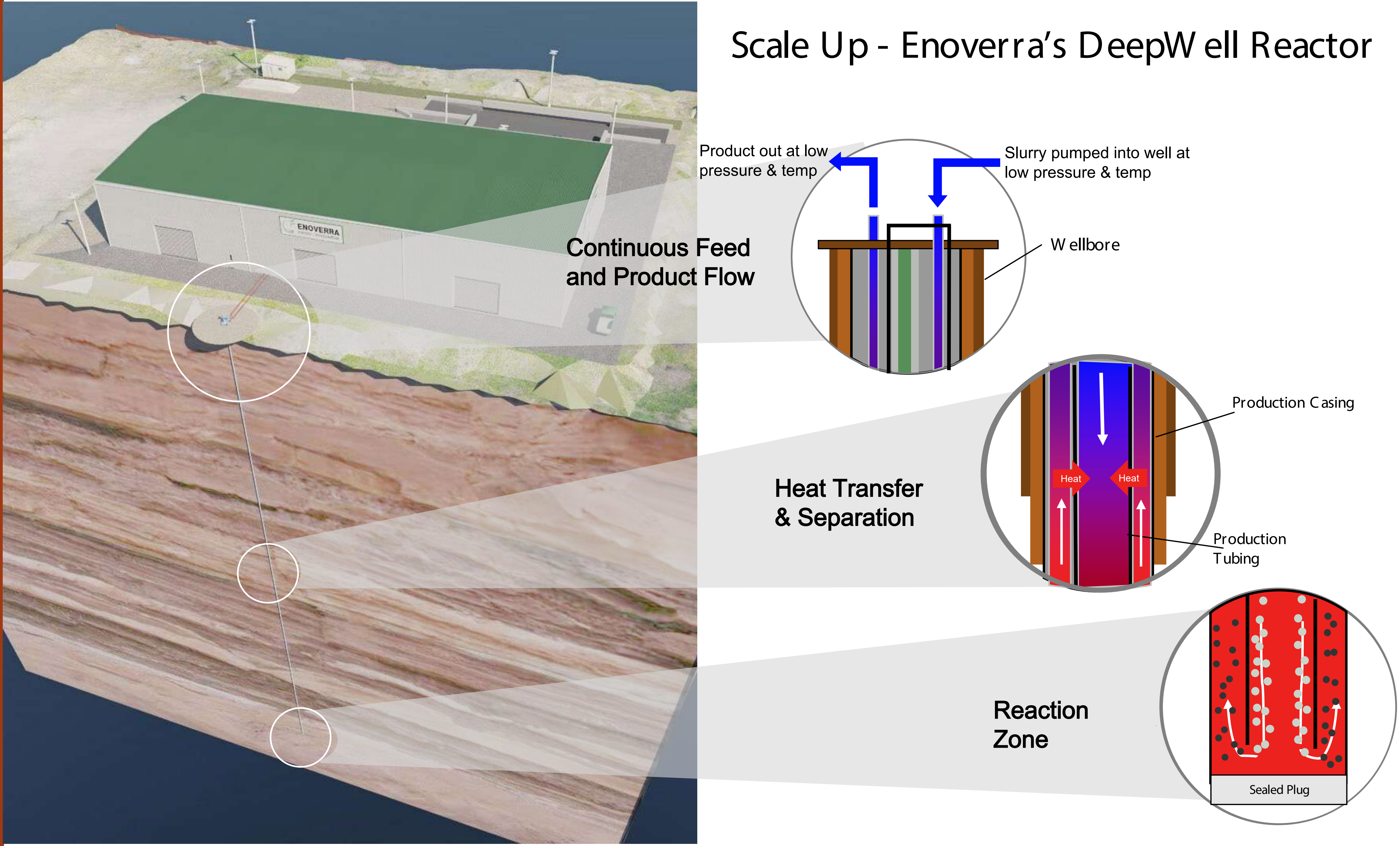
PSD of Feed Woody Biomass Slurry



PSD of Hydrochar



Scale Up - Enoverra's DeepWell Reactor



Continuous Feed and Product Flow

Heat Transfer & Separation

Reaction Zone

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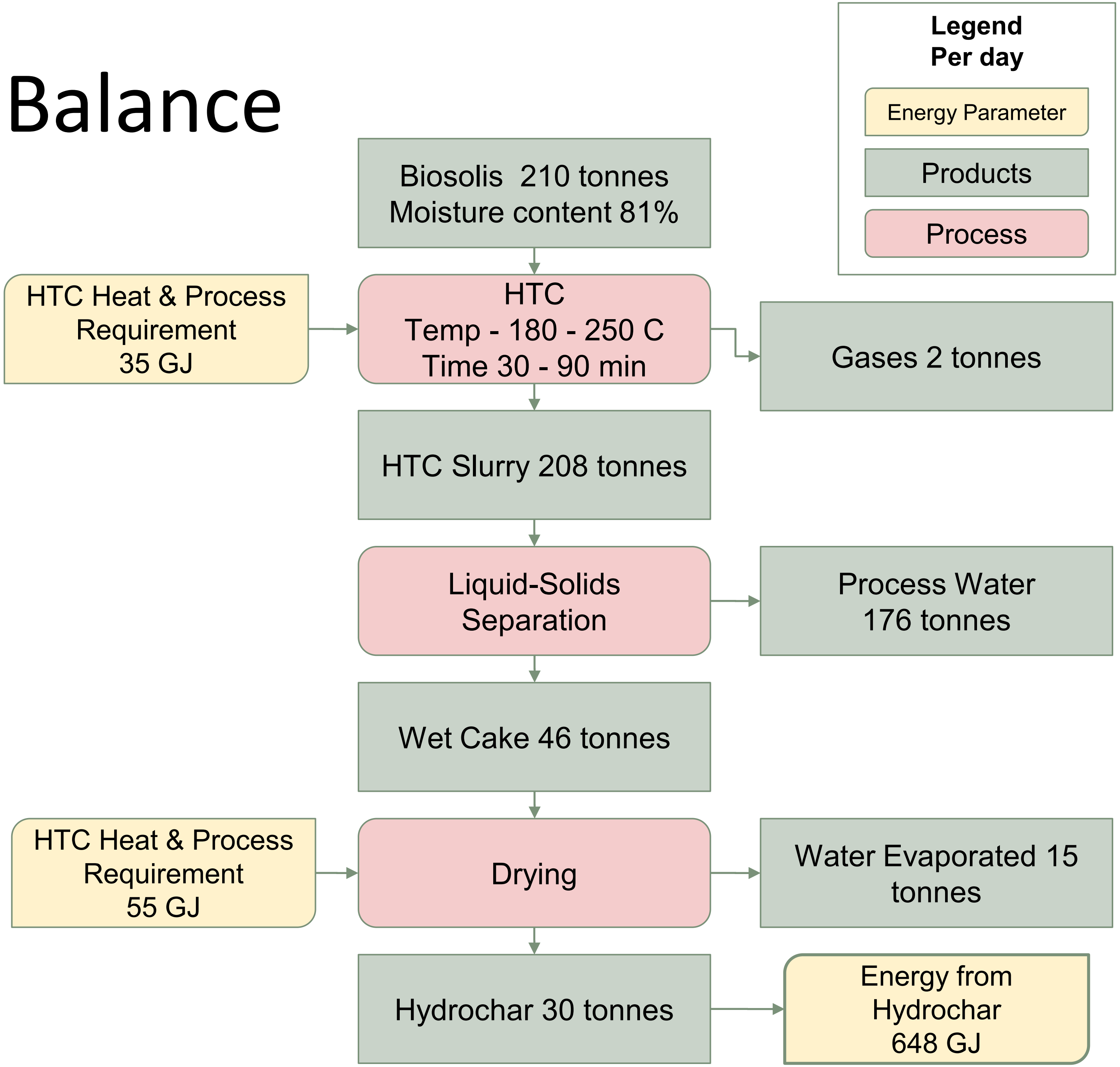
Mass & Energy Balance

- Requirements vary depending on the nature of feedstock, solids loading, reactor size, desired product quality, residence time, and operating temperature.
- The overall yield of hydrochar, on a dry basis, was 61%.
- Wet hydrochar cake - used as soil amendment without drying.
- Drying is the largest consumer of energy. After drying, hydrochar can be used as fuel.
- Process water: make-up water for the HTC or irrigation.
- 6 X more energy than consumed.



Legend
Per day

Energy Parameter
Products
Process

Biosolis 210 tonnes
Moisture content 81%

HTC Heat & Process
Requirement
35 GJ

HTC
Temp - 180 - 250 C
Time 30 - 90 min

Gases 2 tonnes

HTC Slurry 208 tonnes

Liquid-Solids
Separation

Process Water
176 tonnes

Wet Cake 46 tonnes

HTC Heat & Process
Requirement
55 GJ

Drying

Water Evaporated 15
tonnes

Hydrochar 30 tonnes

Energy from
Hydrochar
648 GJ

Benefits of Hydrochar

Avoids feedstock pre-drying

Enhanced hydrophobicity & Improved dewatering efficiency

High nutrient recovery

Generates 6 x more energy than it consumes as fuel source

Reduces pharmaceuticals & PFAS chemicals

High char conversion

Onsite Operations

Lower environmental impact & lowest energy consumption compared to other thermochemical processes

Challenges

Drying of hydrochar cake when used as fuel: energy intensive consuming more than the HTC process itself.

Contaminants: Depending upon waste biomass feedstock used - may contain heavy metals.

Organic acids in water phase: if not acceptable as fertilizer or recycled with feed - may require aerobic or anaerobic digestion or return to WWTP.

Limited commercial application & history: permitting, long term impact of corrosion and deposition on reactor & HX and CAPEX/OPEX.

Summary

Main Focus: Pilot-scale study was successful in converting high water content waste biomass into hydrochar.

Hydrothermal Carbonization: Significant energy and environmental advantages over other thermochemical conversion processes.

Benefits of Hydrochar:

- Acts as a soil amendment, improving soil quality.
- Serves as a carbon-neutral fuel similar to lignite, aligning with sustainability goals.
- Potential as cement and smelting additive
- Enriches soil with nutrients and sequesters carbon.

Key Waste Sources: WWTP sludge, forestry waste, landfill biowaste, and agricultural waste are ideal candidates.

Conclusion: HTC presents a promising approach to manage waste biomass, offering environmental benefits and energy solutions.

SESSION 3

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Corrosion (Resistance) in Hazardous Waste Incinerators

International Conference on Thermal Treatment Technologies & Hazardous Waste Combustors,

September 13-14 2023, Charlotte NC, USA

Air & Waste Management Association

Johannes Boersma – Gouda Refractories
Annelies Niewijk – Gouda Refractories
Zhenlan Gao – Suez Groupe

Outline

- Corrosion Resistance in Hazardous Waste Incinerators
    - Experimental setup Crucible test
    - Results Crucible test
    - Experimental setup SEM imaging
    - Results SEM imaging
    - Wear ratio
    - Summary

Crucible test

- Introduction
  - Crucible test
    - 10 commercial chromia-corundum bricks from various sources

	A	B	C	D	E	F	G	H	I	J
Density (g/cm3)	3.46	3.38	3.20	3.53	3.54	3.42	3.35	3.36	3.44	3.43
Porosity (%)	12.9	16.1	14.7	12.5	11.5	13.0	13.0	13.4	12.4	13.5
Cold Crushing Strength (MPa)	125	146	121	157	105	111	108	141	117	138
SiO_2 (%)	1.75	0.90	7.40	2.08	2.24	2.21	2.40	1.99	2.38	1.88
Al_2O_3 (%)	84.08	84.57	76.58	72.77	79.44	83.42	85.99	79.54	75.58	72.25
Fe_2O_3 (%)	0.06	0.10	0.28	0.18	0.07	0.11	0.09	0.10	0.15	0.10
ZrO_2 (%)	3.79	3.92	3.20	4.59	4.19	3.71	5.29	5.50	5.33	4.40
Cr_2O_3 (%)	9.57	10.08	11.46	19.65	12.86	9.60	4.77	11.39	14.98	19.80

- Performance ranking
  - Based on dimensions of reaction zone
  - Based on Wear ratio

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Crucible test

- Experimental setup (DIN 51069-2)
  - Crucible test dimensions
    - Diameter of 40 mm; depth of 35 - 45 mm
    - Crucible covered with a lid
  - 30 grams of representative slag
    - Typical composition: 30% Fe_2O_3, 15% CaO, 3% Na_2O
  - Firing
    - Gas fired kiln
    - Heating rate of 1 °C/min
    - Holding time 96 hrs at 1400 °C
    - Free cooled at the end of the test

Crucible test

- Experimental setup (DIN 51069-2)
  - Analysis
    - Visual inspection
    - Analysis with SEM imaging

Crucible test

- Results - Crucible test

(A)

(B)

Crucible test

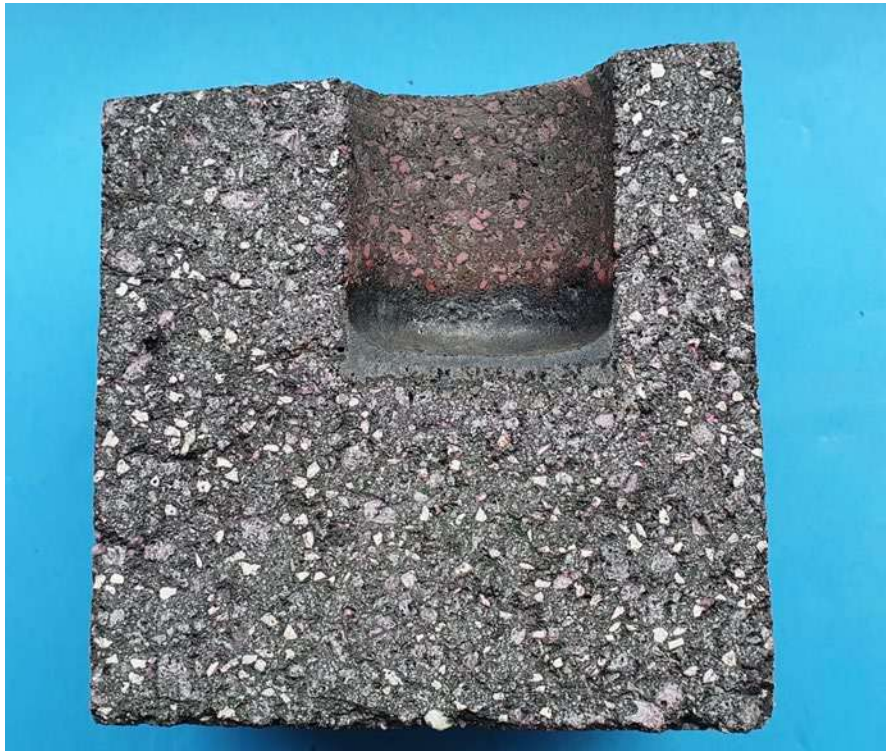
- Results - Crucible test

(C)

(D)

Crucible test

- Results - Crucible test



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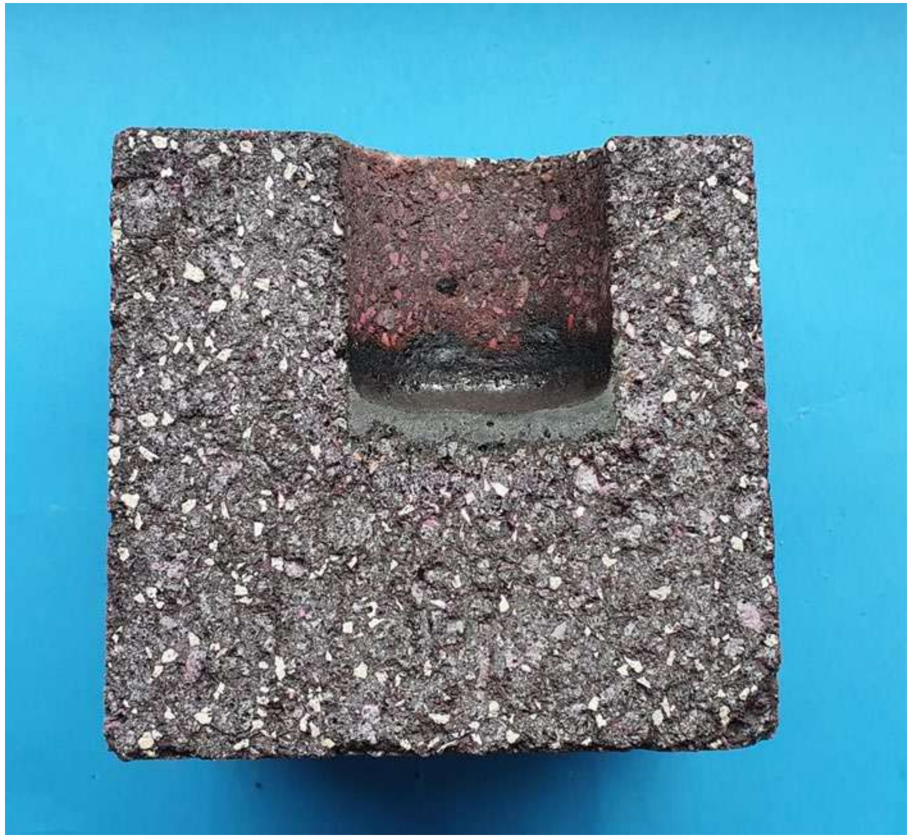
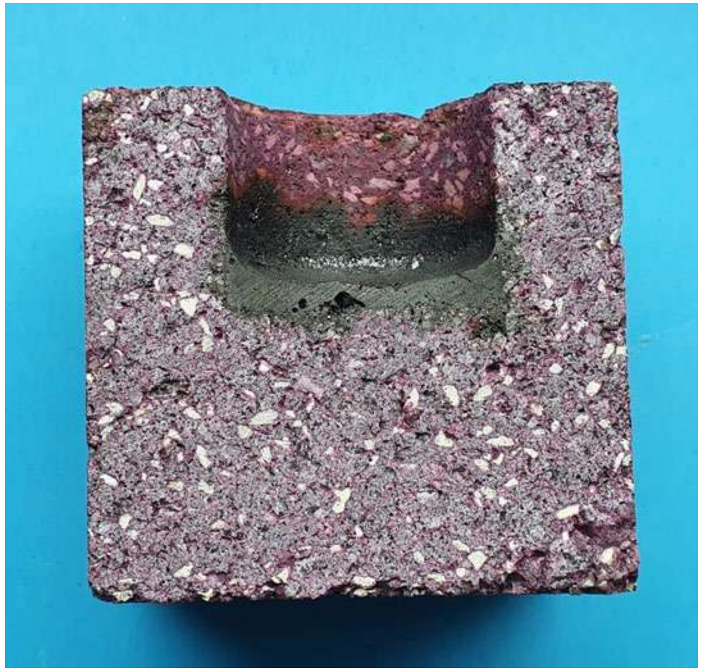


(F)

Crucible test

- Results - Crucible test



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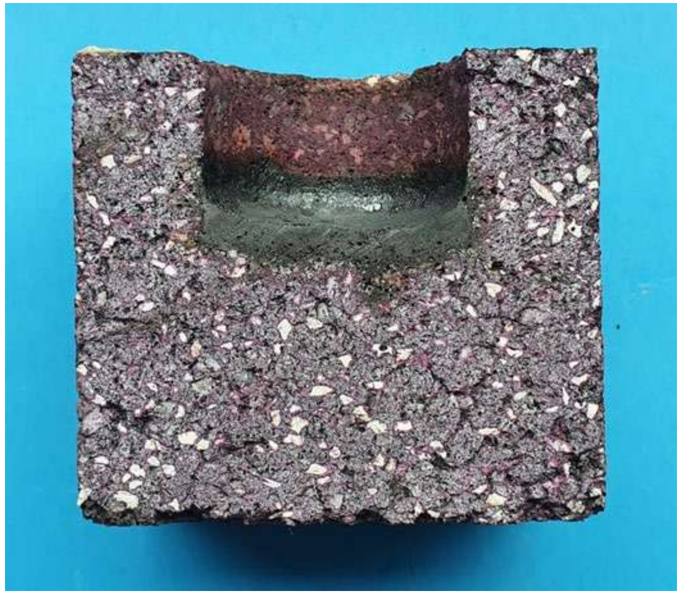

(H)

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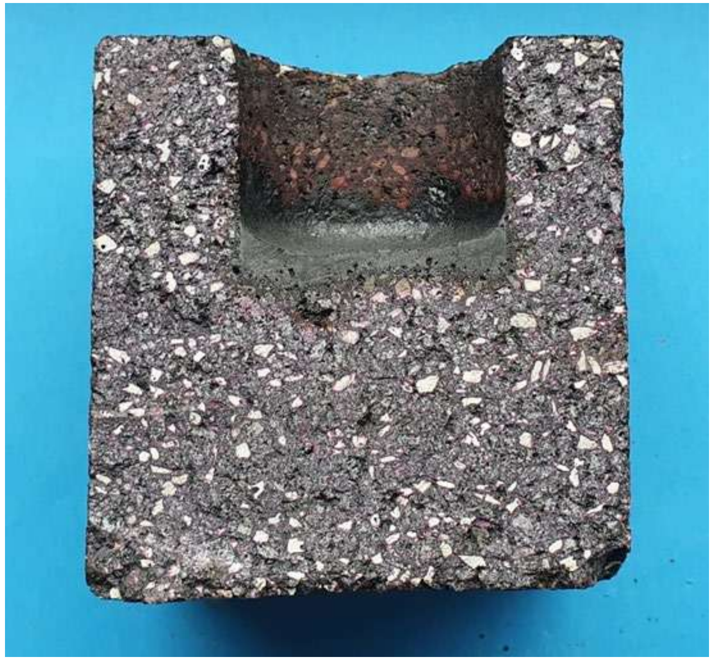
Crucible test

- Results - Crucible test

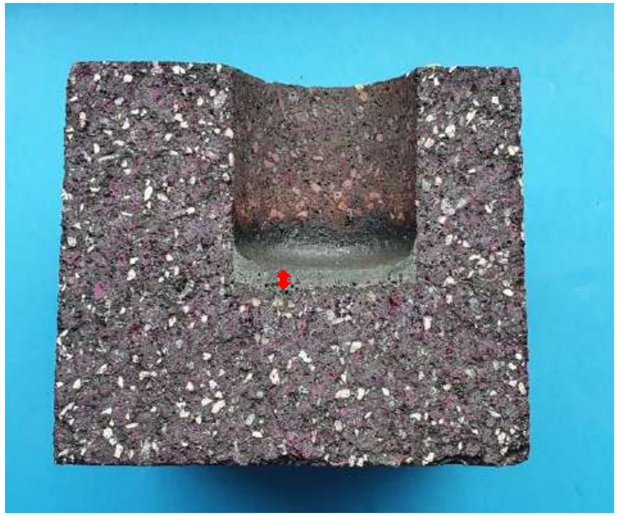
(I)



(J)

Crucible test

- Results - Crucible test
  - Infiltration depth



	Infiltration depth (mm)
A	3
B	4
C	2
D	4
E	3
F	4
G	5
H	5
I	5
J	4

Crucible test

- Results - Crucible test
  - Difference in infiltration depths
  - Composition of infiltrated zone
    - Slag?
    - Corroded brick?
    - Combination of both?

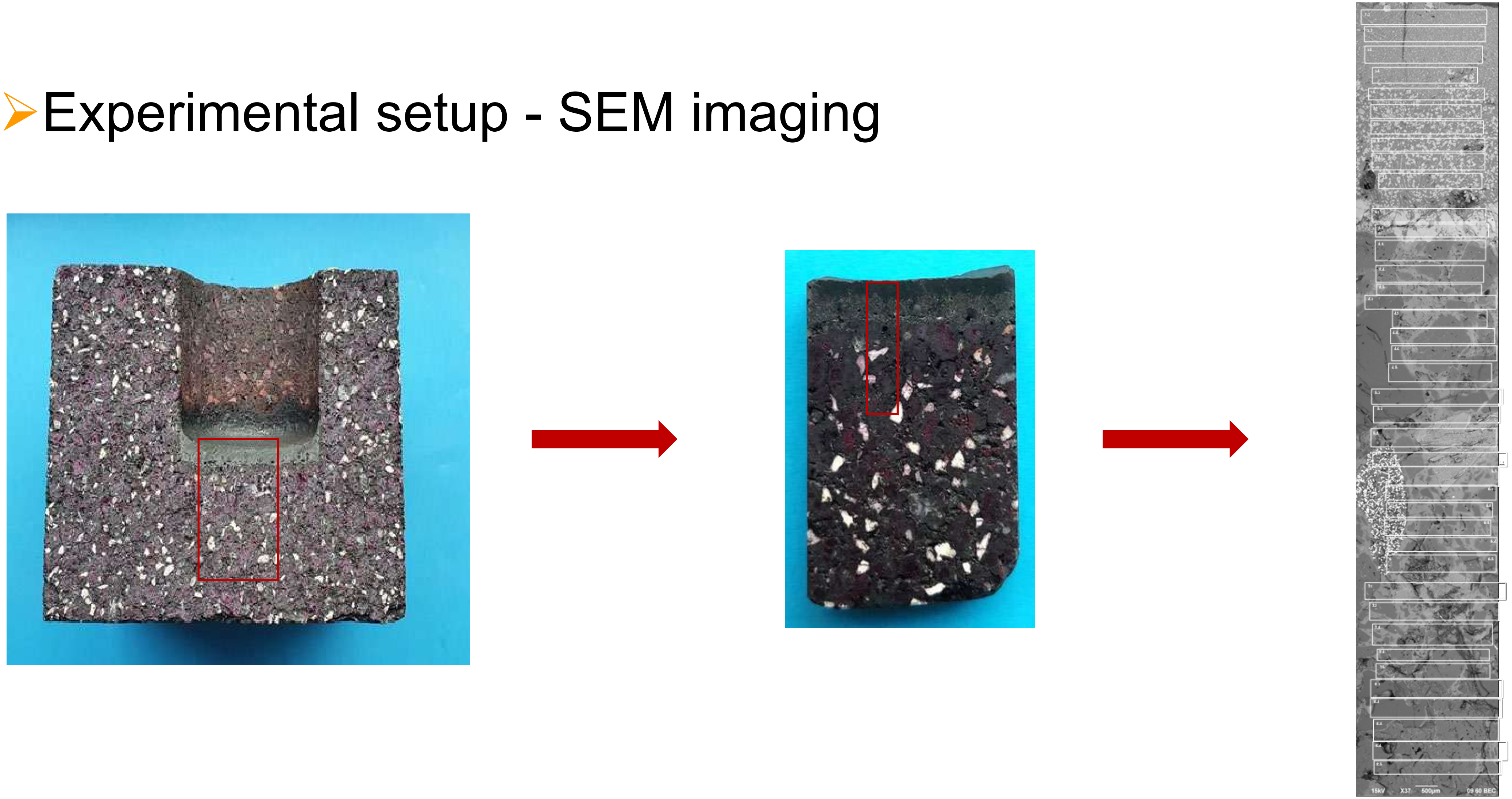
  - No conclusions to be drawn

SEM imaging

- Experimental setup - SEM (Scanning Electron Microscopy) imaging
  - Fine polished samples
  - Carbon coated
  - Backscattered electron imaging
  - 1 profile consists of 9 separate SEM images

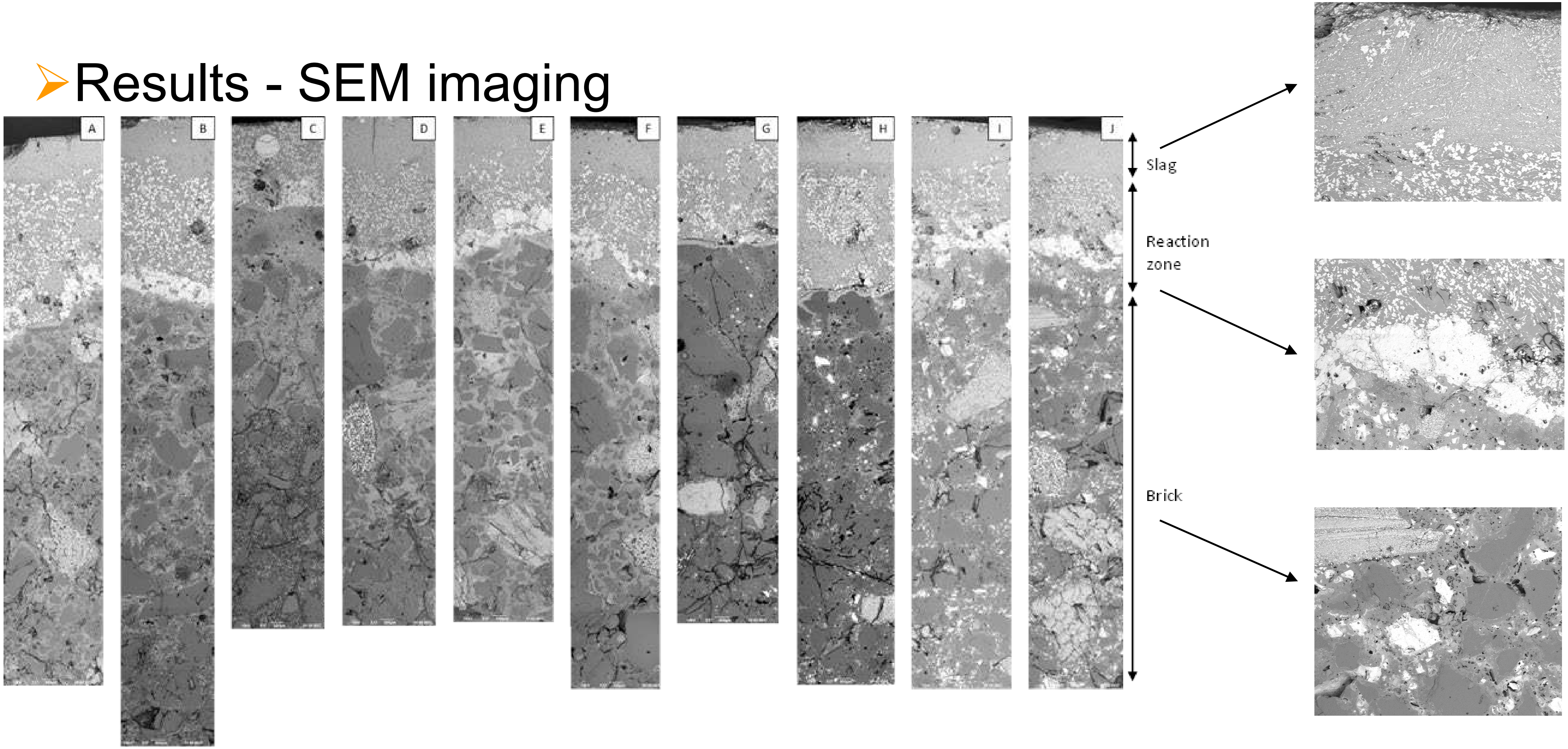
SEM imaging

- Experimental setup - SEM imaging



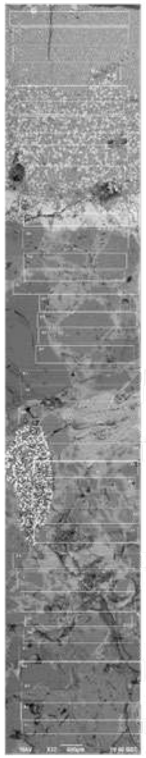
SEM imaging

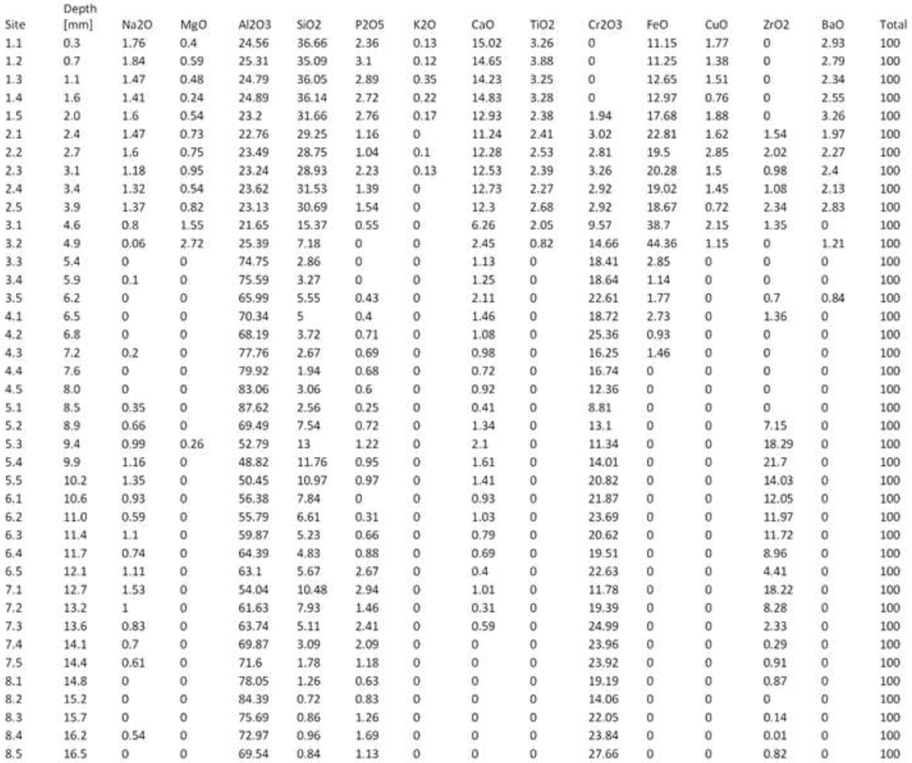
- Results - SEM imaging



SEM imaging

- Experimental setup: Infiltration - EDS (Energy Dispersive X-Ray Spectroscopy) analyses





Site	Depth [mm]	Na2O	MgO	Al2O3	SiO2	P2O5	K2O	CaO	TiO2	Cr2O3	FeO	CuO	ZrO2	BaO	Total
1.1	0.3	1.76	0.4	24.56	36.66	2.36	0.13	15.02	3.26	0	11.15	1.77	0	2.93	100
1.2	0.7	1.84	0.59	25.31	35.09	3.1	0.12	14.65	3.88	0	11.25	1.38	0	2.79	100
1.3	1.1	1.47	0.48	24.79	36.05	2.89	0.35	14.23	3.25	0	12.65	1.51	0	2.34	100
1.4	1.6	1.41	0.24	24.89	36.14	2.72	0.22	14.83	3.28	0	12.97	0.76	0	2.55	100
1.5	2.0	1.6	0.54	23.2	31.66	2.76	0.17	12.93	2.38	1.94	17.68	1.88	0	3.26	100
2.1	2.4	1.47	0.73	22.76	29.25	1.16	0	11.24	2.41	3.02	22.81	1.62	1.54	1.97	100
2.2	2.7	1.6	0.75	23.49	28.75	1.04	0.1	12.28	2.53	2.81	19.5	2.85	2.02	2.27	100
2.3	3.1	1.18	0.95	23.24	28.93	2.23	0.13	12.53	2.39	3.26	20.28	1.5	0.98	2.4	100
2.4	3.4	1.32	0.54	23.62	31.53	1.39	0	12.73	2.27	2.92	19.02	1.45	1.08	2.13	100
2.5	3.9	1.37	0.82	23.13	30.69	1.54	0	12.3	2.68	2.92	18.67	0.72	2.34	2.83	100
3.1	4.6	0.8	1.55	21.65	15.37	0.55	0	6.26	2.05	9.57	38.7	2.15	1.35	0	100
3.2	4.9	0.06	2.72	25.39	7.18	0	0	2.45	0.82	14.66	44.36	1.15	0	1.21	100
3.3	5.4	0	0	74.75	2.86	0	0	1.13	0	18.41	2.85	0	0	0	100
3.4	5.9	0.1	0	75.59	3.27	0	0	1.25	0	18.64	1.14	0	0	0	100
3.5	6.2	0	0	65.99	5.55	0.43	0	2.11	0	22.61	1.77	0	0.7	0.84	100
4.1	6.5	0	0	70.34	5	0.4	0	1.46	0	18.72	2.73	0	1.36	0	100
4.2	6.8	0	0	68.19	3.72	0.71	0	1.08	0	25.36	0.93	0	0	0	100
4.3	7.2	0.2	0	77.76	2.67	0.69	0	0.98	0	16.25	1.46	0	0	0	100
4.4	7.6	0	0	79.92	1.94	0.68	0	0.72	0	16.74	0	0	0	0	100
4.5	8.0	0	0	83.06	3.06	0.6	0	0.92	0	12.36	0	0	0	0	100
5.1	8.5	0.35	0	87.62	2.56	0.25	0	0.41	0	8.81	0	0	0	0	100
5.2	8.9	0.66	0	69.49	7.54	0.72	0	1.34	0	13.1	0	0	7.15	0	100
5.3	9.4	0.99	0.26	52.79	13	1.22	0	2.1	0	11.34	0	0	18.29	0	100
5.4	9.9	1.16	0	48.82	11.76	0.95	0	1.61	0	14.01	0	0	21.7	0	100
5.5	10.2	1.35	0	50.45	10.97	0.97	0	1.41	0	20.82	0	0	14.03	0	100
6.1	10.6	0.93	0	56.38	7.84	0	0	0.93	0	21.87	0	0	12.05	0	100
6.2	11.0	0.59	0	55.79	6.61	0.31	0	1.03	0	23.69	0	0	11.97	0	100
6.3	11.4	1.1	0	59.87	5.23	0.66	0	0.79	0	20.62	0	0	11.72	0	100
6.4	11.7	0.74	0	64.39	4.83	0.88	0	0.69	0	19.51	0	0	8.96	0	100
6.5	12.1	1.11	0	63.1	5.67	2.67	0	0.4	0	22.63	0	0	4.41	0	100
7.1	12.7	1.53	0	54.04	10.48	2.94	0	1.01	0	11.78	0	0	18.22	0	100
7.2	13.2	1	0	61.63	7.93	1.46	0	0.31	0	19.39	0	0	8.28	0	100
7.3	13.6	0.83	0	63.74	5.11	2.41	0	0.59	0	24.99	0	0	2.33	0	100
7.4	14.1	0.7	0	69.87	3.09	2.09	0	0	0	23.96	0	0	0.29	0	100
7.5	14.4	0.61	0	71.6	1.78	1.18	0	0	0	23.92	0	0	0.91	0	100
8.1	14.8	0	0	78.05	1.26	0.63	0	0	0	19.19	0	0	0.87	0	100
8.2	15.2	0	0	84.39	0.72	0.83	0	0	0	14.06	0	0	0	0	100
8.3	15.7	0	0	75.69	0.86	1.26	0	0	0	22.05	0	0	0.14	0	100
8.4	16.2	0.54	0	72.97	0.96	1.69	0	0	0	23.84	0	0	0.01	0	100
8.5	16.5	0	0	69.54	0.84	1.13	0	0	0	27.66	0	0	0.82	0	100

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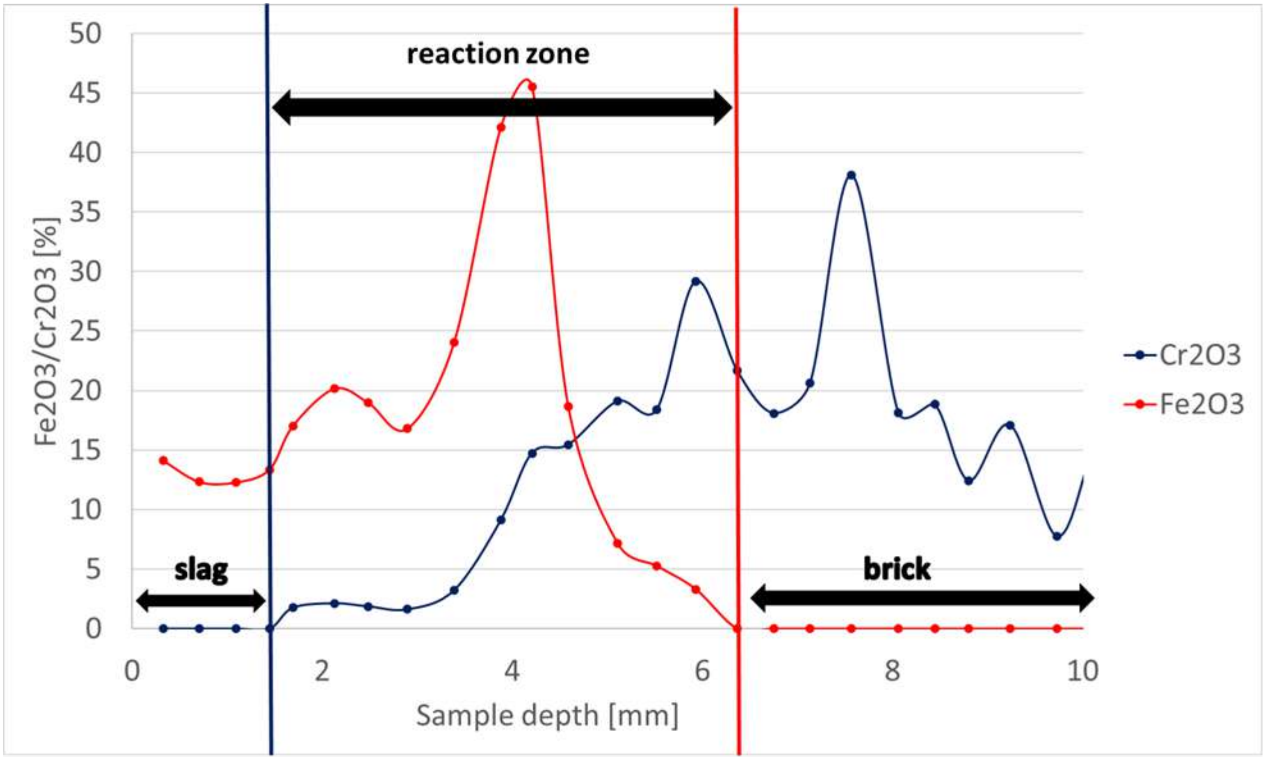
SEM imaging

- Results - SEM imaging
  - Cr_2O_3
    - Present in brick, not in slag
  - Fe_2O_3
    - Present in slag, not in brick

  - Subdivision Zones
    - Slag: the zone where $Cr_2O_3 = 0$
    - Brick: the zone where $Fe_2O_3 = 0$
    - Reaction zone: the zone between slag and brick

SEM imaging

- Results - SEM imaging



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SEM imaging

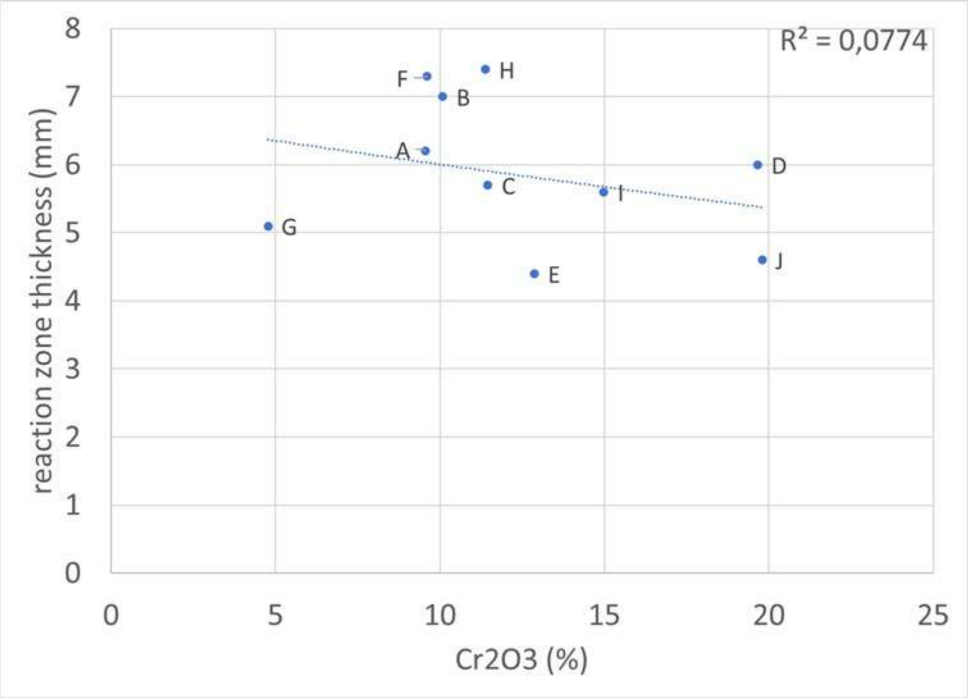
- Results - SEM imaging

	Cr_2O_3 = 0 (mm)	Fe_2O_3 = 0 (mm)	Reaction zone (mm)	Infiltration depth (mm)
A	1.3	7.5	6.2	3
B	1.0	8.0	7.0	4
C	0.0	5.7	5.7	2
D	1.6	7.6	6.0	4
E	1.2	5.6	4.4	3
F	1.2	8.5	7.3	4
G	0.6	5.7	5.1	5
H	1.5	8.9	7.4	5
I	1.5	7.1	5.6	5
J	1.5	6.1	4.6	4

- No relation between Reaction zone and I depth

SEM imaging

- Results - SEM imaging



- No relation between Cr_2O_3 concentration and reaction zone

Wear ratio

- Wear ratio
  - Residual slag layer
    - Thicker slag layer means less corrosion
    - All slag layers should have the same size
      - Continuously supply of slag in real operation
    - Slag layers scaled to referential thickness
    - Reaction zones will be corrected accordingly

	Slag layer (mm)	Reaction zone (mm)
G	0.6	5.1
J	1.5	4.6

→

	Corrected slag layer (mm)	Corrected reaction zone (mm)
G	1.0 (= 0.6 / 0.6)	8.5 (= 5.1 / 0.6)
J	1.0 (= 1.5 / 1.5)	3.1 (= 4.6 / 1.5)

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Wear ratio

- Wear ratio
  - Dimensionless number characterizing corrosion severeness

$$\textit{Wear ratio of brick } x\ (-) = \frac{\textit{reaction zone thickness of brick } x\ (mm)}{\textit{remaining slag layer thickness of brick } x\ (mm)}$$

Wear ratio

- Wear ratio

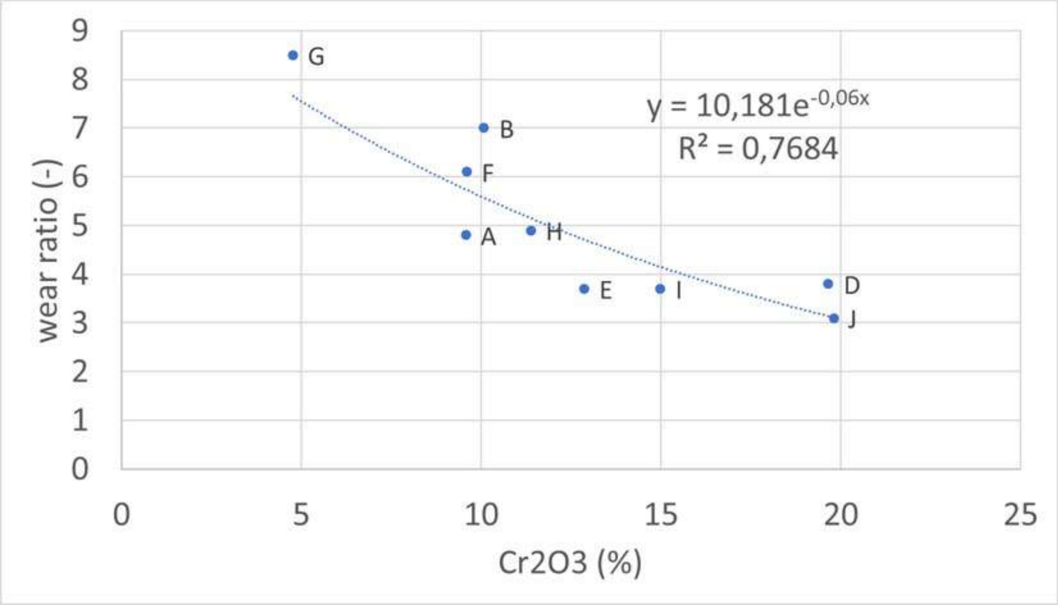
	Slag layer (mm)	Reaction zone (mm)
A	1.3	6.2
B	1.0	7.0
C	0.0	5.7
D	1.6	6.0
E	1.2	4.4
F	1.2	7.3
G	0.6	5.1
H	1.5	7.4
I	1.5	5.6
J	1.5	4.6

	Wear ratio (-)
A	4.8
B	7.0
C	∞
D	3.8
E	3.7
F	6.1
G	8.5
H	4.9
I	3.7
J	3.1

- C highest Wear ratio / poorest corrosion resistance
- In line with real-life observation

Wear ratio

- Wear ratio
  - Relation Cr_2O_3 - Wear ratio



Wear ratio

- Wear ratio
  - Relation Cr_2O_3 - Wear ratio
    - The higher the Cr_2O_3 concentration, the lower the wear ratio
    - The enhancing effect is decreasing
      - Cr_2O_3 from 5% to 10%: big effect
      - Cr_2O_3 from 15% to 20%: small effect
      - Cr_2O_3 > 25%: doubtful

    - In line with real-life observation
      - Cr_2O_3 of 15% is cost-effective optimum

Summary

- Summary
  - Crucible test of 10 commercial chromia-corundum bricks
  - No conclusions based on visual inspection
  - Introduction of Wear ratio
    - Relation with Cr_2O_3-content
    - Results in line with real-life observation

- Questions?
  - johannes.boersma@goudarefractories.com

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New Considerations for Refractory Lining Design

Ryan McDonald
Application Specialist
Energy, Environmental, and Chemical

HWI A MEMBER OF CALDERYS

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Table of Contents

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Refractory Basics

Refractory Basics

- Resists high temperature
- Resists chemical alteration
- Hard, but brittle
- High mechanical strength
- Good insulators
- Inorganic, non metallic materials
- Typically oxides
  - Al_2O_3, SiO_2, CaO, P_2O_5

Raw Materials

Chromic Oxide

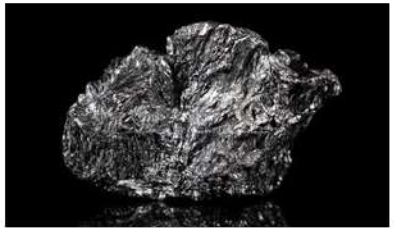
Magnesia

- White fused
- Dead burned

Alumina Zirconia Silicate

Dolomite

Vermiculite



Graphite

Halite

Insulated Refractory Linings

Insulated Refractory Linings

Insulating Fire Brick

Insulating Monolithic

Ceramic Fiber

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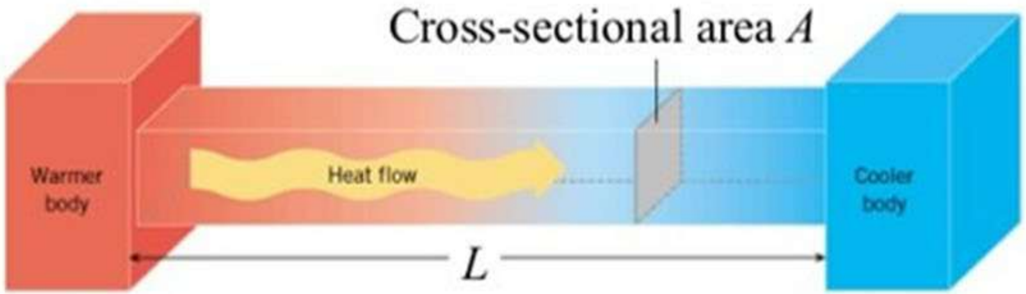
Insulated Refractory Linings

Pro's

- Decreased Shell Temperature
- Increased Energy Savings
- Safety
- Fuel Reduction

Con's

- Overheated Vessel
- Increased Lining Complexity
- Advanced Dry Out Considerations



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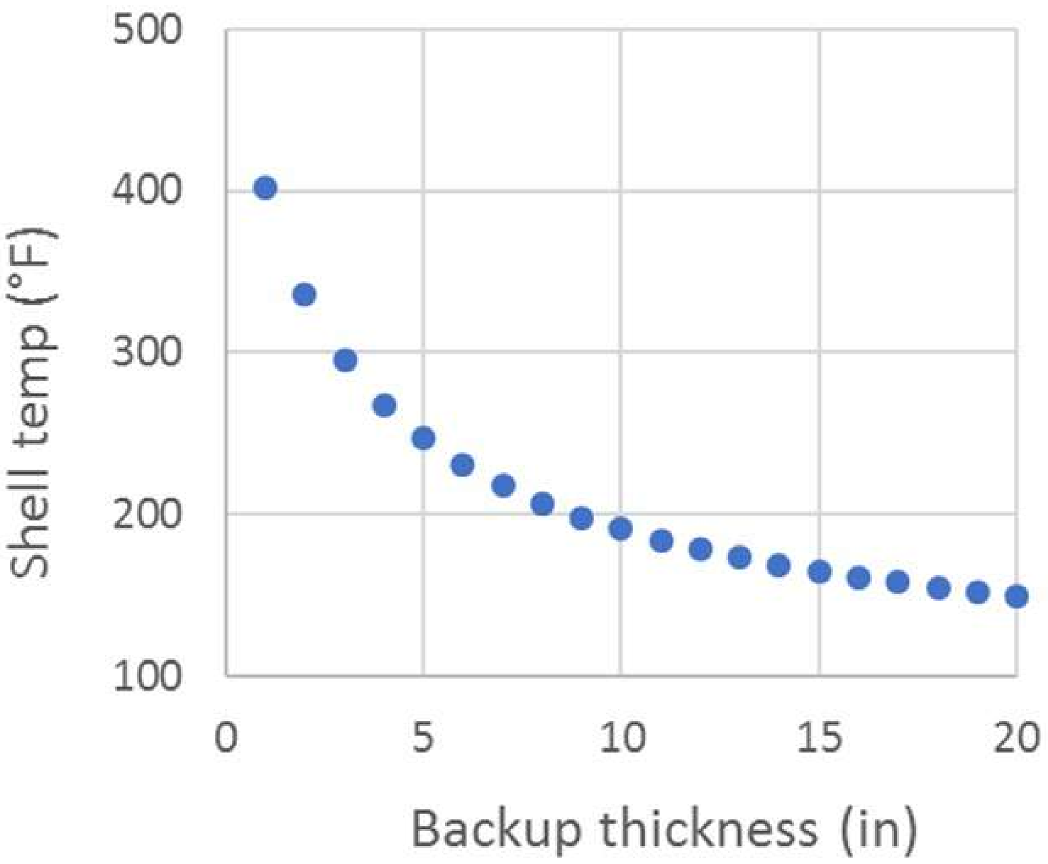
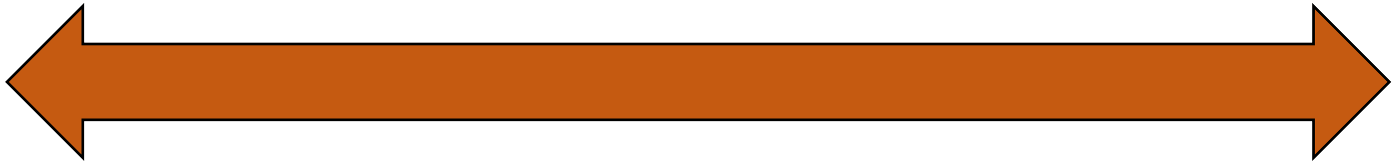
Point of Diminishing Returns



Middleweight Refractory



Lightweight
Low Strength
Most Insulating

Dense
High Strong
Less Insulating

Middleweight
Medium Strength
Medium Insulating Capabilities

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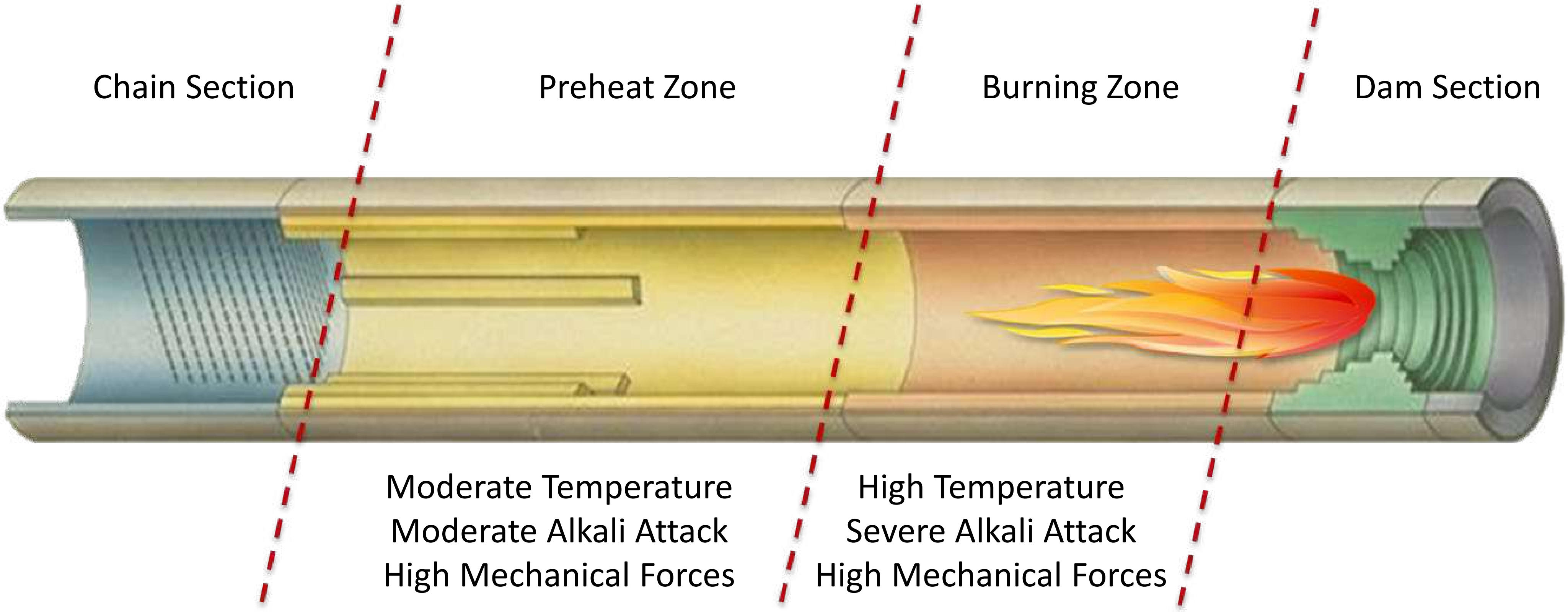
Zoning and Lining Design



Moderate Temperature
Moderate Alkali Attack
High Mechanical Forces

High Temperature
Severe Alkali Attack
High Mechanical Forces

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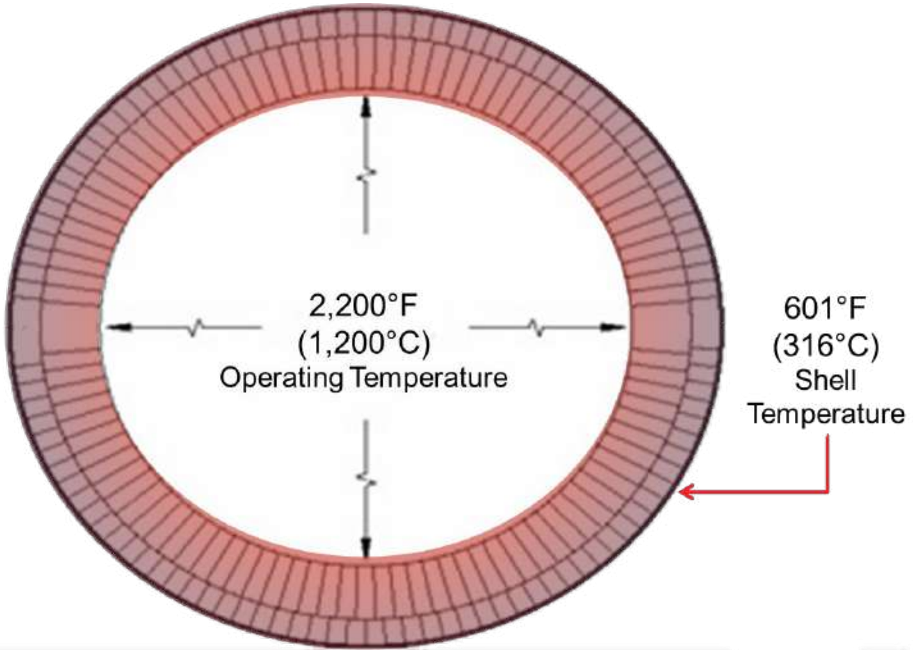
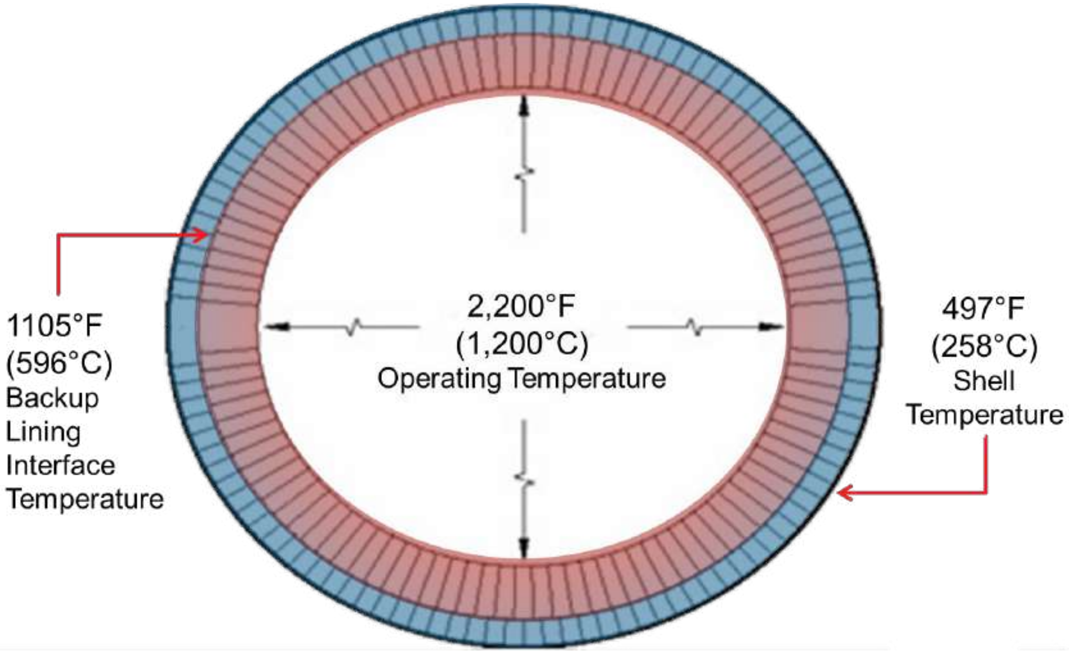
9” Hard Brick



9” Hard Brick
1.5” Middleweight Brick



Refractory Recycling

Refractory Recycling

- Unused Brick Recycling

- Most refractory brick
  - Alumina Silica
  - Chromic Oxide Containing
  - Magnesia Containing

- Crush unused brick and recycled in batts
  - Percentage put back into new brick at plants

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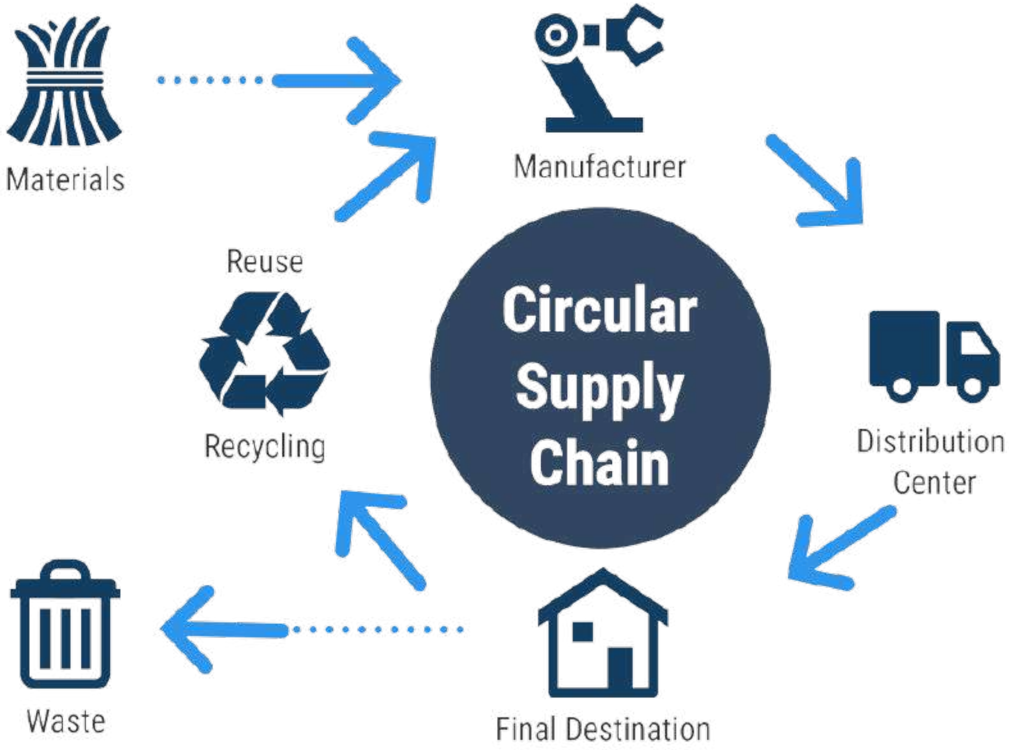
Used Refractory Recycling

- High Value Raw Materials
- Minimal chemical alteration
- Used to make same product, or new lower-end product?
- Constant Supply
- Minimum labor
  - Sorting vs Cutting



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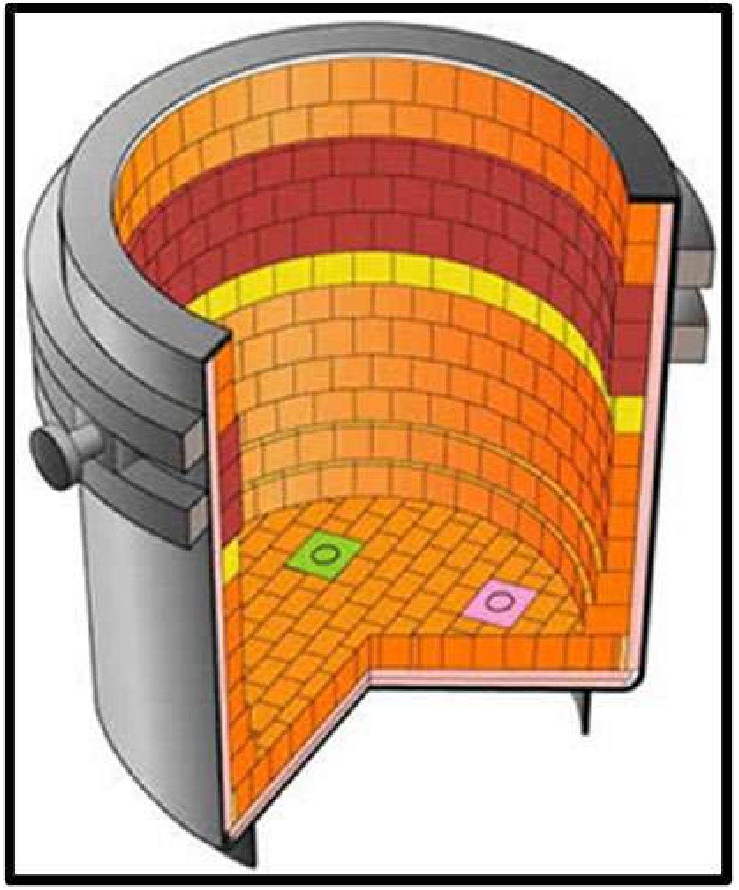
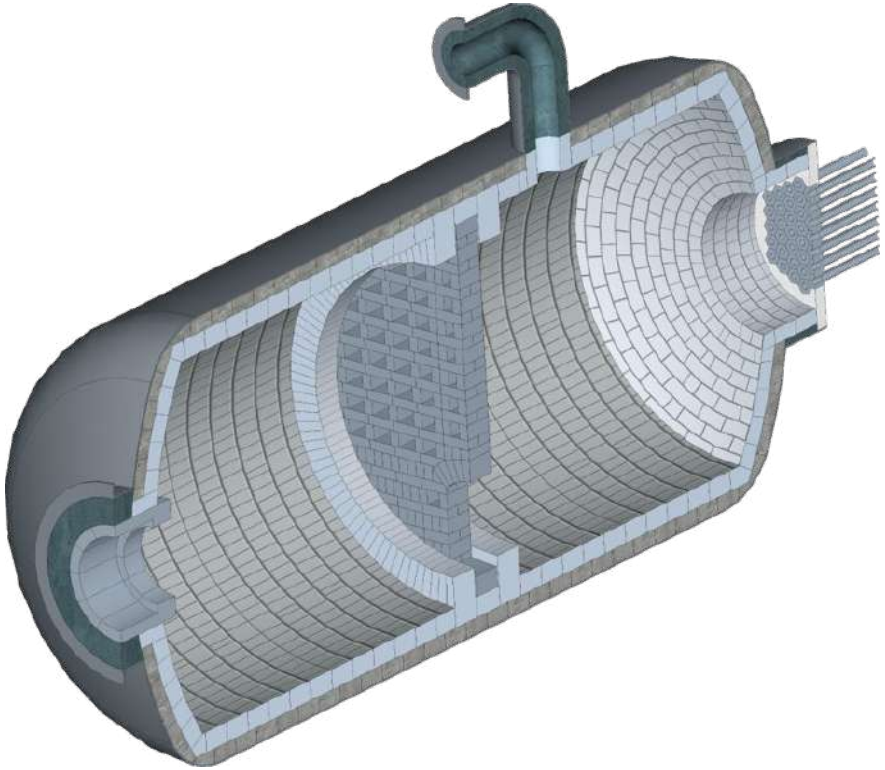
Magnesia Carbon Brick

- Used Magnesia Carbon bricks in Steel Ladles
- High volume of brick used
- Valuable raw material
- Used MgC brick can be recycled up to 20% in new MgC brick



Tabular Alumina Brick

- Tabular Alumina brick recovered from a Sulfur Recovery Unit
- XRF / XRD ran to determine chemistry
- Possible recycling into a variety of products



Tear Out: Sort & Clean Used Furnace Lining → Processor: Crush & Scalp Used Furnace → Fusion: (Pelletize), Melt, Fusion → Processor: Crush, Size CA40 → Product

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Alumina Chrome Brick

- New trials of recycling Alumina Chrome brick in Secondary Copper furnaces
- Possibility of turning recycled brick into a fused alumina-chromia aggregate

Conclusions

- New refractory technologies are being developed to promote ongoing ESG efforts
- More efficient lining design
    - Middleweight Refractory
    - Efficient Zoning
- Ongoing trials and studies for recycling high value refractory raw materials

Questions?

Thank You!!!

Ryan McDonald
RMcDonald@thinkHWI.com
412-403-1407

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Lessons from Failure Analyses in Challenging Refractory Application Environments

Presenter: Tim Marth
co-authors: Dr. Dana Goski, Dominic Loiacona

ALLIED
MINERAL
PRODUCTS

Typical failure mechanisms?

Multiple Factors to consider

Temperature

Working temperature and its distribution

Operating Environment

Oxidizing or Reducing atmosphere, CO, H_2 content

Thermal Cycling

Is the process continuous or not

Chemistry

Composition of the charge material or slag or vapors

Mechanical Loads, Abrasive Wear

Stress, mechanical abuse or abrasion

Others

Structure, Heat-Flow calculation, Slag build up, etc.

Failure Analysis Studies

Refractory Failure or Shortened Service Life - Factors

- Poor Installation Practices
- Improper Refractory Selection
- Thermal-Mechanical Stress during Operation
- Thermal-Chemical Reactions during Operation
- Poor Process Control or Abnormal Operating Conditions
- Commissioning (initial heat up and dry out)

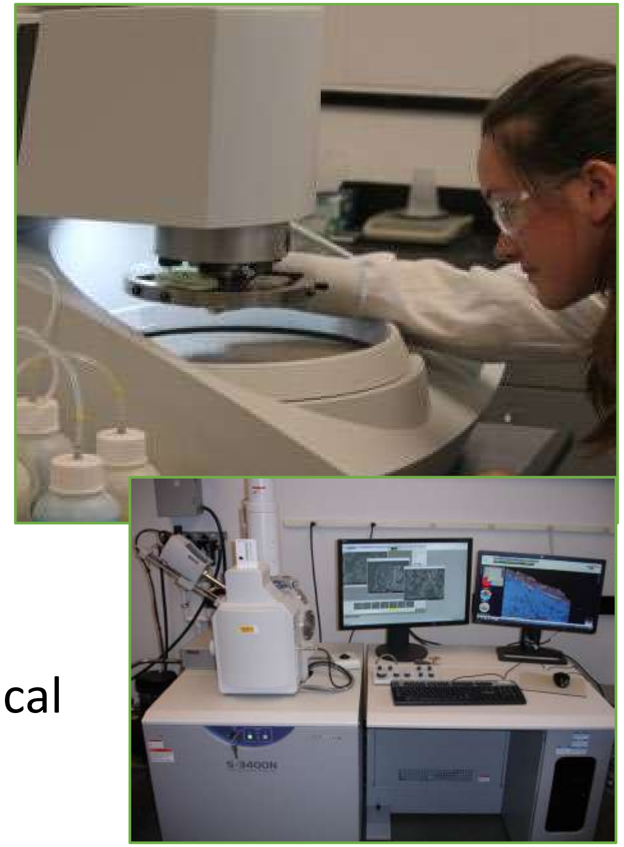
Failure Analysis of spent refractory

- What was the mode of failure?
- What caused it?
- How can it be prevented in the future?

Failure Analysis Studies

Common Challenges

- Received Samples – Info can be limited
- Where exactly did sample come from?
- What product is it? Is it even ours?
- How and when was it installed?
- What other pieces of the puzzle are missing?



Go-to tools:

Visual observations, microscopy (optical & SEM-EDS), chemical & mineralogical analysis (XRD & XRF), and physical properties

Each technique gives one piece of the puzzle

Case Study A: Mechanical Damage in Cement Rotary Kiln Cooling System

Damaged area between dropouts

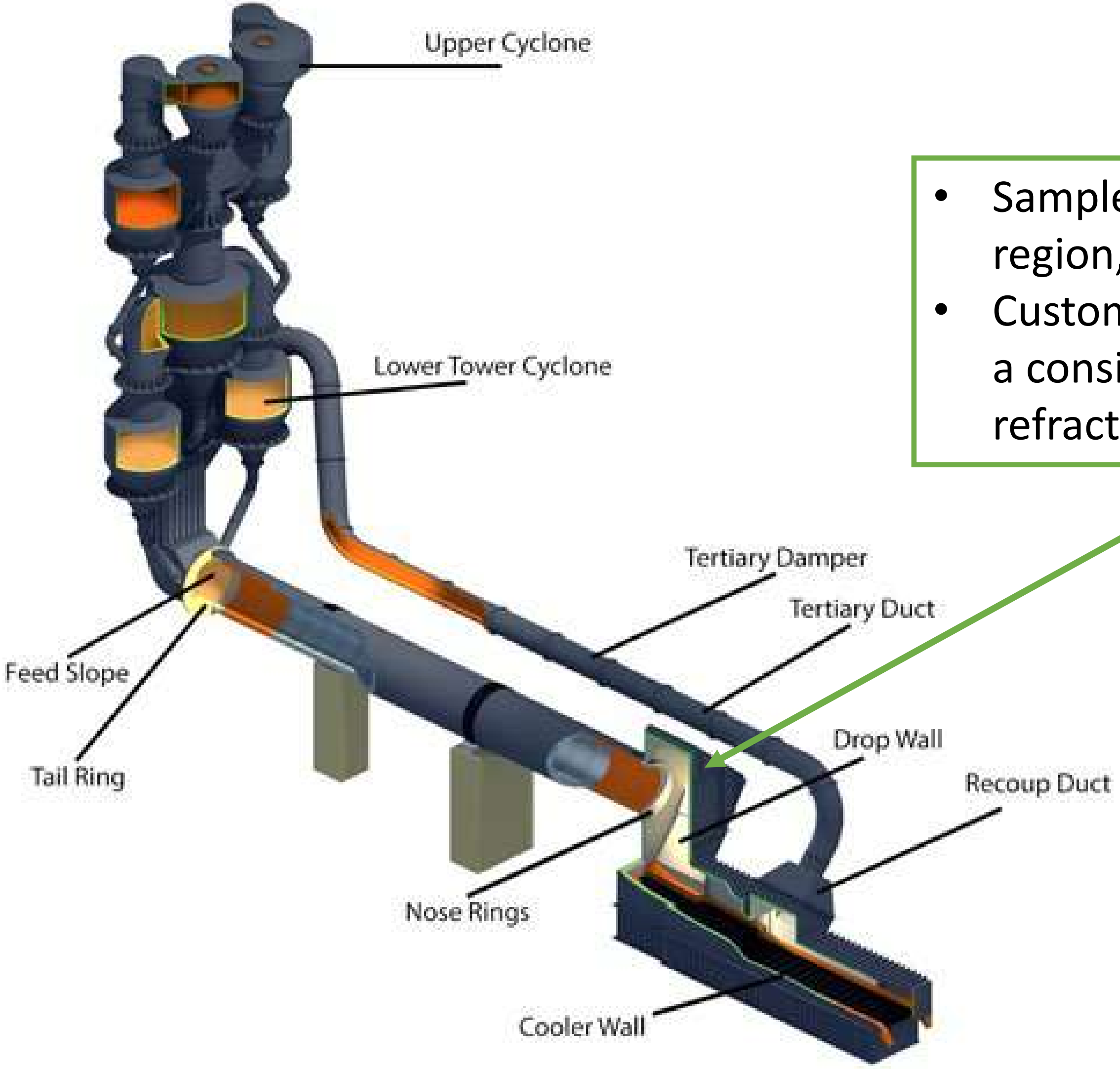
43% Al_2O_3 / 28% SiC, Cement Bonded Product – as received

70% Alumina, Colloidal Silica Bonded Product – as received.

Note: Horizontal Laminations

Customer submitted these samples in order to generate suggestions for refractory campaign life improvement

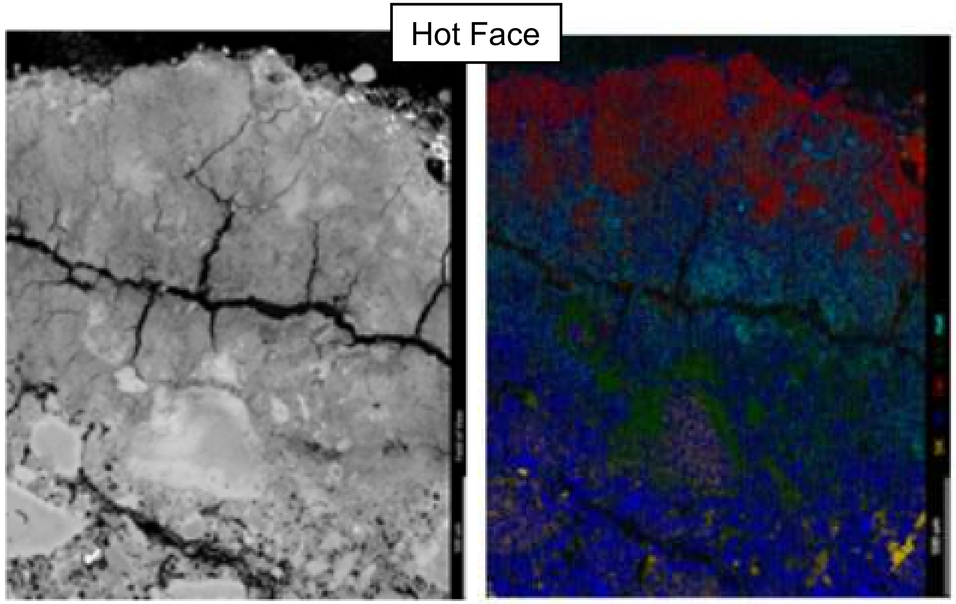
Samples were cross-sectioned and prepared for SEM analysis



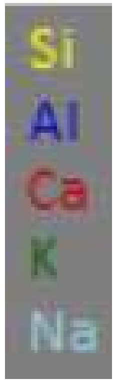
- Samples Collected from Drop Wall region, near cooler
- Customer reports that this region is a consistently problematic area for refractory lifespan

Case Study A: SEM Hot Face Analysis

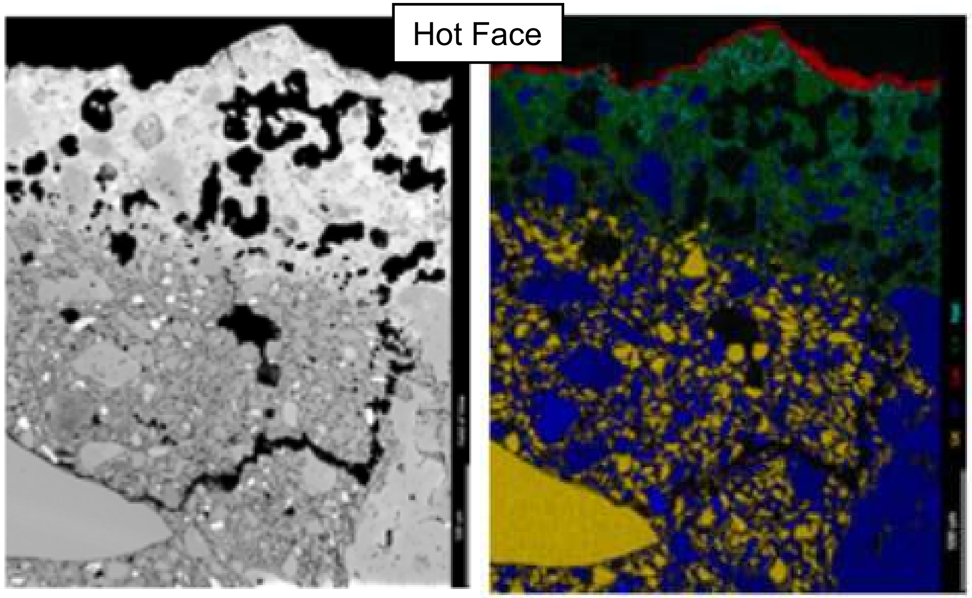
70% Al_2O_3,Colloidal Silica Bonded Product – Sectioned and Polished



K_2O - 13.9%
Na_2O - 6.0%
CaO – 12.6%



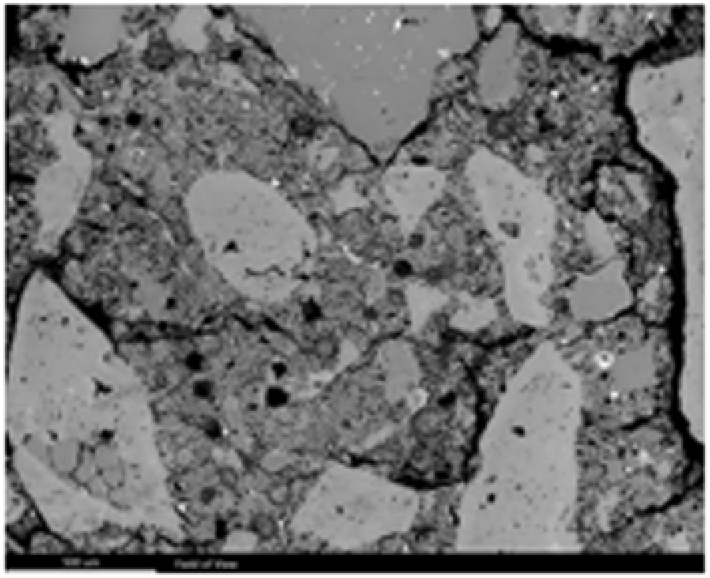
43% Al_2O_3 / 28% SiC, Bonded Product – Sectioned and Polished



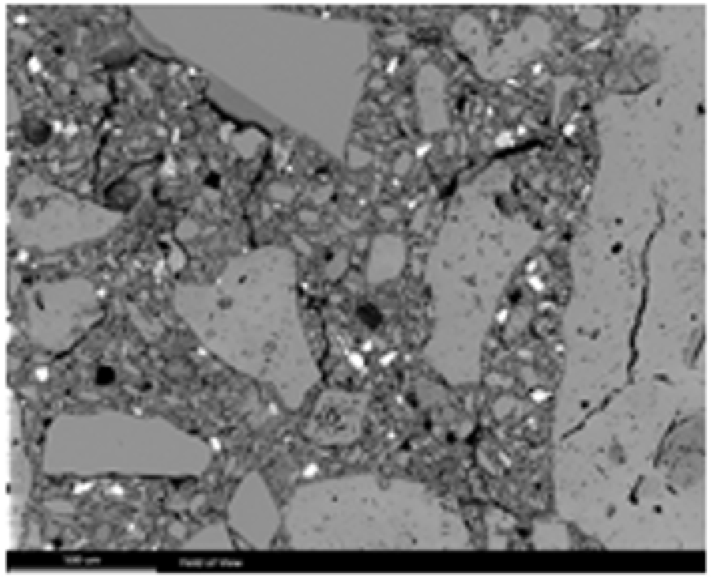
K_2O - 6.0%
Na_2O - 2.0%
CaO – 4.4%

Case Study A: SEM Microcrack Analysis

70% Al_2O_3,Colloidal Silica Bonded Product – Sectioned and Polished



43% Al_2O_3 / 28% SiC, Bonded Product – Sectioned and Polished



- Microcracks were observed at the hot face and on the internal region of the samples. The cracks were more severe in the 70% Al_2O_3 sample.
- Alkali penetration was not severe, so mechanical damage is likely mode of failure
- Source of mechanical damage could be thermal or structural in nature

Case Study A: Conclusion and Recommendations

Conclusion:

- Possible that kiln shell is flexing and transferring mechanical loads and stresses to refractory
- The evidence is consistent with mechanical failures rather than, originally suspected failure due to alkali attack or thermal stresses

Recommendations

- Alter the anchoring systems
- Combine ceramic refractory anchors with existing metal anchors
- Refractory with high HMOR value – plasticity at high temperatures
  - Vibration cast - to maximize density
- Add cold joint to mechanically isolate refractory in contact with rotary kiln shell, and the cooler elbows

Case Study B: Alkali Attack in Liquid Hazardous Waste Incinerator

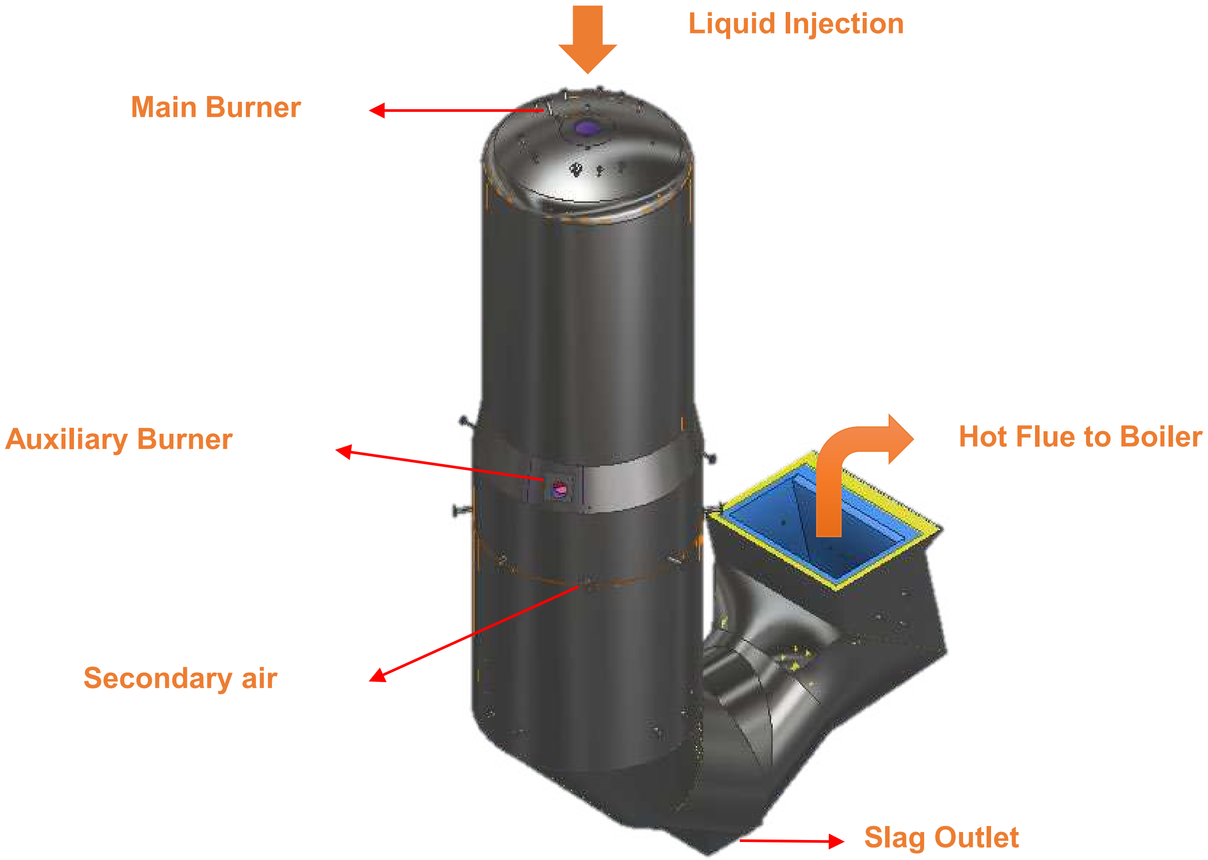
Liquid Waste Incinerator lined with 85% alumina brick and castable

Working Temp – 1150ºC at flue outlet, 1500ºC near burner

Operators try to control liquid feed's content to below 0.4% Fluorine, below 2% alkali

- 200 MT/Day capacity

Previous lining only lasted 20 days in service before failing



Visual Inspection of Lining and Failed Refractory

XRF and XRD Testing – Spalled pieces

	Failed Castable	Failed Brick
Compound	**Wt. (%)**	**Wt. (%)**
SiO_2	6.0	10.4
TiO_2	0.2	0.3
Al_2O_3	71.6	69.0
Fe_2O_3	0.2	0.2
MgO	0.8	0.2
CaO	1.8	0.1
Na_2O	15.7	15.2
K_2O	0.1	0.2
P_2O_5	0.3	0.2
SO_3	2.4	1.6

XRD Phases Detected – both samples
- Corundum (α-Al_2O_3)
- Beta Alumina ($NaAl_{11}O_{17}$)
- Carnegieite ($Na_2O \cdot Al_2O_3 . 2SiO_2$)


Piece of failed castable


Piece of failed brick

Alkali attack reactions

- Alkali Vapors infiltrate refractory, condense in pores.
- Form expansive phases with refractory components between 750-1200 °C
- Volume expansion and stress causes failure as material cracks or spalls

Aluminosilicates (Mullite, Fireclay, Chamotte)	$\xrightarrow{K_2O \text{ or } Na_2O}$	$K_2O \cdot Al_2O_3 \cdot 6SiO_2$ $K_2O \cdot Al_2O_3 \cdot 4SiO_2$ $K_2O \cdot Al_2O_3 \cdot 2SiO_2$ $Na_2O \cdot Al_2O_3 \cdot 2SiO_2$	Orthoclase Leucite Kalsilite Carnegieite	*Up to 55% Expansion*
Alumina	$\xrightarrow{K_2O \text{ or } Na_2O}$	$Na_2O \cdot 11Al_2O_3$ $K_2O \cdot 11Al_2O_3$	Na β-Alumina K β-Alumina	*Up to 25% Expansion*

Alkali resistant additives (SiC, ZrO_2 compounds) can help to protect refractory

Alkali Cup Testing – Modified FL Smidth Test

Procedure:

- Prefire Refractory, Core Drill cavity, fill with reactive compounds
  - 70% NaOH, 15% Na_2SO_4, 15% Na_3PO_4 – known contaminants in customer's application
- Mortar lid, Fire cup at 1500 ^{0}C for 5 hour hold

Materials Tested:

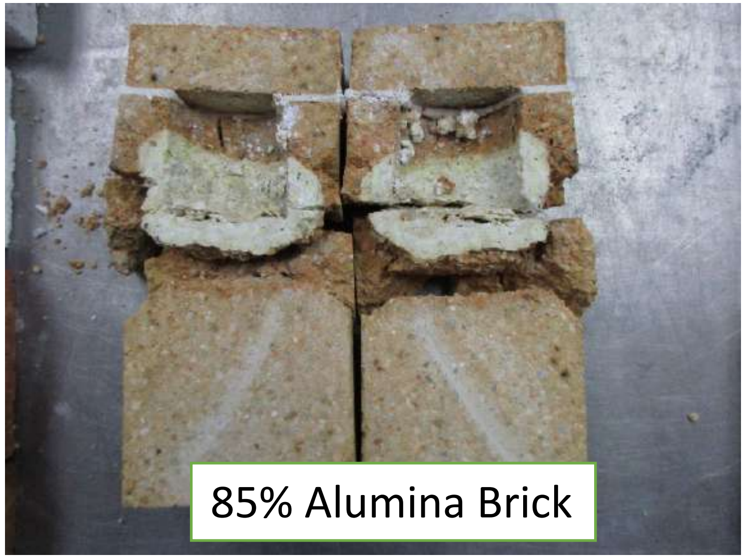
- 65% Alumina Brick
- 85% Alumina Brick
- High Alumina Castable (98% Al_2O_3)
- Castables with Alkali Resistant ***(AR)*** Additives

A: 55% Al_2O_3, 5% SiC, 1% ZrO_2
B: 60% Al_2O_3, 8% SiC
C: 75% Al_2O_3, 4% SiC, 3% ZrO_2
D: 72% Al_2O_3, 4% ZrO_2
E: 52% Al_2O_3, 24% ZrO_2

Materials cross-sectioned, ranked by performance

Failed Samples – Cracks from alkali attack

65% Alumina Brick

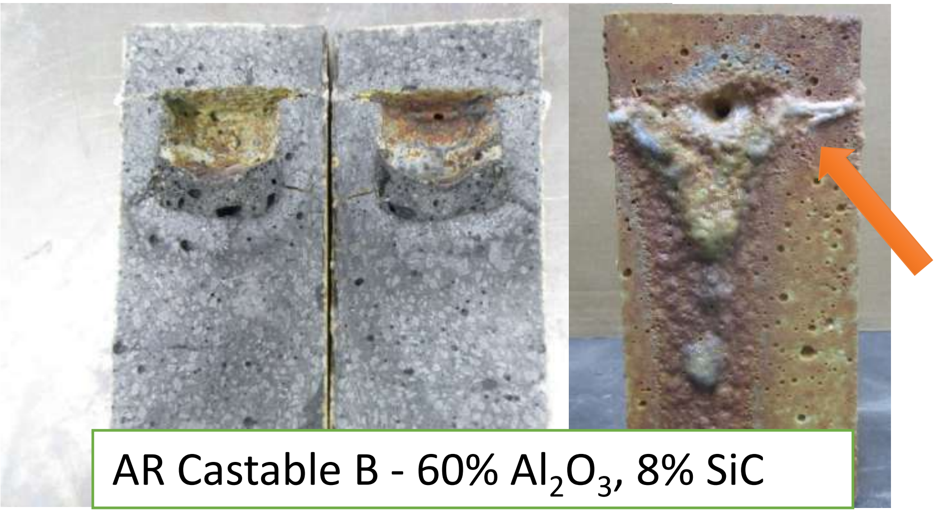


85% Alumina Brick

High Alumina Castable

Expansive phase formation from formation of alkali aluminates and alkali aluminosilicates

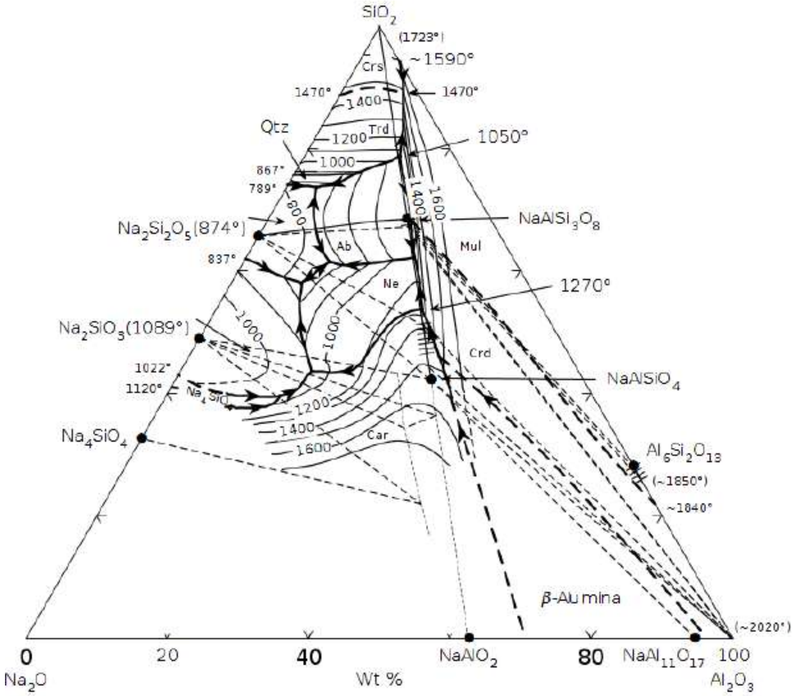
Failed Samples – Liquid Phase Formation (partial melting)



AR Castable B - 60% Al_2O_3, 8% SiC

AR Castable E: 52% Al_2O_3, 24% ZrO_2

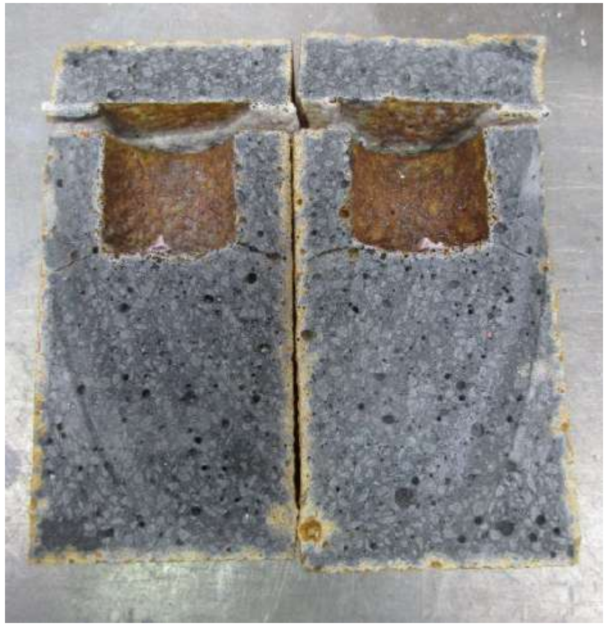
- AR Castable B had slight liquid phase formation
- AR Castable E had ***severe*** liquid phase formation
- Cup testing at 1500°C is uncommon and severe, normally done at 1000°C



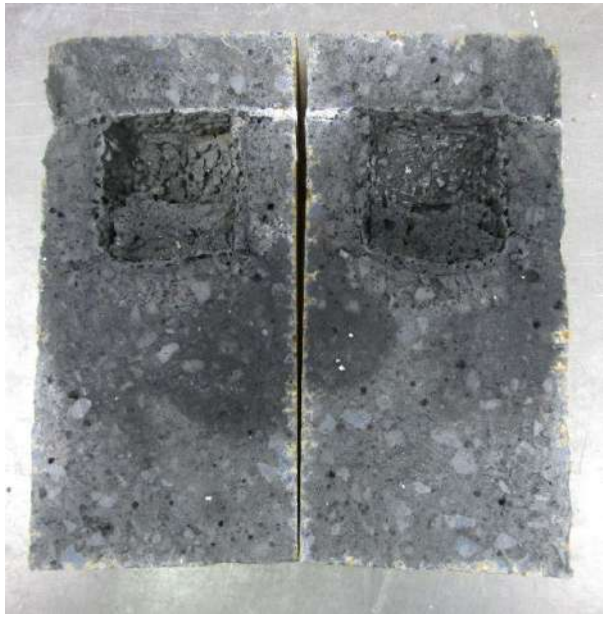
Passed Samples

AR Castables A, C, D all performed well – no cracking or bloating

- Castables C and D contained alkali, while it escaped through porosity of Castable A
- Castable D has some internal corrosion, but still passed test



AR Castable A
55% Al_2O_3, 5% SiC, 1% ZrO_2



AR Castable C
75% Al_2O_3, 4% SiC, 3% ZrO_2

AR Castable D
72% Al_2O_3, 4% ZrO_2

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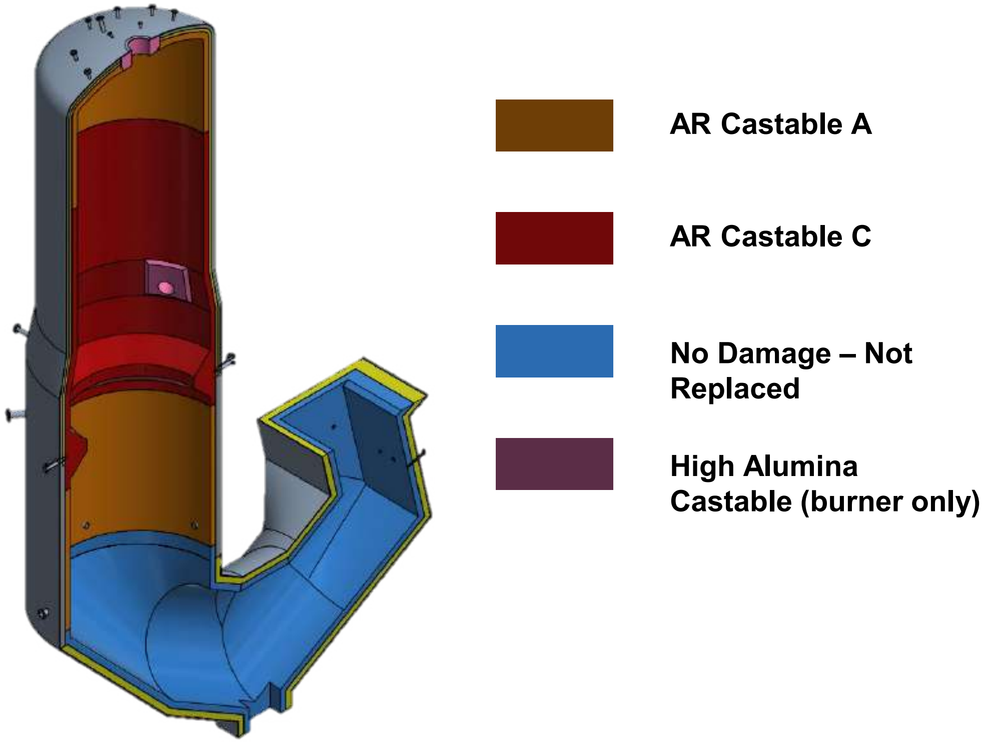
Case Study B: Conclusion and Recommendations

Conclusion:

- Formation of expansive alkali phases caused refractory failure
- Better refractory choices are likely available
- Cup Testing Identified better products for this application

Recommendations:

- High Alumina Castable must be used at burner tip due to extremely high maximum use temperature
- AR Castable C used close to burner due to higher maximum temperature limit.
- AR Castable A is suitable for areas further from the burner



Results: Lining installed via pump casting, still performing after 43 months of service.

Previous brick lining only lasted 20 days before failure

New Analytical Technique Development

International Journal of
Ceramic Engineering
& Science

The American Ceramic Society

RESEARCH ARTICLE | Open Access

Alkali resistance testing methodology and development: Focus on mullite based castables

Katherine Haines, Kasandralee Byrd, David Lankard

First published: 09 April 2022 | https://doi.org/10.1002/ces2.10131

- Sample prep methods optimized
    - Porosity kept consistent
    - Prepped with fine particles (50F) only
    - Focus on mineralogical phase changes
- Use of polished thin sections
- Innovative techniques for detailed characterization
- Assess progressive changes from alkali exposure:
    - under lab test conditions
    - in situ

Example characterization results

Fig. 1. Post-test cross section of 8M.

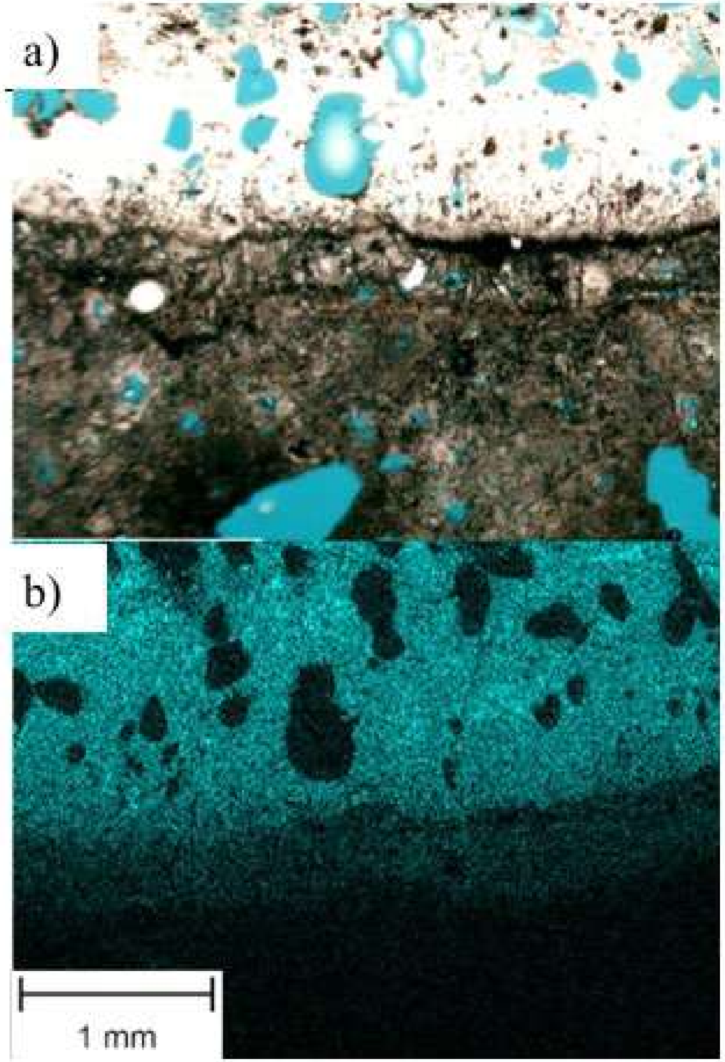


Fig. 3. a) Cross polarized microscopy at 25x magnification of 8M. b) Sodium map of the same area.

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Example characterization results

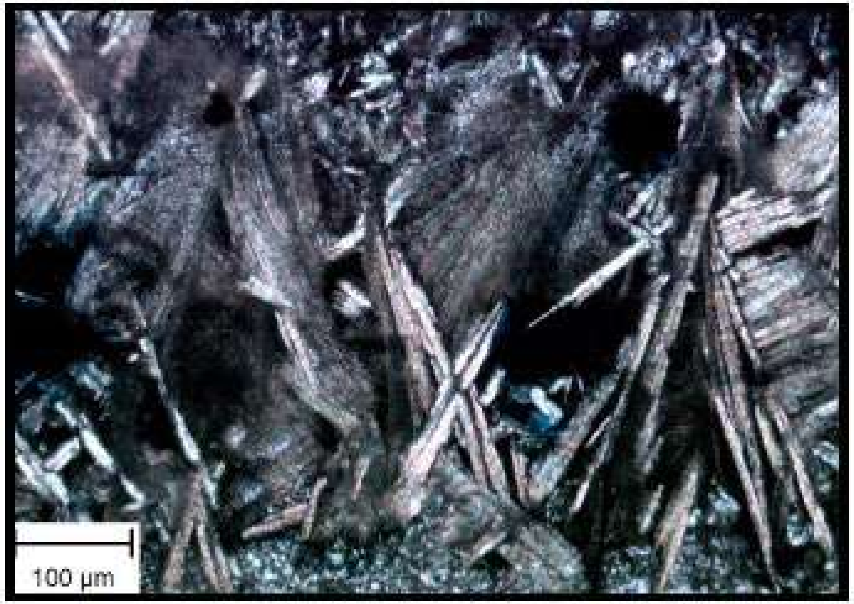

Fig. 4. Cross polarizing micrograph at 200x magnification of the elongate crystals found in 8M post-test.

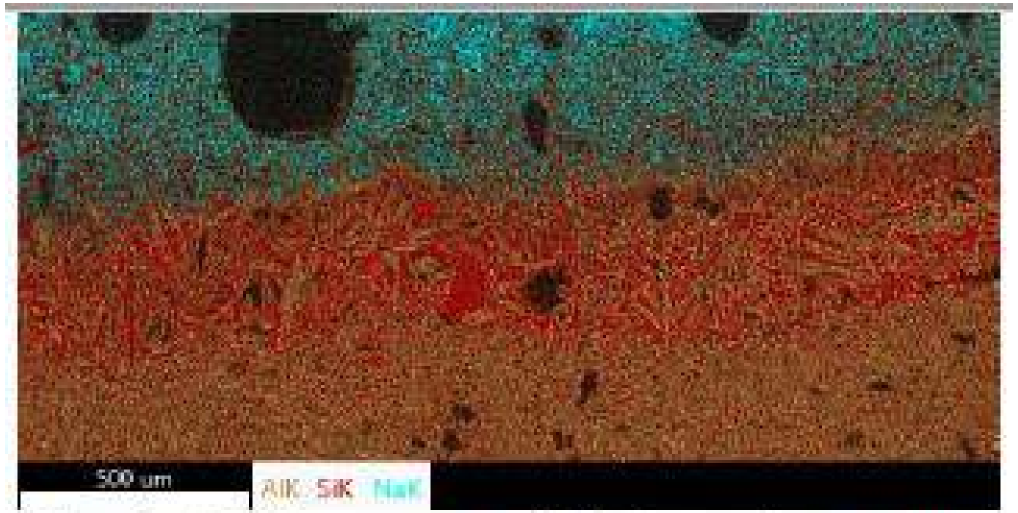

Fig. 6. Sodium map of 8M reaction zone. Al (orange), Si (red) and Na (blue).

Overall Conclusion

After action reporting & analysis – clues leading to a comprehensive look at how material performed:

- What was the mode of failure?
- Initial observations can be misleading – what *actually* happened?
- How can analytical tools help our investigation?

Looking forward:

Ongoing efforts to understand failure mechanisms:

  Refine and optimize analytical techniques
  Combine analysis with experience of industry experts, and data analysis tools

Leverage growing understanding and continuous learning:

- To extend campaign life
- Strive to prevent in future?
- Can better refractory selection solve problems?
- Should other solutions be explored?
- Technical Service adds value complimenting the value of the refractory itself

Thank You!

Interesting in collaborating?

Visit our booth to start a conversation.

Contact me at:
tim.marth@alliedmin.com

Thank you Dr. Dana Goski, Dominic Loiacona, Tim Hoyt, Vincent Li, Dave Lankard, Kate Haines, and Kassy Byrd for contributing to this presentation!

SESSION 4

Clean Harbors Aragonite PFAS Test Program Results

40th IT3 International Conference on Thermal Technologies
& Hazardous Waste Combustors
Sponsored by AWMA
September 13-14, 2023 Charlotte, NC

Mike Crisenbery (Clean Harbors), Bill Troxler (Focus Environmental),
Frank Barranco, John Kumm, Steve Yankay
(EA Engineering Science and Technology)

Presentation Overview

- Aragonite facility overview
- Test program overview
- Sampling & analytical program
- PFAS spiking protocol
- PFAS mass balance and DRE calculations
- Fluorine mass balance
- Total organic precursor assay
- Test program summary

Project Objectives

- Measure DRE for spiked compounds (PFOA, PFOS, PFHxS, HFPO-DA)
- Perform process PFAS mass balance
- Measure hydrogen fluoride (HF) stack emissions
- Perform a fluorine mass balance
- Assess “hidden mass” of PFAS in AFFF wastes with total oxidizable precursor assay (TOPA)

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Clean Harbors - Aragonite Utah

Combustion & Emission Control Systems

- Combustion System
  - Slagging rotary kiln (~1,000-1,100°C)
  - Afterburner (~1,120-1,150°C)
- Emission Control System
  - Spray dryer
  - Baghouse
  - Saturator
  - Wet Scrubber
  - Induced draft fan
  - Stack

Testing Teams

June 2021 Test

- EA Engineering, Science & Technology
- Focus Environmental
- Montrose AQ Services
- Enthalpy Analytical

February 2022 Test

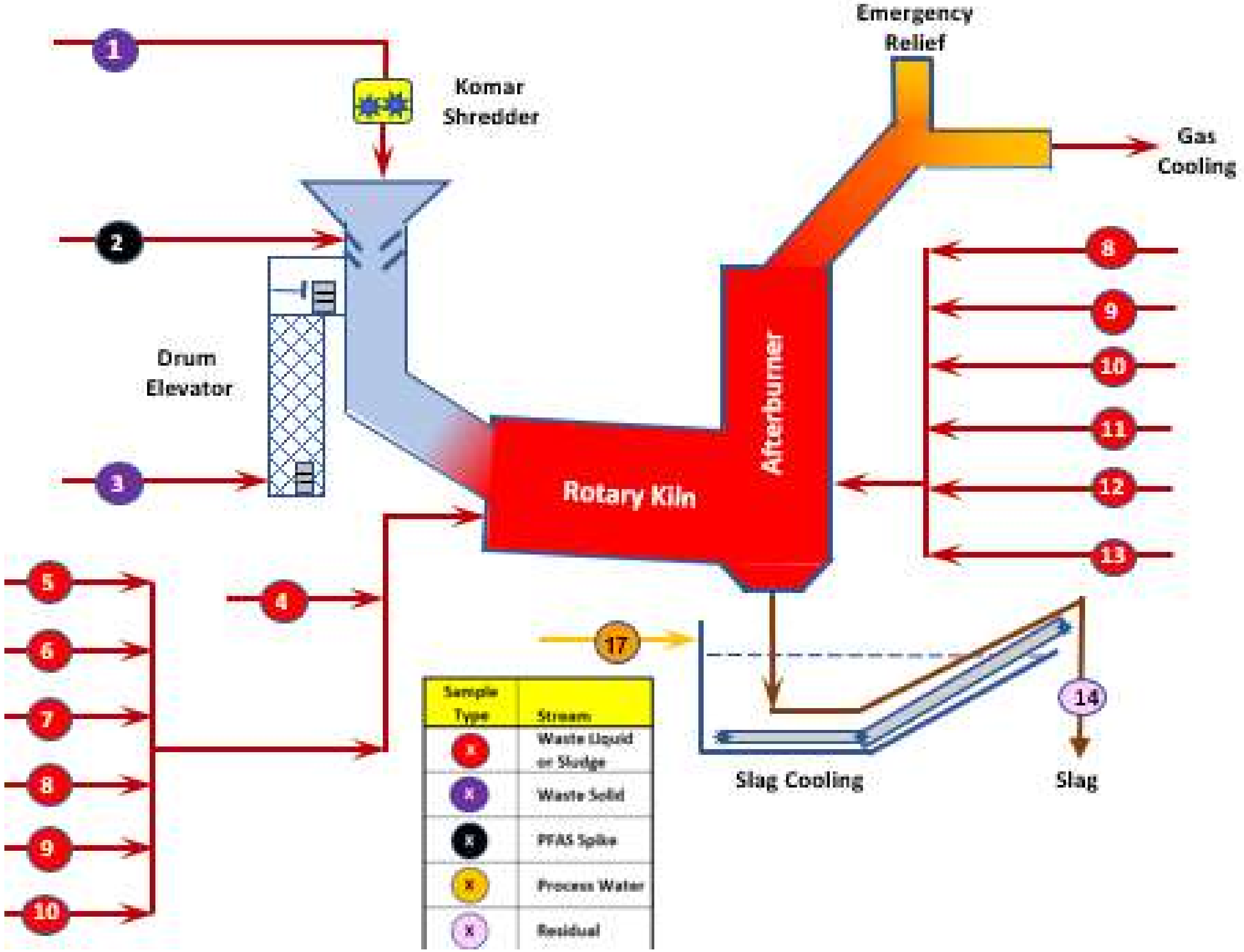
- EA Engineering, Science & Technology
- Focus Environmental
- Alliance Source Testing
- Eurofins

Planned Test Conditions - Feed Streams

Test Condition	Runs	Test Condition Description	Normal Waste Feeds	Spiked PFAS	AFFF(a)
1	1-3	Baseline	X	---	---
2	4-6	PFAS Spiking	X	X	---
3	7-9	AFFF Feed	X	---	X

(a) AFFF inadvertently fed during Runs 1-8 through sludge port.

Combustion System Sampling Points



Sample Type	Stream
x	Waste Liquid or Sludge
x	Waste Solid
x	PFAS Spike
x	Process Water
x	Residual

Sampling Point	Stream
1	Komar Solids
2	PFAS Spike
3	Containerized Solids
4	Sludge Port
5	Direct Burn - Drums
6	Direct Burn - Trucks
7	Direct Burn - Rob Roller
8	High Btu Liquid
9	Fuel Oil
10	Used Motor Oil
11	Aqueous Liquid
12	Corrosive Waste
13	AFFF from Tote
14	Slag
17	Process Water

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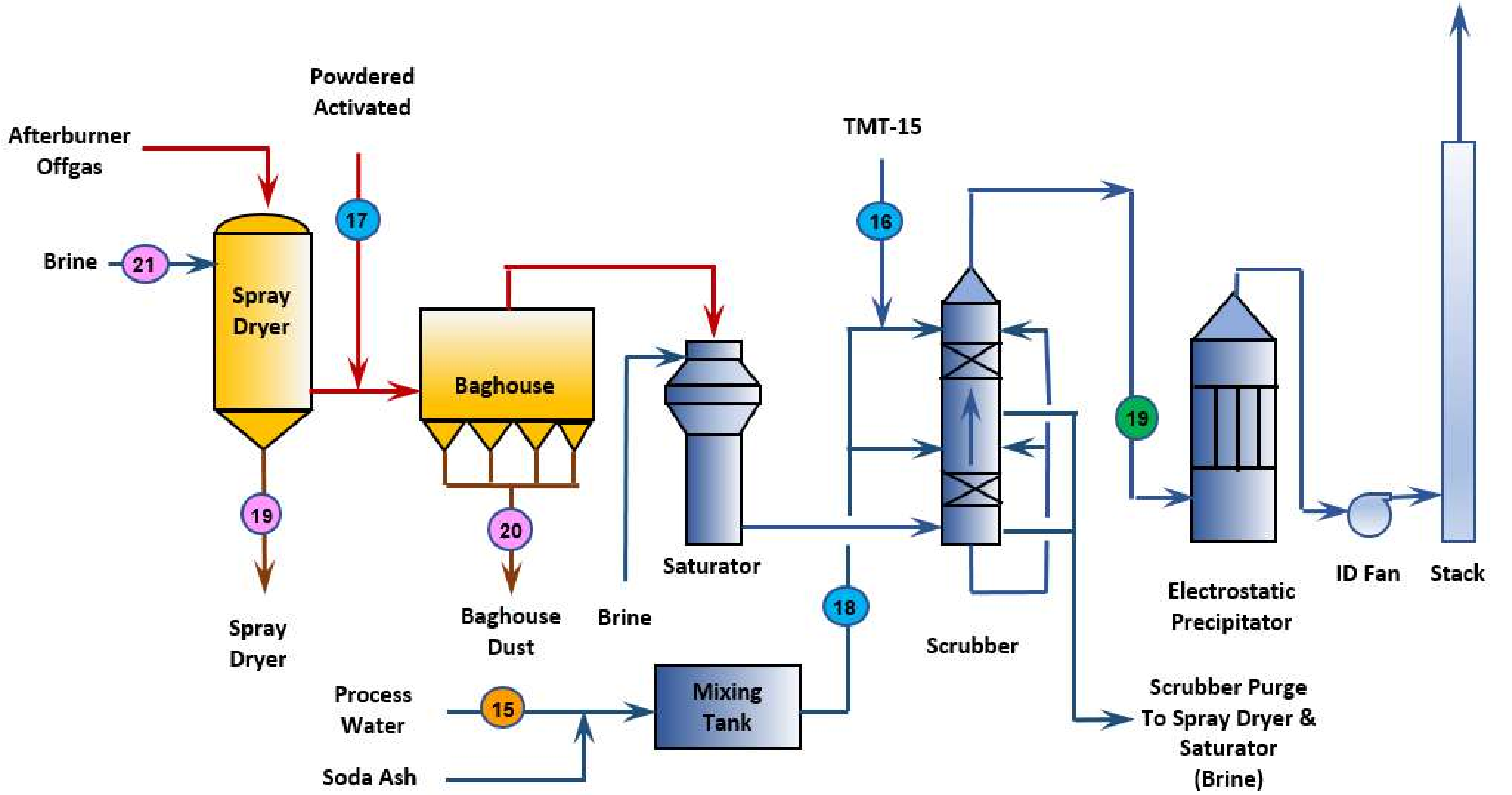
Emission Control System Sampling Points



Sampling Location	Material
15	Process Water
16	TMT-15
17	Powdered Act. Carbon
18	Soda Ash Solution
19	Spray Dryer Solids
20	Baghouse Dust
21	Brine
20	Stack Gas

Sampling and Analytical Methods

- Stack gas sampling methods

PFAS	EPA OTM-45
HF	EPA Method 26A

- Analytical methods
  - PFAS - DoD Quality Systems Manual (LC/MS/MS)
  - HF - EPA Method 26A (ion chromatography)
  - Total fluoride - EPA Method 340.2 (ion selective electrode)
  - Total oxidizable precursor assay (TOPA) - (Houtz et.al.)

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PFAS Spiking Calculations

- Spiking compounds: PFOA, PFHxS, PFOS, and HFPO-DA
- Calculated mass of each PFAS compound required to demonstrate >99.9999% DRE based on:
    - Stack gas flow rate
    - Stack gas sample volume
    - Detection limit of PFAS compound
    - Include contingency for unknowns

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PFAS Spiking Material Preparation

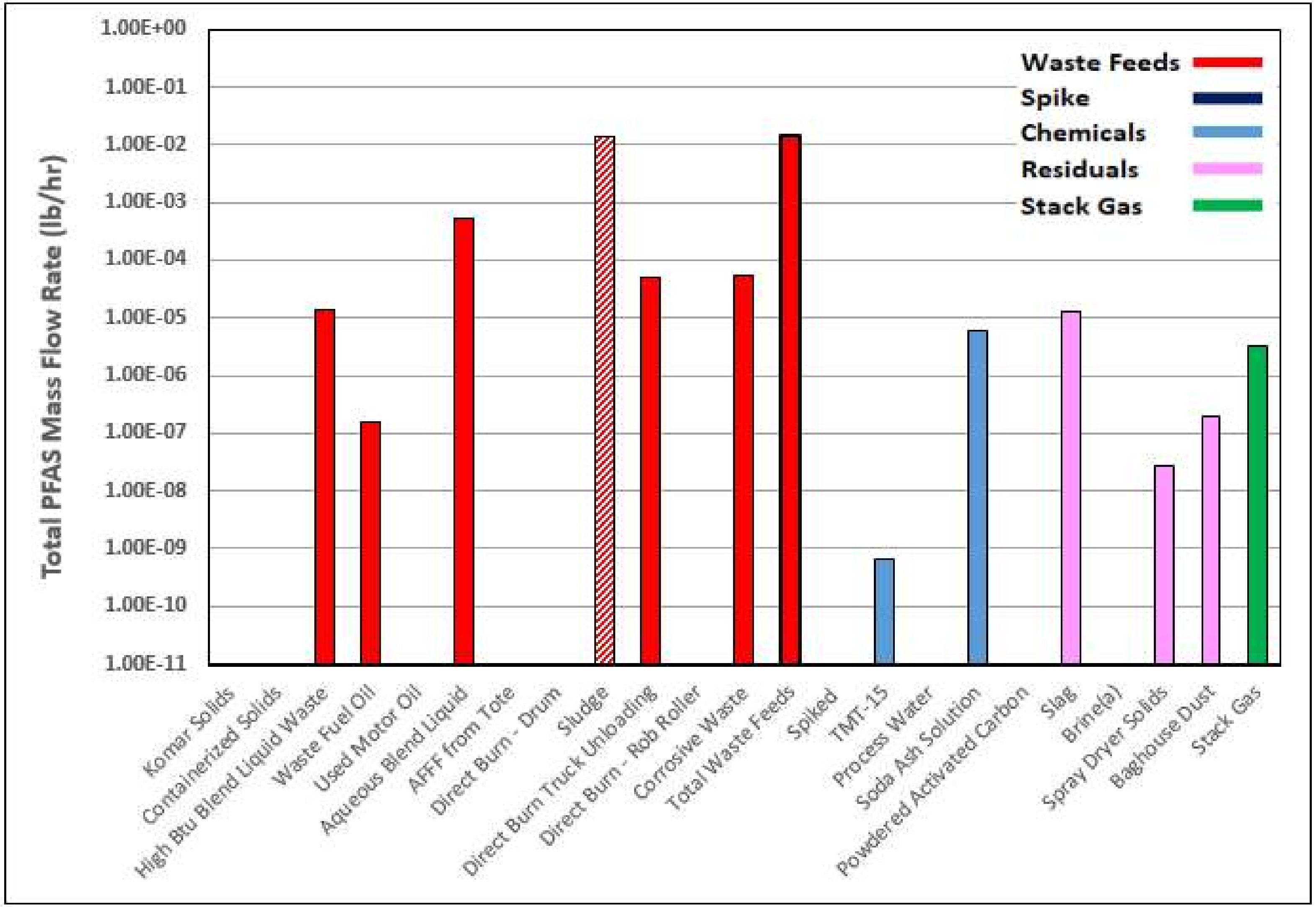
Pre-weighed bottles of spiking materials
bundled in cardboard box

Process for inserting PFAS
spiking bottles into
numbered cardboard boxes

Conservative Mass Balance & DRE Calculations

- PFAS not measured in solid waste feed streams
- PFAS in process water and chemical inputs to the gas cleaning systems included in mass balances but not in DRE calculations
- Concentration of zero used for PFAS non-detects in waste feed, chemical, process water, and residual streams
- PFAS non-detects concentration in stack gas assumed at the MDL
- DREs biased low based on conservative assumptions

PFAS Mass Balance - Test Condition 1 (Baseline)



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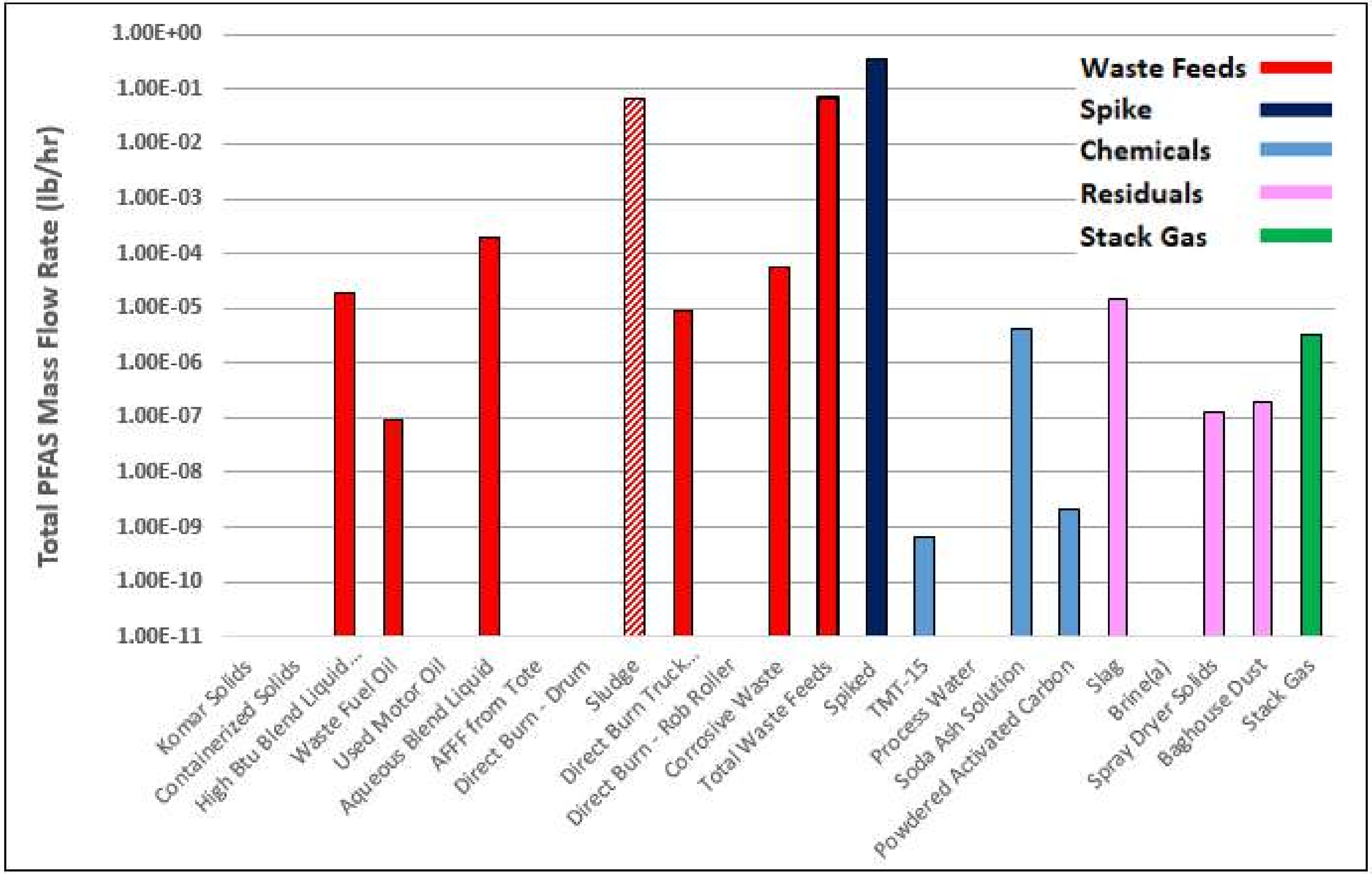
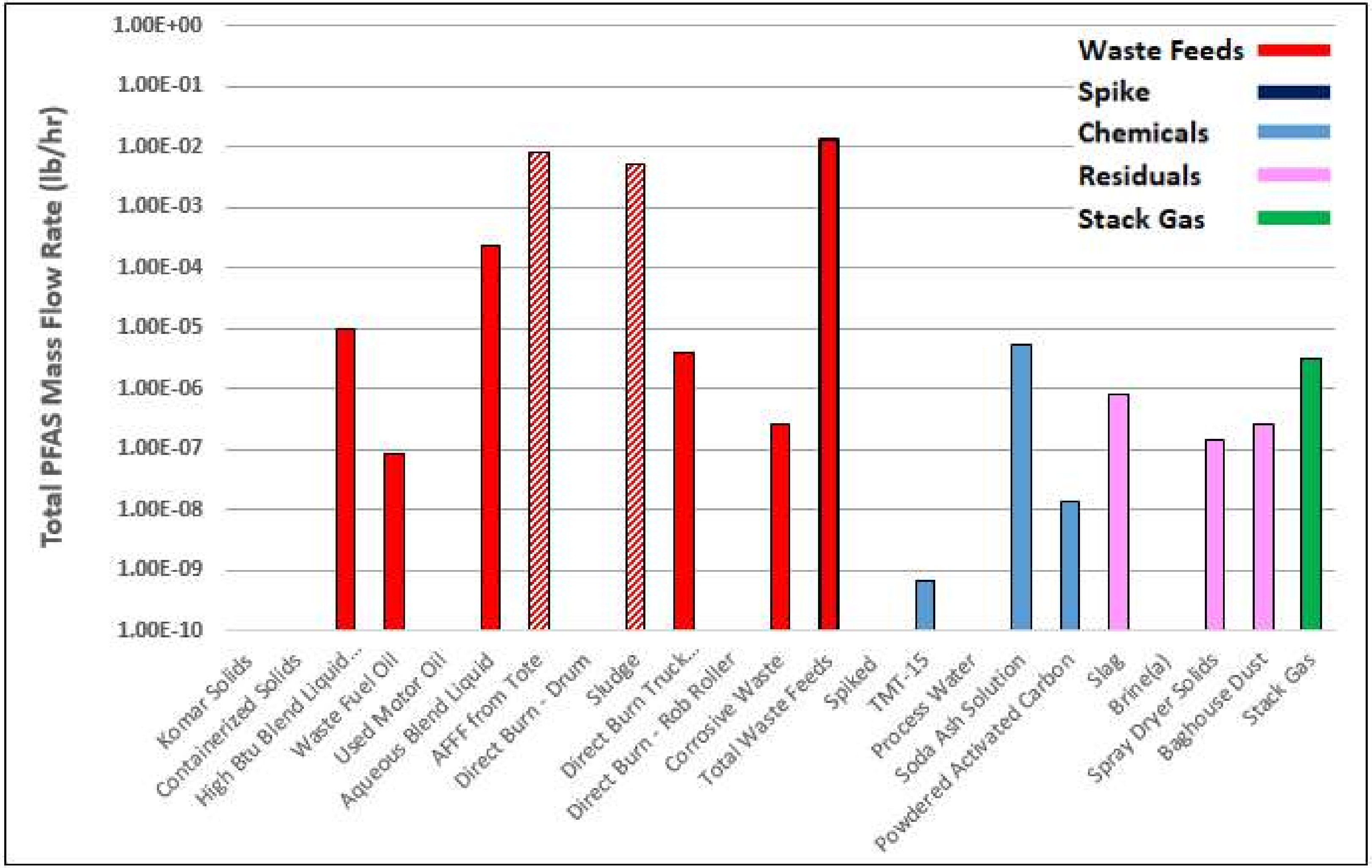
PFAS Mass Balance - Test Condition 2 (PFAS Spiking)



PFAS Mass Balance - Test Condition 3 (AFFF Feed Test)



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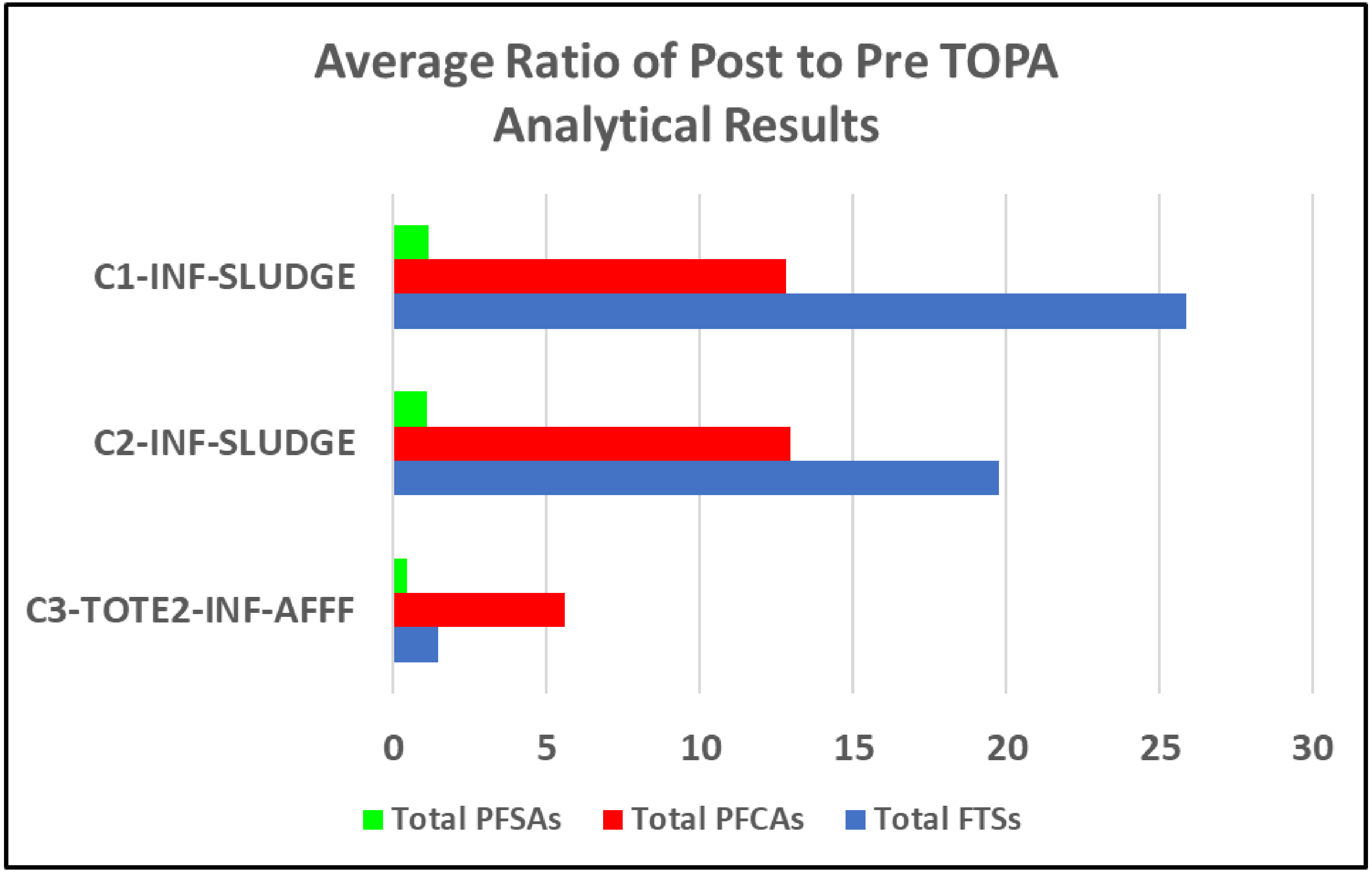
Total Oxidizable Precursor Assay (TOPA)



DRE Results

Compound	Test Condition/ Run No.								
	TC #1 (Baseline)			TC #2 (PFAS Spike)			TC #3 (AFFF Feed)		
	1	2	3	4	5	6	7	8	9
Spiked Compounds									
PFOA	🩷	🔵	🟣	🟢	🟢	🟢	🩷	🩷	🟣
PFHxS	🔵	🔵	🔵	🟢	🟢	🟢	🔵	🩷	🟣
PFOS	🟡	🟡	🔵	🟢	🟢	🟢	🔵	🔵	🩷
HFPO-DA	ND	ND	ND	🟢	🟢	🟢	ND	ND	ND
Native Compounds									
6:2 FTS	🔵	🔵	🔵	🟡	🟡	🟡	🟡	🟡	🟡
8:2 FTS	🔵	🔵	🔵	🟡	🟡	🟡	🟡	🟡	🟡
10:2 FTS	🔵	🔵	🔵	🔵	🔵	🔵	🔵	🔵	🔵

🟢 DRE > 99.9999%
🟡 DRE > 99.999%
🔵 DRE > 99.99%
🩷 DRE > 99.9%
🟣 DRE > 99%

ND - Non-detect in all waste feed streams

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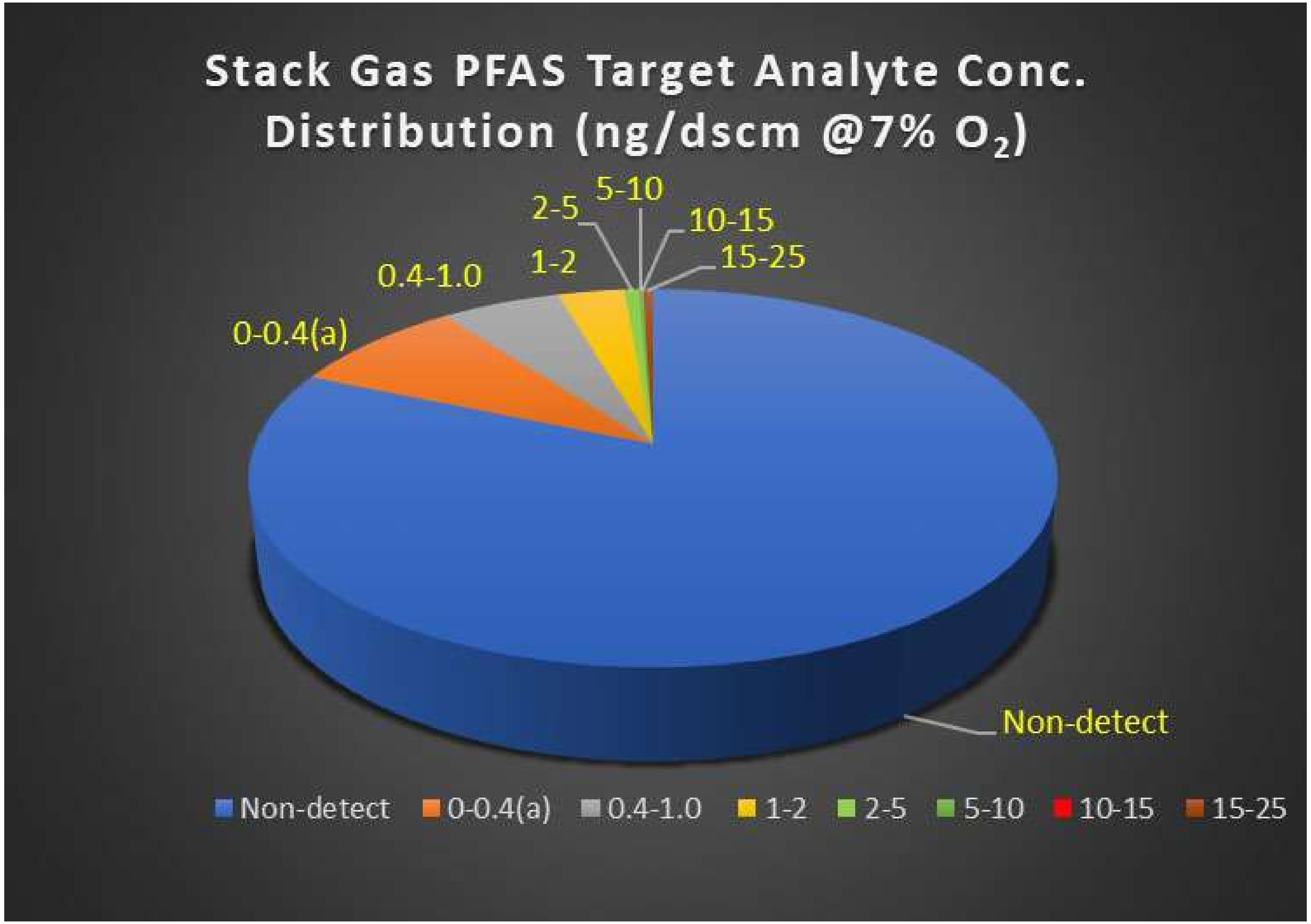
Stack Gas PFAS Compound Concentrations



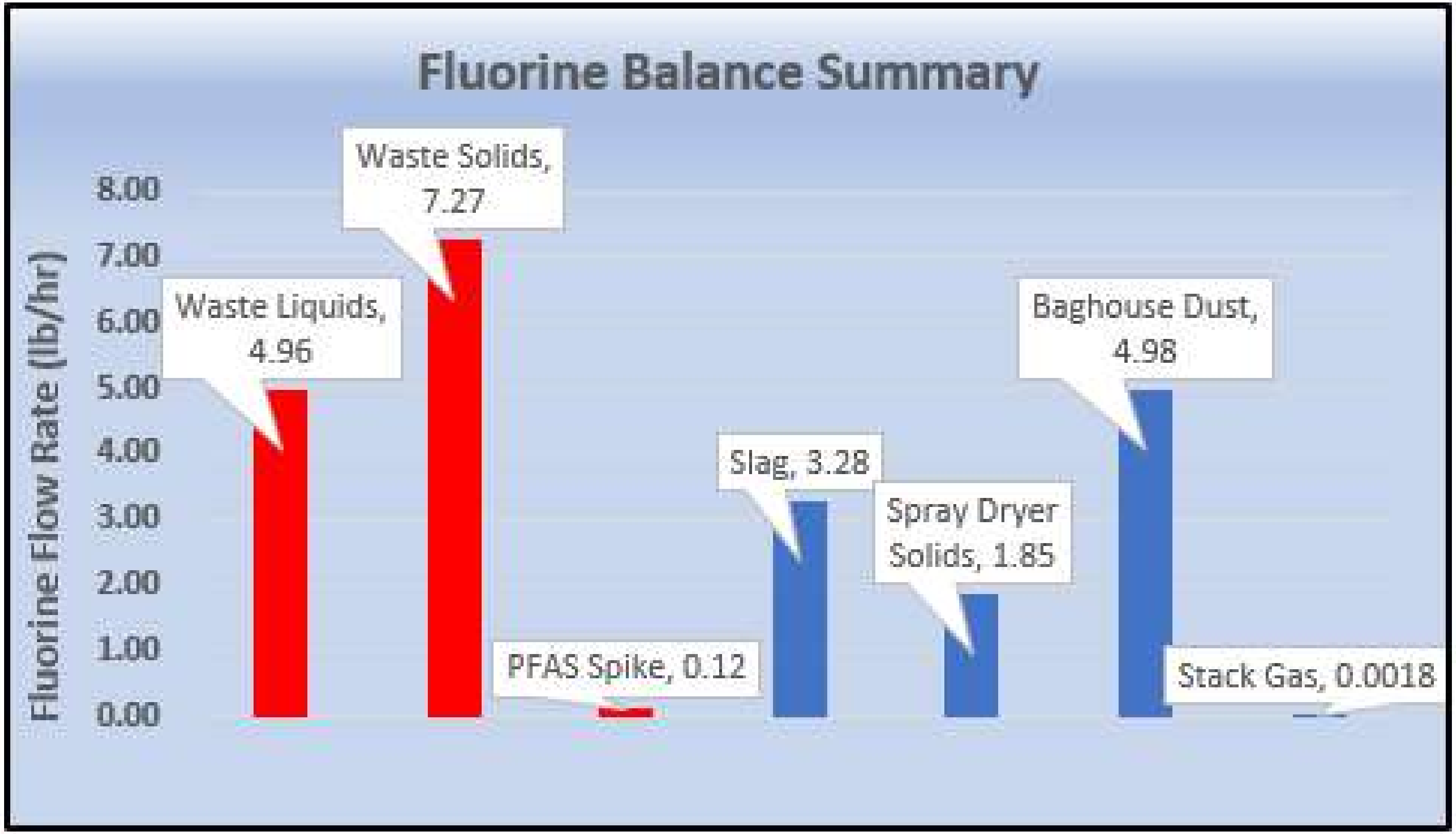
Hydrogen Fluoride Stack Emission Results

Test Condition	Fluoride(a) in Liquid & Sludge Wastes & PFAS Spikes (lb/hr)	HF Stack Gas Conc. (ppmv @7% O_2)	HF(b) Emission Rate (lb/hr)	HF Removal Efficiency (%)
TC #1 (Baseline)	2.58	0.07	0.006	99.77
TC #2 (PFAS Spiking)	2.76	0.10	0.009	99.70
TC #3 (AFFF Feed)	2.76	0.11	0.010	99.67
Average	2.70	0.09	0.008	99.72

(a) Excludes estimated fluorine in solids waste streams.

(b) Clean Air Act Hazardous Air Pollutant Emission Limit for HF = 10 tons/yr (2.28 lb/hr)

Fluorine Balance Summary
February 2022 Test



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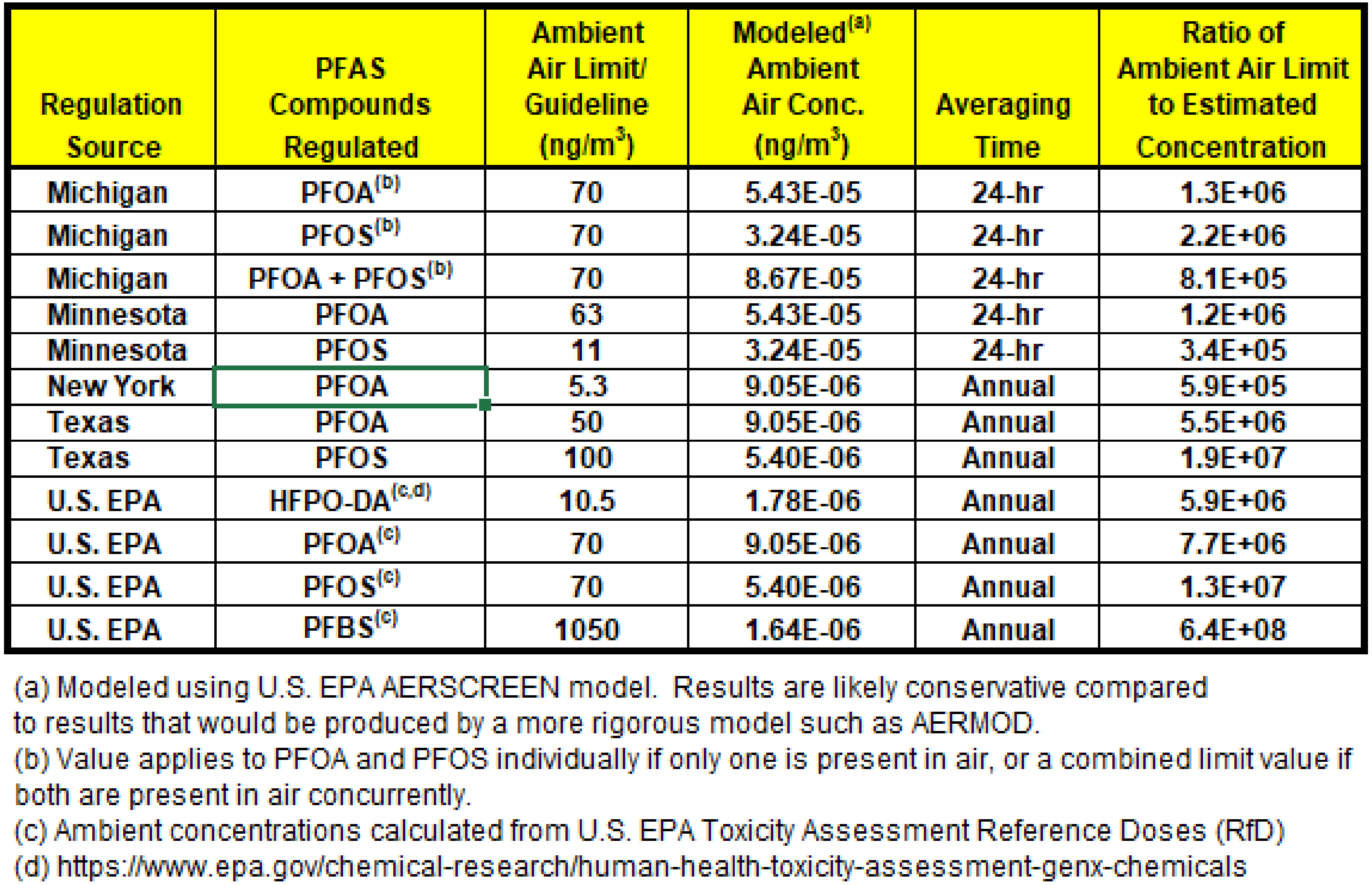
Conclusions - Fluorine Balance

Fluorine mass balance was not a useful tool because:

- Fluorine in target analyte PFAS ~0.04% of total fluorine in waste feeds
- Fluorine in stack gas comprises ~0.02% of the total fluorine in all residual streams
- Fluorine mass balance closure not accurate for individual test runs
- Fluorine mass balance closure improves as multiple runs or days are averaged

Ambient Air Impacts



Regulation Source	PFAS Compounds Regulated	Ambient Air Limit/ Guideline (ng/m^3)	Modeled$^{(a)}$ Ambient Air Conc. (ng/m^3)	Averaging Time	Ratio of Ambient Air Limit to Estimated Concentration
Michigan	PFOA$^{(b)}$	70	5.43E-05	24-hr	1.3E+06
Michigan	PFOS$^{(b)}$	70	3.24E-05	24-hr	2.2E+06
Michigan	PFOA + PFOS$^{(b)}$	70	8.67E-05	24-hr	8.1E+05
Minnesota	PFOA	63	5.43E-05	24-hr	1.2E+06
Minnesota	PFOS	11	3.24E-05	24-hr	3.4E+05
New York	PFOA	5.3	9.05E-06	Annual	5.9E+05
Texas	PFOA	50	9.05E-06	Annual	5.5E+06
Texas	PFOS	100	5.40E-06	Annual	1.9E+07
U.S. EPA	HFPO-DA$^{(c,d)}$	10.5	1.78E-06	Annual	5.9E+06
U.S. EPA	PFOA$^{(c)}$	70	9.05E-06	Annual	7.7E+06
U.S. EPA	PFOS$^{(c)}$	70	5.40E-06	Annual	1.3E+07
U.S. EPA	PFBS$^{(c)}$	1050	1.64E-06	Annual	6.4E+08

(a) Modeled using U.S. EPA AERSCREEN model. Results are likely conservative compared to results that would be produced by a more rigorous model such as AERMOD.
(b) Value applies to PFOA and PFOS individually if only one is present in air, or a combined limit value if both are present in air concurrently.
(c) Ambient concentrations calculated from U.S. EPA Toxicity Assessment Reference Doses (RfD)
(d) https://www.epa.gov/chemical-research/human-health-toxicity-assessment-genx-chemicals

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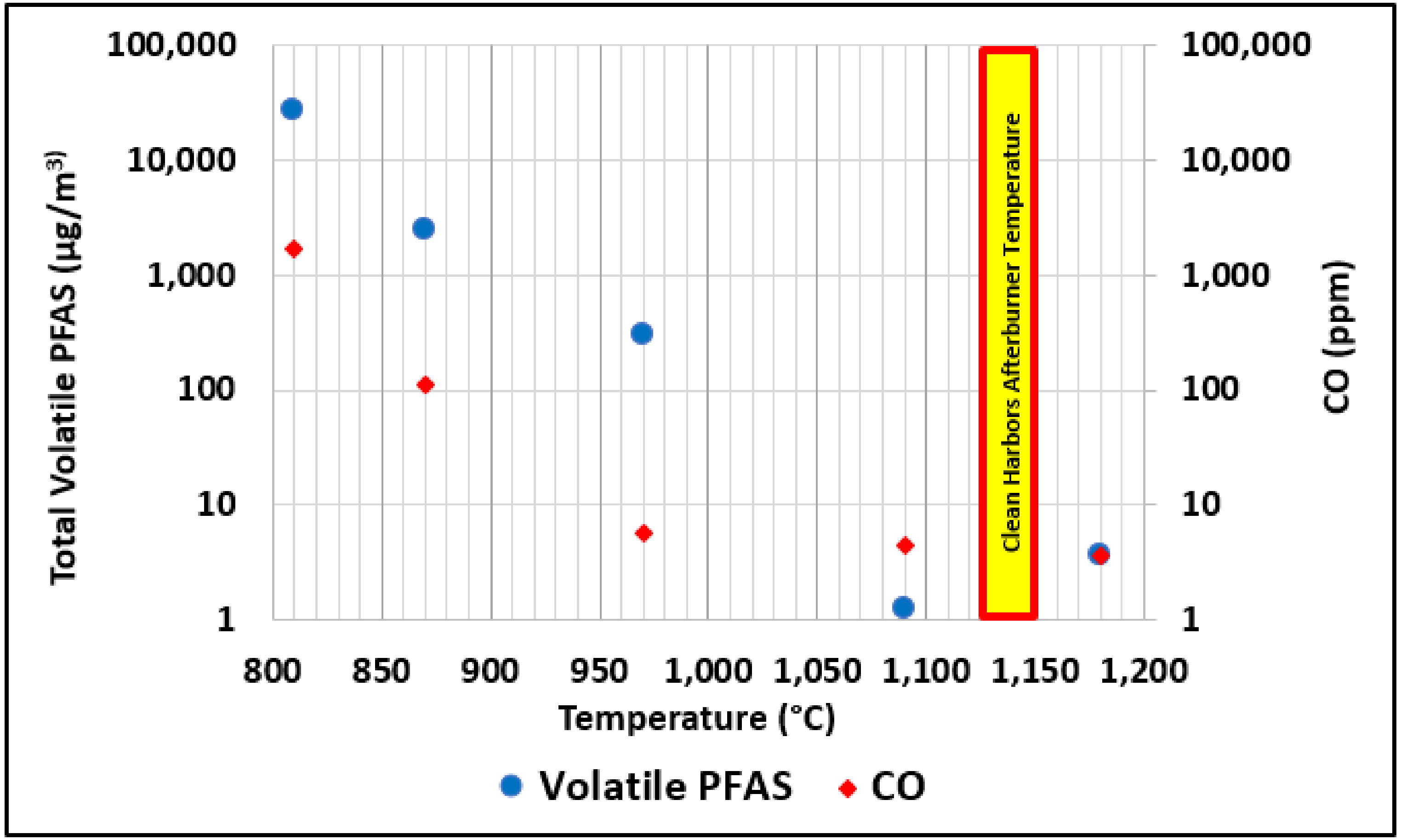
Overlay of Aragonite Afterburner Temperature with EPA Total Volatile PFAS and CO Data(a)



(a) Source: Erin P.Shields et. al, "Pilot-Scale Thermal Destruction of Per- and Polyfluoroalkyl Substances in a Legacy Aqueous Film Forming Foam", ACS ES&T Engineering, May 16, 2023.

Summary of DRE and Emission Results

DRE

- >99.9999% DRE for spiked PFAS compounds during spiking runs
- 99.99-99.999% DRE for FTS compounds, all runs

PFAS Emissions

- 90% of stack gas PFAS analyte concentrations <0.4 ng/dscm @7%O_2 (dioxin/furan TEQ emission standard)

PFAS Modeled Ambient Concentrations

- 2-8 orders of magnitude below existing state and EPA air limits/guidelines based on assuming stack NDs = MDL

HF Emissions

- Average HF emission rate >2 orders of magnitude below Clean Air Act HAP major source threshold (10 tons/yr)

PIC Emissions

- Operating temperature was well above value at which EPA demonstrated PICs were destroyed

Questions?

Contact Information

Mike Crisenbery
Clean Harbors
E-mail: CrisenberyM@CleanHarbors.com
Phone: (513) 383-6441

Bill Troxler
Focus Environmental, Inc.
E-mail: Wltroxler@Focusenv.com
Phone: (865) 368-7130

A&WMA IT3/HWC Conference, September 13-14, 2023, Charlotte, NC

OHIO LUMEX®

WORLDWIDE LEADER
Environmental & Process Monitoring

Metal HAP Emissions
Continuous Monitoring with Sorbent Traps

SBIR Project – Phase I Summary and Phase II Updates

Alexandra Sipershteyn & Jonathan Cross

Presentation Outline

- ▷ **What is SBIR?**
- ▷ **What is the proposed concept?**
- ▷ **What are the research objectives and what’s the timeline?**
- ▷ **What is the performance of this new method so far?**
- ▷ **What are the critical obstacles we’ve found so far and how are we addressing them?**

SBIR Metals Research - Overview

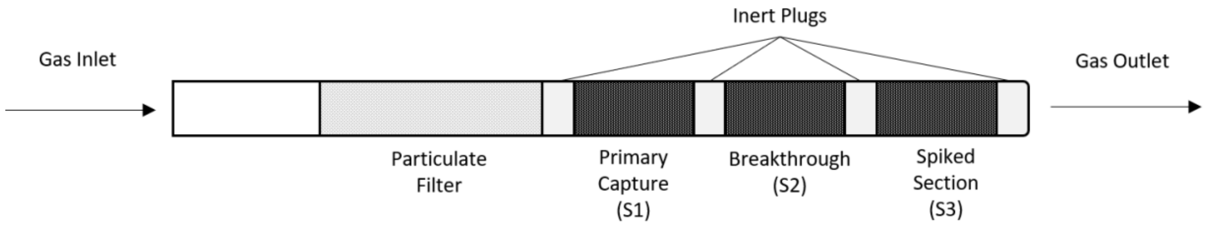
- **Small Business Innovation Research (SBIR)**
    - Foster innovation that aligns with government interests.
    - Several government agencies offer funding through this program, including EPA.

- **EPA SBIR Topic on Metals Analysis**
    - EPA has identified a need for a cost-effective monitoring technology for hazardous air pollutant (HAP) metals.
    - Current approach relies on periodic Method 29 analysis.
    - Sources of interest include hazardous waste combustors, secondary metal smelting, iron and steel, metal scrap recycling, and other sources.

AMERICA'S SEED FUND
SBIR

POWERED BY
EPA

SBIR Research – Proposed Concept



- **Metal HAP Sorbent Trap**
  - Repetitive in-stack sampling and periodic analysis of time-integrated samples collected over several days. Modeled after PS 12B for mercury measurement.
- **Method Features**
  - Sampling through a filter and into a 3-section sorbent trap.
  - Target metals include Sb, As, Be, Cd, Cr, Co, Cu, Pb, Mn, Ni, Se, and Hg Laboratory analysis by ICP-MS
- **Performance Targets and Quality Controls**
  - Pair agreement, spike recovery, and breakthrough
  - Low background concentrations

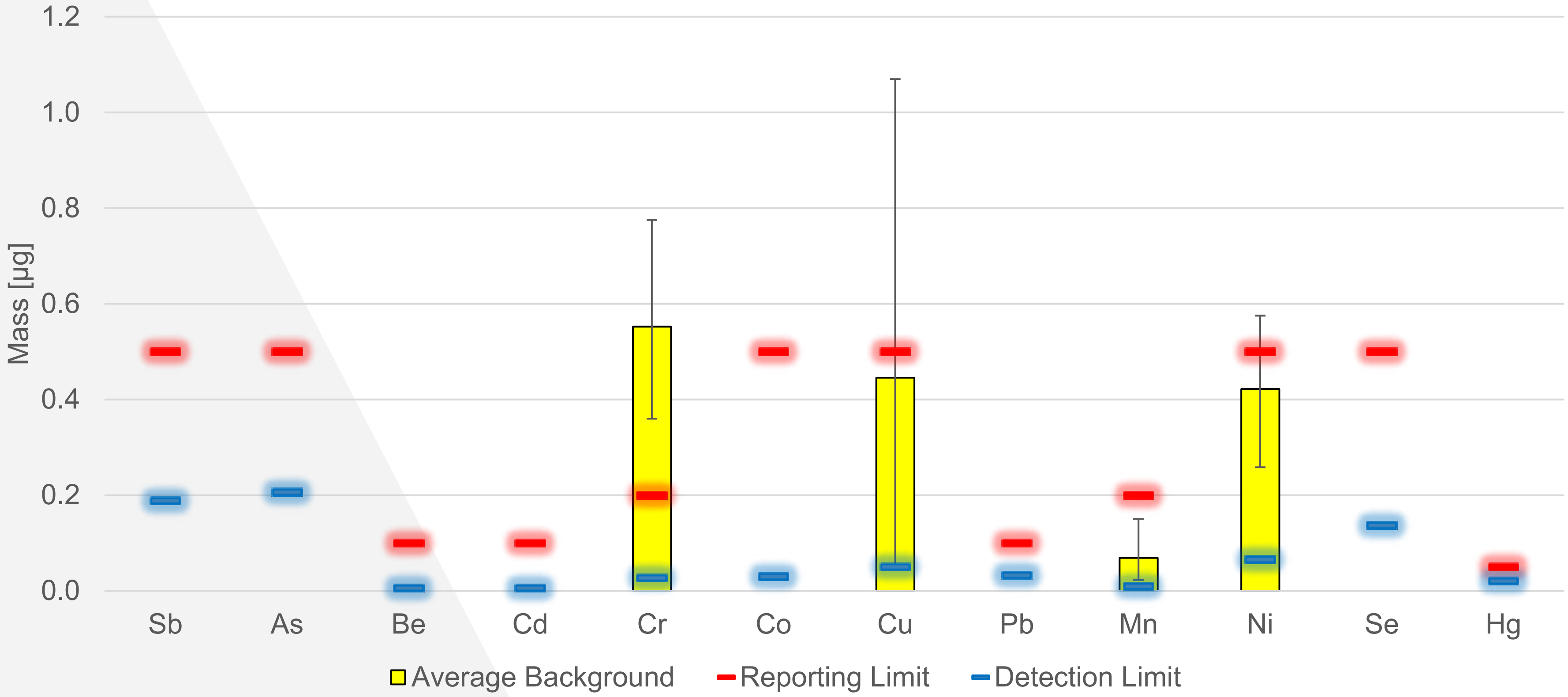
SBIR Research Objectives and Timeline

- **Phase I – Completed in June 2022**
  - Objective: Basic proof of concept
  - Synthesized, treated, and tested three sorbent materials
  - Measured background metals, direct spike recovery, and simulated stack gas spike recovery
- **Phase II – October 2022 to October 2024**
  - Objective: Full validation of the method and commercialization
  - Improve method sensitivity and background levels
  - Scale up production
  - Add and test particulate filter with long-duration automated isokinetic sampling during field tests
  - Perform modified Method 301 against Method 29
- **Phase II Supplement – Through October 2025**
  - Objective: Reduce sampling duration to create true alternative to Method 29
  - Need incredible material purity for this to work

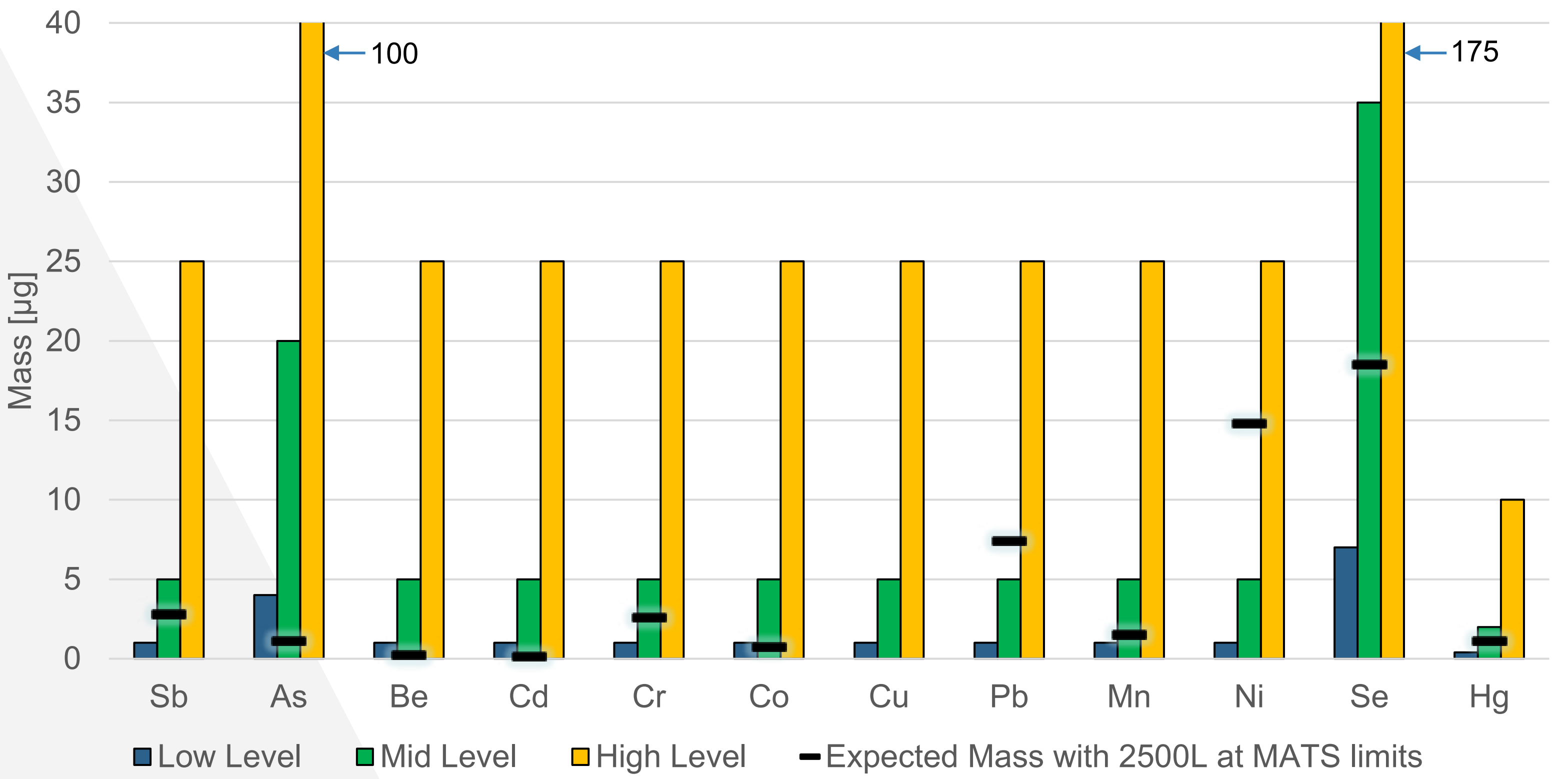
SBIR Phase I – Synthesis

- **Synthesis**
  - Three materials were synthesized/treated
    - Sorbent #1 performed OK but we had less control over quality
    - Sorbent #2 had great physical qualities and good performance
    - Sorbent #3 has the most potential for enhancement but is difficult to scale up

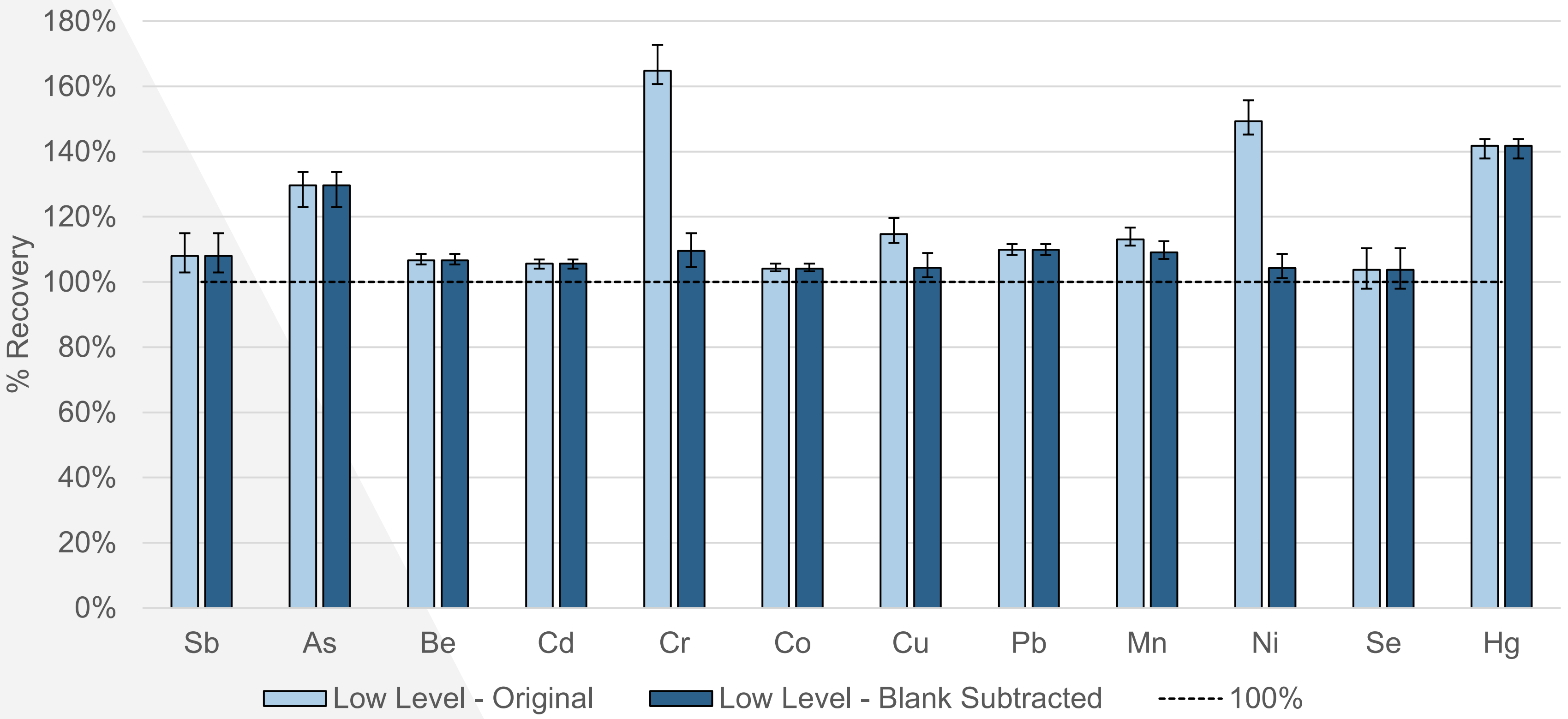
Blank Background Metal Mass vs. RL and DL



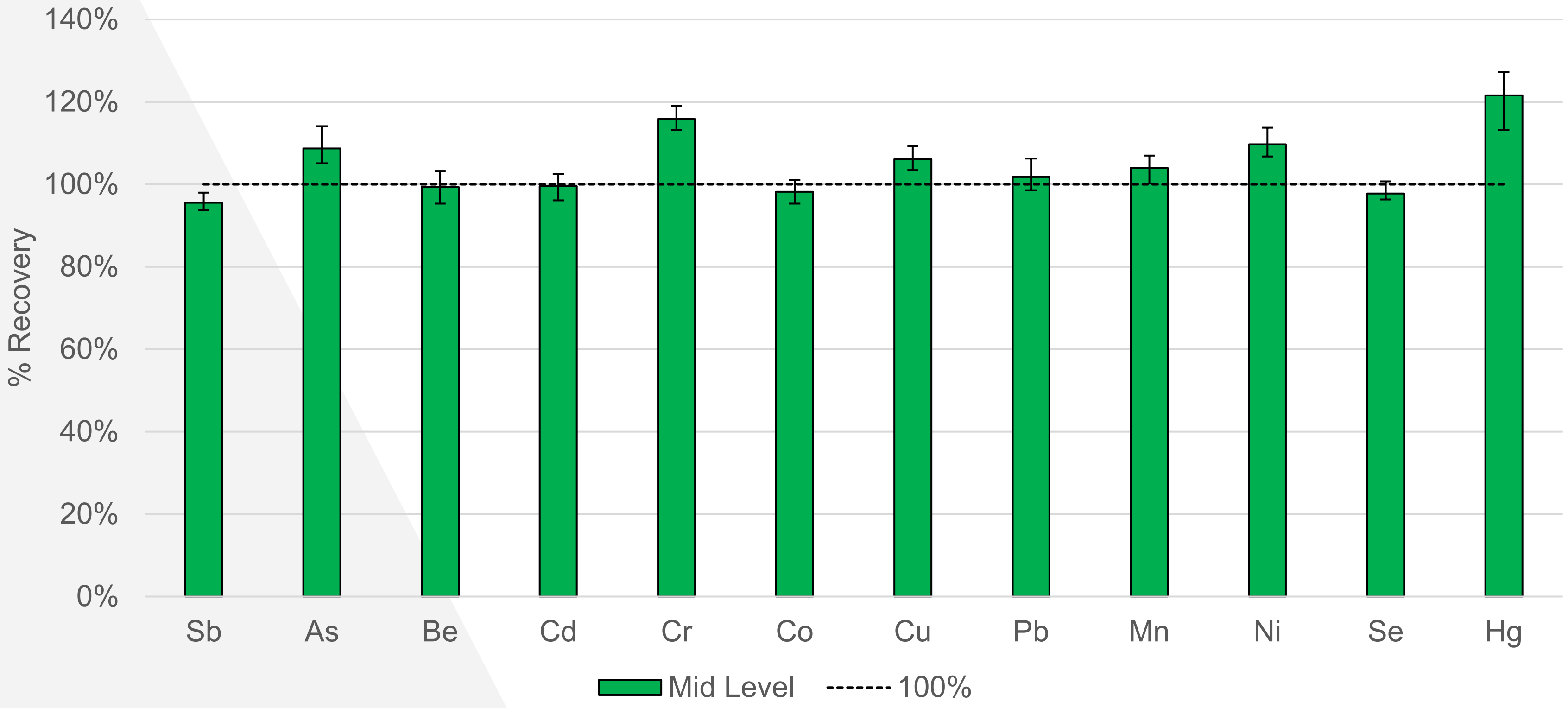
Spike Masses



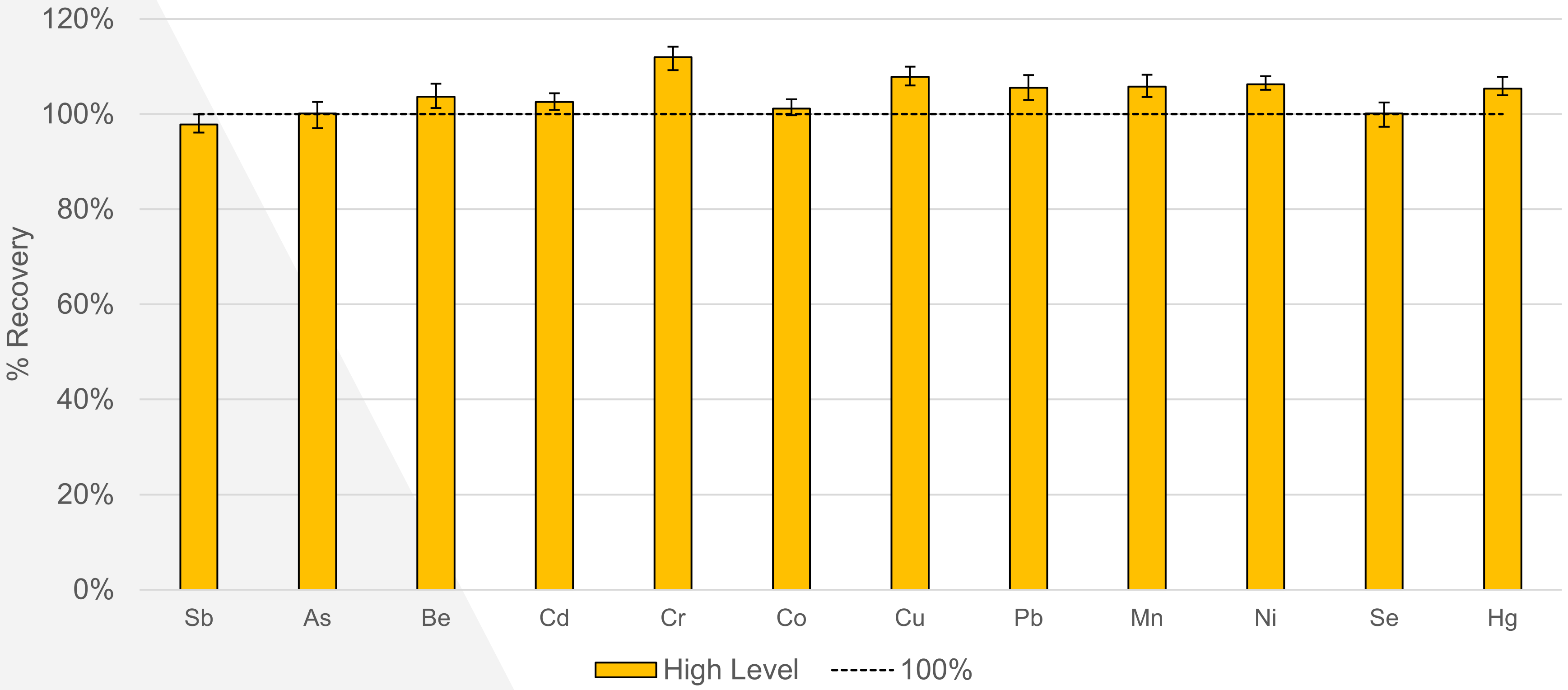
Average Direct Spike Recovery - Low



Average Direct Spike Recovery - Mid



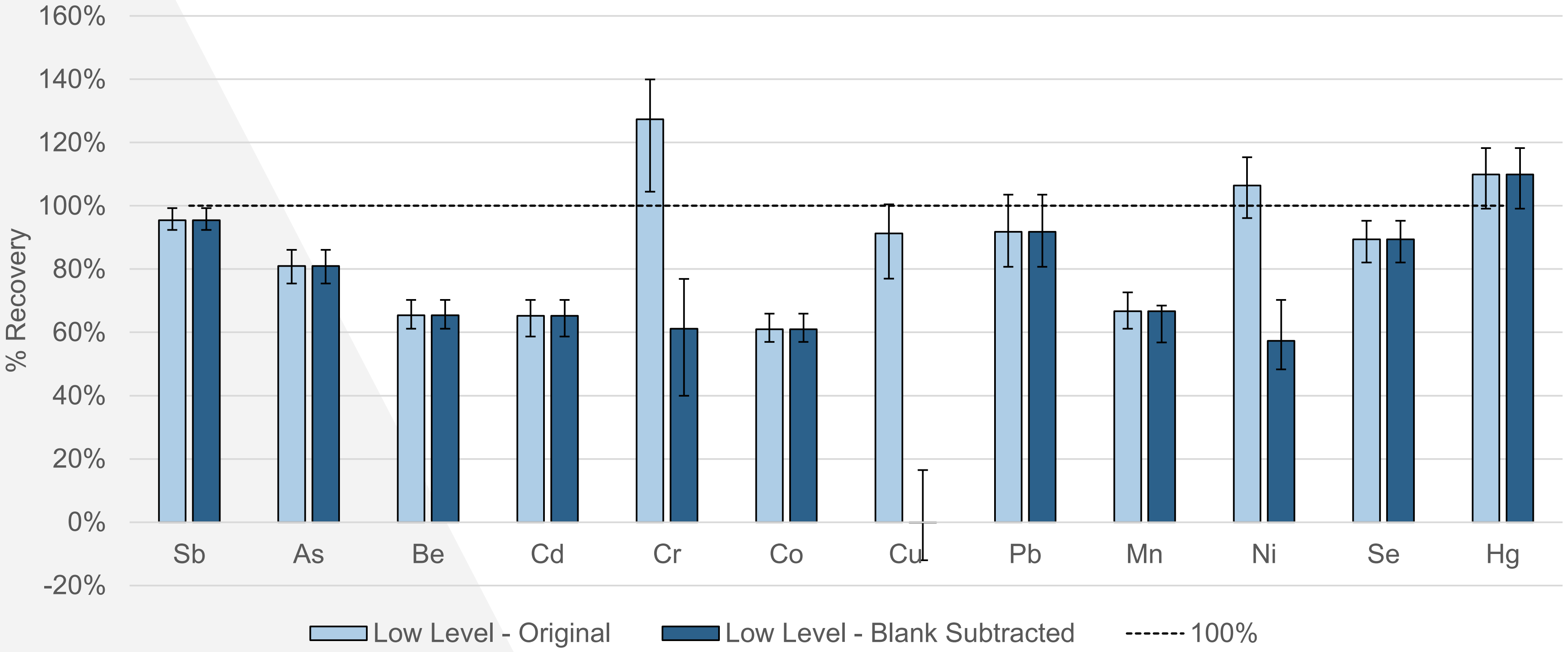
Average Direct Spike Recovery - High



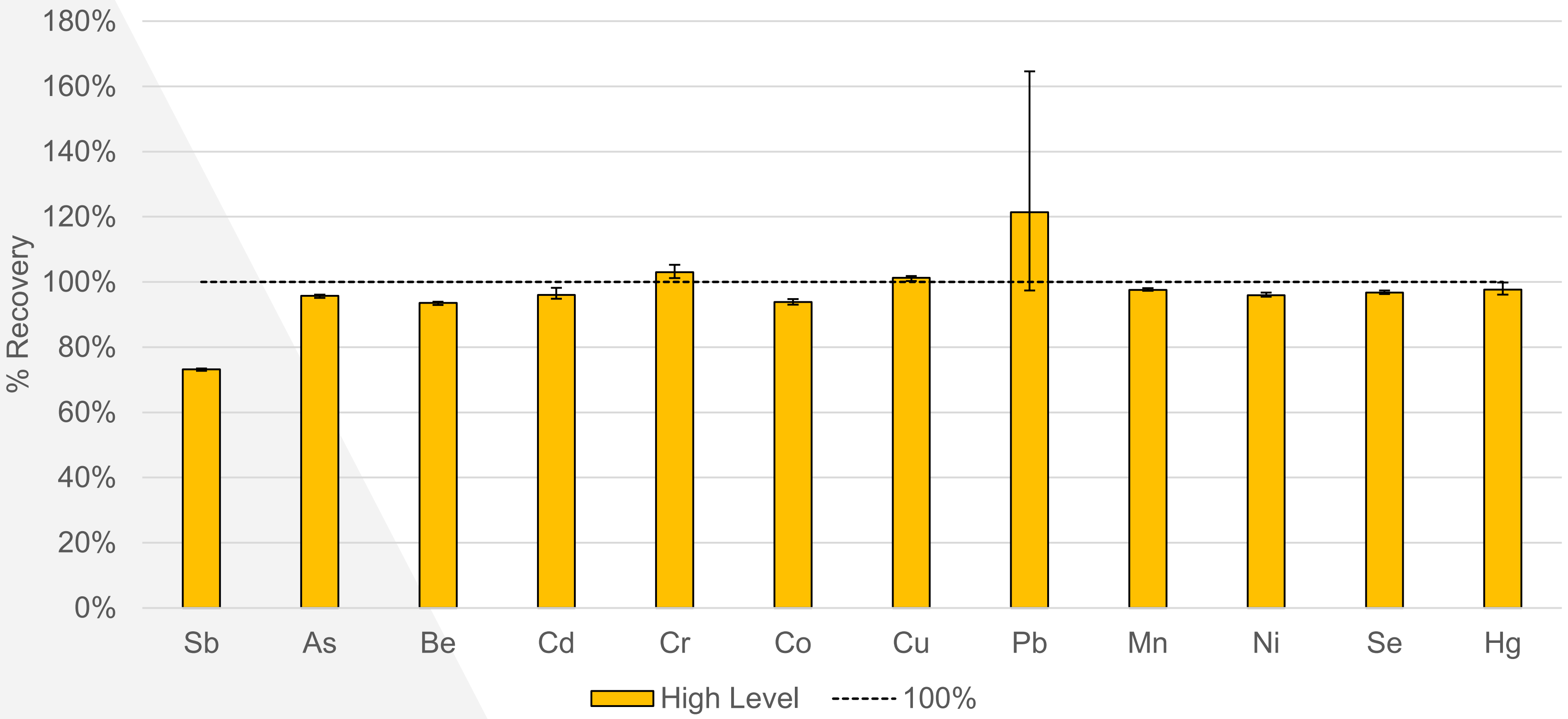
SBIR Phase I – Simulated Stack Gas Spike Recovery

- **Simulated Stack Gas System at Ohio Lumex**
  - 10% moisture, 160ppm SO2, 120°C, 7 days of sampling
- **Spike Recoveries**
  - Sorbent traps were fully assembled with three sections, the third section being spiked at one of two levels (low and high).
  - Three traps at each level, for each material
- **Limitations**
  - Sorbent traps were fully assembled with three sections, the third section being spiked at one of two levels (low and high).
  - Metals were not introduced – no effective way to introduce metals in test system (other than mercury)
  - Real sample matrices may be more complex
  - Actual field testing required – to be done in Phase II

Average Simulated Stack Gas Spike Recovery - Low



Average Simulated Stack Gas Spike Recovery - High



Concentration Limits

Metal	MATS [$\mu g/m^3$]	Hazardous Waste Combusters - Existing Sources [$\mu g/m^3$]	Hazardous Waste Combusters - New Sources [$\mu g/m^3$]	Municipal Waste Incinerators – prior to 9/1994 [$\mu g/m^3$]	Municipal Waste Incinerators – 9/1994 – 12/2005 [$\mu g/m^3$]	Municipal Waste Incinerators – after 12/2005 [$\mu g/m^3$]
Sb	1.12					
As	0.44	92 [1] (a)(4)	23 [1] (b)(4)			
Be	0.09	92 [1] (a)(4)	23 [1] (b)(4)			
Cd	0.06	230 [2] (a)(3)	10 [2] (b)(3)	35	20	10
Cr	1.04	92 [1] (a)(4)	23 [1] (b)(4)			
Co	0.3					
Pb	2.96	230 [2] (a)(4)	10 [2] (b)(3)	400	200	140
Mn	0.59					
Ni	5.92					
Se	7.4					
Hg	0.44	130 (a)(2)	8.1 (b)(2)	50	50	50

1 - Combined concentration of As, Be, and Cr, corrected to 7% O2

2 - Combined concentration of Cd and Pb, corrected to 7% O2

[40 CFR 63.1219(a)(4)]
[40 CFR 63.1219(a)(3)]
[40 CFR 63.1219(a)(2)]

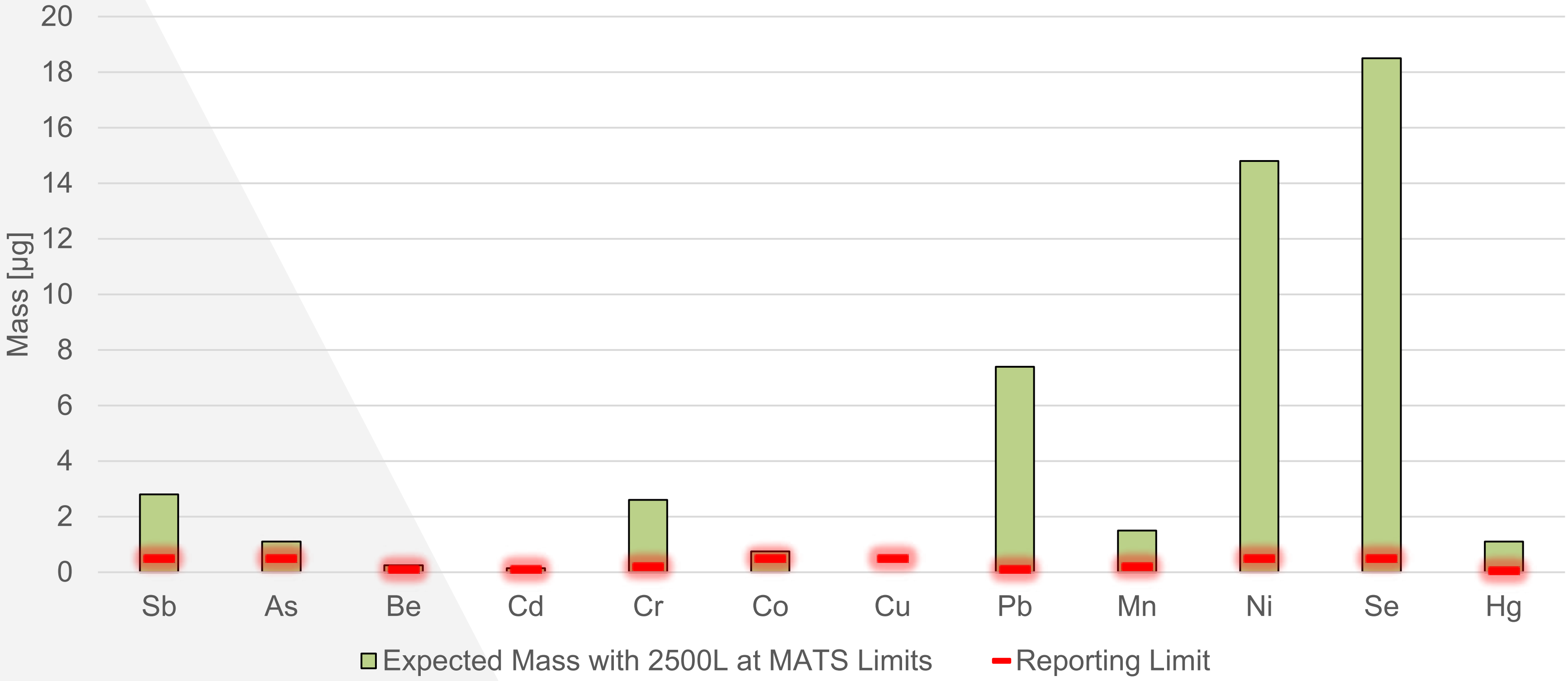
[40 CFR 63.1219(b)(4)]
[40 CFR 63.1219(b)(3)]
[40 CFR 63.1219(b)(2)]

[40 CFR Part 60 Subpart Cb]

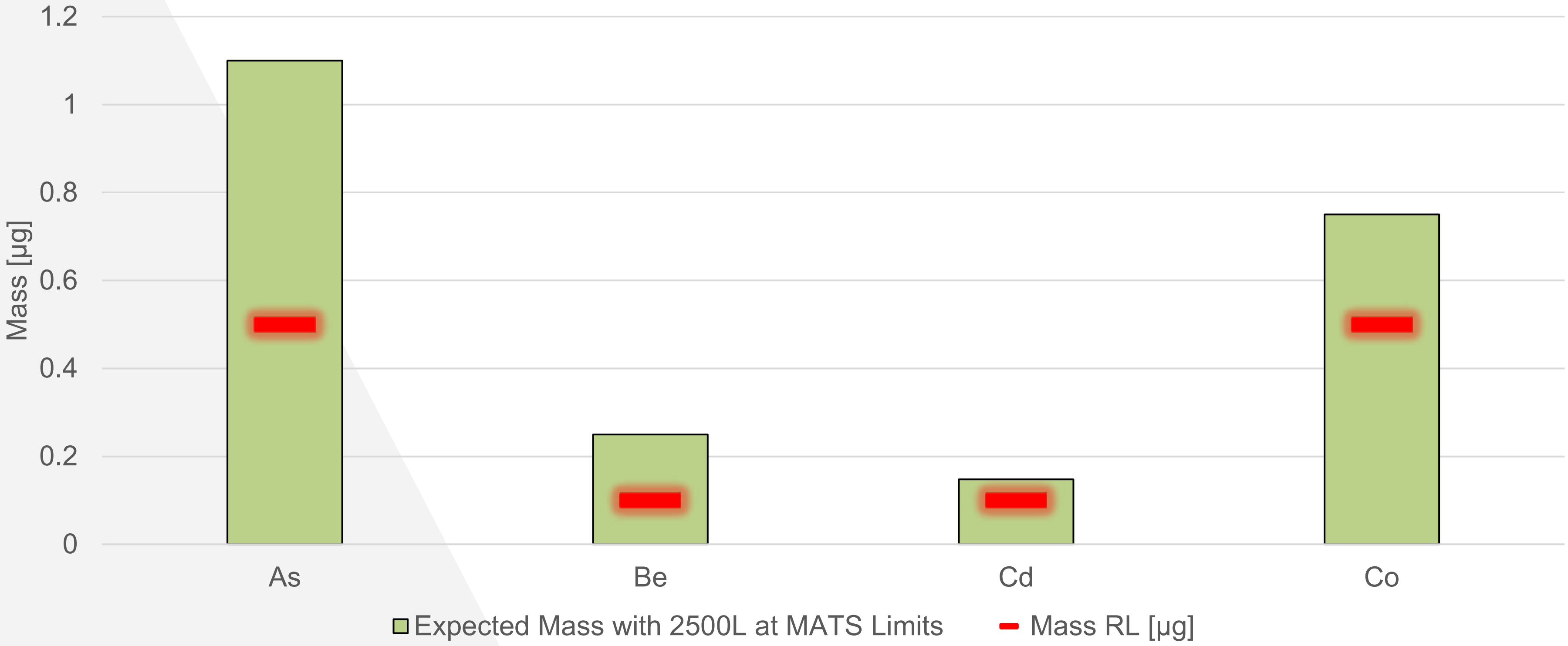
[40 CFR Part 60 Subpart Eb]

[40 CFR Part 60 Subpart Eb]

Method Sensitivity – All Metals



Method Sensitivity - Challenging Metals



Conclusions and Phase II Objectives

- **Material background concentrations must be reduced**
  - Significant influence from material background, especially chromium
  - Material production must be repeatable, scalable, and produce material with extremely low background metals.
- **Laboratory environment must be extremely clean**
  - Several analysis results indicated samples were contaminated during material production, sample preparation, digestion, and/or analysis.
  - Ohio Lumex is building a laboratory expansion designed specifically to work with trace metals, including positive pressure rooms, HEPA air filtration, and zero metallic surfaces.
- **Sensitivity must be improved**
  - Current sensitivity is barely sufficient for 2500L of sample gas at MATS limits. In order to measure lower concentrations or reduce the sample volume, sensitivity must be improved.
- **Field testing must be performed to test real sampling conditions**
  - After all other improvements are made, a modified Method 301 will be performed against Method 29.
  - An optional third year of research will be performed to develop a 30B analogue for short-term testing as a direct alternative to Method 29, if sensitivity is sufficiently improved.

QUESTIONS???

OTM-45 Unique Sources and Lessons Learned

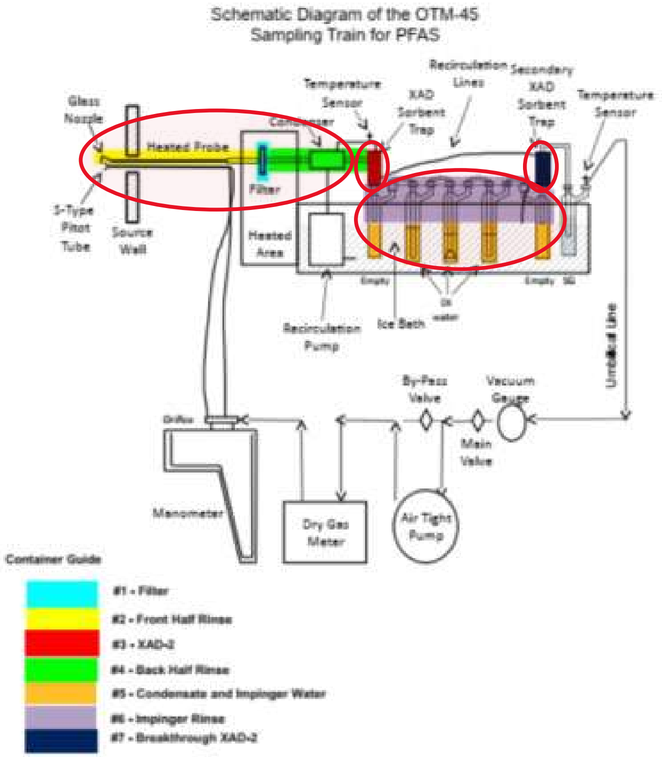
Jesse Rocha
Regional Manager
Alliance
TECHNICAL GROUP

Why are you testing and how will data be used?

- Investigative
- Research and Development
- Compliance
- For the fun of it!

Typical OTM-45 Tests

- Stack
  - Procedure to promote consistency in testing.
  - Intended for trace levels but can be modified for higher concentrations
  - Isokinetic Sampling Train
  - 7 field fractions
  - Reported as 4 analytical fractions
- Ambient
  - Modified to FH and XAD, only



Good Practices for the Isokinetic Sample Train

- Try to use as little PTFE as possible
- Glass frits for the filter assemblies
- Parafilm instead of Teflon tape
- Prep o-rings, brushes, funnels with the same cleaning procedure as the filter assemblies, condensors, impingers, and connecting glassware
- Dedicated recovery glassware for each sampling location
- Rinse the sample probe before the first use and heat to a higher-than-expected temperature (we use 350°F for 2 hours)

But, what about unique or atypical source locations?

Landfill Leachate Evaporator Stack

- Investigative test
  - Test ports did not meet Method 1 criteria
  - Flue Gas Temperature of ~220°F and saturated moisture
  - Discussed with the laboratory and determined sampling should be limited to a condensate collection volume (6 liters) as opposed to a dry gas volume target.
- Test Results
  - Low flow profile (~11 fps)
  - Single point sampling (non-isokinetic) to collect approximately 6 liters of condensate
  - 99.8% Moisture
  - 1-hr test collected ~0.6-0.7 dscf of flue gas
  - *Observation:* Higher levels of PFAS in the FH fraction

Landfill Leachate Evaporator Stack

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Pyrolysis Unit

- Investigative Test
  - Biosolids treatment
  - Screening test to determine levels of PFAS before the pollution control device
  - Test location was the exit of reaction chamber (inlet to pollution control device)
  - 4” pipe with a single test port (did not meet EPA Method 1 criteria)
  - Previous flow screening determined that the sources had turbulent flow; used EPA GD-008 to estimate flow rate
  - Expect high particulate loading
- Test Results
  - 700°F flue gas temperature
  - Single point sampling (constant rate @ 0.5 cfm)
  - High Particulate Matter (required a filter changeout during the test)
  - *Observation:* HFPO-DA hits on BH and Impinger fractions

Carbon Regeneration

- Investigative Test
  - Multiple Hearth Exhaust to Afterburner
  - Refractory-lined square duct with single test 4” test port (did not meet EPA Method 1 criteria)
  - Concern on the effects of the laboratory extraction procedure because of the particulate matter makeup (activated carbon)
- Test Results
  - 600°F flue gas temperature
  - Low flow profile (~15 fps)
  - Used cyclone knockout due to high particulate matter
  - Isokinetic sample: 4 points across a single plane/test port
  - *Awaiting PFAS lab results*

Thermal Desorption Unit

- Pilot Study
  - Thermal Desorption Exhaust
  - Batch process
  - Small 1” Exhaust Pipe
  - Low Volume Exhaust (~17-18 cf/hour maximum)

Planned Approach

- Modified test methods:
  - OTM-45 – using a low-volume sampling system (non-isokinetic)
  - Hydrogen Fluoride collected and recovered in NaOH impingers prior to the OTM-50 canister
  - Total Fluoride collected in a separate canister
- 4-8 hour test runs (dependent on exhaust volume)

(Testing on hold for approved funding)

Other Inquiries for PFAS Sampling

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- Semiconductor Facilities
  - Fabrication
    - Chemical used to manufacture semiconductor and related devices (photoresist liquids, etch chamber gases, containers, and high purity water) could contain PFAS
  - Room Exhaust Ducts
    - Predominately room air
  - Some discussed methods for sampling:
    - Titanium probe to Modified OTM-45 sample train
    - OTM-50

Laboratory Notifications to Think About

- Moisture Weight Gain on XAD traps
  - Higher moistures can have an effect on surrogate recoveries.
  - Target is 80% MeOH/20% H_20 in the final extraction.
  - XAD weight gains alert the lab in case they need to handle the extraction process differently.
  - Can become a time factor to make sure the H_20 fraction is correct.
  - Annotate the weight gains on the COCs.
- High Carbon Particulate Loading
  - May need to consider a carbon disulfide extraction.
  - Method 18 carbon sorbent trap solvent of choice is carbon disulfide to strip the VOCs off.

QA Samples

- OTM-45 QA Samples
  - Sampling Train Field Blank
    - **One per test series –** multiple conditions require multiple STFB’s
    - Full sample train with previously used glassware
    - Test location; leak checked; heated and held for the same duration as the test run
  - Sampling Train Proof Blank
    - **One per test series –** multiple conditions require multiple STPB’s
    - Unused glassware without media (i.e., filter, XADs, DI Water)
    - Test location; leak checked; heated and held for the same duration as the test run
  - Field Sample Media Blank
    - Trip Blank, Reagent Blank

QA Samples

- Samples = Data = additional cost ($$).
- Because of this, some clients are electing for a scaled down version of QA Samples such as Trip Blanks, Reagent Blanks, and a single STPB.

Conclusion

- Sampling unique sources requires a clear understanding of how the data should be used and interpreted.
  - Determine the objectives
  - Involve your subcontracted laboratory in early communications for unusual sources
  - Document and explain normal procedures and any modifications to these procedures that may have been used for the test
  - Collect the level of QA samples that meet the needs for your test objectives

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- Acknowledgements
  - Dr. William Anderson, Eurofins TestAmerica

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THANK YOU

Jesse Rocha – Regional Manager
Alliance Technical Group
jesse.rocha@AllianceTG.com

Air and Waste Management Association IT3

International Conference on Thermal Treatment Technologies & Hazardous Waste Combustors

A Survey of EPA Sampling and Analysis Strategies for the Characterization of PFAS Off-Gas from Thermal Treatment Systems

September 14, 2023 – Charlotte, NC

Co Authors:
William C. Anderson, Ph.D.
Courtney M. Adkins

eurofins | Environment Testing

Statement the Problem

New Sampling and Analysis Methods are Needed to Complete the Spectrum of PFAS Characterization

OTM-45	OTM-55	OTM-50
Semi-Volatile	Semi-Volatile	Volatile
Polar	Non-Polar	Non-Polar

Statement of the Problem, Continued

The objective is to identify what is formed when PFAS is burned under the various Incineration Conditions applied to Wastes today

- Hazardous Waste Incinerators
- Municipal Waste Incinerators
- Sewage Sludge Incinerators
- Medical Waste Incinerators
- Thermal Oxidizers

Some Chemistry to Help Our Perspective

$$CH_4 + 2O_2 \xrightarrow{\Delta} CO_2 + 2H_2O$$

Some Chemistry to Help Our Perspective

$$CH_4 + 2O_2 \xrightarrow{\Delta} CO_2 + 2H_2O$$

$$CF_4 + O_2 \xrightarrow{\Delta} CO_2 + H_2O + HF$$

Some Chemistry to Help Our Perspective

$$CH_4 + 2O_2 \xrightarrow{\Delta} CO_2 + 2H_2O$$

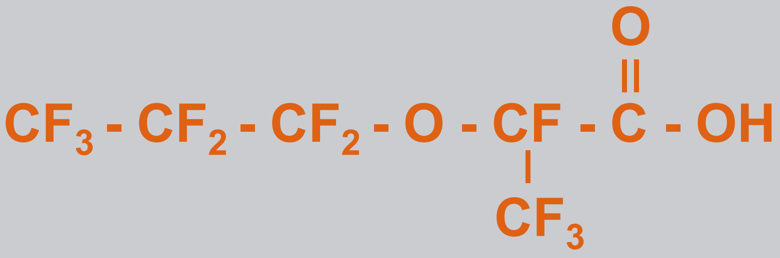
$$CF_4 + O_2 \xrightarrow{\Delta} CO_2 + H_2O + HF$$

$$CF_4 + 2CH_4 + 4O_2 \xrightarrow{\Delta} 3CO_2 + 2H_2O + 4HF$$

Some Chemistry to Help Our Perspective

Thermal Destruction of GenX

(2,3,3,3-Tetrafluoro-2(1,1,2,2,3,3,3-heptafluoroproproxy) propanoic acid)



$$CF_3 - CF_2 - CF_2 - O - \underset{\displaystyle CF_3}{\underset{|}{CF}} - \overset{\displaystyle O}{\overset{||}{C}} - OH$$

$$C_6F_{11}O_3H + 3CH_4 + 8O_2 \xrightarrow{\Delta} 9CO_2 + H_2O + 11HF$$

Some Chemistry to Help Our Perspective

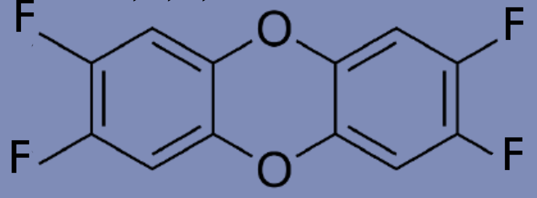
- Not Every Compound Burns So Cleanly
- Thermal Destruction of Hexafluoroethane
- Free Radical Formation

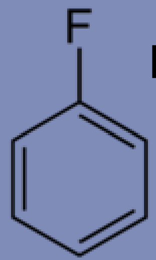
$$CF_3 - CF_3 \xrightarrow{\Delta} CF_3\bullet \quad \bullet CF_3$$

Products of Incomplete Combustion (PICs)

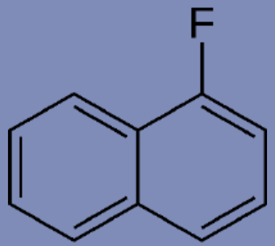
These are compounds that are formed when combustion reactions aren't completed stoichiometrically, or post-combustion products are formed.

2,3,7,8-TFDD

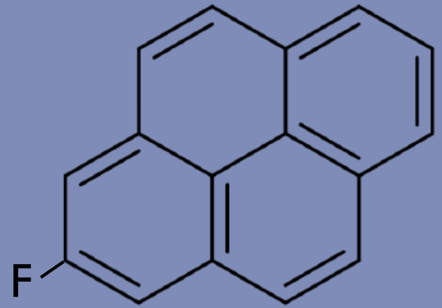




Fluorobenzene

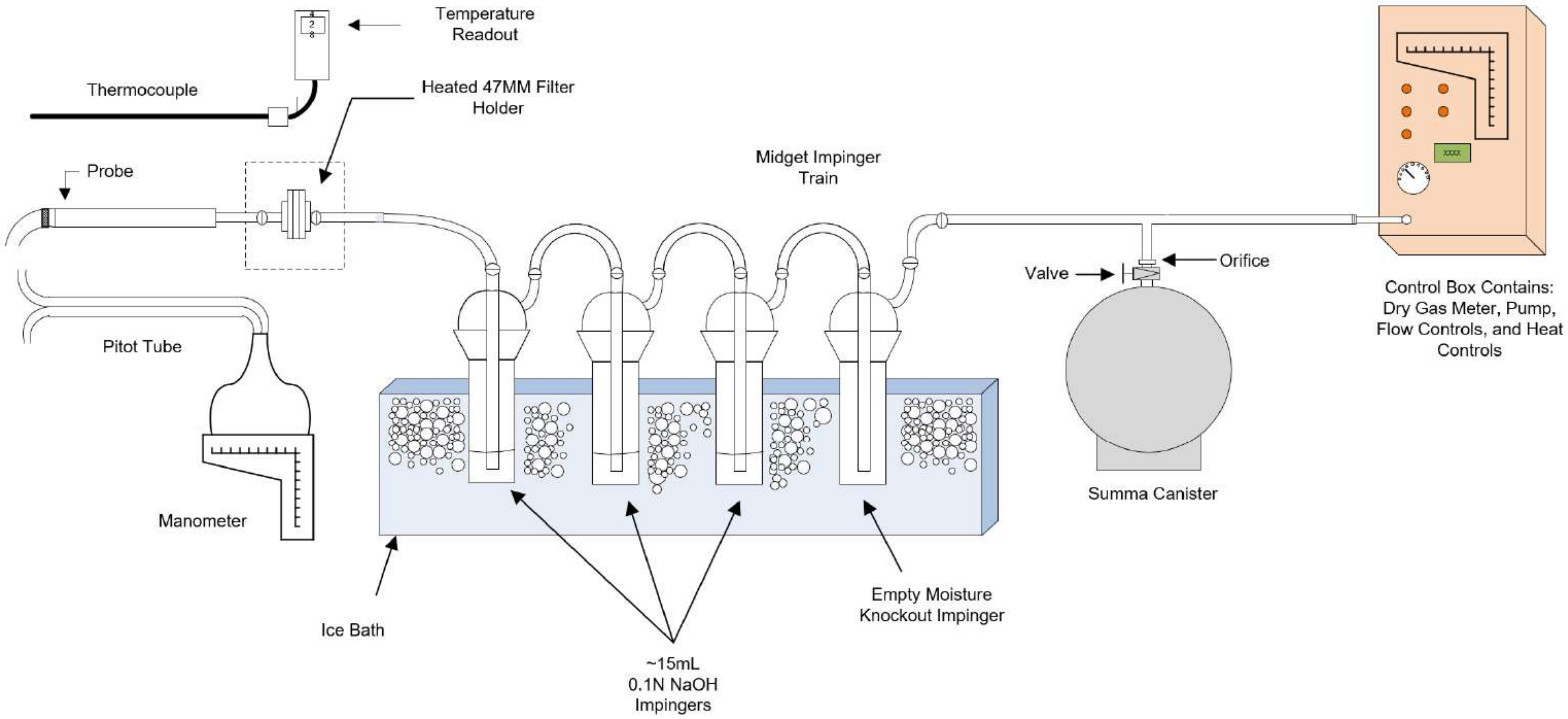


1-Fluoronaphthalene



1-Fluoropyrene

OTM-50 Sampling and Analysis for Volatile PFAS Compounds in Source Air



OTM-50 Target Analyte List

Carbon	Target	CAS No.
C1	Tetraflouromethane	75-73-0
	Chlorotrifluoromethane	75-72-9
	Chlorodifluoromethane	75-45-6
	Trichlorofluoromethane	75-69-4
	Fluoroform	75-46-7
	Difluoromethane	75-10-5
	Fluoromethane	593-53-3
C2	Hexafluoroethane	76-16-4
	Tetraflouroethylene	116-14-3
	Pentafluoroethane	354-33-6
	1,1,1,2-Tetrafluoroethane	811-97-2
	1,1,1- Trifluoroethane	420-46-2
C3	Hexafluoropropylene	116-15-4
	Hexafluoropropene oxide	428-59-1
	Octafluoropropane	76-19-7
	1H-Heptafluoropropane	2252-84-8
C4	Perfluorobutane	355-25-9
	1H-Nonafluorobutane	375-17-7
	Octafluorocyclobutane	115-25-3

Carbon	Target	CAS No.
C5	Dodecafluoro-n-pentane	678-26-2
	1H-Perfluoropentane E-1	375-61-1
	Octafluorocyclopentane	559-40-0
C6	Tetradecafluorohexane	355-42-0
	1H-Perfluorohexane	355-37-3
C7	Hexadecafluoroheptane	335-57-9
	1H-Perfluoroheptane	375-83-7
C8	Perfluorooctane	307-34-6
	1-H-Perfluorooctane E-2	335-65-9

Tentatively Identified Compounds

- Identifies Compounds beyond the target analyte list
- Utilizes a GC/MS Software of Over 250,000 Compounds
- Estimates a concentration for Each Additional Peak
- Can be used as a General Survey Tool For the Evaluation of PICs

The ORD TIC Guidelines

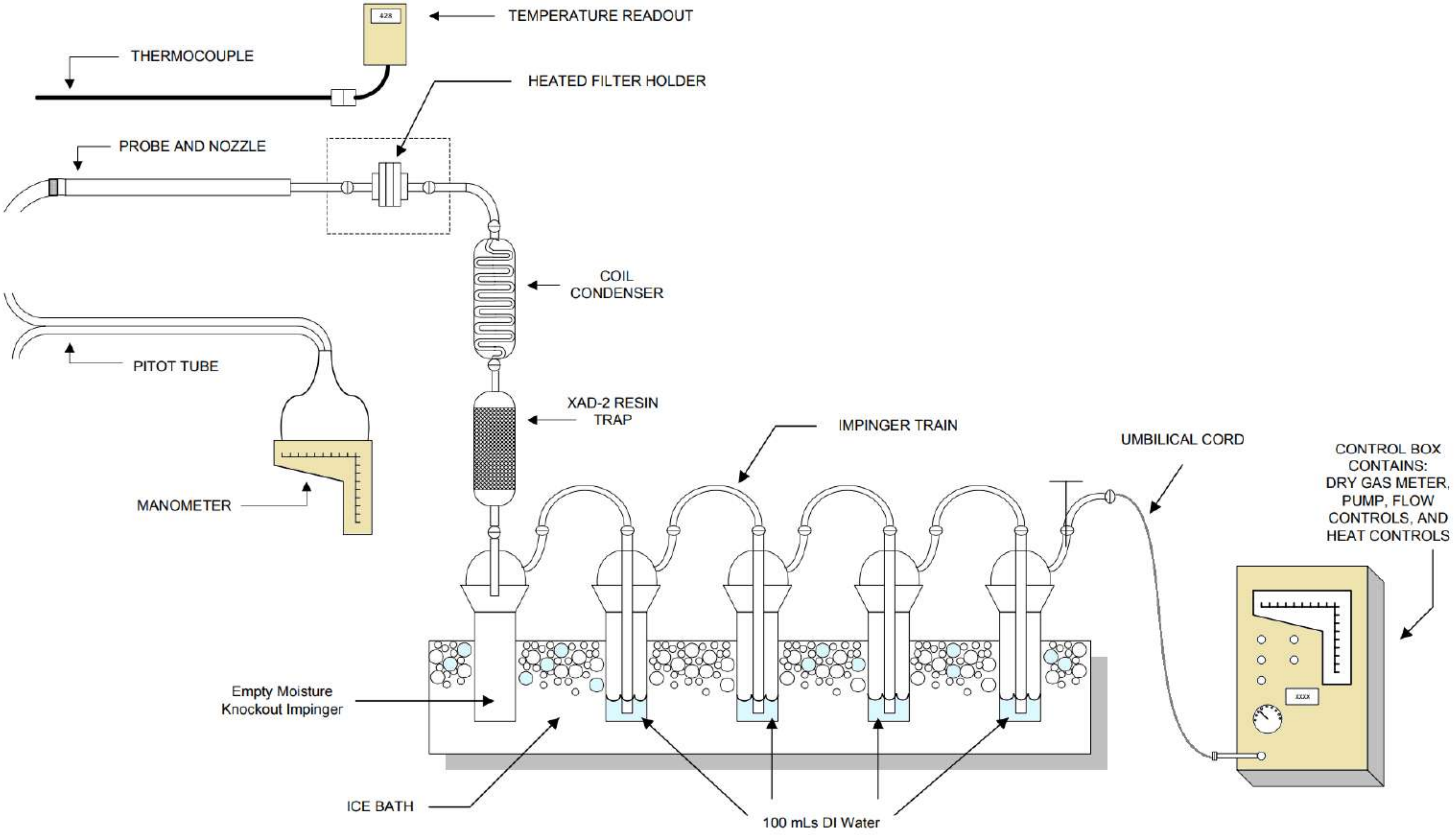
- How Much Chromatographic Information Lies Outside the Target Analyte List?
- Can Tentatively Identities be Given to Peaks.
- Are there Patterns that Overlay the Data Sets?

OTM-55

Sampling and Analysis for Semi-Volatile PFAS Compounds in Source Air

- This Method is a Non-Polar PFAS Method
- Includes Telomer Alcohols (FTOHs)
- Uses GC/MS and GC/MS/MS Method 8270 Instrumentation
- The Emphasis of this Data Collection is PIC Identification

OTM-55



428
TEMPERATURE READOUT
THERMOCOUPLE
HEATED FILTER HOLDER
PROBE AND NOZZLE
COIL CONDENSER
PITOT TUBE
XAD-2 RESIN TRAP
IMPINGER TRAIN
UMBILICAL CORD
CONTROL BOX CONTAINS: DRY GAS METER, PUMP, FLOW CONTROLS, AND HEAT CONTROLS
MANOMETER
XXXX
Empty Moisture Knockout Impinger
ICE BATH
100 mLs DI Water

OTM-55 Target Analyte List

Category	Target	CAS No.
Halogenated Benzenes	Fluorobenzene	462-06-6
	Pentafluorobenzene	363-72-4
	Hexafluorobenzene	392-56-3
	1,3,5-Trifluorobenzene	372-38-3
	1,2,3-Trifluorobenzene	1489-53-8
	1,2,4-Trifluorobenzene	367-23-7
	1-Chloro-4-fluorobenzene	352-33-0
	1-chloro-2-fluorobenzene	348-51-6
	1-chloro-3-fluorobenzene	625-98-9
	4-Bromofluorobenzene	460-00-4
	1,3-Dibromo-5-fluorobenzene	1435-51-4
	1-Bromo-2-fluorobenzene	1072-85-1
	1-Bromo-3,5-difluorobenzene	461-96-1
	1,2-Dibromo-4,5-difluorobenzene	64695-78-9
	Benzene, 1,3-dibromo-2,4,5,6-tetrafluoro-	1559-87-1
	Benzene, 1,2-dibromo-3,4,5,6-tetrafluoro-	827-08-7
	1-Bromo-2,3,4,5-tetrafluorobenzene	1074-91-5
	Bromopentafluorobenzene	344-04-7
	2-Bromo-4-chloro-1-fluorobenzene	1996-30-1
Halogenated Phenols and Carboxylic Acids	4-fluorophenol	371-41-5
	2-Chloro-4-fluorophenol	1996-41-4
	3-Chloro-4-fluorophenol	2613-23-2
	4-fluorobenzoic acid	456-22-4
	2',4'-Difluorobiphenyl-3-carboxylic acid	656304-77-7
	4-fluoro-1-naphthoic acid	573-03-5

Category	Target	CAS No.
Halogenated Biphenyls	1,1'-Biphenyl, 4-bromo-4'-fluoro-	398-21-0
	2,2'-Dibromooctafluorobiphenyl	5576-19-2
	4-chloro-2-fluoro-1,1'-biphenyl	39224-18-5
	3-chloro-4-fluoro-1,1'-biphenyl	1803002-70-1
	4-Bromo-3-chloro-2-fluoro-1,1'-biphenyl	2755717-23-6
	2-Bromo-4-chloro-6-fluorobiphenyl	2244107-72-8
	2-Fluorobiphenyl	321-60-8
	4-Fluorobiphenyl	324-74-3
	2,2'-Difluorobiphenyl	388-82-9
	4,4'-Difluorobiphenyl	398-23-2
	2,4-difluorobiphenyl	37847-52-2
	3,3'-Difluorobiphenyl	396-64-5
	2,3,4,5,6-pentafluorobiphenyl	784-14-5
	3-Bromo-4-fluorobiphenyl	306935-88-6
	4,4'-Dihydrooctafluorobiphenyl	3883-86-1
	Decafluorobiphenyl	434-90-2
Halogenated Naphthalenes and Other PAHs	1-Bromo-4-fluoronaphthalene	341-41-3
	1-Fluoronapthalene	321-38-0
	2-Fluoronaphthalene	323-09-1
	1-Bromo-5-fluoronaphthalene	315-56-0
	2-bromo-6-fluoronaphthalene	324-41-4
	2-bromoheptafluoronaphthalene	27041-17-4
	2-Fluorofluorene	343-43-1

OTM-55 vs. OTM-45 Sequential Extraction

- One (1) Sampling Train vs. Two (2) Sampling Trains Employed on-on-site to Collect the Stack Samples
- Complexity in the Analytical Laboratory is Increased
- Comprehensive Sampling Train for PFAS

THANK YOU

Environment Testing

SESSION 5

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Current State of Dry Sorbent Injection (DSI) Solution

Control # IT3-03
Gerald Hunt
Ian Saratovsky PhD
September 14, 2023
Air & Waste Management Association

Lhoist

Sorbacal®

Agenda

- DSI Technology Synopsis
- System Design Considerations
- Engineered Hydrated Lime Sorbents (EHLS)
- Acid Gas Control Capabilities
- DSI Performance Optimization
- Disposal Considerations
- Total Cost of Ownership (TCO) Solution
- Conclusion

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DSI Technology Synopsis

What is it? Who is using it?

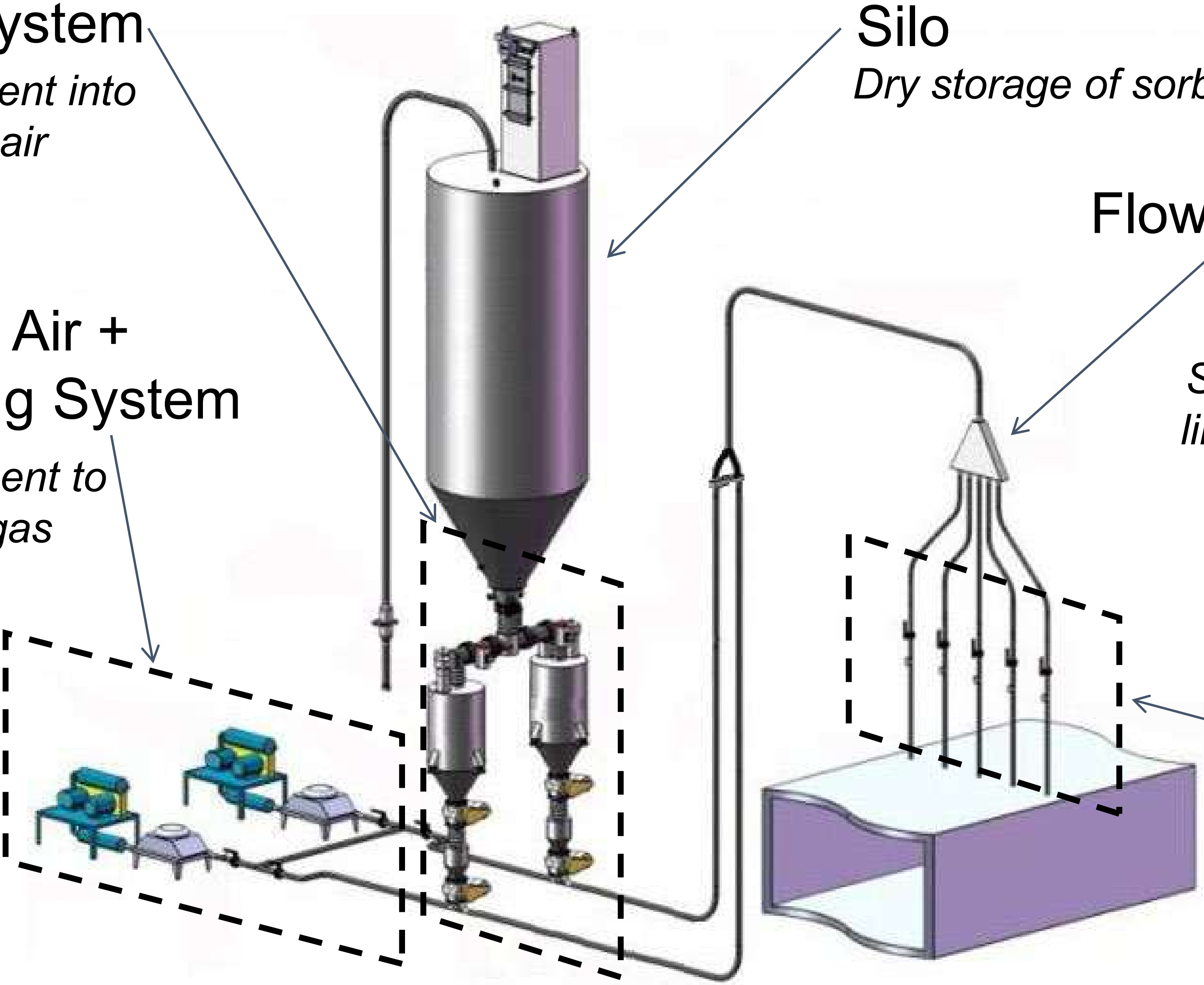
Dry Sorbent Injection (DSI): Dry injection of an alkaline sorbent (calcium, sodium) into an exhaust gas to chemically ‘scrub’ or neutralize acid gases such as sulfur dioxide (SO_2), sulfuric acid (SO_3/H_2SO_4), hydrogen chloride (HCl) and hydrogen fluoride (HF). Scrubbed acid gases captured as solid residue.

- Coal fired power plant (SO_2, SO_3, HCl)
- Cement (SO_2, HCl)
- Biomass (SO_2, HCl)
- Glass (SO_2, HCl)
- Pulp & Paper (SO_2, HCl)
- Universities (HCl)
- Aluminum Smelters (SO_2, HCl, HF, Hg, D/F)
- Carbon Black (SO_3)
- Calcined Pet Coke (SO_2, SO_3)
- Fiberglass (SO_2)
- Chemicals (HCl, Hg)
- Brick and Tile (SO_2, HCl, HF)

Hundreds of DSI Systems Installed and Operating in the US over Past 20 Years

DSI Technology Synopsis

System Overview



Dosing System

Meters sorbent into motive air

Silo

Dry storage of sorbent

Flow + Sorbent Partitioning Device

Splits sorbent flow from single line to multiple injection lances

Motive Air + Conditioning System

Carries sorbent to exhaust gas

Injection Lances

Distributes sorbent into exhaust gas

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System Design Considerations

Design for Maximum Reliability

- Storage Silo Sizing
  - *Consider supplier logistics*
- Inventory Monitoring/Management
  - *Reliable silo level monitoring technology*
- Sorbent Flowability
  - *Fluidizing air, mechanical vibration*
- Pneumatic Conveying System
  - *Sorbents are not inert with ambient air*
- Conveying Piping/Elbows
  - *Length, elbow bend radius, elbow materials of construction*
- Volumetric vs. Gravimetric Feed
  - *Value in loss-in-weight measurements*
- Venting
  - *Minimize conveying air back flowing through feed train*
- Design Feed Rate
  - *Important for metering system sizing as well as turn-down; worst case for storage silo sizing*
- Injection Grid
  - *Sorbent must contact acid gases to react*
- Sorbent Selection
  - *Consideration for dosage rate and density*

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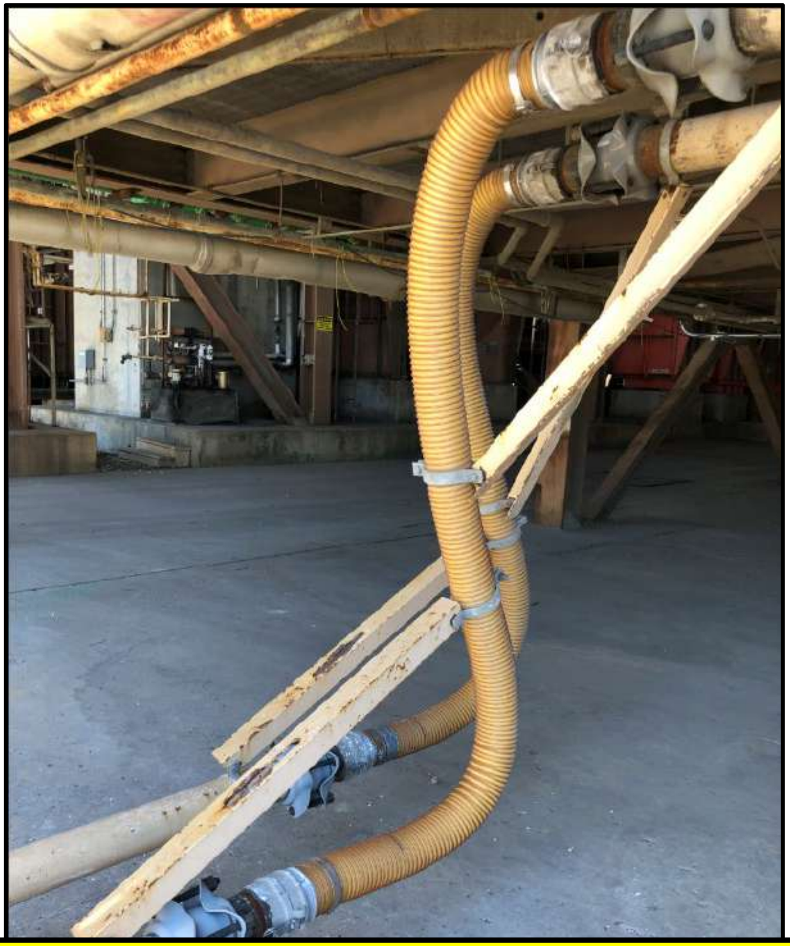
System Design Considerations

Key Equipment Design Considerations – A Quick Example

Common DSI configuration → elbow scaling/plugging every 6-8 weeks

“This is how we’ve always done it”



Polyurethane hose elbows in operation > 2 years without a single downtime due to scaling/plugging

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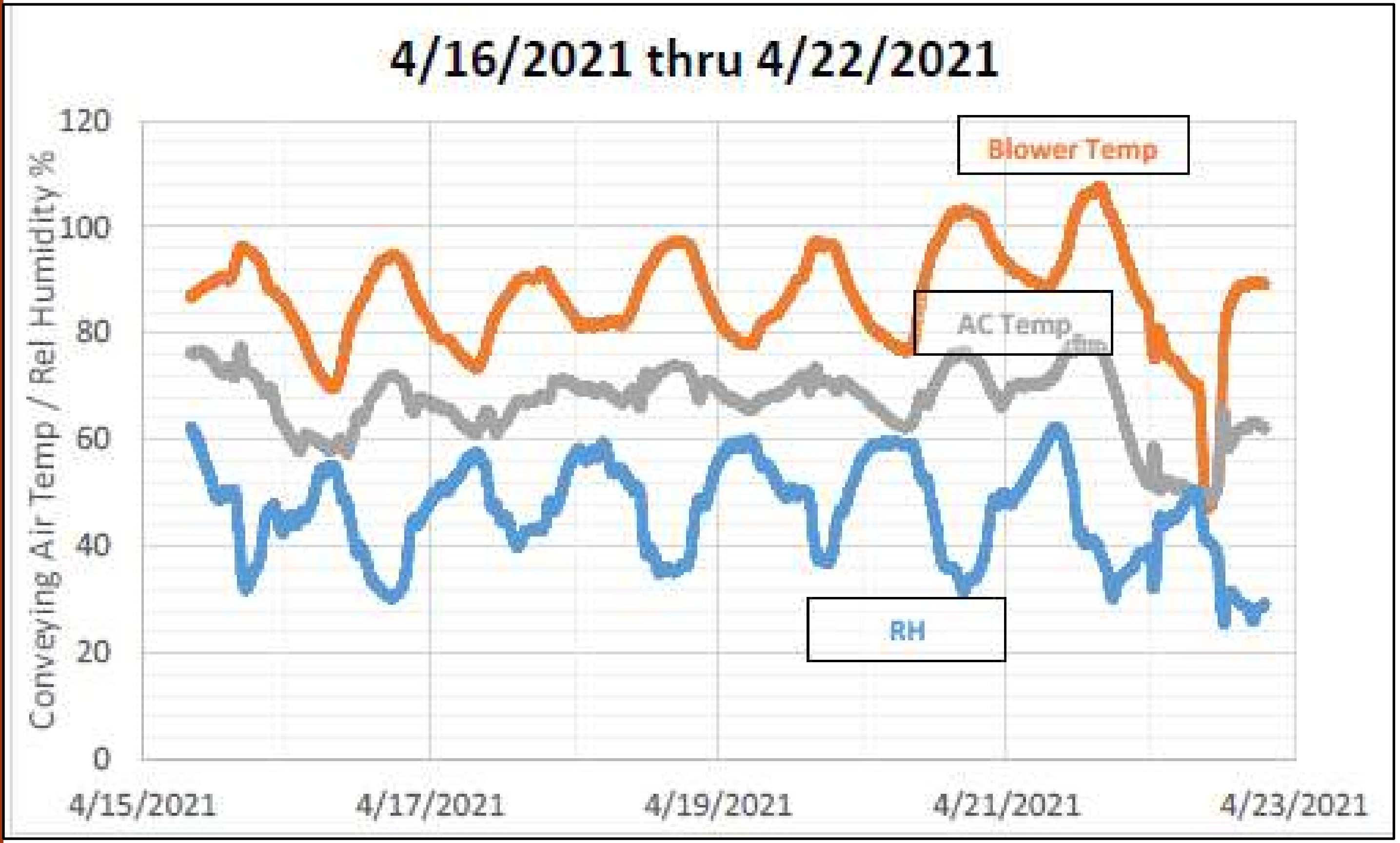
System Design Considerations

Key Equipment Design Considerations – Carbonation Scaling



- Reducing conveying air relative humidity (RH) to < 8% significantly reduces carbonation
  - *Supported by literature as well as operating experience*
- Conveying air temperature varies with night and day
- While not intuitive may be times to cool conveying air and times to not cool it

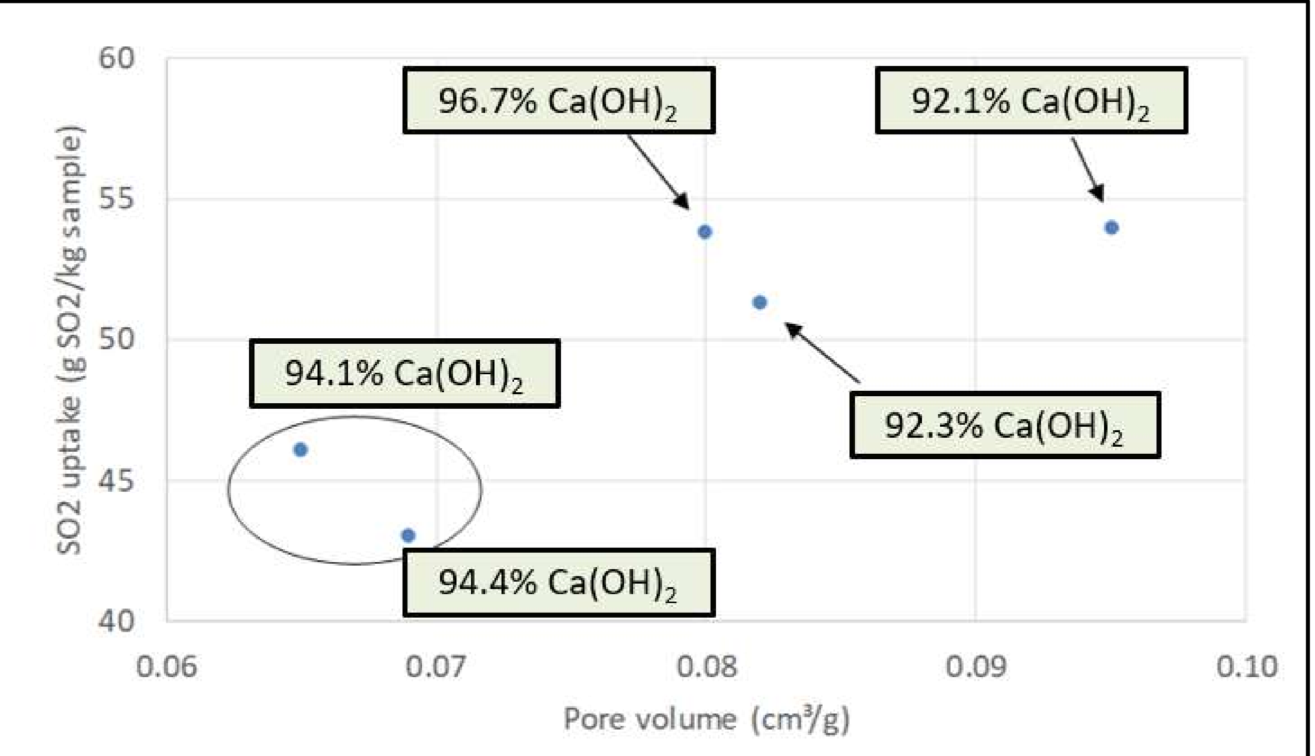
Valuable data can be gained via dew point transmitter

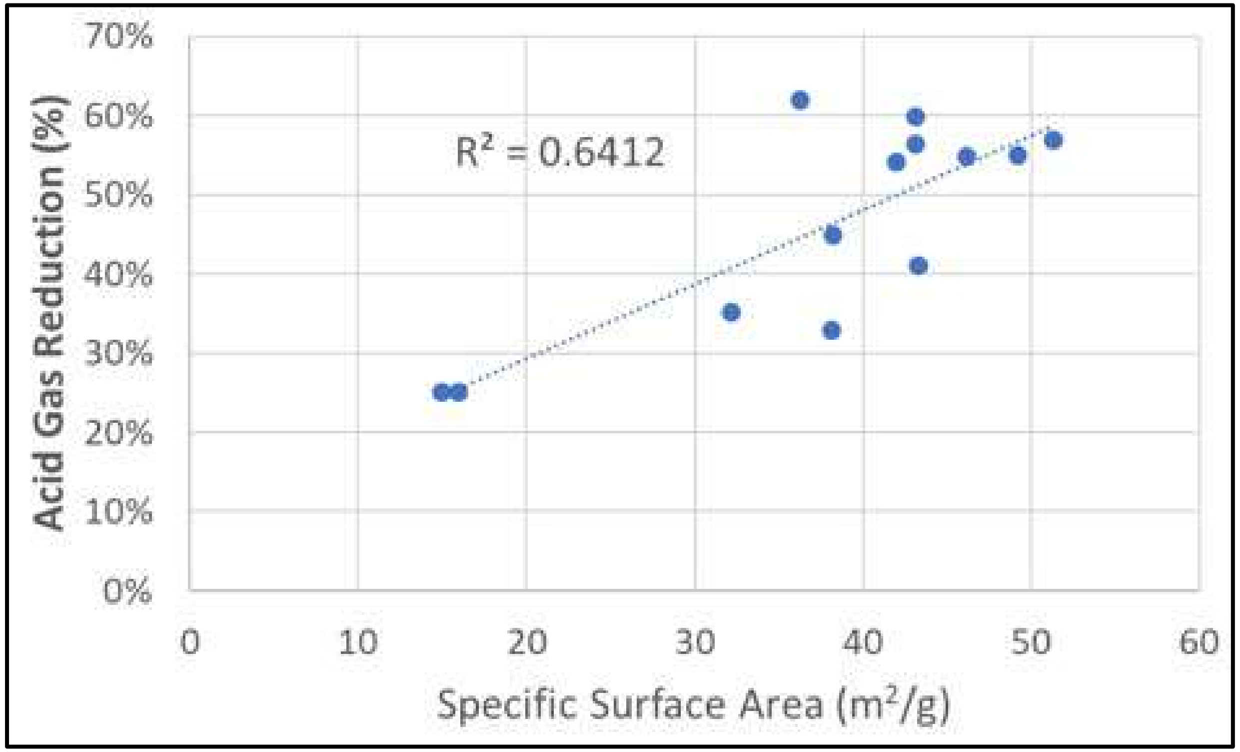
Engineered Hydrated Lime Sorbents (EHLS)

What Properties Matter for Dry Scrubbing Applications?

Is purity important? **Yes**

But is it the <u>most</u> important property? **No**





Is surface area important? **Yes**

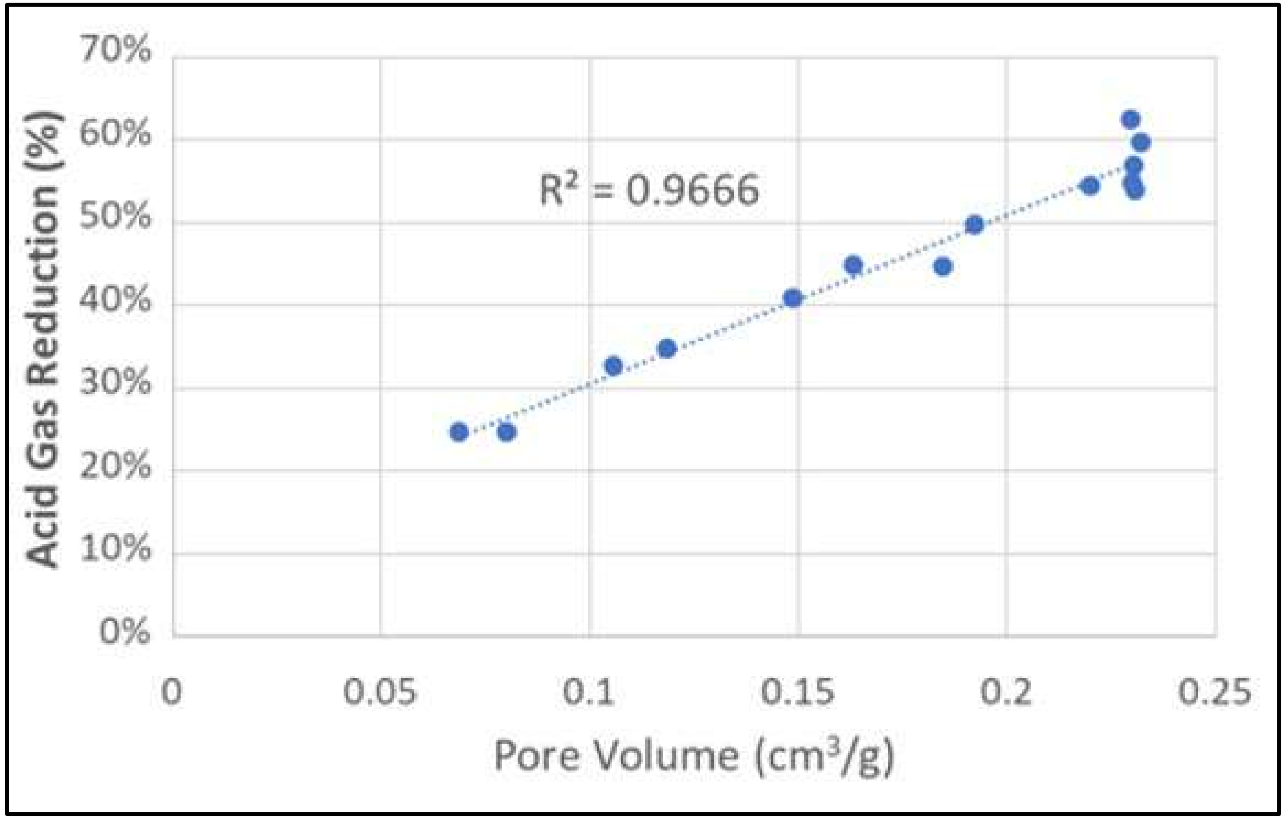
But is it the <u>most</u> important property? **No**

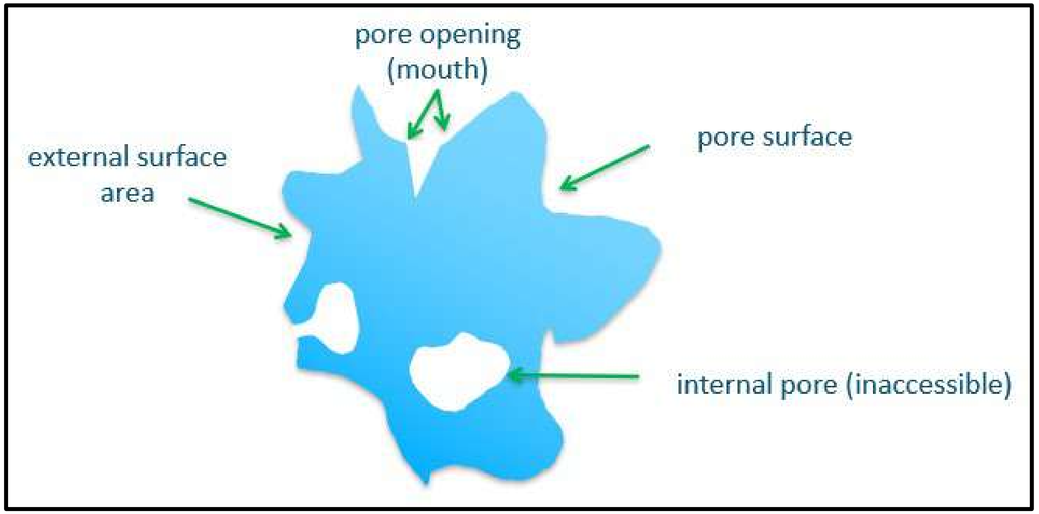
Engineered Hydrated Lime Sorbents (EHLS)

What Properties Matter for Dry Scrubbing Applications?

Is pore volume important? **Yes**

But is it the most important property? **Yes**





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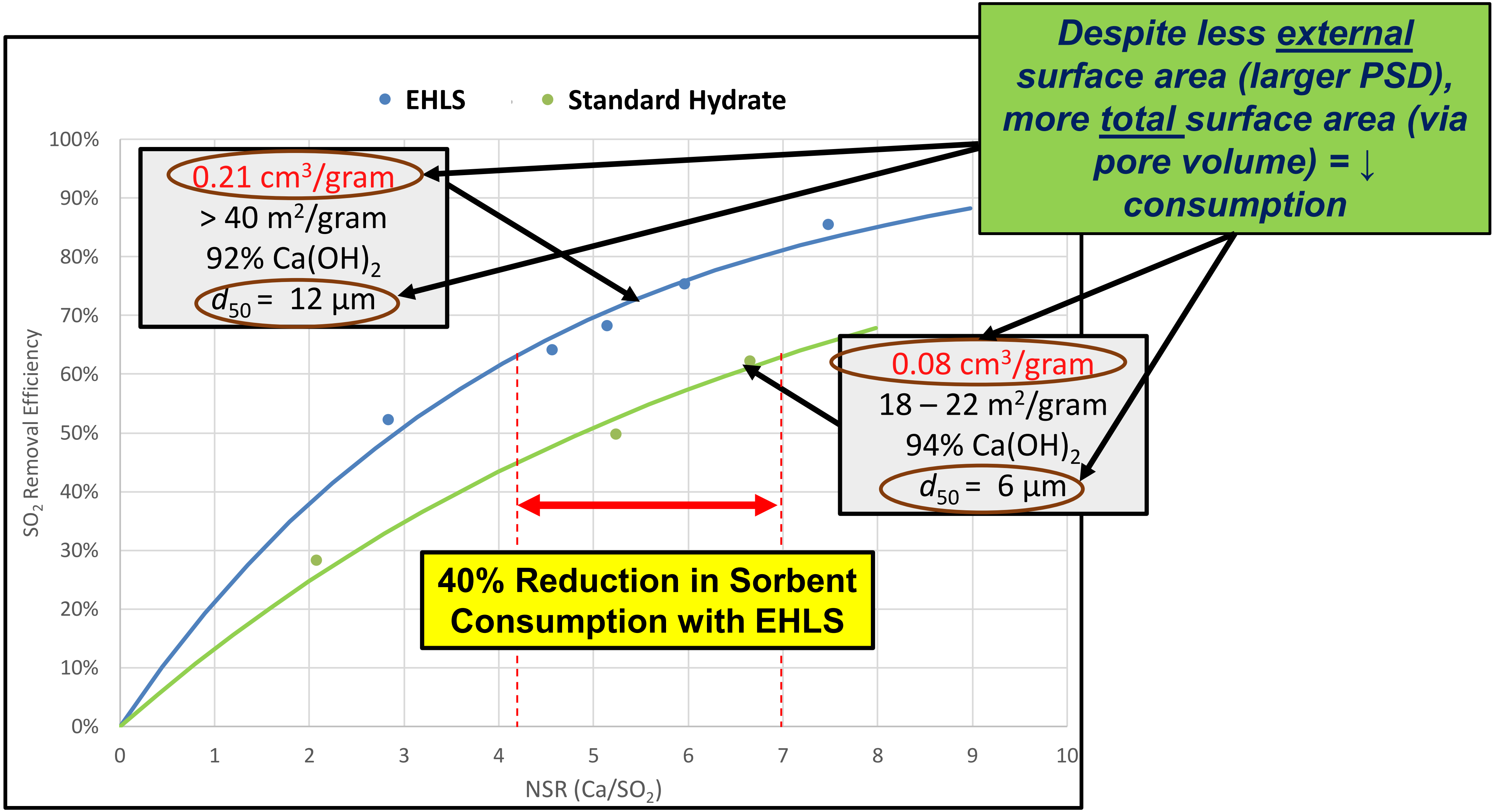
Internal Surface Area + External Surface Area = Total Surface Area

Driven by Pore Volume *Driven by Particle Size*

Engineered Hydrated Lime Sorbents (EHLS)

An Example – Standard Hydrated Lime vs. EHLS in DSI Application



Despite less <u>external</u> surface area (larger PSD), more <u>total</u> surface area (via pore volume) = ↓ consumption

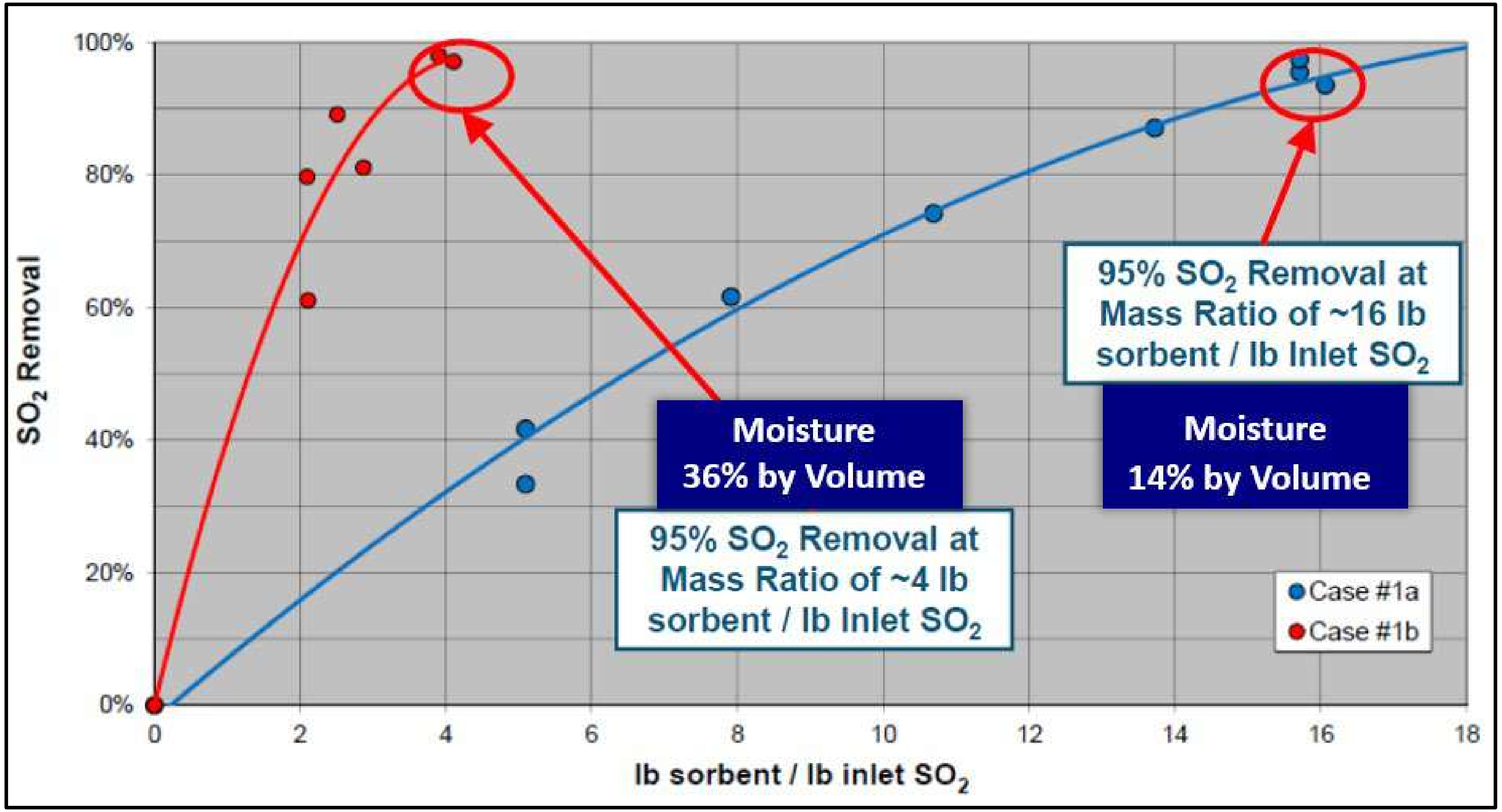
$0.21\ cm^3/gram$
$> 40\ m^2/gram$
$92\%\ Ca(OH)_2$
$d_{50} = 12\ \mu m$

$0.08\ cm^3/gram$
$18 – 22\ m^2/gram$
$94\%\ Ca(OH)_2$
$d_{50} = 6\ \mu m$

40% Reduction in Sorbent Consumption with EHLS

Acid Gas Control Capabilities

DSI with EHLS – SO_2 Removal



Moisture 36% by Volume

95% SO_2 Removal at Mass Ratio of ~4 lb sorbent / lb Inlet SO_2

Moisture 14% by Volume

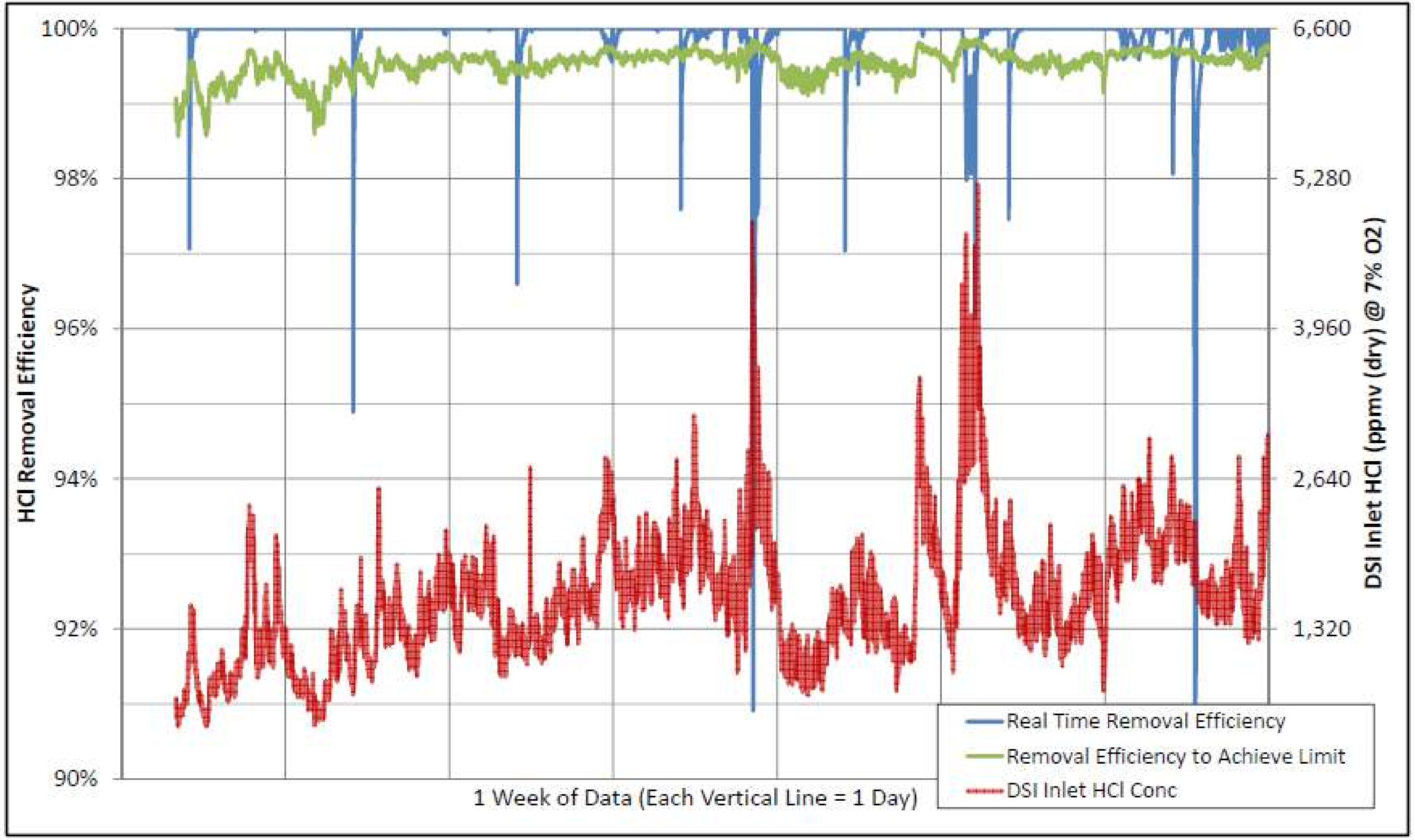
95% SO_2 Removal at Mass Ratio of ~16 lb sorbent / lb Inlet SO_2

- Proof of concept DSI trial executed within days
- EHLS successful demonstrating > 95% SO_2 removal efficiency
- Importance of gas moisture content evident from trial

Demonstrated > 95% SO_2 Removal

Acid Gas Control Capabilities

DSI with EHLS – HCl Removal



- HCl data based on week-long DSI trial with EHLS at waste incinerator
- Stringent averaging period for compliance (3-hour rolling average)
- Sustained 99% HCl removal with highly variable emission profile

Demonstrated > 99% HCl Removal

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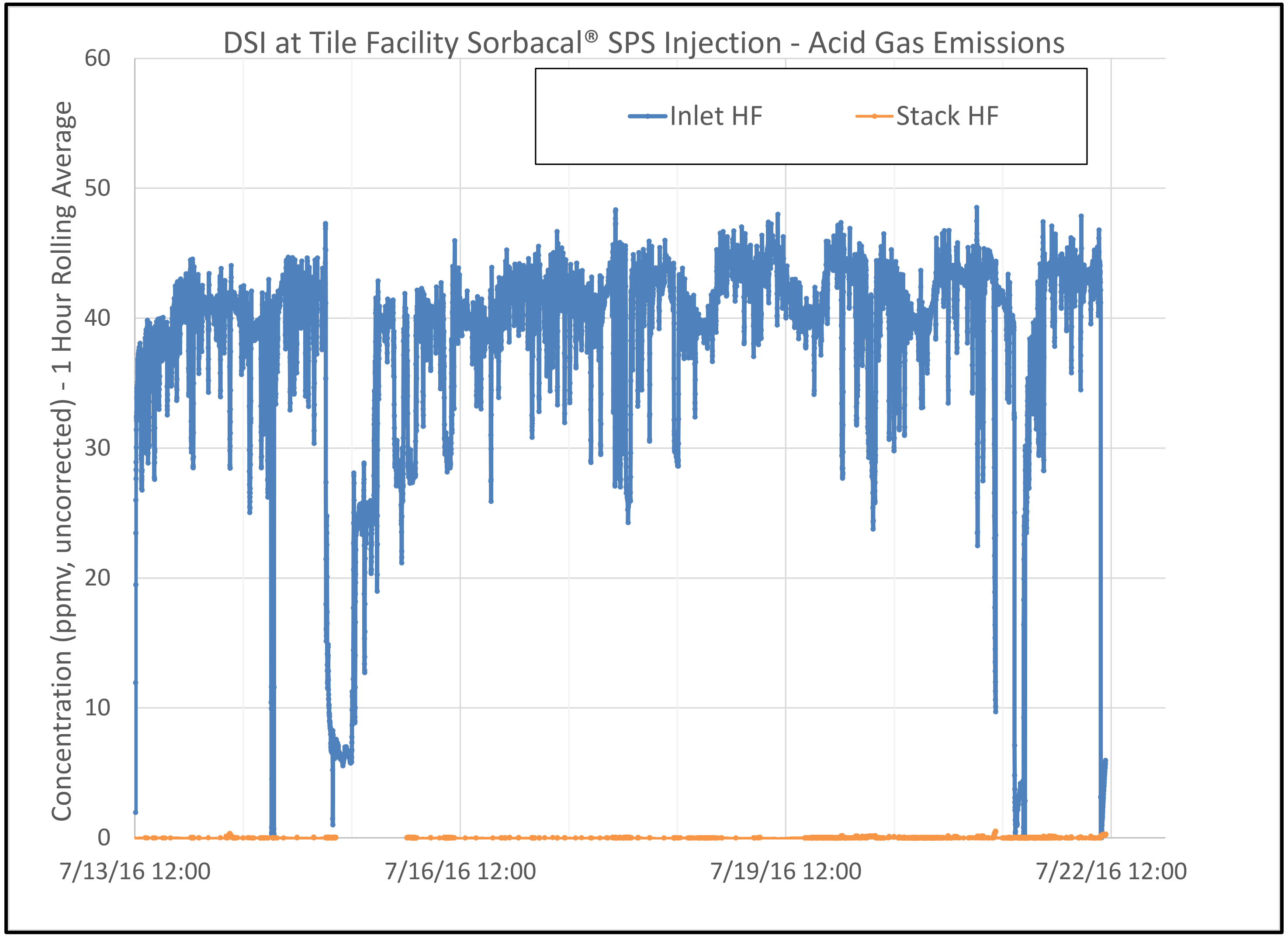
Acid Gas Control Capabilities

DSI with EHLS – HF Removal



- Site initially used sodium sorbent (SO_2, HCl) and commodity hydrated lime (HF)
- Driver for alternative solution was due to generating hazardous residue
- Testing EHLS achieved following;
  - Compliance with SO_2, HCl and HF
  - Residue = non-hazardous
- Converted to use of single sorbent (EHLS)

Demonstrated > 99% HF Removal (More Reactive than HCl)

Acid Gas Control Capabilities

DSI with EHLS – Heavy Metal (Selenium) Removal

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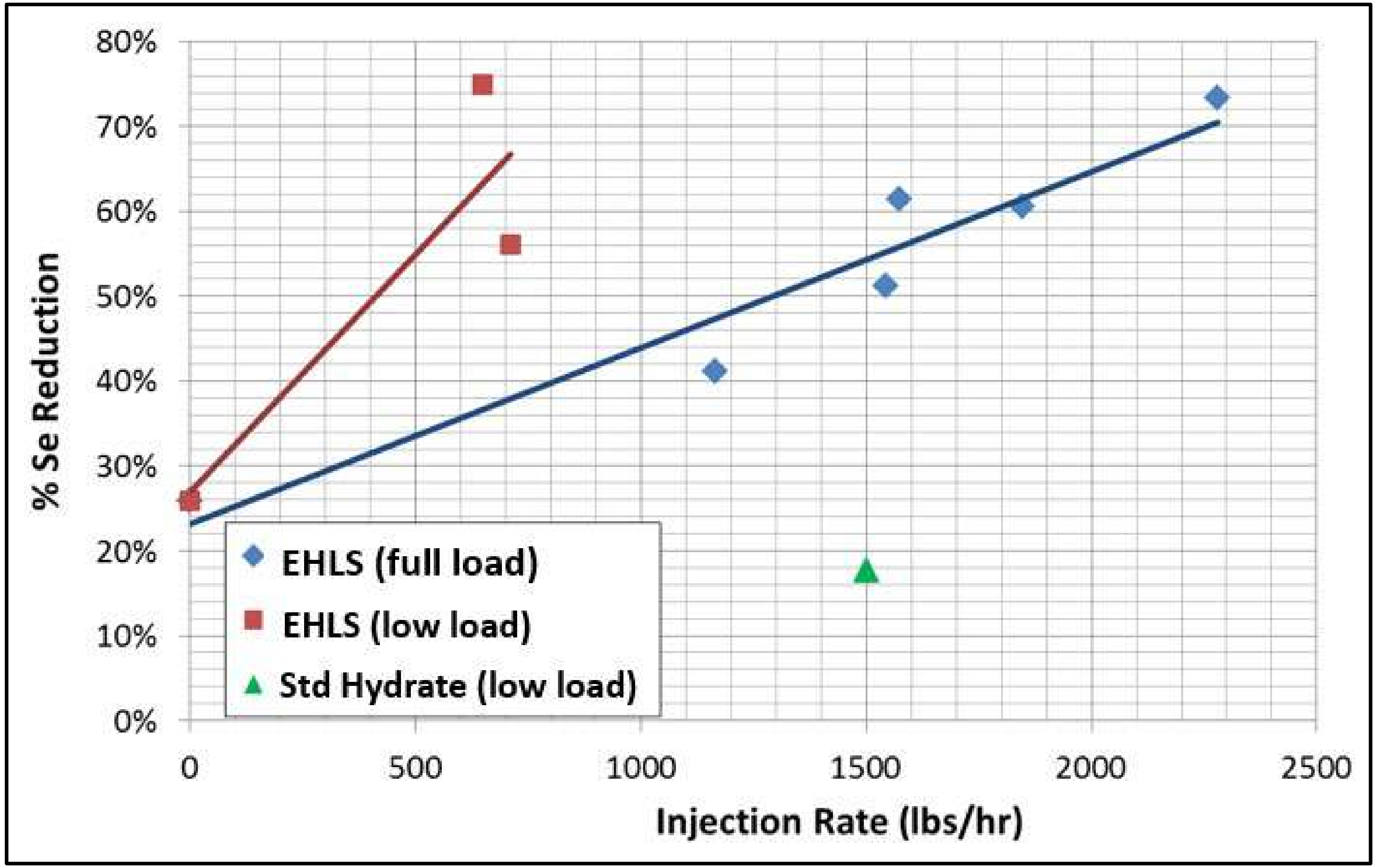

- DSI trial from a coal fired utility
- EHLS selenium removal >> standard hydrated lime selenium removal
- DSI with EHLS can be potential solution to reduce selenium emissions and/or into water treatment processes

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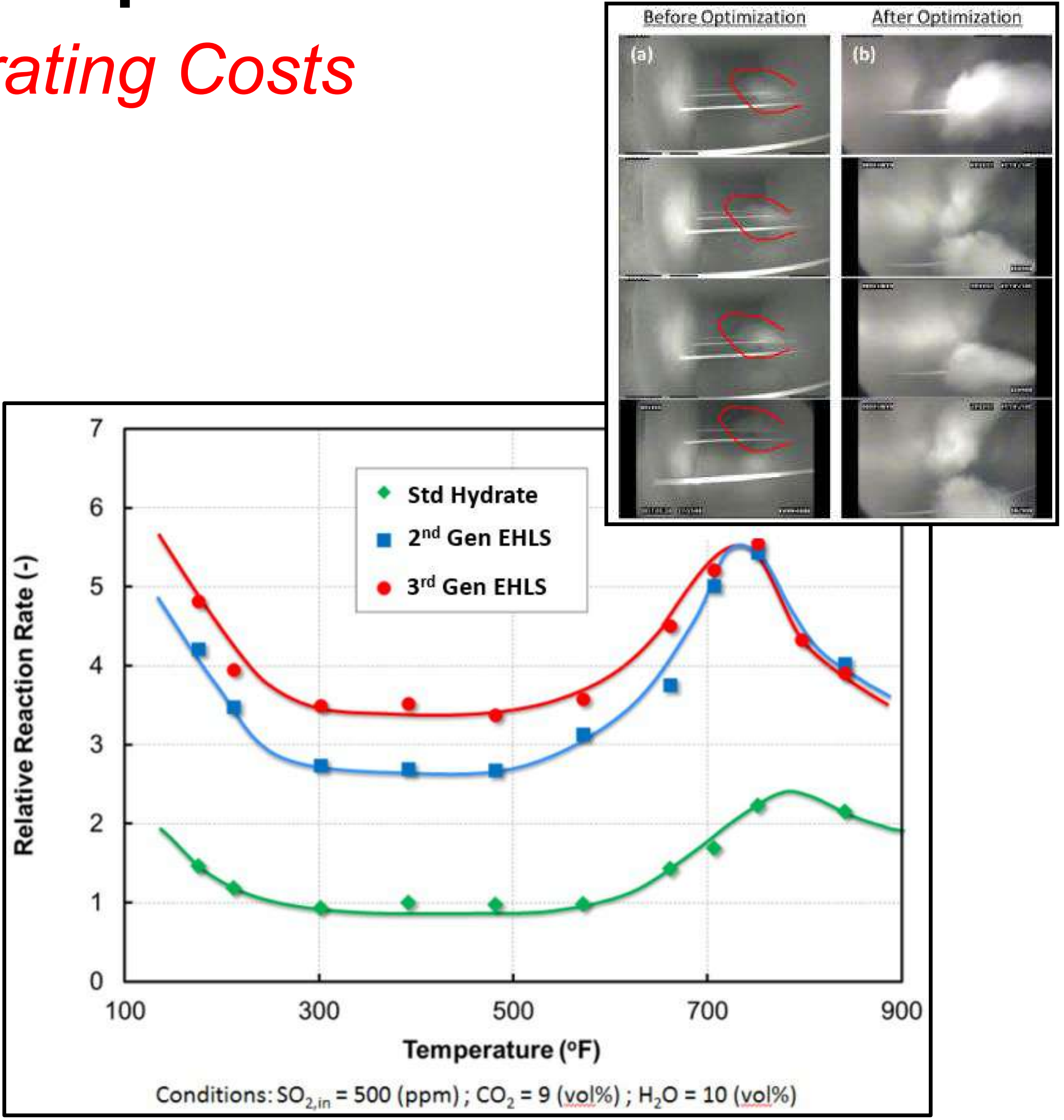
DSI Performance Optimization

Optimization Operating Costs

- Baghouse/Filter Operation
  - *Operation can impact DSI efficacy*[1]
- Sorbent Selection
  - *Lowest delivered $ ≠ lowest annual spend*
- Injection Location
  - *Site specific selection based on target acid gas, process conditions, balance of plant considerations as well as existing access constraints*
- Sorbent Dispersion
  - *Still common to see single injection lance*
  - *Sorbent cannot react with something it does not contact*



Conditions: $SO_{2,in}$ = 500 (ppm) ; CO_2 = 9 (vol%) ; H_2O = 10 (vol%)

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1. *"Implementation of Baghouse Cleaning Changes to Improve Sorbent Injection Systems". Rooney, J., Carstens, A., Daghlian, J., Simko, W.; 2014 MEGA Symposium.*

Disposal Considerations

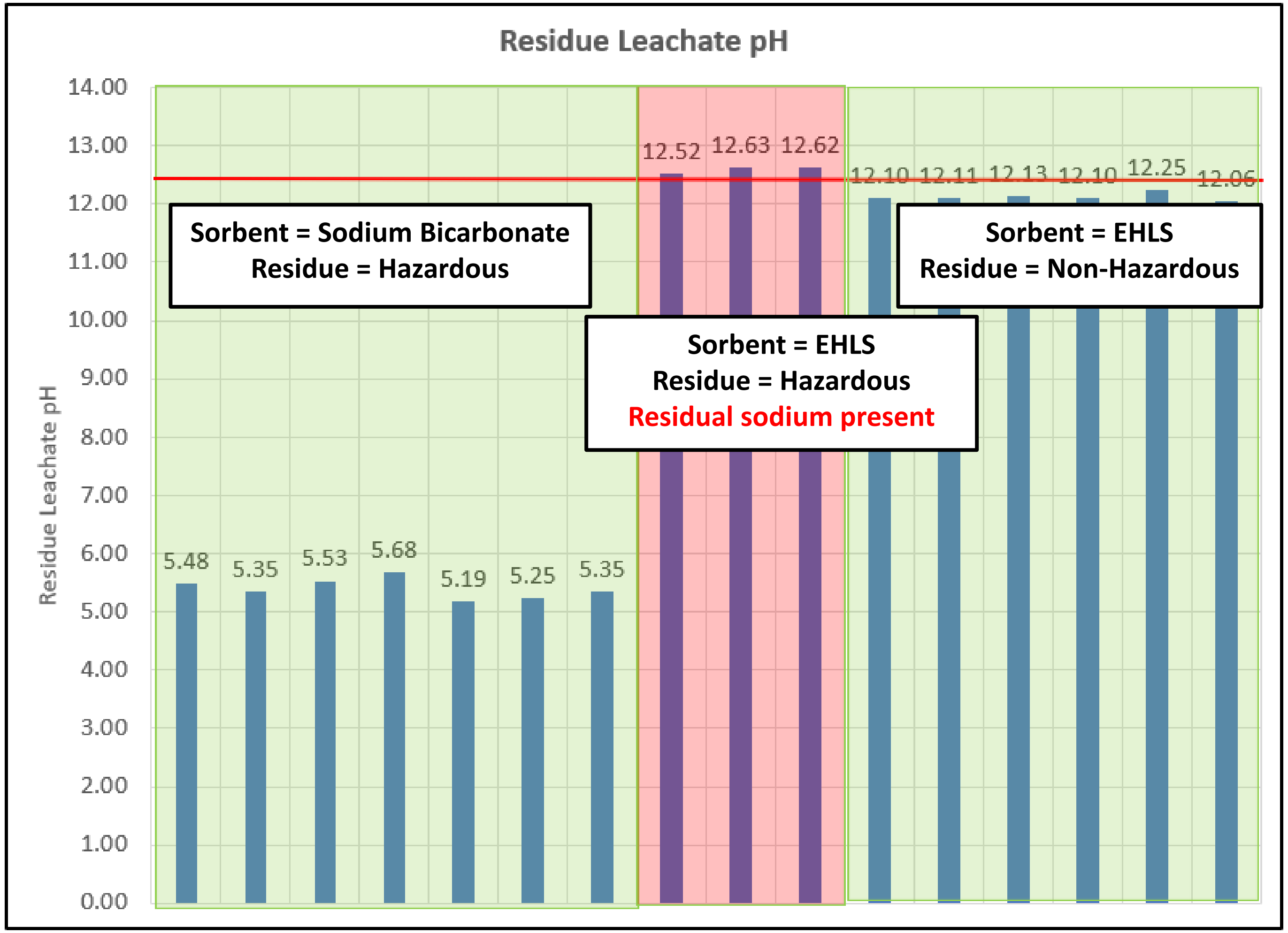
Sometimes the "Tail Wags the Dog"

- DSI user generating hazardous waste due to selenium leaching while using sodium bicarbonate
  - *Switched to EHLS*
  - *Initially did not achieve non-hazardous classification*
- Additional lab analyses provided supporting evidence to extend testing longer
  - *Selenium leaching eventually decreased below RCRA limit*
  - *Achieved non-hazardous disposal classification with EHLS*

Disposal Considerations

Sometimes the "Tail Wags the Dog"

- Additional analysis during sorbent transition provided key data
  - *$Ca(OH)_2$ has pH of 12.45 at 25°C*
  - *Calcium and sodium co-mingling can produce sodium hydroxide which can increase pH > 12.5*
  - *Once residual sodium fully purged the byproduct pH < 12.5 (non-hazardous)*



Sorbent = Sodium Bicarbonate
Residue = Hazardous

Sorbent = EHLS
Residue = Hazardous
Residual sodium present

Sorbent = EHLS
Residue = Non-Hazardous

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Total Cost of Ownership (TCO) Solution

What is the 'Right' Sorbent for my Application?

- Lowest $/ton delivered price ≠ lowest cost for compliance
  - *Decide based on total cost of ownership (TCO)*
  - *Sorbent delivered pricing and reactivity/consumption*
  - *Relative residue disposal costs*
  - *Balance of plant impacts*

TCO Example on DSI Application

Sorbent		EHLS	Standard Hydrate	
Delivered Price	$/ton	$245	$193	**EHLS has higher delivered price**
Consumption	tons/year	450	750	**EHLS has lower consumption rate**
Sorbent Annual Spend	$/year	$110,250	$144,750	**EHLS has lower annual sorbent spend**
Disposal Cost	$/ton	$30	$30	
Waste Disposed	tons/year	450	750	**EHLS has lower residue generation**
Disposal Annual Spend	$/year	$13,500	$22,500	**EHLS has lower annual disposal spend**
Total Cost of Ownership	**$/year**	**$123,750**	**$167,250**	**EHLS has lowest TCO**

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Conclusion

Seek Solutions Oriented Partners, Not Vendors

- When an operational issue occurs…"what's wrong with the sorbent?"
- Equipment supplier blames the sorbent, sorbent supplier blames the equipment, end user stuck in the middle
- Multiple vendors who can sell a widget but lack fundamental understanding of the solution or only looking to sell something
- End users only familiar with <u>their</u> system and <u>their</u> issues
- Solutions oriented partners understand solution and how to optimize cost and reliability

Thank You!

Gerald (Jerry) Hunt
Gerald.Hunt@lhoist.com

Greg Filippelli, PE
Greg.Filippelli@lhoist.com

Dr. Ian Saratovsky
Ian.Saratovsky@lhoist.com

Travis Reynolds
Travis.Reynolds@lhoist.com

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The Ship & Shore Environmental Mindset

- Ship & Shore Environmental (S&SE), a woman-owned global corporation, specializes in engineering, designing, constructing, installing, and servicing custom air pollution control systems for various industries to eliminate harmful emissions from industrial manufacturing operations.

- With over 23 years of experience, S&SE has been instrumental in improving global air quality through its innovative systems.

- We continuously evolve our technology to address emerging industry sectors and environmental challenges, all while proudly contributing to the fight against climate change every day.

Presentation Overview

1. Abstract
2. Background (Challenges & Limitations)
3. Multi-Stage Thermal Oxidizer
4. Final Process Design
5. Fabrication
6. Installation
7. Conclusion

Abstract

- Ship & Shore Environmental (S&SE) is your complete source for industrial *air pollution* **capture and control**.

- A biogas company consulted S&SE to develop a custom ***99% efficient Multi-Stage Direct-Fired Thermal Oxidizer*** with downstream heat recovery capability to be combined to a pyrolysis furnace and condensers (installed upstream) in order to thermally oxidize four (4) waste streams high in sulfur and nitrogen, while limiting NOx formation.

Background

Challenges

The waste streams contain sufficient nitrogen content that if directly oxidized in a standard thermal oxidizer (TO), an excessive amount of NOx would form.

Limitations

Limited space (35 ft. X 19 ft.) and potential excess production of NOx due to waste streams high in nitrogen provided unique challenges for the S&SE engineering team.

Multi-Stage Thermal Oxidizer

FOR VOC CONTROL & ABATEMENT

- **Multi-Stage DFTOs** operate with sufficient excess oxygen and temperature to destroy the combustibles from the initial stage, while keeping oxygen and temperatures sufficiently low to avoid the reformation of thermal NOx.

- A quench media is required to minimize the temperature of subsequent stages and recycle flue gas (RFG) provides **maximum heat recovery.**

Multi-Stage Thermal Oxidizer

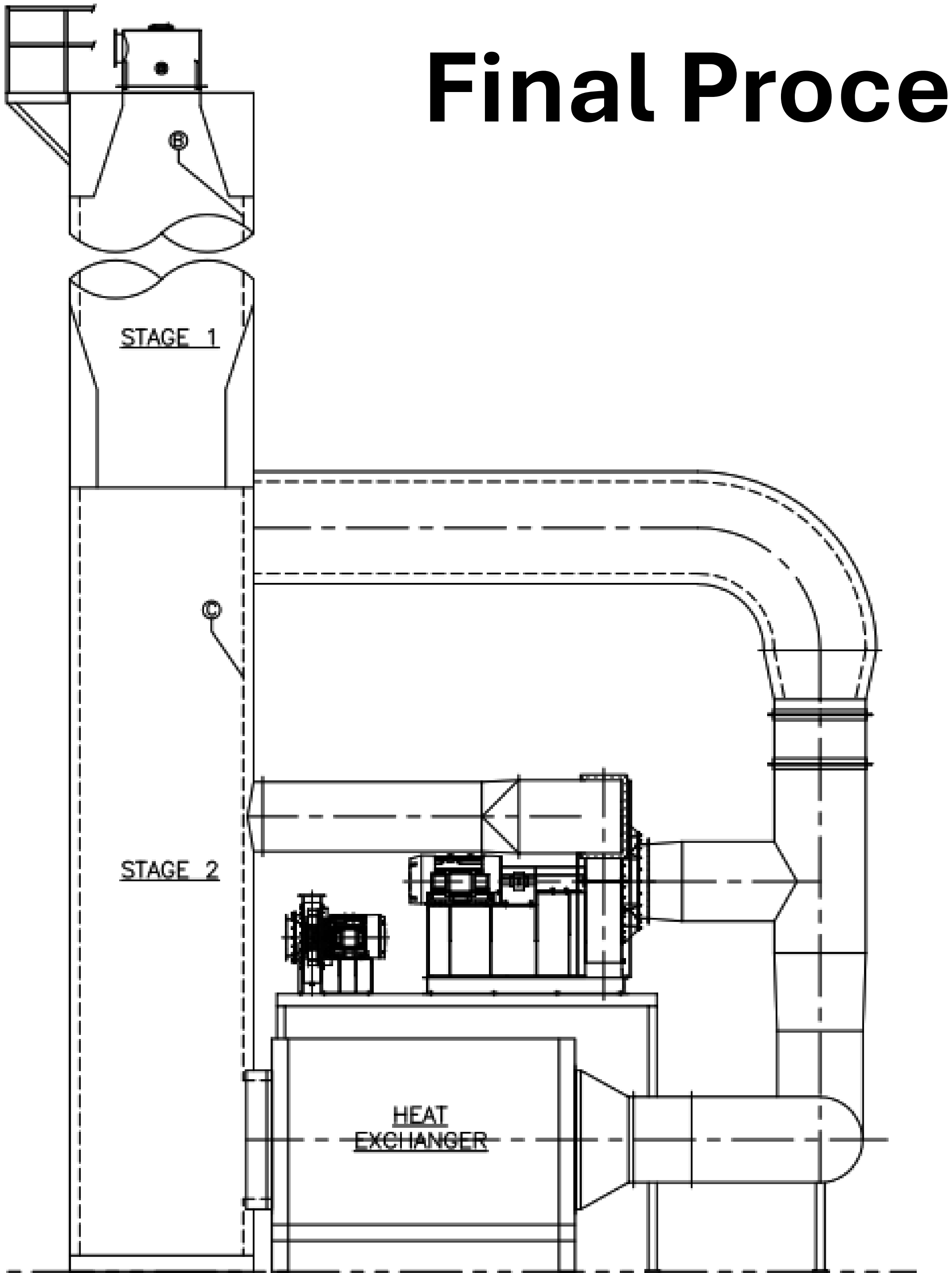
FOR VOC CONTROL & ABATEMENT

- Two processes are used in the Multi-Stage Thermal Oxidizer:
  - **Three stages:** initial reducing stage, quench stage to cool flue gas, and a third oxidation stage.
  - **Two stages:** initial reducing stage, RFG for quench, and a second oxidizing stage with RFG and excess air. The two-stage process simplifies control and reduces costs compared to the three-stage process.

Final Process Design

- The initial stage operates at 2150°F with 1+ second residence time, generating excess CO and H2 in an oxygen-starved setting.
- This controls nitrogen oxides by converting bound nitrogen compounds to N2 instead of NOx.
- The second chamber completes oxidation at 1650°F, and the exothermic waste streams minimize natural gas use, mainly during start-up.
- Exhaust gas is split: half goes to a heat exchanger for plant applications, while the other half is directed to a quench.

Final Process Design



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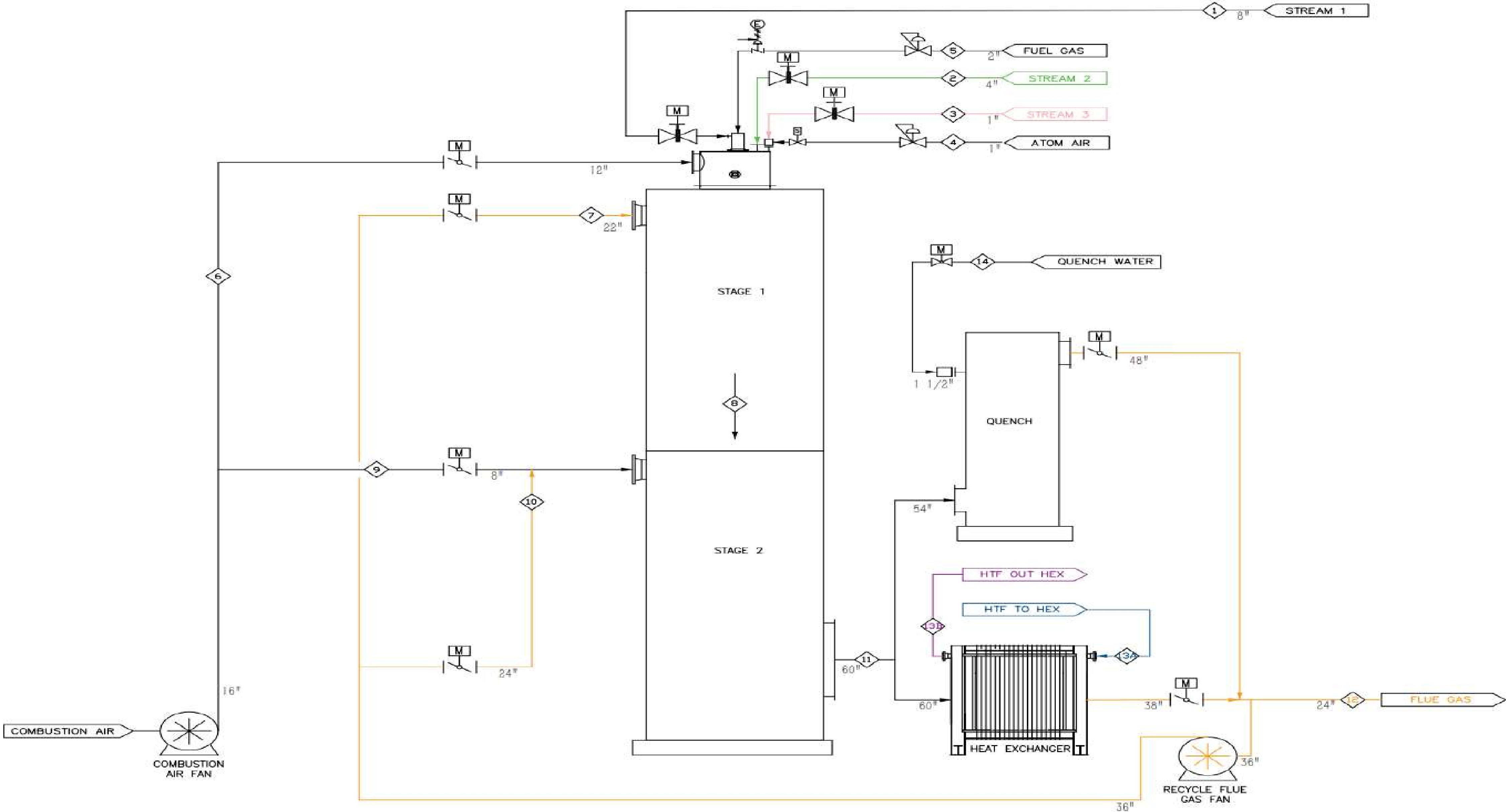
Final Process Flow Diagram (PFD)



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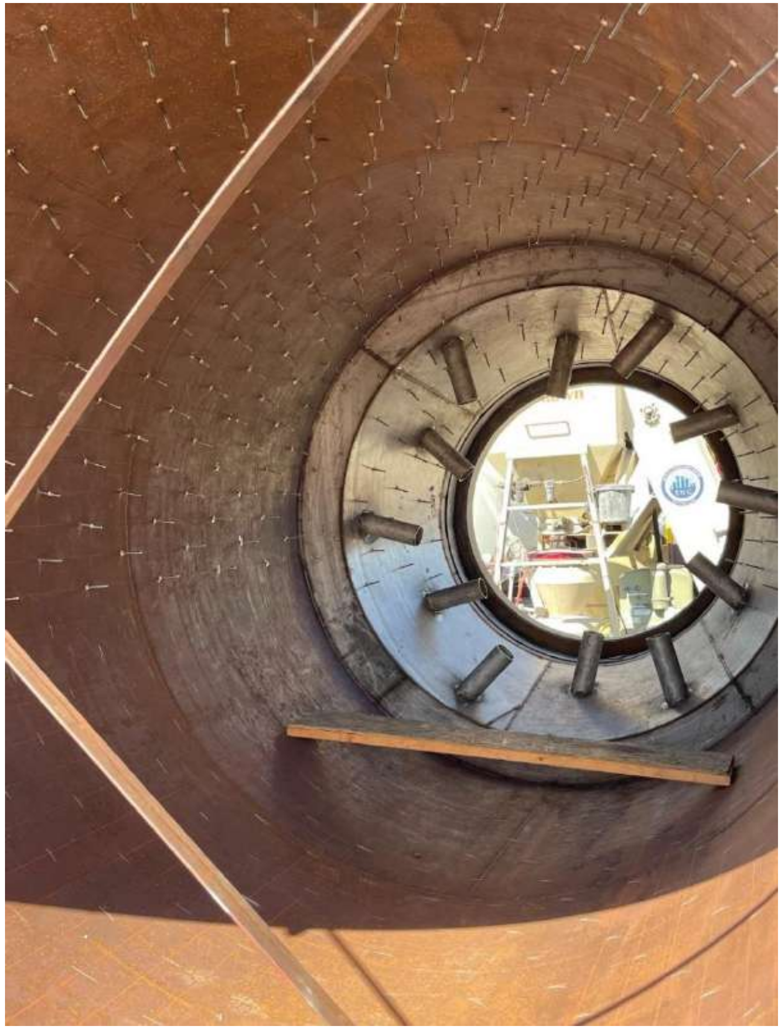
Final Process Design

Stream Name			STREAM 1			STREAM 2			STREAM 3			ATOMIZING AIR FOR STREAM 3 LIQUID		
Component	Formula	mw	lb/h	lbmole/h	wt%	lb/h	lbmole/h	wt%	lb/h	lbmole/h	wt%	lb/h	lbmole/h	vol%
Carbon	C	12.01	904.136	75.275	48.382%	152.145	12.667	29.400%	96.420	8.028	25.570%			
Hydrogen	H	1.01	194.834	193.294	10.426%	2.743	2.721	0.530%	19.552	19.397	5.185%			
Nitrogen	N	14.01	36.322	2.593	1.944%				7.824	0.559	2.075%			
Sulfur	S	32.06	2.049	0.064	0.110%	9.522	0.297	1.840%	4.393	0.137	1.165%			
Oxygen	O	16.00	725.320	45.334	38.813%	353.090	22.069	68.230%	60.352	3.772	16.005%			
Ash	Ash	60.08	6.089	0.101	0.326%									
Water (liq)	H2O(l)	18.02							188.542	10.466	50.000%			
Heat Transfer Fluid	Dowtherm Q	DTQ												
Fuel Gas	CH4	16.04												
Carbon monoxide	CO	28.01												
Carbon dioxide	CO2	44.01												
Hydrogen	H2	2.02												
Water (vapor)	H2O (v)	18.02												
Nitrogen	N2	28.01										72.4	2.58	79.05%
Nitrogen Dioxide	NO2	46.01												
Oxygen	O2	32.00										21.9	0.68	20.95%
Hydrogen Sulfide	H2S	34.08												
Sulfur dioxide	SO2	64.06												
TOTAL			1,868.75	60.74	100.000%	517.50	25.36	100.000%	377.08	----	100.000%	94.3	3.27	100.00%
Molecular Weight (lb/lbmole)			30.77			20.41			-----			28.85		
Pressure, "w.c.-g (psig)			-5.0			-5.0			(75)			(85)		
Temperature, °F			1200			176			176			77		
FLOW RATE, scfm (gpm)			384			86			(1.0)			20.7		
FLOW RATE, acfm			1,226			106			----			----		
LOWER HEATING VALUE, Btu/lb			8,867			8,395			11,447			----		
HEAT RELEASE, mmBtu/h			16.571			4.344			4.316			----		
SENSIBLE ENERGY, mmBtu/h			0.63			0.02			0.00					

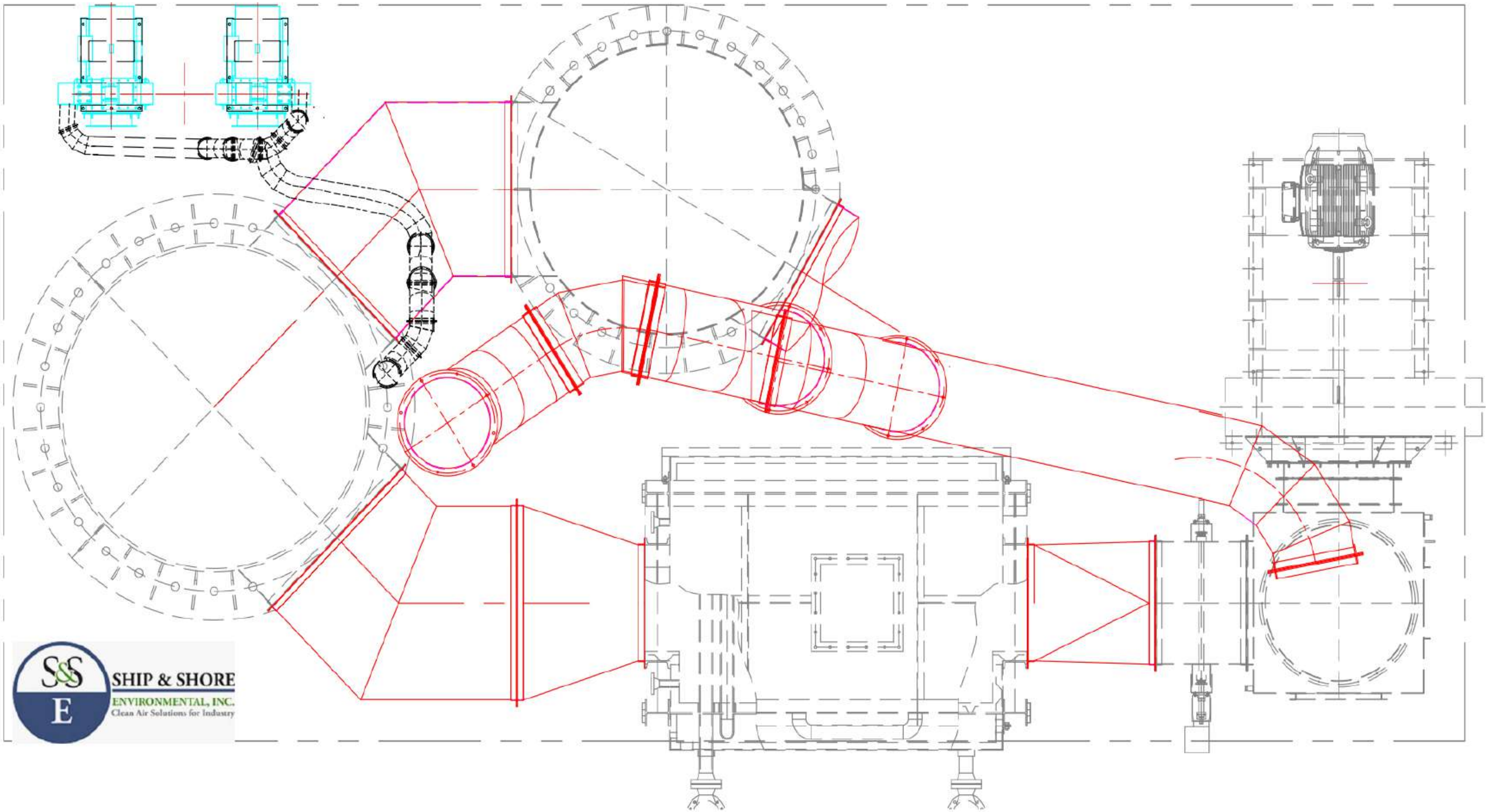
Final Process Design (Fabrication)



Burner is installed at top of Multi-Stage TO

- All streams mix at the burner exit with a designed vortex profile.
- Anchors with caps are installed beforehand.
- The refractory consists of 2 layers: 9" Thick Lo-Erode® for the Thermal Oxidizer and 6" thick Lo-Abrade® for the Quench.
- Ducts from the Thermal Oxidizer and heat exchanger have 6" refractory, while other process ducts are SS, maintaining temperatures above 750°F.
- A recycle line minimizes combustion fuel for process heating, ensuring a 99% destruction efficiency and a guaranteed 200 ppmV of NOx.

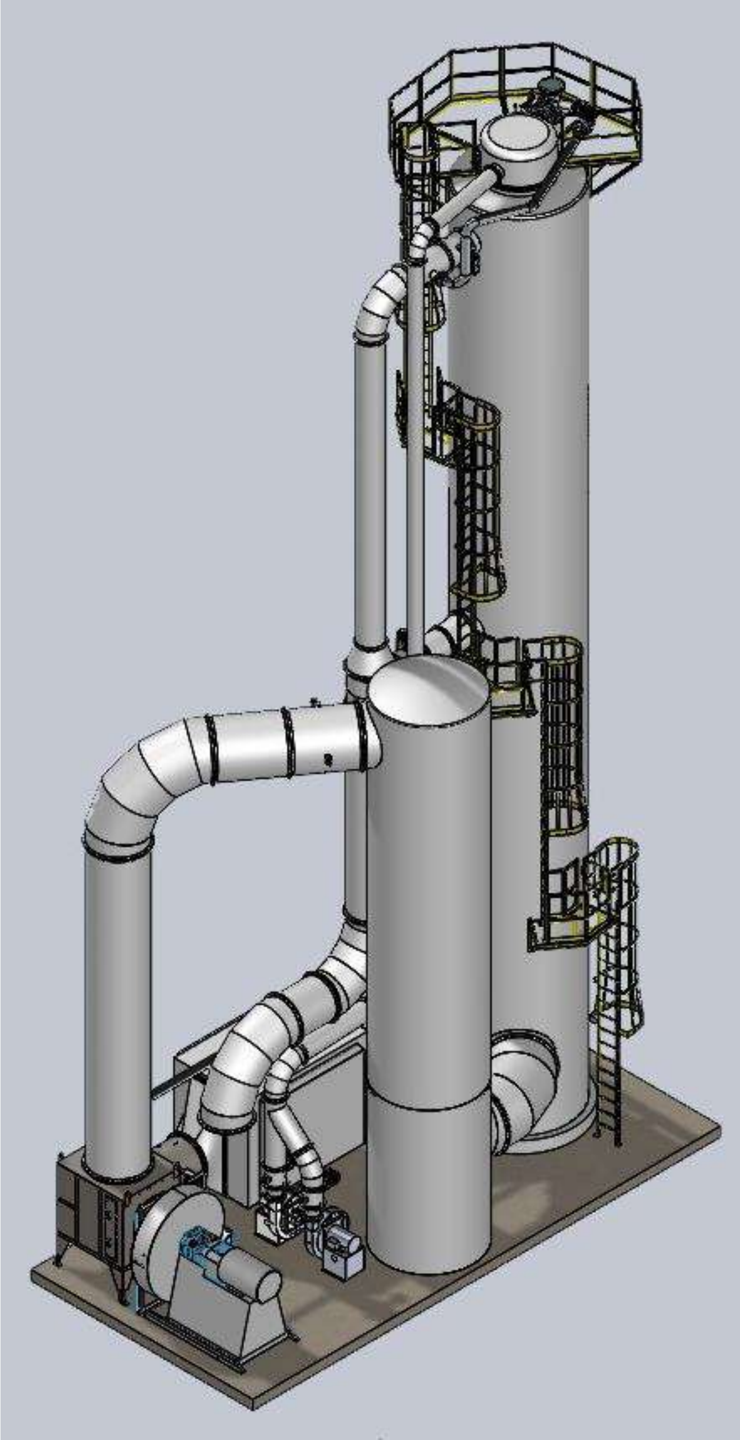
Installation



IT3/HWC

Charlotte
2023

SHIP & SHORE
ENVIRONMENTAL, INC.
Clean Air Solutions for Industry



Conclusion

- S&SE designed the system to fit the limited space, utilizing a vertical/down-fired burner.
- This design eliminates potential ash/particle effects on the burner.
- Despite not using natural gas for combustion, the heat exchanger recycles and redistributes heat throughout the plant at no extra cost.
- The system efficiently combines recycled flue gas and waste gas heat for combustion, reducing NOx formation by 99% with minimal natural gas usage.

HIGH EFFICIENCY CATALYTIC FILTRATION FOR NOX AND PARTICULATE EMISSION CONTROL IN INTEGRATED STEEL PLANTS

IT3 Conference - 2023
September 14, 2023
Charlotte, NC

Tarun Poddar
W. L. Gore & Associates, Inc.

Together, improving life

GORE

Contents

- Background
- Technology, product and application overview
- Application in steel plants
- Conclusive remarks
- Questions

Driving Forces for Pollutants Abatement

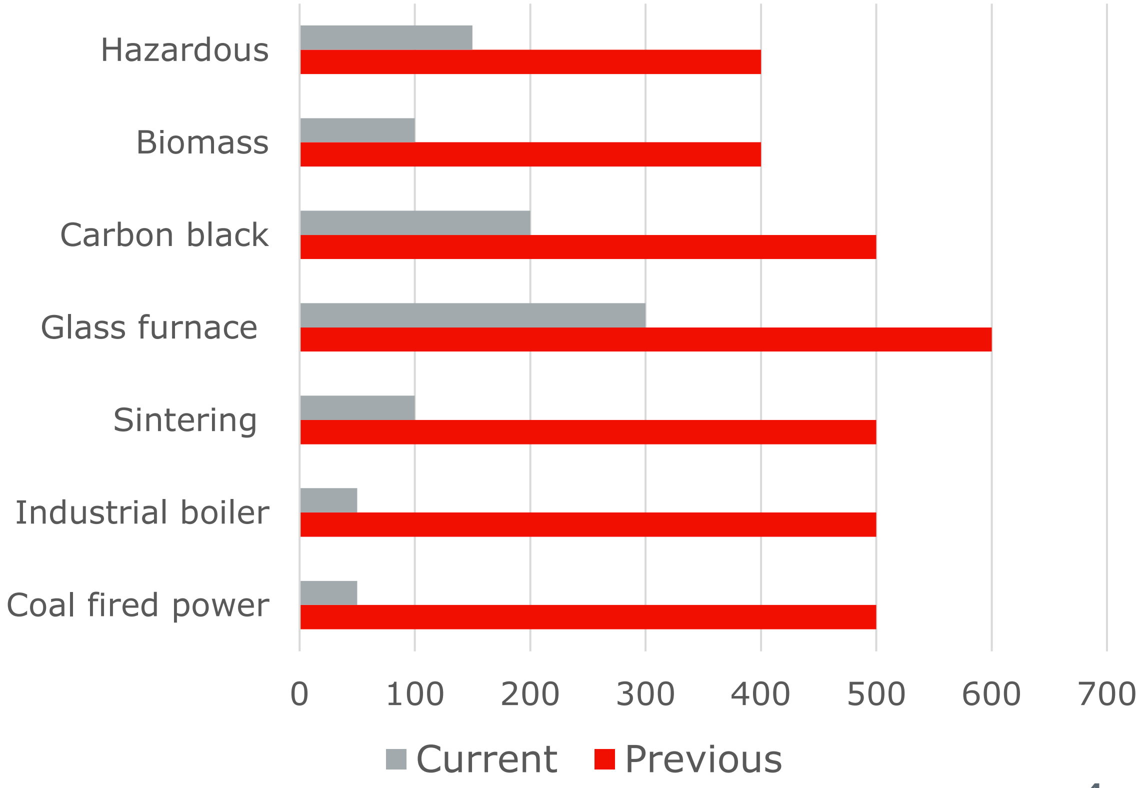
- Awareness and demand for clean and healthy environment
- Increasingly strict regulations
- Incentives

Continuous Enforcement of Regulations for NOx Emissions

European NOx Emission limit (mg/Nm^3)

European Directive (IED) = 150 mg/Nm^3
Austria = 70
Netherlands and others = 80
France (for tax rebate) = 80
Italy (regionally) = 80
Switzerland = 80
Regional = 50

China NOx Emission limit (mg/Nm^3)



GORE® DeNOx Catalytic Filter Bags -

An innovative product for reliable & costeffective solution - NOx, ammonia & dioxin/furun reduction

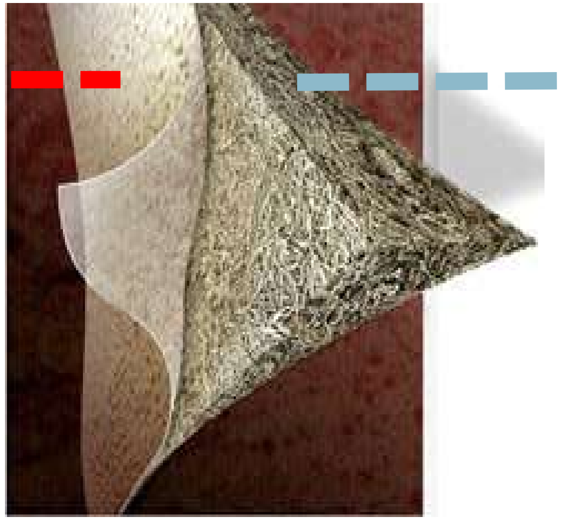
Overview

- *Technology*
- *Product*
- *Application*

Concept of Catalytic Filtration Technology

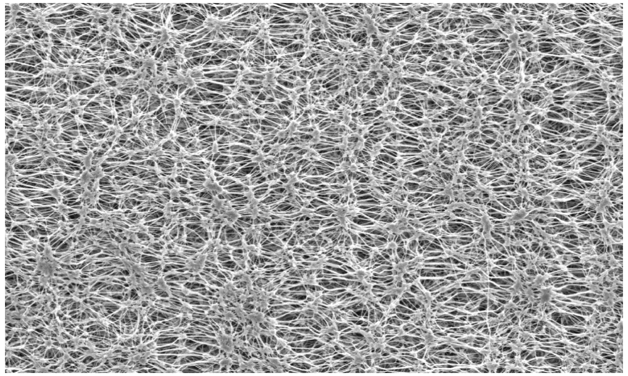
Combines particulate filtration & catalytic reaction in a single unit

Dirty & polluted flue gas



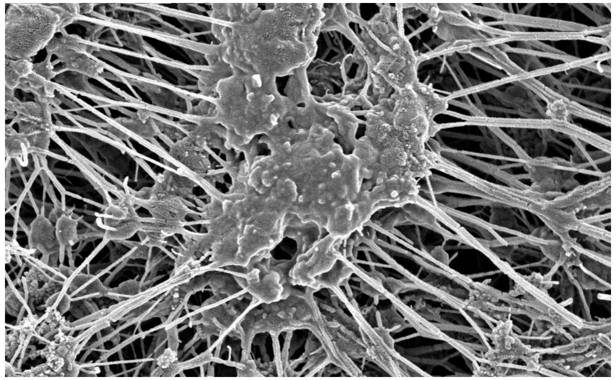
Clean flue gas

Expanded PTFE membrane



Efficient filtration of particulates

Catalyst-filled felt



Efficient contact with catalyst

A Long-term Leader in Innovative Filtration Technology

History of Gore particulate filtration & gas phase remediation

1972	1998	2013	2015	2018	2020
Membrane-based particulate filtration	**GORE® REMEDIA® Catalytic Filter Bags**	**GORE® Mercury Control System**	**GORE® DeNOx Catalytic Filter Bags**	**Generation 2 GORE® REMEDIA® Catalytic Filter Bags**	**Generation 2 GORE® DeNOx Catalytic Filter Bags**

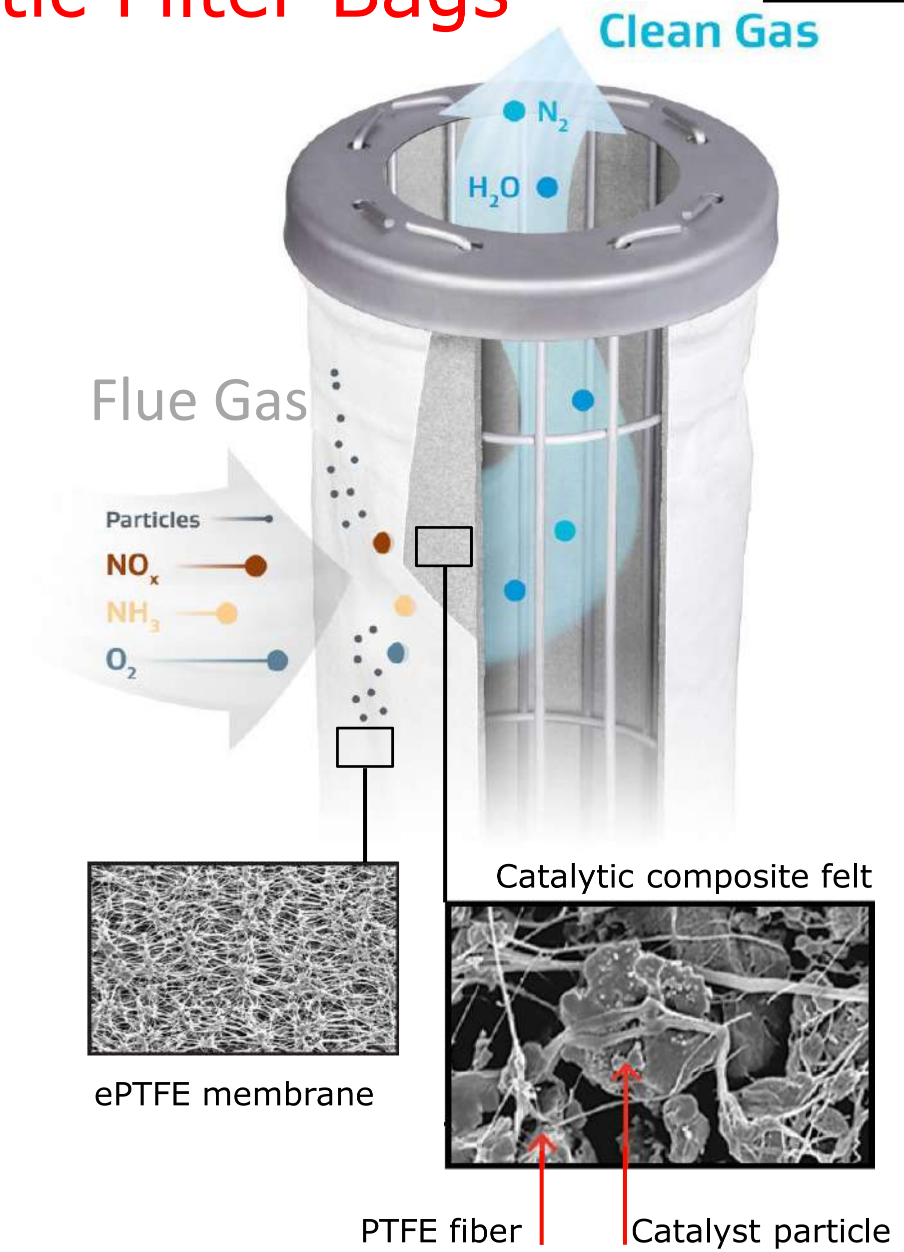
NOx Removal by GORE® DeNOx Catalytic Filter Bags

For NOx & NH_3 reduction

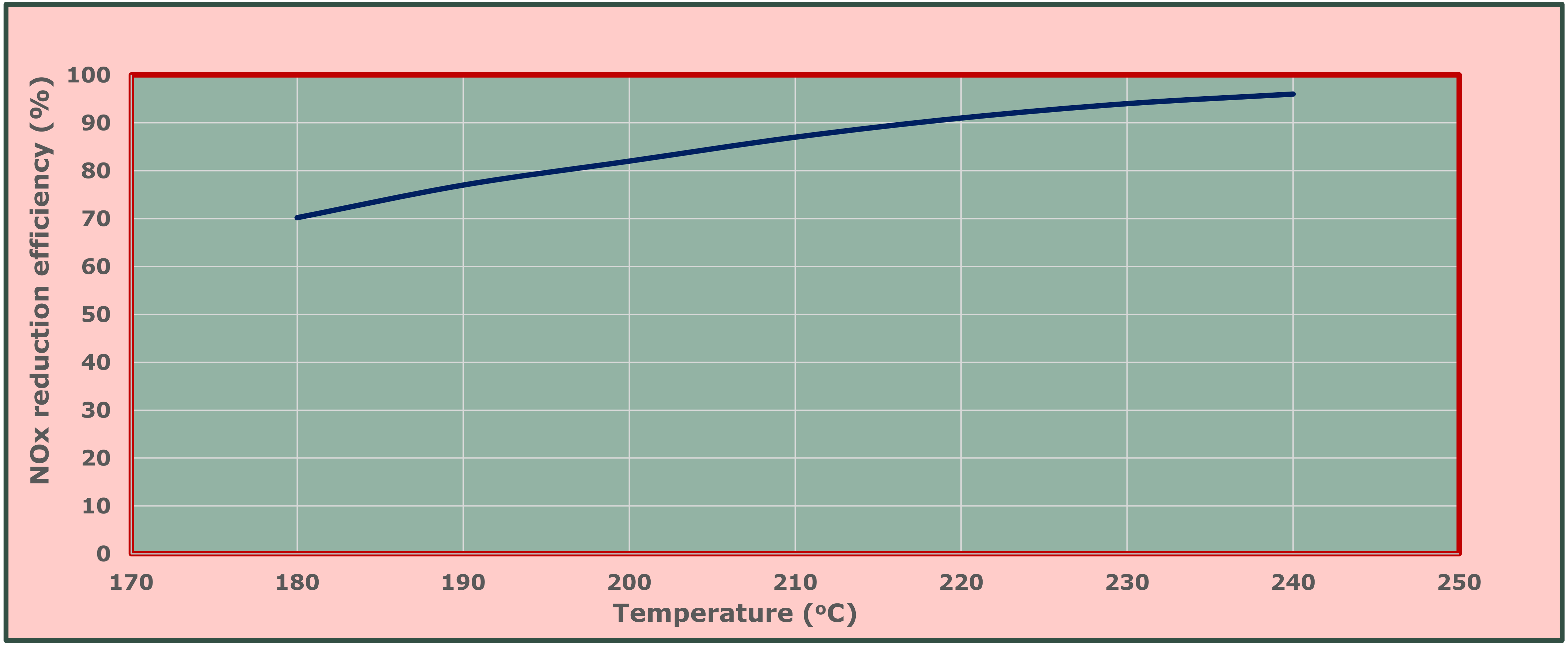
- Particulate filtration & destruction of NOx in one unit
  - Outer ePTFE membrane for efficient particulate removal
  - Catalytic composite felt for Nox and NH_3 reduction

$$
\begin{aligned}
4NO + 4NH_3 + O_2 &\rightarrow 4N_2 + 6H_2O \\
4NO_2 + 8NH_3 + 2O_2 &\rightarrow 6N_2 + 12H_2O
\end{aligned}
$$

- Reaction is more efficient at temperatures >180°C
- Temperature limitation for continuous use: 260°C



DeNOx Performance of Gore DeNOx Catalytic Bags



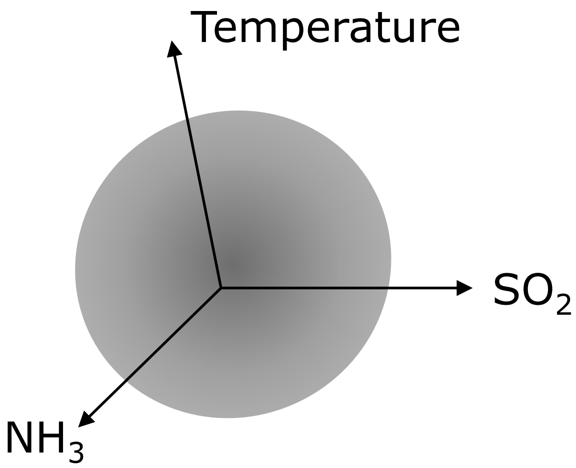
- *Example performance chart. Actual performance will depend on the process conditions.*

Undesired Reactions and Catalyst Fouling

Ammonia salt formation on catalyst

Impact

- NOx reduction efficiency
- Catalytic bag-filter life



$$2\,SO_2 + O_2 \rightarrow 2\,SO_3$$

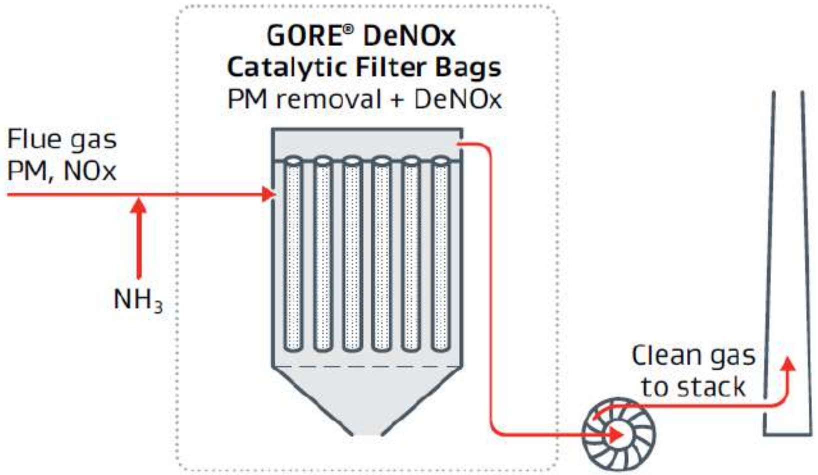
$$NH_3 + SO_3 + H_2O \rightarrow NH_4HSO_4$$

$$2NH_3 + SO_3 + H_2O \rightarrow (NH_4)_2SO_4$$

Solution

- Implementation of optimized process conditions (ammonia, SO_2 and temperature)
  - ➢ Gore application support

Requirements for Gore DeNOx Technology



- Existing or new baghouse
- Average baghouse temperatures: 180°C to 260°C
- NH_3 at the inlet of the baghouse
- Low SO_2 (0 – 50 mg/Nm^3) at the exit of the baghouse

All catalytic filter bags are custom-designed and manufactured

Proven Technology

Commercial applications since 2015

Worldwide applications

- **Municipal waste Incineration**
- **Hazardous waste Incineration**
- **Medical waste incineration**
- **Steel industry (sinter and lime plants)**
- **Chemical manufacturing**

- **Source of NOx is not important, process conditions are**

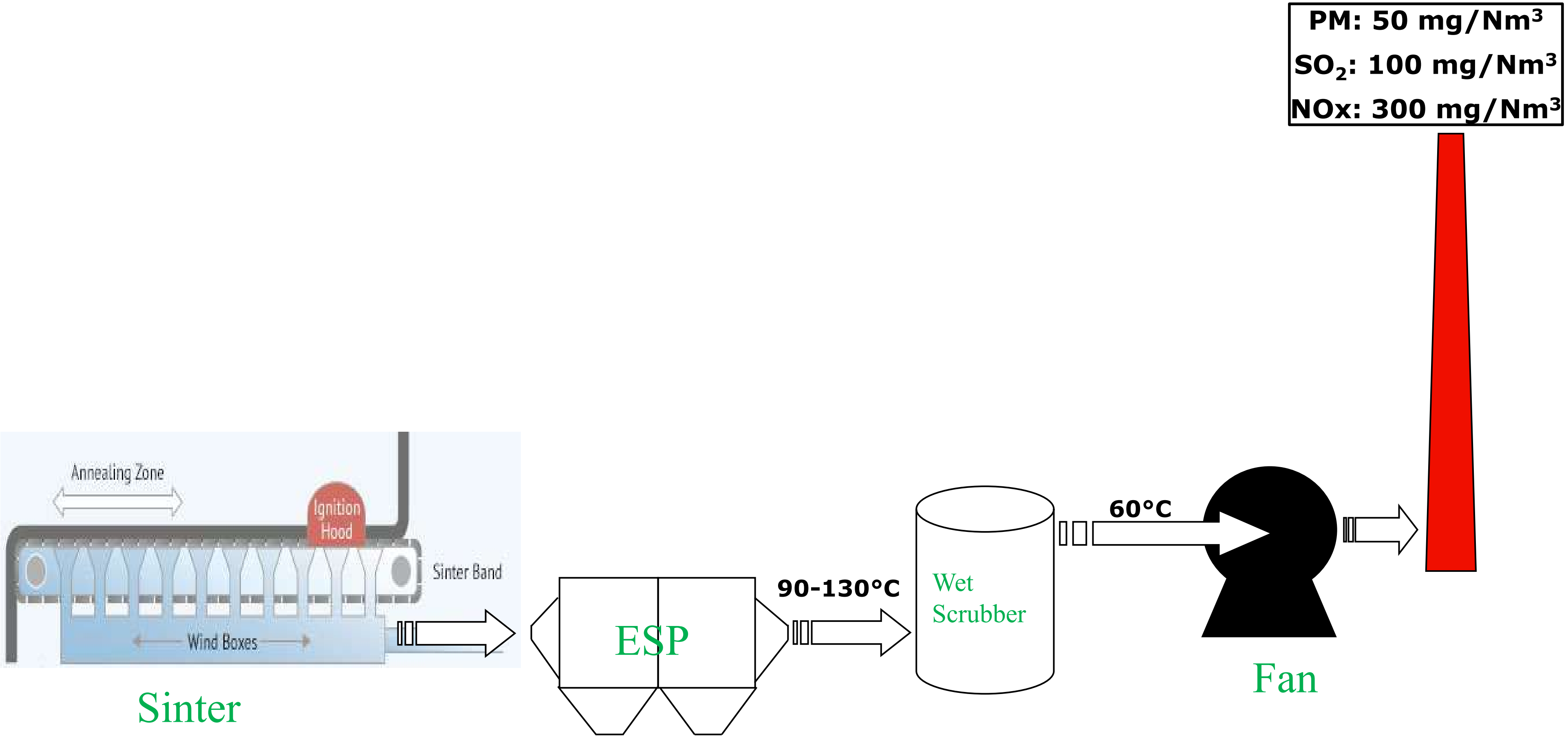
GORE® DeNOx CATALYTIC FILTER BAGS -

An innovative product for reliable & costeffective solution - NOx, ammonia & dioxin/furun reduction

Application in steel plants

- *Flue gas from sinter plants*
- *Flue gas from lime plants*

Sinter Flue Gas Cleaning Process Before DeNOx Process



PM: 50 mg/Nm^3
SO_2: 100 mg/Nm^3
NOx: 300 mg/Nm^3

Sinter

ESP

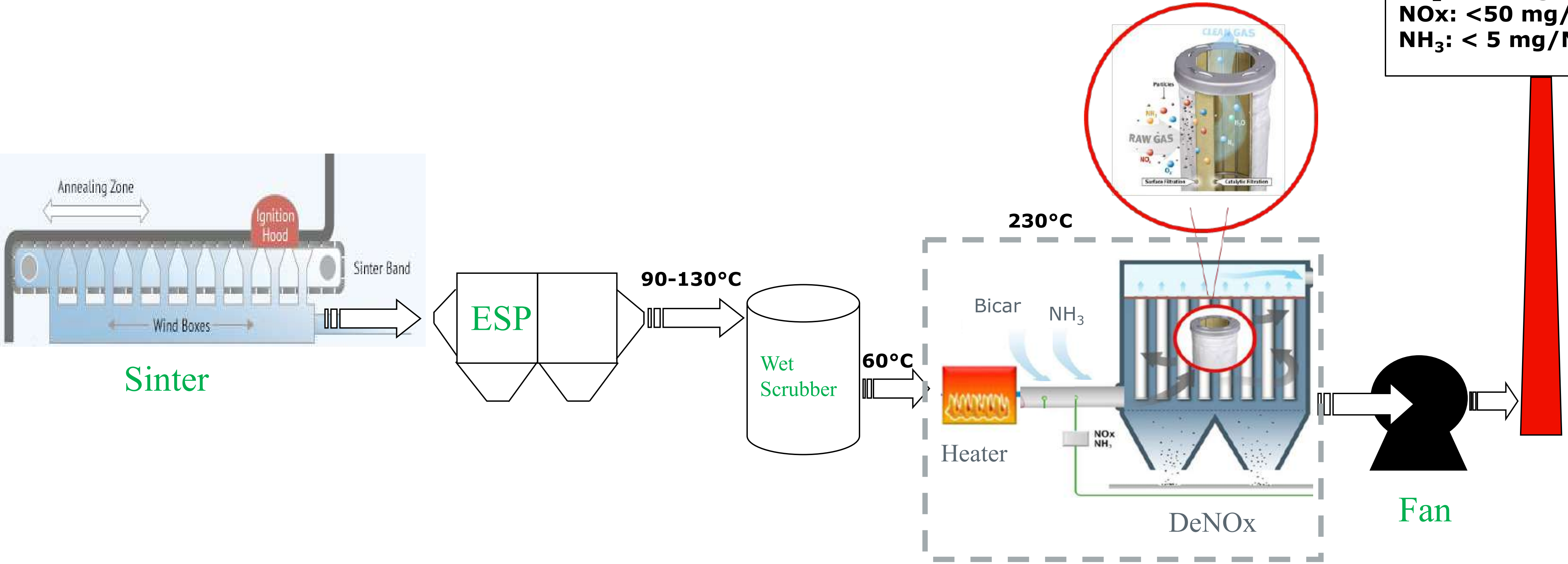
90-130°C

Wet Scrubber

60°C

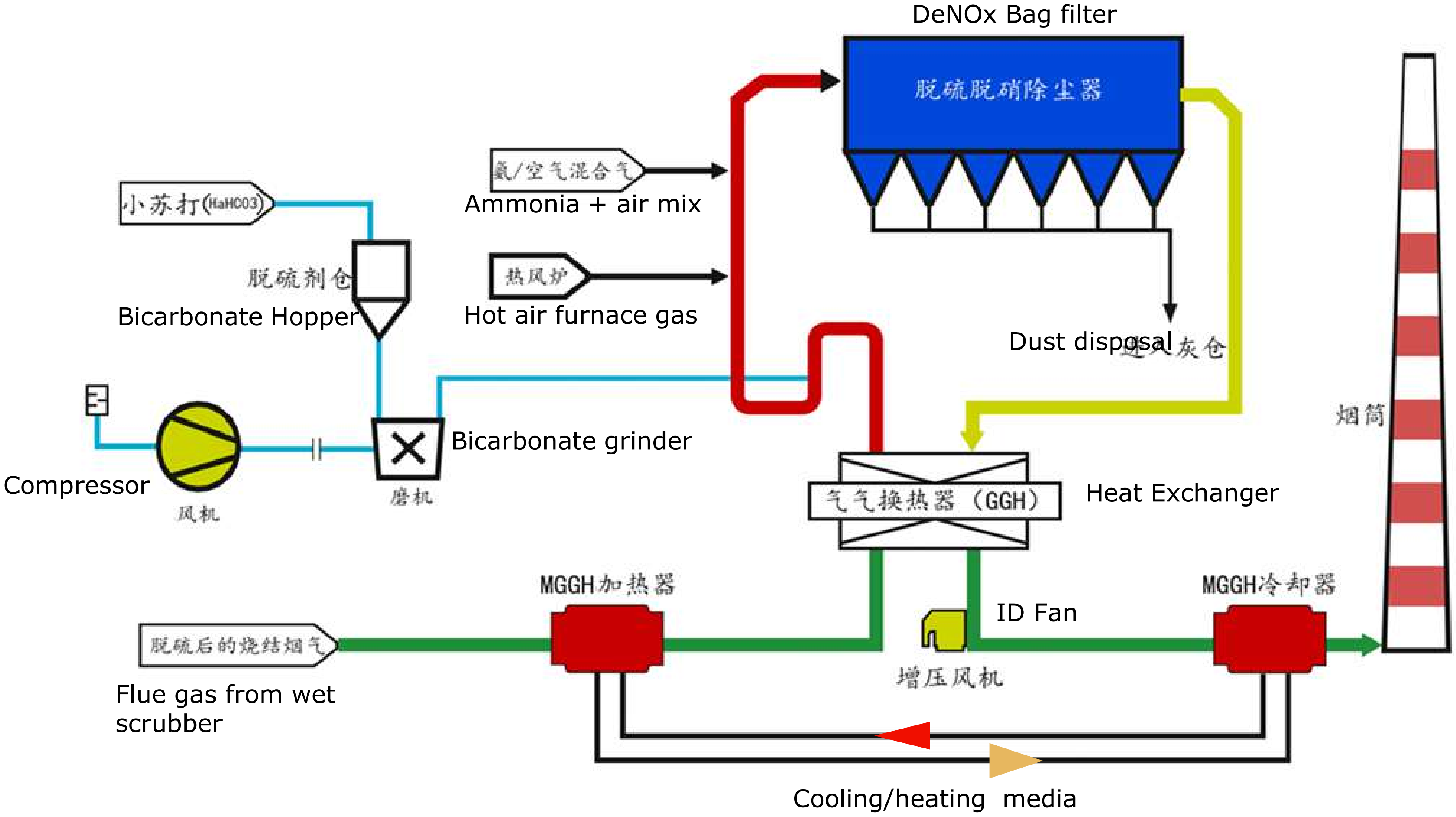
Fan

Proposed DeNOx Process With Catalytic Filters



PM: <5 mg/Nm3
SO_2: <40 mg/Nm3
NOx: <50 mg/Nm3
NH_3: < 5 mg/Nm3

Schematic of the DeNOx System Installed



Target emissions

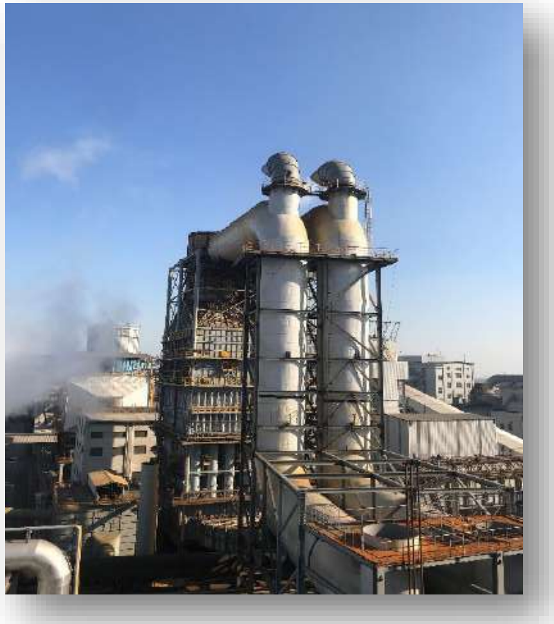
PM: <5 mg/Nm³
SO_2: <10 mg/ Nm³
NOx: <50 mg/ Nm³
NH_3: < 5 mg/ Nm³

Required conditions

Outlet SO_2: <10 mg/ Nm³
Inlet NOx: <300 mg/ Nm³
Temperature: >230C
ACR: < 0.9 m/min

Integrated Steel Plant in China

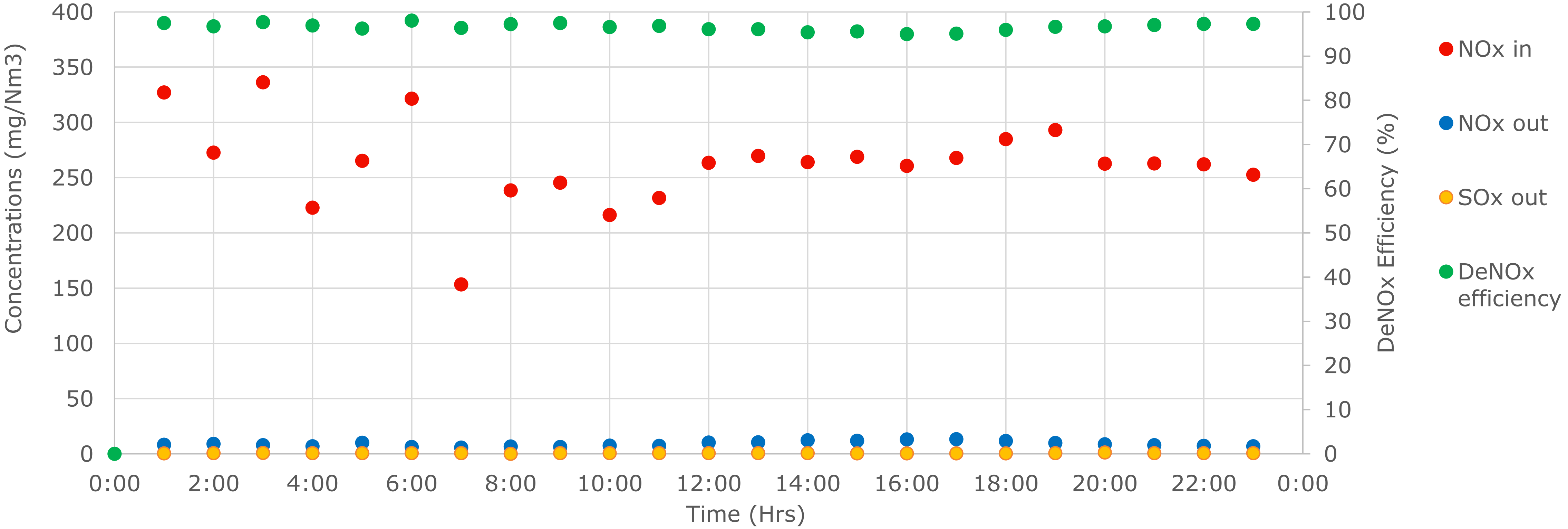
NOx reduction of sinter flue gas



- Combined flue gas flowrate of 1.8 million Nm^3/hr
- Line #3 was installed in October, 2019 with 8,064 DeNOx bags
- Line #4 was installed in November, 2019 with 9,408 DeNOx bags
- Total filtration area (for both lines) of 65,834 m^2

Sinter Plant in Steel Manufacturing

DeNOx performance at the startup (Line -4)

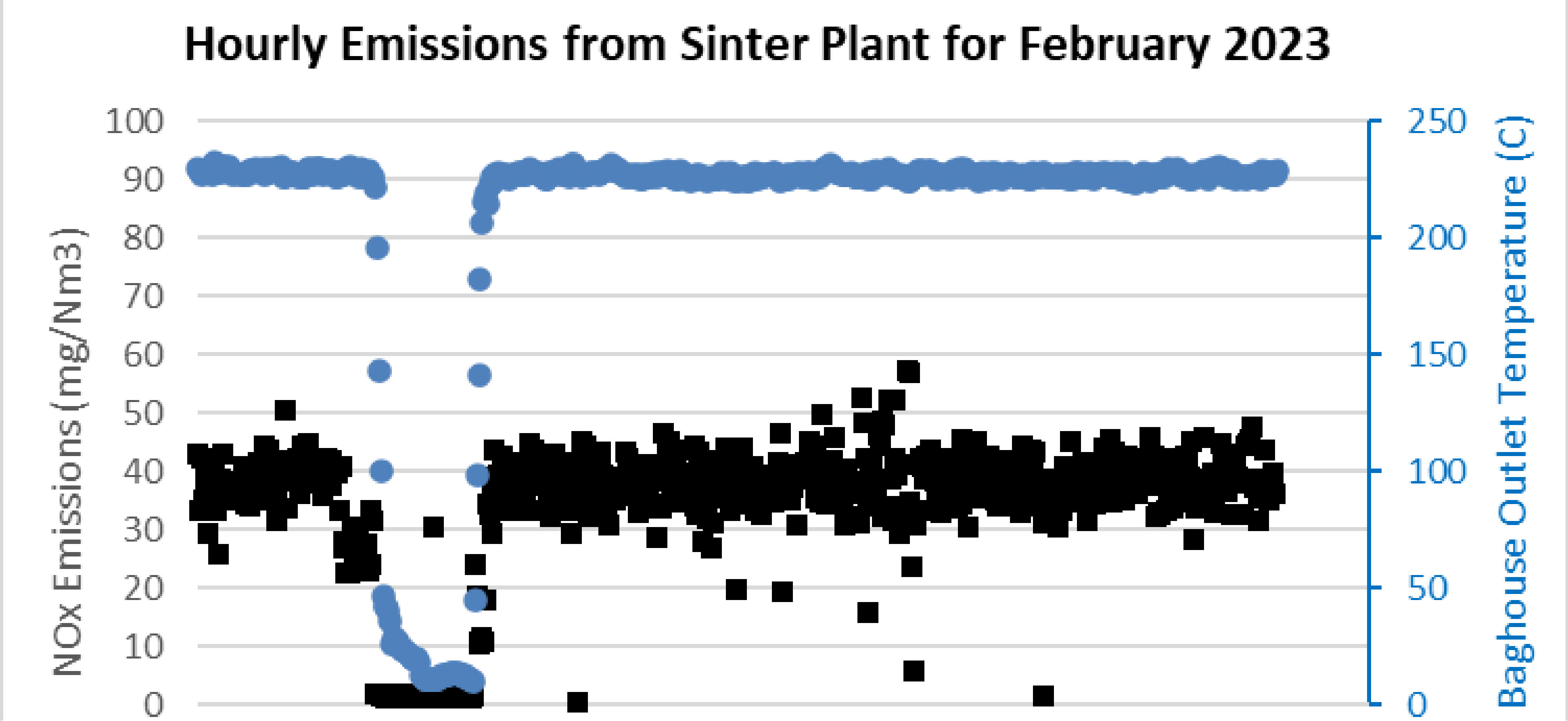


Inlet NOx : 200 to 350 mg/Nm^3
Outlet NOx: ≈ 10 mg/Nm^3
Average efficiency : ≈ 97%

Inlet SOx : 125 to 25 mg/Nm^3
Outlet SOx: ≈ 2 mg/Nm^3
Average efficiency : ≈ 97%

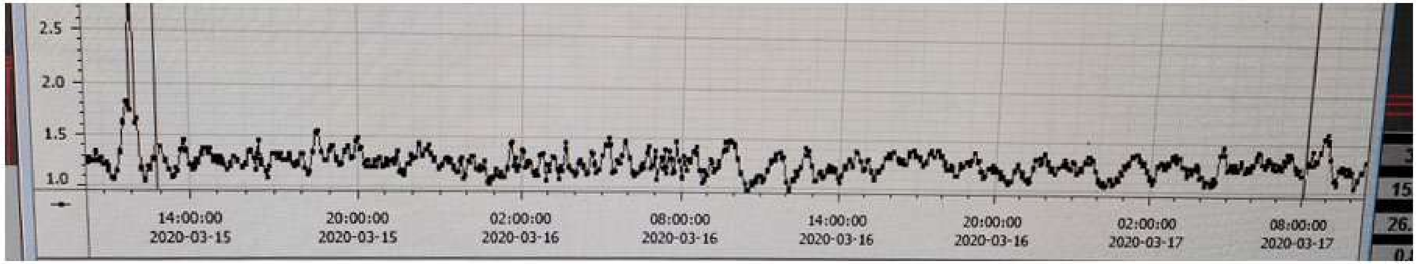
Average Temp: 230C
Average ACR : 0.9 m/min
F-F DP : 0.7 kPa

NOx Emission and Baghouse Temperature – Snapshot

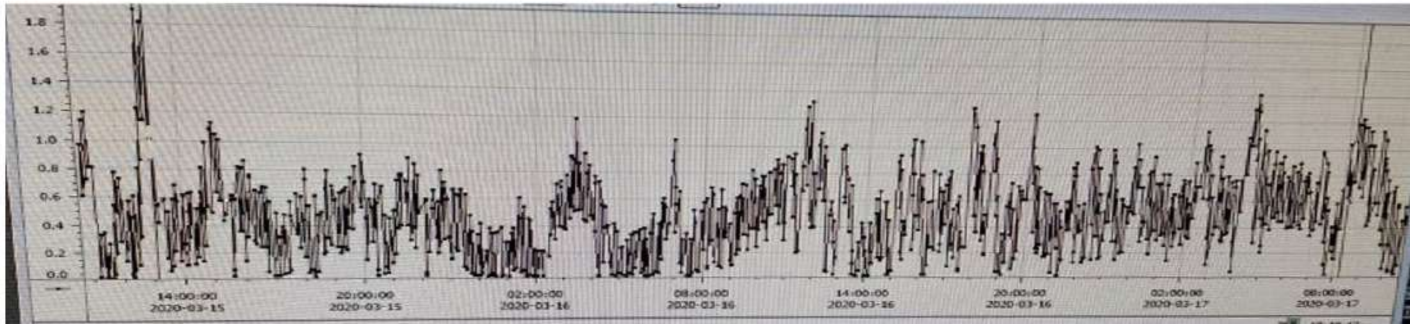


Key Performance Snapshots with Catalytic Filtration

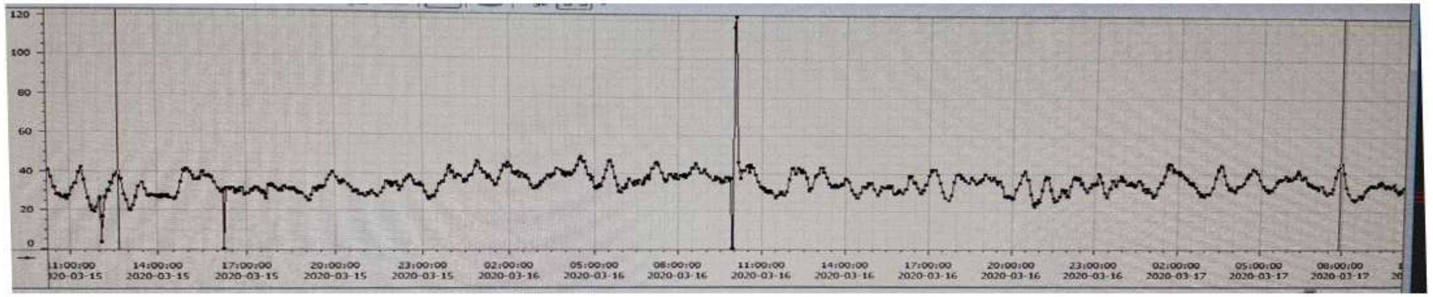
Total PM : < 2mg/Nm^3



Ammonia slip : < 2mg/Nm^3



NOx emission : < 50mg/Nm^3



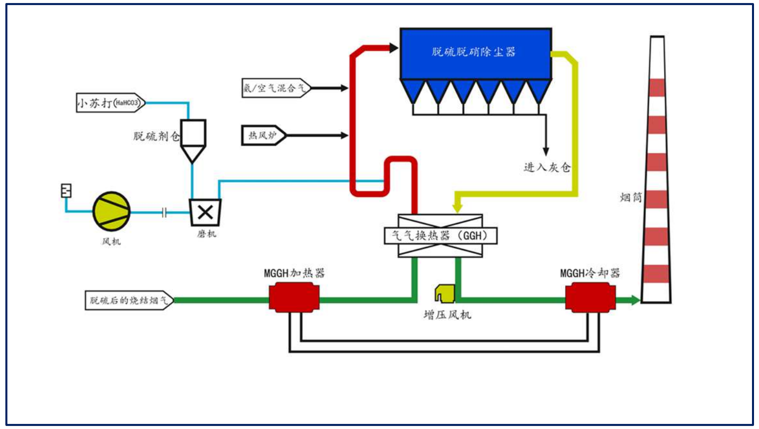
Process Parameters and Performance Summary

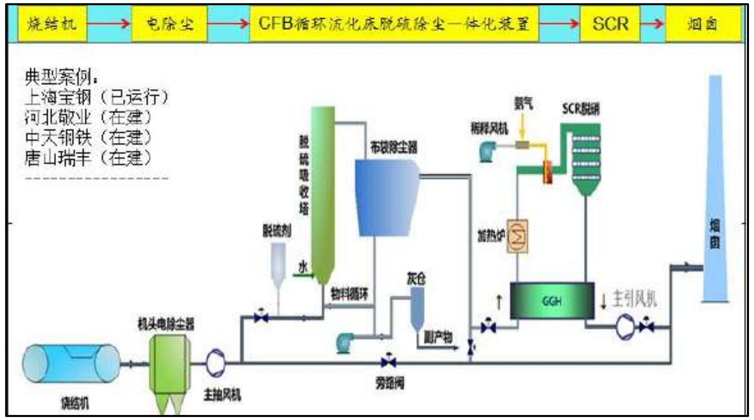
Required process parameters	Target	Actual
NOx inlet, mg/Nm^3	N/A	200-400
SO_2 outlet, mg/Nm^3	<10	<5
Superficial velocity, m/min	<0.9	<0.9
Bag house temperature, °C	230	225-235

Performance data	Target	Actual
NOx emission, mg/Nm^3	<50	<40
Ammonia slip, mg/Nm^3	<5	<2
PM, mg/Nm^3	<5	<2
Pressure drop,Pa	not specified	800
Dioxin Furan, TEQ/Nm^3	<0.1	0.03
Stable DeNOx efficiency achieved, %	not specified	84-85
Maximum DeNOx efficiency achieved, %	not specified	97

OPEX Comparison Between Catalytic Filters and SCR

DeNOx Technology	**GORE® DeNOX Catalytic Bags**		**SCR**
Sinter	Line #3	Line #4	Line #5
SOx Reduction Technology	Old Wet FGD + Bicarbonate	Old Wet FGD + Bicarbonate	New Semi-dry CFB
# Bags	8064	9408	Not applicable
DeNOx Operating Temp	225 – 235 °C	225 – 235 °C	280 – 300 °C
2020 Capacity (tpd Sinter)	6435	6526	7990
2023 Capacity (tpd Sinter)	5060	5800	5980
2020 OPEX* (RMB/ton Sinter)	12.586	12.645	13.35
2023 OPEX* (RMB/ton Sinter)	15.726	16.138	20.204





Lime Kiln Application in an Integrated Steel Plant, China

Rotary Kiln

Highlights

- Total of 7 lines – 7 baghouses
- 4 Rotary kilns & 3 Shaft kilns
- Total flowrate: 800,000 Nm^3/hr
- Total number of filters: 10,430
- Total filtration area: 25,922 m^2

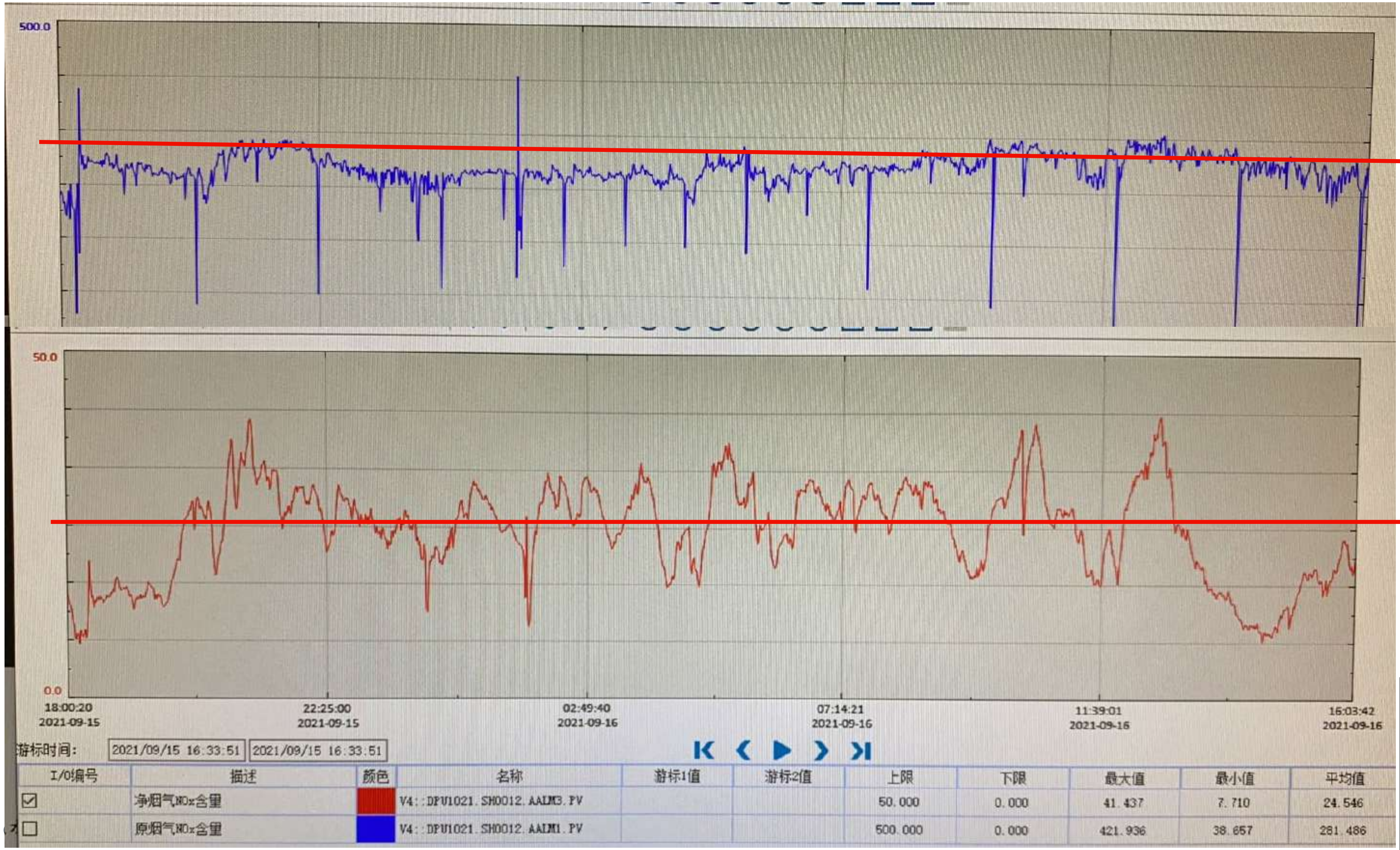
Shaft Kiln

Process Parameters and Performance Summary

Required process parameters	Target	Actual
NOx inlet, mg/Nm^3	N/A	<300
SO_2 outlet, mg/Nm^3	<10	<10
Superficial velocity, m/min	<1	<1
Baghouse temperature, °C	230	220-240

Performance data	Target	Actual
NOx emission, mg/Nm^3	<50	<50
Ammonia slip, mg/Nm^3	<3	<3
PM, mg/Nm^3	<5	<5
Pressure drop,Pa	not specified	800- 900
Dioxin Furan, TEQ/Nm^3	N/A	N/A
Stable DeNOx efficiency achieved, %	not specified	83-85
Maximum DeNOX efficiency achieved, %	not specified	>91

Performance Snapshot – DeNOx Efficiency



游标时间: 2021/09/15 16:33:51 2021/09/15 16:33:51

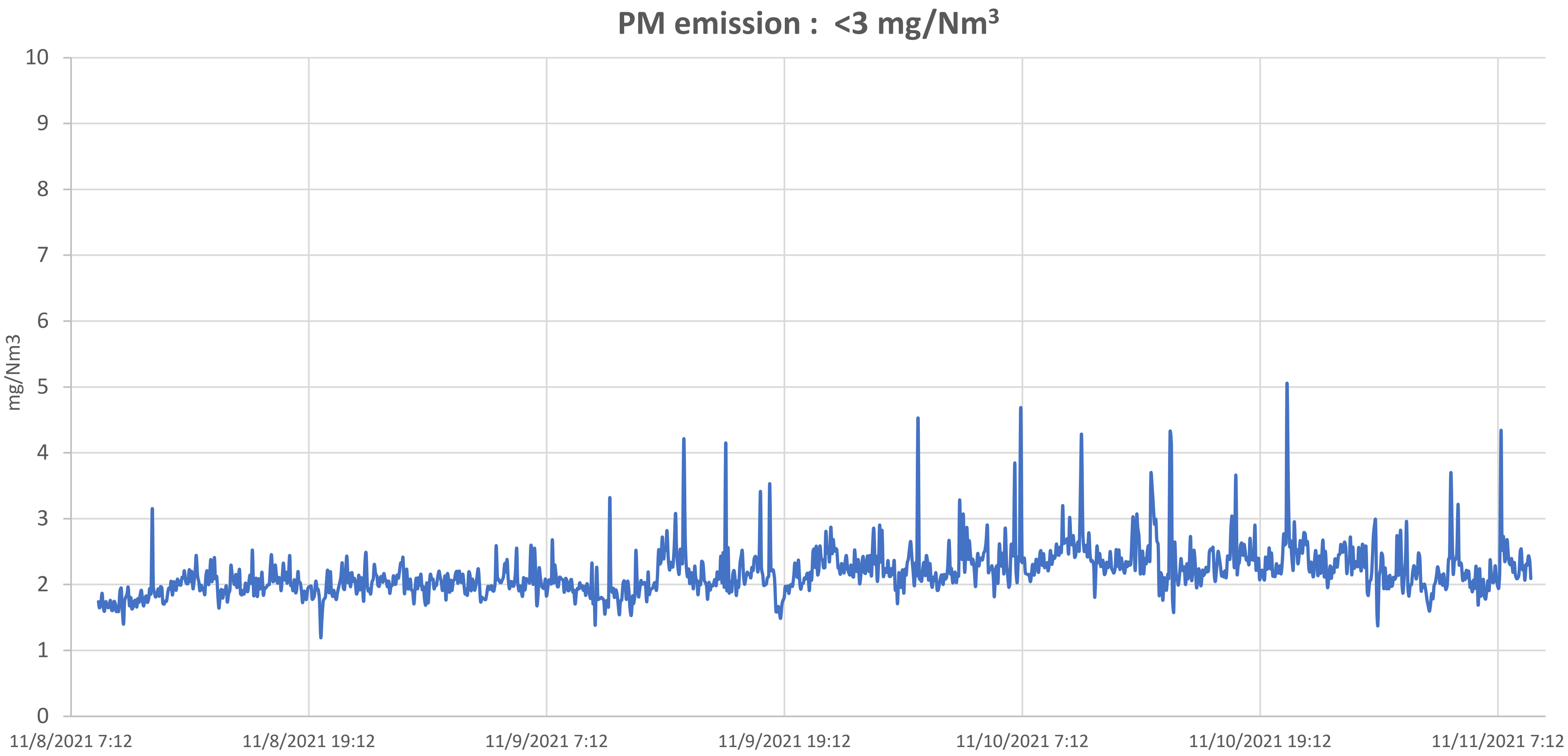
I/O编号	描述	颜色	名称	游标1值	游标2值	上限	下限	最大值	最小值	平均值
☑	净烟气NOx含量	🟥	V4::DPU1021.SH0012.AALM3.PV			50.000	0.000	41.437	7.710	24.546
□	原烟气NOx含量	🟦	V4::DPU1021.SH0012.AALM1.PV			500.000	0.000	421.936	38.657	281.486

Inlet NOx:
280mg/Nm^3

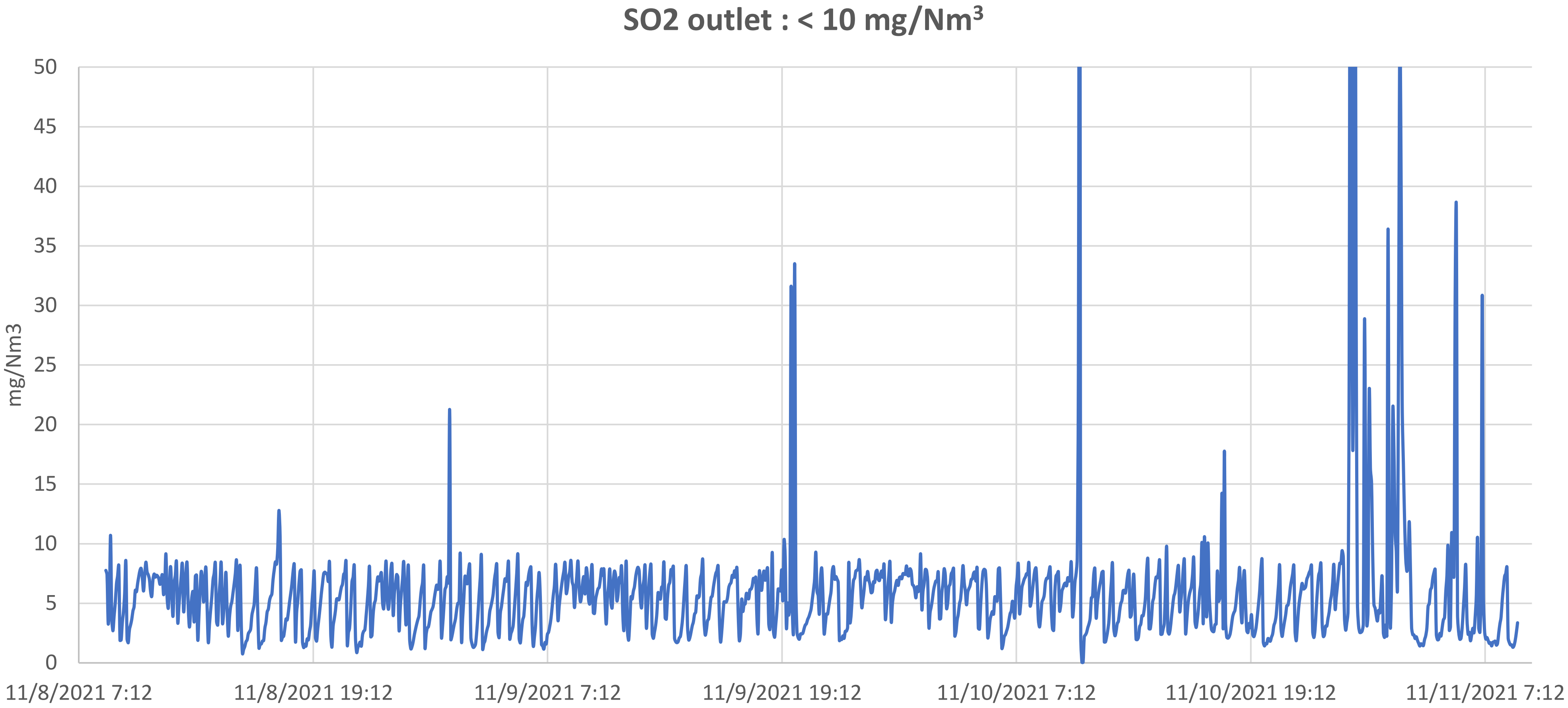
outlet NOx:
25mg/Nm^3

NO$_x$ conversion is ~91%

Performance Snapshot – PM Emission



Process Parameter Snapshot – SO_2 Outlet



Conclusive Remarks

Gore catalytic filtration technology proven to be effective in meeting stringent NOx regulations

High DeNOx efficiency with low NOx emission: > 95% achievable

Low ammonia slip : < 3 mg/Nm^3

Meeting Dioxin /Furan emission as a co-benefit

Proper process conditions are required to maintain DeNOx performance over lifetime of the filters

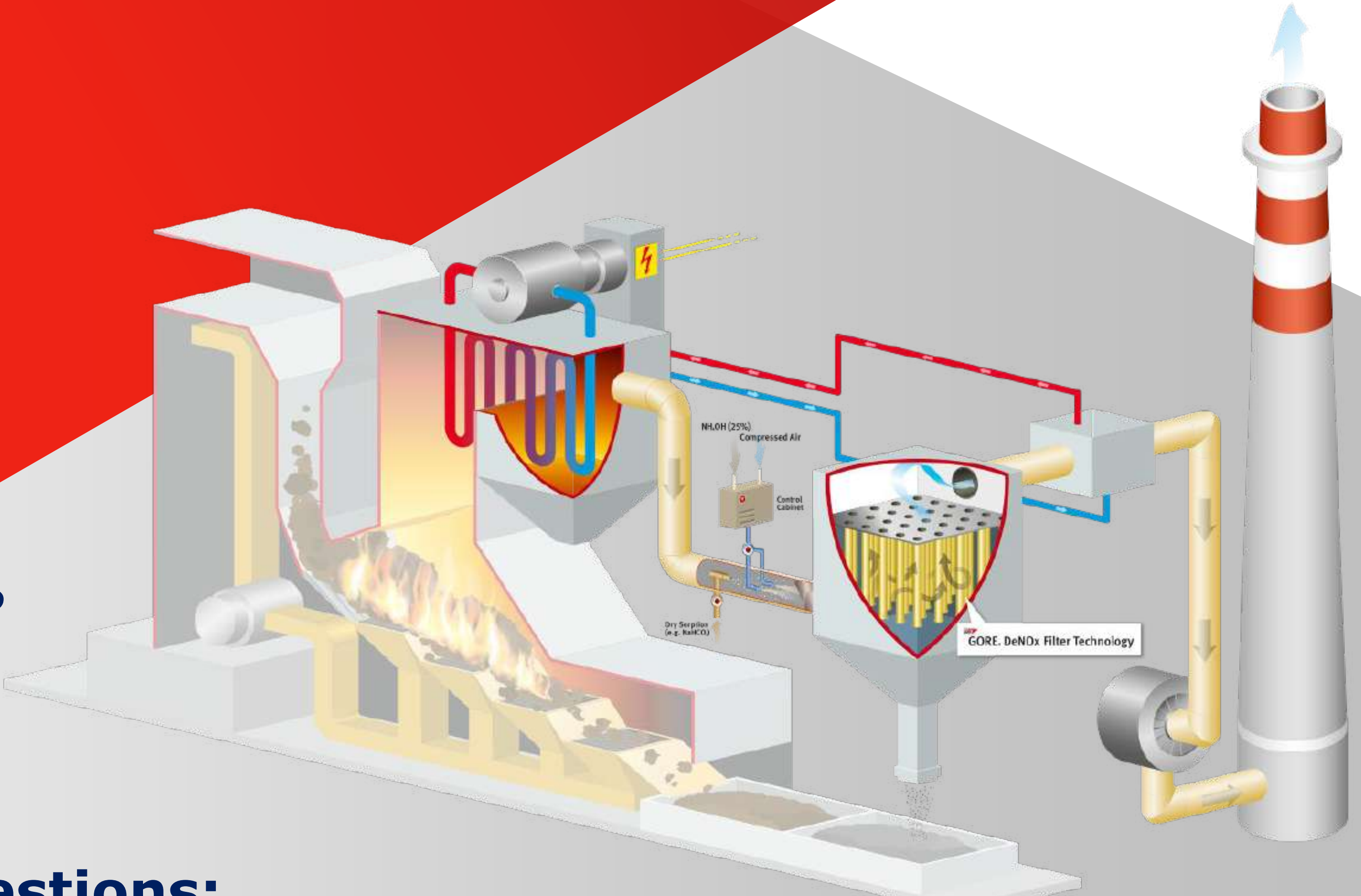
Easy implementation without additional equipment or real-estate footprint- uses existing baghouses

Possible lower cost of ownership compared to conventional Honeycomb SCR

OBRIGADO
GRACIAS
THANK YOU
고맙습니다
ありがとう

GRAZIE
DANKE
謝謝
TACK

Questions?



Please contact with any questions:

- Tarun Poddar - W. L. Gore & Associates, Inc.
- tpoddar@wlgore.com

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GORE

IT3-31: Phosphorus Recovery from Wastewater Treatment Sludges

AWMA IT3 HWC 40th Conference, Charlotte NC, September 2023

By Kai Sartorius and Cornelia Cretiu
SOLVAir®

Summary

O1 _ Phosphorus (P) Essential Element and Resource

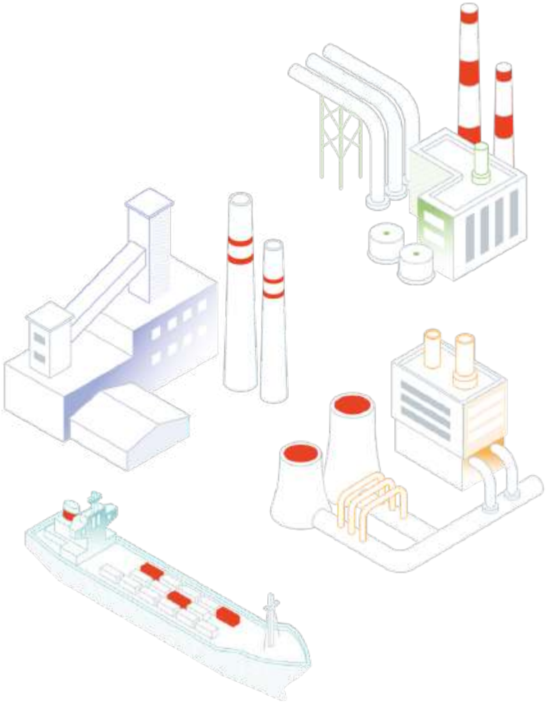
O2 _ Why recover P?

O3 _ Sources of Phosphorus
Why sludge?

O4 _ P recovery methods

O5_ Sodium DSI for acid gas remediation in sludge incineration for P recovery

O6_ Case Study

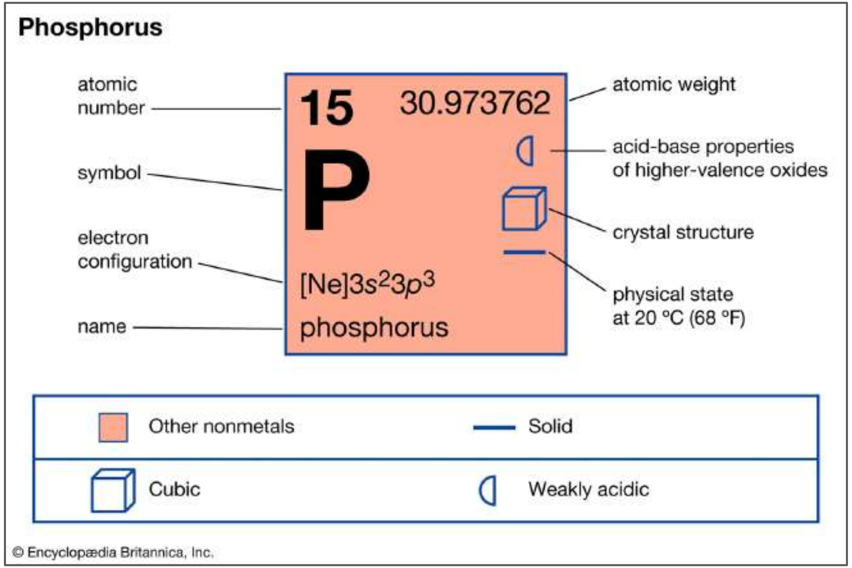


Phosphorus and Human Life

Bones and Teeth contain Phosphates

For the Whole Human: needed for the growth, maintenance, and repair of all tissues and cells, and for the production of the genetic building blocks, DNA and RNA

Sources of Phosphorus: dairy products, meats and poultry, fish, eggs, nuts, legumes, vegetables, and grains



Source: https://www.britannica.com/science/phosphorus-chemical-element/images-videos

Phosphorus (P) as Essential Element

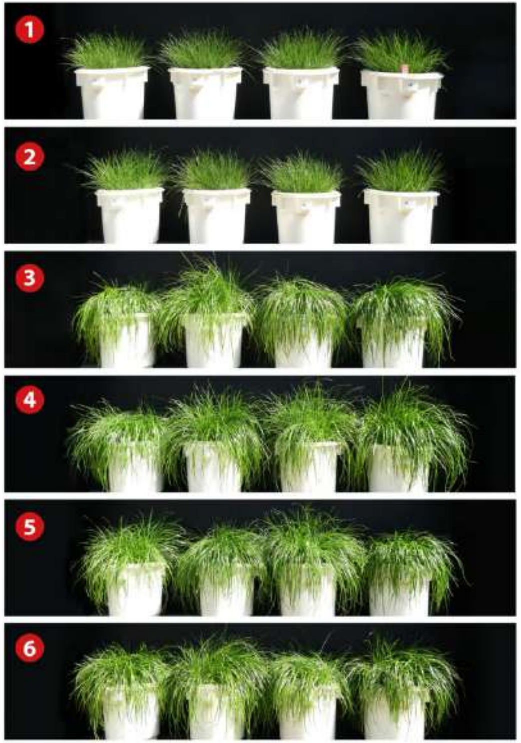


Image Source: https://phos4green.glatt.com/de/verwertung/pflanzversuche/

1 = no fertilizer

2 = raw phosphate

3 - 5 = different fertilizers based on sludge incineration ashes

6 = commercial fertilizer

"To put it simply, there is no life on Earth without phosphorus," explained Prof Penny Johnes of Bristol University.

Ref.:https://www.theguardian.com/environment/2023/mar/12/scientists-warn-of-phosphogeddon-fertiliser-shortages-loom

P is a Limited Resource

EU Critical Raw Materials Act:
The EU defined 34 critical and strategic raw materials, including Phosphorous and Phosphorit

Around 85% of the phosphate rock reserves are located in five countries: Morocco (70%), China (5%), Egypt (4%) Algeria (3%), and Syria (3%).

>85% of the total P-demand is imported

P-recovery from sewage sludge can cover about 50% of the total demand

P Recovery and EU and Global Initiatives

P is considered a critical Element

Germany will make P-recovery **mandatory** for big (2029) and medium (2032) sized waste water treatment plants. Big- and medium sized plants treat >90% of the total waste water volume.

Not signed yet, but similar initiatives expected in the surrounding countries (Austria, Switzerland, Netherlands).

Globally, there are a lot of initiatives and projects under large international organizations: UN, World Bank

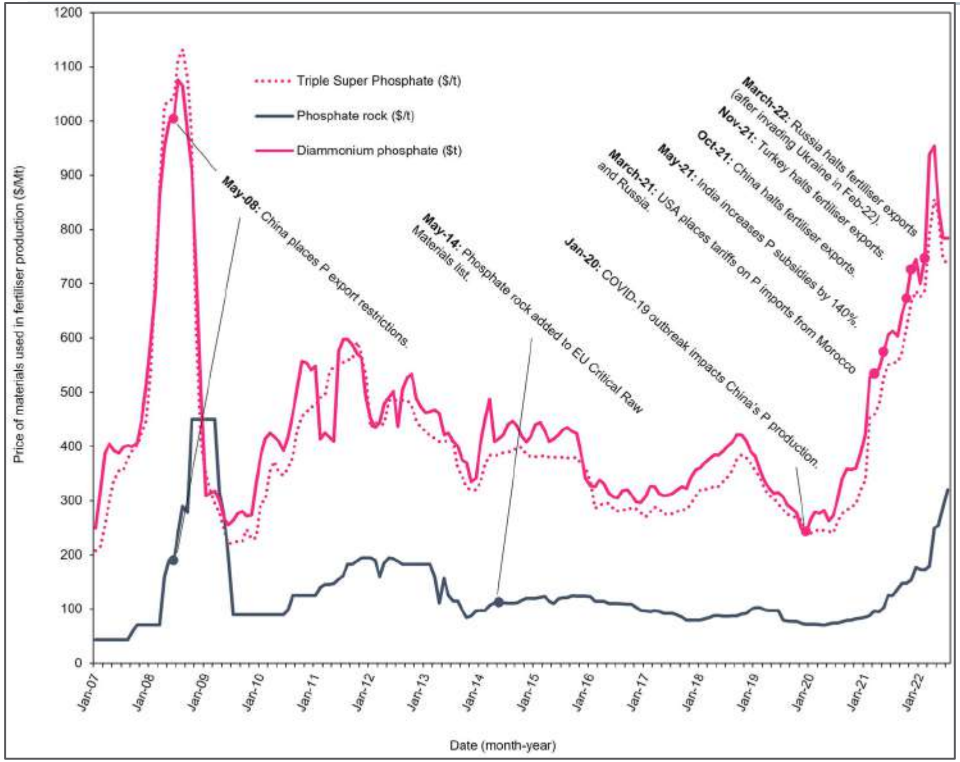
P Sources: Natural and Recoverable

Large deposits of guano were the first "ores" mass exploited

Agricultural and Human sources
"Wastewater contains nitrogen and phosphorus from human waste, food and certain soaps and detergents."
Source:https://www.epa.gov/nutrientpollution/sources-and-solutions-wastewater#:~:text=Wastewater%20contains%20nitrogen%20and%20phosphorus,of%20nitrogen%20and%20phosphorus%20pollution.

Scientists talk about a "Phosphogeddon" term that was toned down lately
Source: "https://www.theguardian.com/environment/2023/mar/12/scientists-warn-of-phosphogeddon-fertiliser-shortages-loom"

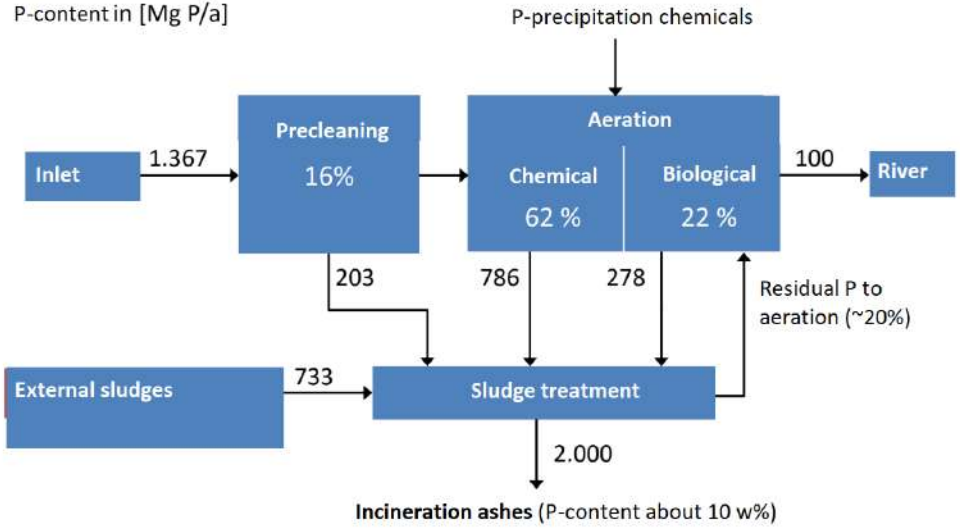
Price of Phosphate Rock and Phosphate fertilizer



- Valuable commodity with highly volatile price connected to food safety
- Circular economy possible with tight management
- Knee-jerk governmental triggers
- Global problem with a potential solution

Source;
https://www.frontiersin.org/articles/10.3389/fsufs.2023.1088776/full

Concentrate the source: Sludge Incineration


P-content in [Mg P/a]

P-precipitation chemicals

Inlet

1.367

Precleaning

16%

Aeration

Chemical

62 %

Biological

22 %

100

River

203

786

278

Residual P to aeration (~20%)

External sludges

733

Sludge treatment

2.000

Incineration ashes (P-content about 10 w%)

P-balance in Hamburg wastewater treatment plant (150 Mm³/year)

(Source: "Erste Erfahrungen aus einer großtechnisch umgesetzten P-Rückgewinnungsanlage in Hamburg", Harald Hanßen, Presentation at *DWA Klärschlammtage 2021*)

To recover the phosphorous, different technologies are available. Recovery from single-source incineration ashes are the most promising as the P-content is the highest.

Direct use of sewage sludges as agricultural fertilizer is banned nowadays, as it contains several pollutants like medical residues and heavy metals.

P-concentration in wastewater: ~0.0001 w%
P-concentration in sludge*: ~0.5 w%
P-concentration in ashes: ~10 w%
*dewatered, 20% dry matter

P Recovery Methods

Basic principle: precipitation of phosphoric minerals from sludge or leachates

The economic efficiency of the method is hinging on the content of recoverable product in the source

Separation methods: selective dissolution, specialized filtration, alkaline leaching and stabilization, wet chemical extraction (e.g., Sephos process, Biocon, Pash process, Eberhard process), high-temperature processes (e.g., Merphec, Susan, ATZ ion bath reactor), bioleaching process (Incore)

https://www.sciencedirect.com/science/article/abs/pii/S0959652616319680#:~:text=At%20the%20moment%2C%20the%20most,struvites%2C%20hydroxyapatites%20or%20calcium%20phosphates.

Cost Effective and Efficient Recovery

Incentive, subsidies and governmental support to ensure agriculture sector needs and food security

All big and medium sized wastewater treatment plants in Germany are forced to recover phosphorus from 2029 on

- From wet phase: >50% P-recovery mandatory
- From incineration ash: >80% P-recovery mandatory

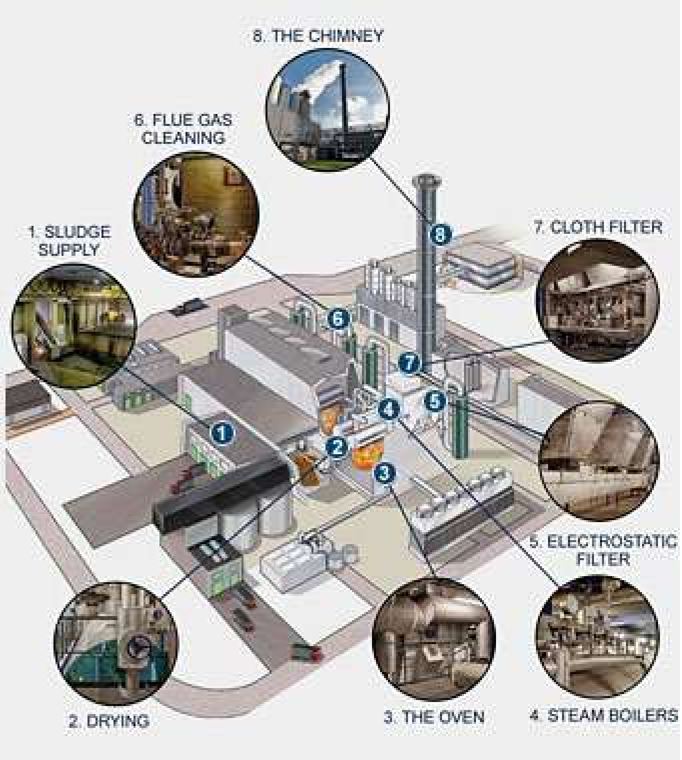


Image: https://www.asme.org/topics-resources/content/sewage-sludge-power

Acid Gas Remediation for Sludge Incineration

Sewage sludge incineration has to meet the same emission standards like waste incineration - the most stringent among all industries.

High efficient flue gas cleaning is mandatory to meet the emission limits: >99% mitigation rate for SOx is needed.

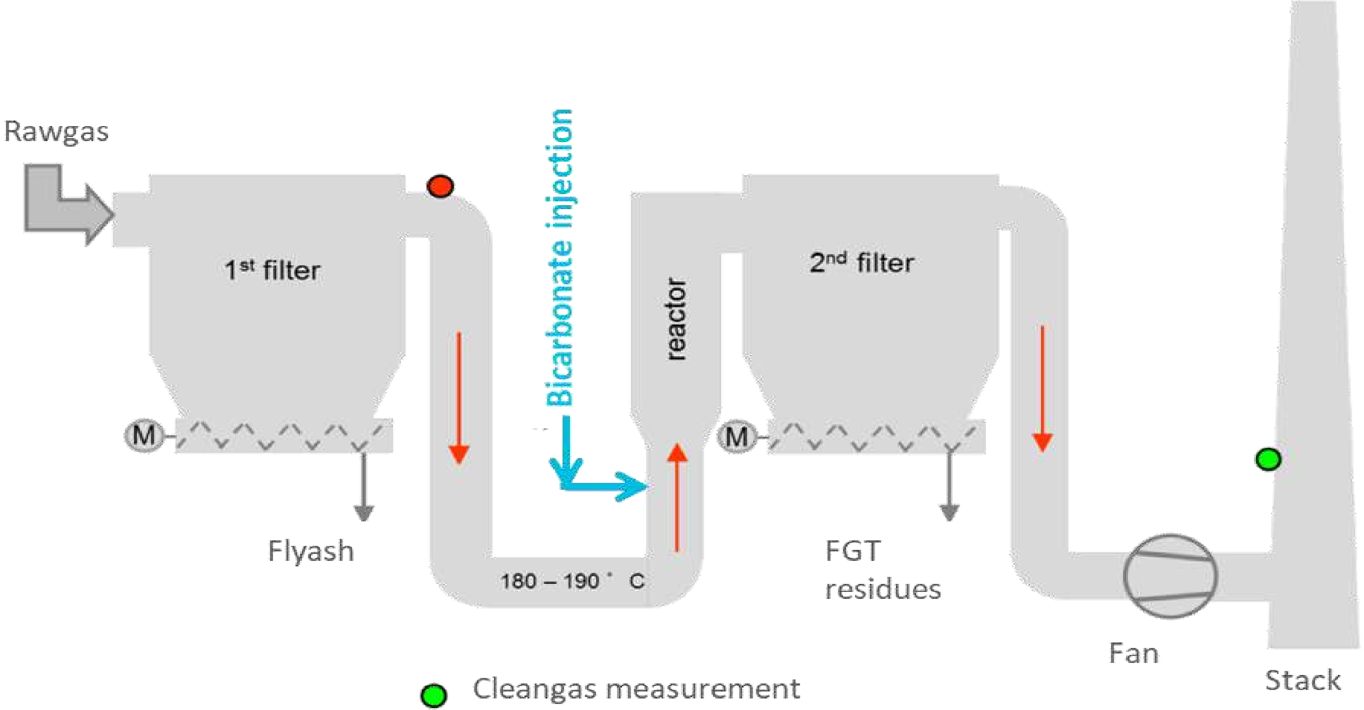
Cofiring of sludge in other incineration plants (coal, waste, cement) is so far a common way of treatment. In the future, only single-source incineration will be possible, due to mandatory P-recovery from the incineration ashes.

European BREF-WI emission limits		
	2006	2019
	mg/Nm³, dry, 11% O_2	**mg/Nm³, dry, 11% O_2**
HCl	10	< 2 - 6
SO_x	50	5 - 30
HF	1.0	< 1.0
NH_3	10	2 - 10
NO_x	200	50 - 120
Dust	10	< 2 - 5

Sodium (Na) and Phosphorus (P)

- Not directly linked, both are important biologically
- Sludge incineration produces acid gases that can be treated with dry sodium sorbents
- Substances found in the ashes from sludge incineration determine the hazardous/non-hazardous category of the residues and recoverable status of resource minerals within
- Two step mitigation is beneficial: avoids dilution of ashes with the highest concentration of P
- Sludge incineration plants are fluidized bed, high dust, makes sense to do the acid gas remediation after removal of the dust

Case Study - GIKW Gdansk (Poland)



🟢 Cleangas measurement
🔴 Rawgas measurement

Case Study - GIKW Gdansk (Poland)

- Burnt sludge:
  6 - 7 t/h, 20% DM
- S-content:
  0.24% (wet)
  1.25% (dry)
- Emission limit SOx:
  50 mg/Nm^3

DAY	SOx Raw gas	Required SOx mitigation	SOLVAir RTU
	mg/m^3 dry	%	kg/h
1	3012	98.3	111.3
2	2955	98.3	123.3
3	2549	98.0	120.0
4	2408	97.9	109.5
5	3081	98.4	105.7
Average	**2801**	**98.2**	**114.0**

Case Study - GIKW Gdansk (Poland)

- Average Stoichiometric Ratio = 1.15
- Avg. bicarbonate consumption: 14 kg/t (wet sludge, 20% DM)
- HSS-lime consumption: >28 kg/t (wet sludge, 20%DM)
    - Not always able to meet the requirements
- Residues generated
    - Bicarbonate: 10 kg/t sludge
    - HSS-lime: > 30 kg/t sludge

SOLVAiR®

vs. HSS lime

Sorbent consumption - 50% ↘

FGT residues - 67% ↘

Conclusions

- P is a critical element suitable to be recovered in circular economy fashion due to its scarcity
- Water treatment sewage sludge is a widely available source for P
- Recovery from sewage sludge can cover a significant amount of P-needs
- Highest P-recovery rates can be achieved from ashes obtained in single-source sludge incineration plants
- Efficient flue gas cleaning is needed for single-source incineration plants (very high SOx-levels to be mitigated)

"Pecunia non olet": attributed to Roman Emperor Vespasian

Questions?

Kai Sartorius
Sales Dev. Mgr. SOLVAir Solutions
Germany
Kai.Sartorius@solvay.com

Cornelia Cretiu
Technical Dev. Engineer SOLVAir
USA
Cornelia.Cretiu@solvay.com

Advanced Gas Cleaning Wet Scrubber Technology for Spodumene Lithium Mineral Processing

Paper #IT3-36 Presented at the 40th International Conference on Thermal Treatment Technologies & Hazardous Waste Combustors, September 13-14, 2023, Charlotte, NC

Andrew C. Bartocci
Envitech, Inc.
2924 Emerson Street- Suite 320
San Diego, CA 92106
Ph: 619-223-9931

ABSTRACT

The desire to reduce greenhouse gas emissions has propelled demand for lithium. Over the next decade, global demand for lithium will continue to grow at a compounded annual rate driven by growth in the electric vehicle (EV) market. Battery demand for lithium is expected to grow from 30% of the lithium market in 2015 to 95% of the market by 2030[1]. Lithium production from spodumene ore will play a significant role in meeting future demand. Spodumene processing relies on a two-step, high temperature, pyrometallurgical process. The first step is calcination followed by roasting. Both steps produce significant emissions that rely on wet scrubber technology to meet emission standards. This paper outlines advanced gas cleaning wet scrubber technology to treat emissions from both steps.

INTRODUCTION

The desire to reduce greenhouse gas emissions has propelled demand for lithium. Over the next decade, global demand for lithium will continue to grow at a compounded annual rate driven by growth in the electric vehicle (EV) market. Battery demand for lithium is expected to grow from 30% of the lithium market in 2015 to 95% of the market by 2030[2]. Lithium production from spodumene ore will play a significant role in meeting future demand. Spodumene processing relies on a two-step, high temperature, pyrometallurgical process. The first step is calcination followed by roasting. Both steps produce significant emissions that rely on wet scrubber technology to meet emission standards. This paper outlines advanced gas cleaning wet scrubber technology to treat emissions from both steps.

Lithium metal can be produced from non-pyrometallurgical processes derived from various mineral sources like saline lakes and geothermal brine. However, spodumene ore remains an important lithium source. The advantage of spodumene compared to brine sources is its higher lithium concentration. Spodumene processing relies on thermal treatment and generally has higher energy and extraction cost compared to brine processing. Spodumene naturally occurs in a compact, low reactivity alpha phase. It must first be transformed to a more porous beta phase with larger surface area and higher reactivity to allow lithium extraction via leaching processes. The phase transformation occurs during calcination above 900°C (1,652°F)[3]. Calcination refers to thermal treatment of a solid chemical compound at a temperature below its melting point to promote a physical change. Calcination typically occurs in an inert environment, however, alpha spodumene is not sensitive to products of combustion. Therefore, a direct fired rotary kiln is used to calcine spodumene ore.

After calcination, the beta phase spodumene concentrate is cooled and mixed with 95% to 97% sulfuric acid. The mixture is roasted in an indirect fired rotary kiln at approximately 250°C (582°F). An exothermic reaction begins at 170°C (338°F)[4]. An indirect fired kiln is used because the beta phase concentrate cannot be exposed to the products of combustion. The roasting step with sulfuric acid allows the lithium to be extracted as a water-soluble sulfate which can then be leeched.

Both thermal treatment steps, calciner and roaster, emit significant pollutants which must be removed. The wet scrubber gas cleaning technology required to treat these emissions is discussed below.

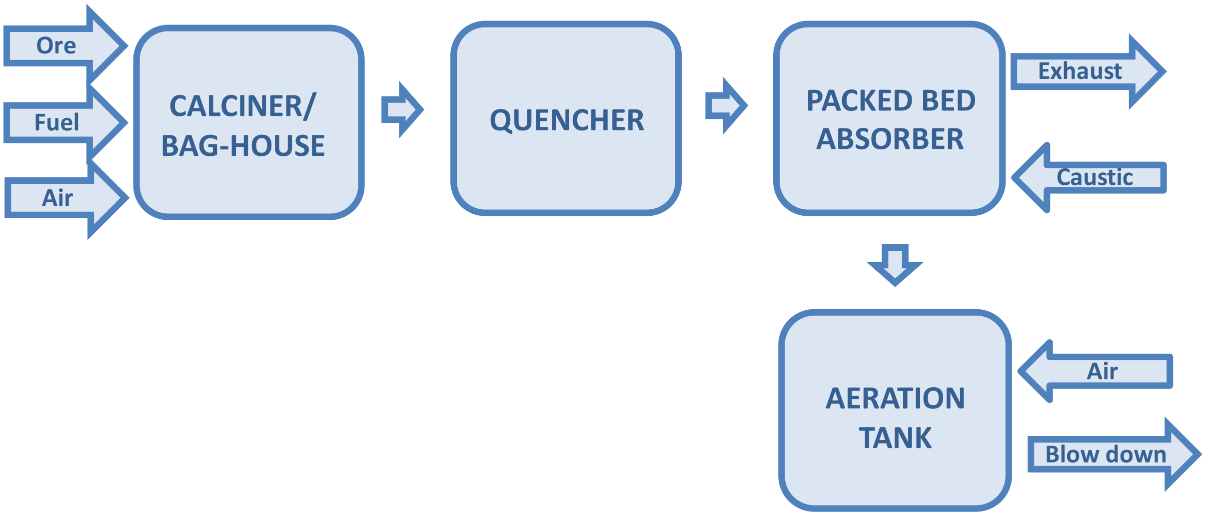
CALCINER GAS CLEANING

The calciner is typically a direct-fired rotary kiln. The exhaust gas contains products of combustion including 20% to 30% moisture. Pollutants can vary from facility to facility depending on the feed composition of specific spodumene ore. Calciners emit significant amounts of particulate matter. Most calciner gas cleaning systems utilize a baghouse to capture particulate. The particulate amount and size depend on upstream processing and how fine the feed ore is milled. A wet scrubber follows the baghouse. The primary pollutant removed by the wet scrubber is SO_2. There may also be low concentrations of HF and NOx present. Typical gas flow rates are less than 50,000 m^3/hr (85,000 acfm) at around 232°C (450°F). In the case of high sulfur loads, forced oxidation may be required to reduce chemical oxygen demand by oxidizing sodium sulfite (Na_2SO_3) to sodium sulfate (Na_2SO_4). A packed bed containing random dumped packing provides high SO_2 removal efficiency. SO_2 emission limits less than 30 mg/dNm^3 and efficiencies greater than 99% are achievable.

General Arrangement

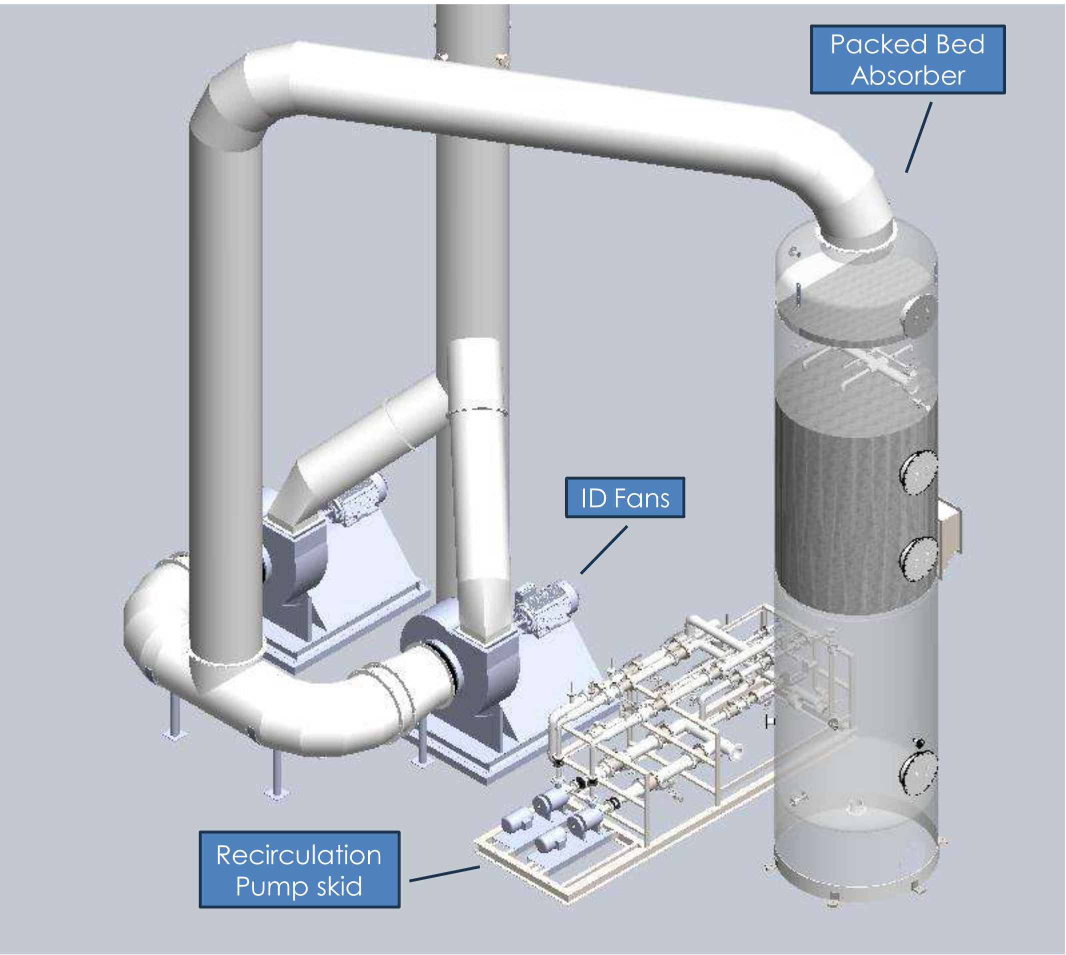
Figure 1 provides a block diagram of a typical spodumene calciner wet scrubber system. The gas is first cooled in an evaporative quencher using recirculated water. In case of a pump failure, an emergency spray nozzle provides an independent source of water controlled by a thermocouple. Excess water collects in the absorber sump. After the quencher, the gas passes through a counter-current packed bed absorber with forced oxidation. The gas enters the bottom of the absorber and flows vertically upward through the packing. Recirculated water is sprayed above the packing and falls by gravity, counter-current to upward flowing gas. Plant supplied sodium hydroxide (NaOH) is metered into the recirculation line to capture SO_2 as gas and recirculated water mix in the packed bed. The recirculation liquid is collected in the scrubber sump and recirculated to the top of the packed bed and to the quencher. Compressed air is blown into the sump to oxidize sulfites to sulfate.

Figure 1: Block diagram of a typical spodumene calciner wet scrubber system.



The gas passes through a mist eliminator at the top of the absorber vessel to remove liquid droplets. After the absorber, the gas passes through an ID fan and is exhausted to atmosphere through a stack. Figure 2 shows an example of a spodumene calciner wet scrubber equipment arrangement.

Figure 2: Example of spodumene calciner wet scrubber.



Design Considerations

Several considerations should be factored into the design of a calciner scrubber. These include design life, material of construction, uptime, reliability, performance, and water balance. The considerations can be impacted by the sulfur load, HF concentration, NOx emission limits, water availability or wastewater discharge constraints.

Design life and material of construction (MOC) go hand in hand. Stainless steel or fiber reinforced plastic (FRP) can be considered for the scrubber vessel, interconnect ductwork, and stack. However, the MOC selection may be impacted if hydrofluoric acid (HF) is in the gas or the particulate. HF is highly corrosive. Concentrations as low as 20 ppm_v can impact stainless steel and design life. FRP is more corrosion resistant than stainless steel and may provide a longer design life if HF is present, even in low concentrations. For FRP selection, it's important to select the correct resin for the expected gas composition to optimize design life. Trade-offs may occur for specific components. For instance, a low-cost alloy may be preferable to an exotic alloy if required lifetimes are more than five years. Similar decisions can be made for the pumps and fans.

Sulfur loading can impact scrubber design by requiring oxidation of sulfite (SO_3) to sulfate (SO_4). This increases the size, complexity, and operating cost. In the case of a low sulfur load, aeration can occur in the sump with minimal impact on the scrubber size. In the case of a high sulfur load, the scrubber sump requires substantial modification to sufficiently oxidize SO_3. For excessive sulfur loads, oxidation may need to take place in a separate oxidation tank. The design must incorporate an adequate aeration diffuser with sufficient sump size and depth to achieve oxidation limits.

Uptime and reliability are important considerations for any mineral processing application. Redundancy with an installed spare for critical rotating equipment including recirculation pumps and fans can help maximize uptime. The equipment has a substantial pre-assembled recirculation pump skid with pre-mounted instruments including transmitters and sensors for flow, pH, and conductivity transmitters. The skid assembly should be organized to optimize maintenance access and isolation capability so that operating personnel can calibrate and maintain critical instruments without shutting down the equipment.

Emission limits can impact scrubber design and capability. Ideally, NOx emission limits are above the calciner NOx emissions. If NOx removal is required, it could increase the cost of the equipment, its complexity, and its operating cost. NOx removal in a wet scrubber is possible but can substantially increase costs.

Water may also be an important consideration for facilities, both in terms of water consumption and wastewater generation. Establishing proper controls and feedback loops help optimize scrubber operation to minimize water consumption and blowdown. For instance, conductivity controls a blowdown valve that maintains the water close to, but below, any solubility limits.

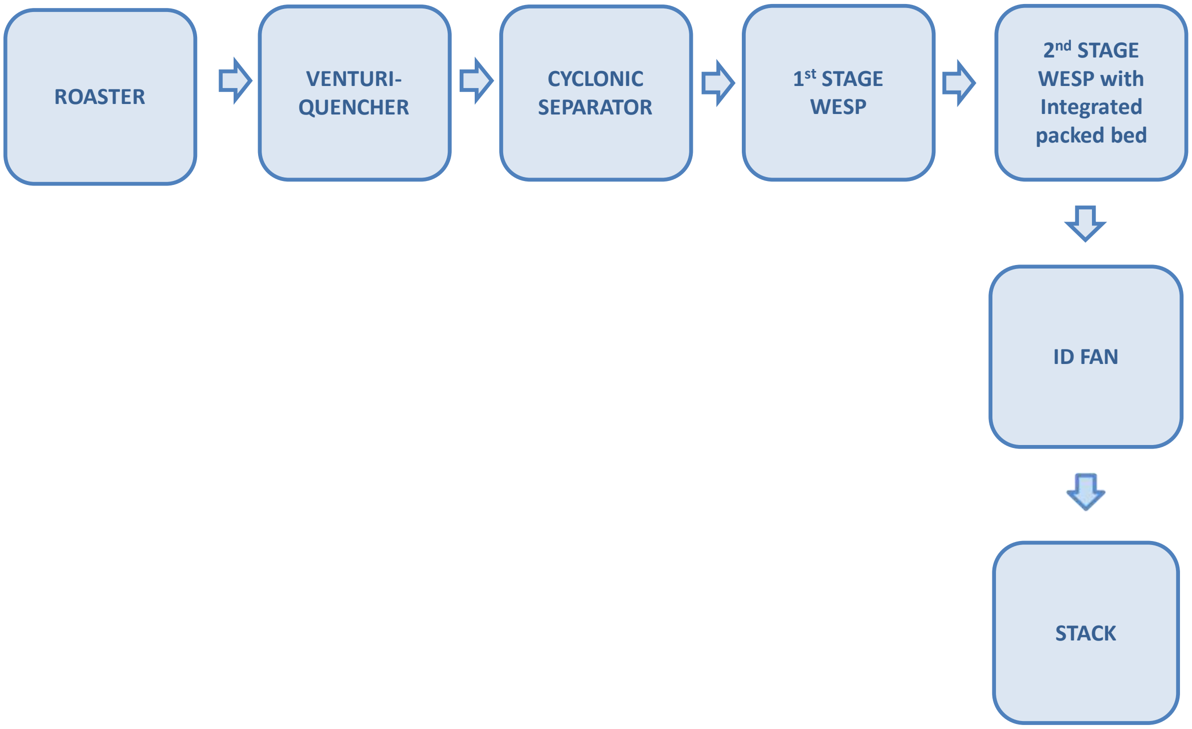
ROASTER GAS CLEANING

After calcination, beta spodumene ore is mixed with sulfuric acid and roasted in an indirect fired kiln at a temperature around 250°C (582°F). The primary emission is evaporated sulfuric acid. Typical roaster exhaust gas flow rates are less than 10,000 m^3/hr (5,900 acfm). The gas contains up to 50% moisture, high concentrations of sulfuric acid, particulate, and SO_2. If fluorine is present in the ore, the sulfuric acid liberates hydrofluoric acid (HF) into the gas stream. Other metals present in the ore may volatilize into the gas in low concentrations. As the gas is cooled downstream and contacted with water, the sulfuric acid will form an aerosol mist that will need to be collected and removed by the gas cleaning equipment. Collection is very exothermic, significantly increasing the temperature of the water as it absorbs sulfuric acid.

General Arrangement

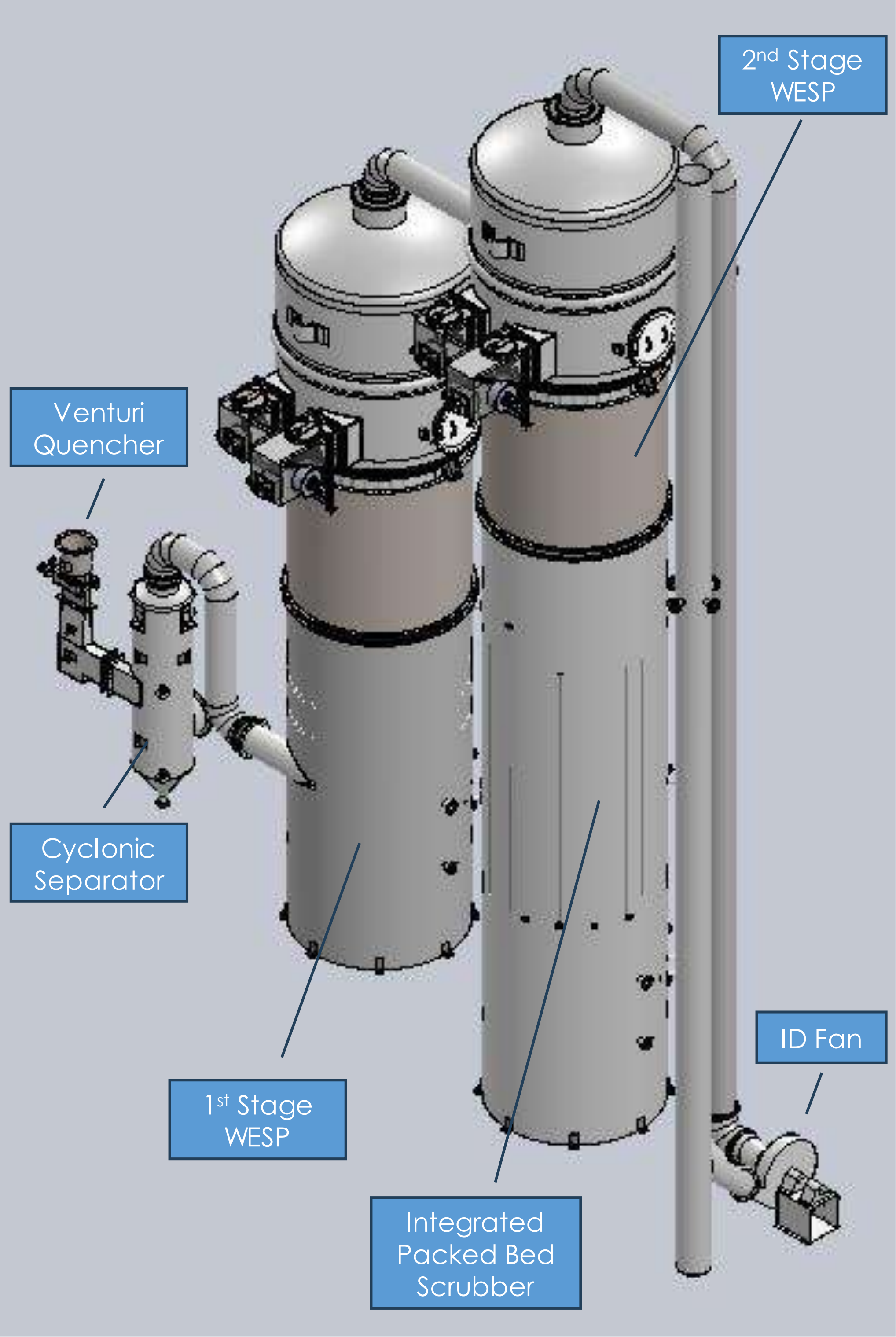
Figure 3 provides a block diagram of a typical spodumene roaster wet scrubber system. The gas first passes through a Venturi quencher to cool the gas to saturation and remove particulate. Excess water flows into the sump of a vertical upflow cyclonic separator. The cyclonic separator removes particulate laden water droplets. A recycle pump recirculates water from the cyclonic separator sump to the Venturi quencher. A blowdown stream purges the system of pollutants. Fresh water is sprayed into the top of the quencher to make-up for water losses.

Figure 3: Block diagram of a typical spodumene roaster wet scrubber system.



After the cyclonic separator, the gas passes through the first stage of an upflow wet electrostatic precipitator (WESP) to collect submicron particulate and sulfuric acid mist. The gas then passes to a second stage upflow WESP with an integrated packed bed absorber. The packed bed is in the bottom conditioning section, below the WESP collector. A spray header above the packed bed and below the collector sprays recirculated water over the packed bed. The water falls by gravity over the packed bed, counter-current to upward flowing gas. Plant supplied sodium hydroxide (NaOH) is metered into the recirculation line. As gas and water mix in the packing, reactions with NaOH remove acid gases from the gas into the water. The recirculation liquid collects in the WESP sump and recirculates to the top of the packed bed. A blowdown stream purges the system of reaction products. A mist eliminator at the top of the WESP removes water droplets from the gas. The gas is then pulled through the system by an ID fan and is exhausted to atmosphere through a stack. Figure 4 shows an example of a spodumene wet scrubber roaster equipment arrangement.

Figure 4: Example of spodumene roaster wet scrubber.



Design Considerations

Like the calciner, similar considerations should be factored into the design of the roaster scrubber. Major vessels after cooling to saturation will be FRP due to the corrosive nature of the gas. The quencher Venturi and first stage WESP collector need to be an alloy steel to withstand the corrosive impacts of sulfuric acid. If HF is present, a higher alloy steel will be required. A critical decision will be the MOC of the second stage WESP collector after scrubbing the acid gases. WESP collector tubes have relatively thin walls. Most designs share a wall between collector tubes, increasing the impact of corrosion. Collectors are expensive and require downtime to replace. Stainless steel could be considered for the second stage collector. It will have a lower capital cost, but the facility may need to factor in a plan to periodically replace the collector.

Operational and performance benefits can be derived from sub-cooling in the first stage WESP with a plate and frame heat exchanger and a source of cooling water. Sub-cooling is used in many other combustion particulate gas cleaning applications like waste incineration and silicon monomer production. Sub-cooling reduces the volumetric flow rate of gas to reduce the WESP collection area. Submicron particles and acid aerosol become nucleation sites for condensation, growing the particles and droplets in size. Condensing vapor sweeps particles with it for collection as it moves toward cold surfaces. Thermal forces from the temperature gradient between gas and cold surfaces enhance collection efficiency. Wetting the particles helps to keep the WESP collector clean, reducing the potential for fouling. Condensed water on the acid aerosol dilutes it, minimizing corrosion of the WESP collector. Finally, sub-cooling reduces the overall gas flow, improving performance. The trade-off is a larger volume of wastewater discharge. The ability to take advantage of sub-cooling will depend on the facility's tolerance for additional wastewater.

Performance limits may also impact the system design. In general, a spodumene roaster is designed to reduce particulate, SO_2, and sulfuric acid aerosol. If a facility has other stringent emission limits for specific heavy metals that may be present in the ore, it may impact the collection area of the WESP to meet the performance limits. This can increase the capital and operating costs.

Like the calciner, reliability is important. Redundancy can be provided on critical rotating equipment for pumps and fans. Isolation capability and access can be designed into the piping and instrument arrangement to maximize uptime.

CONCLUSION

Policy making to reduce global warming is driving demand for lithium. Efforts are underway to develop lithium sources in Australia, Europe, and North and South America. Spodumene ore will play a significant role in meeting the growing lithium demand. Thermal processing is required to extract the metal from Spodumene ore. Advanced wet scrubber technologies will play a critical role to enable lithium extraction from spodumene sources in an environmentally responsible way. Differences in ore deposits and local regulatory requirements will require adjustments to gas cleaning. It's important to partner with an experienced technology provider that can optimize a solution to meet the facilities specific needs or constraints.

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KEY WORDS

Spodumene lithium gas cleaning, roaster gas cleaning, calciner gas cleaning, wet scrubber, wet electrostatic precipitator, WESP, SO_2 scrubber, mineral processing scrubber.

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2023

Advanced Gas Cleaning Wet Scrubber Technology for Spodumene Lithium Mineral Processing

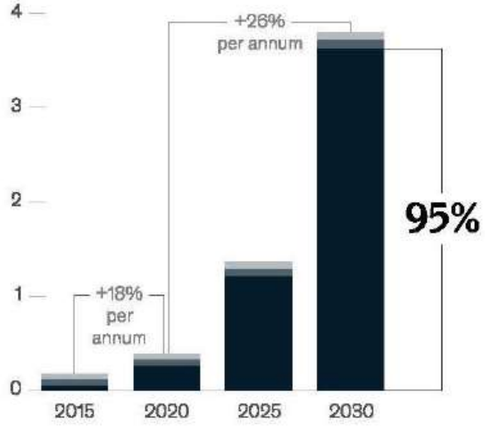
Paper # 36

Andrew Bartocci – Envitech Sales Manager

Outline

- Background: Spodumene lithium mineral processing
- Calciner scrubber block diagram/arrangement
- Calciner scrubber design considerations
- Roaster scrubber block diagram/arrangement
- Roaster scrubber design considerations
- Summary

Background



- Greenhouse gases has propelled lithium demand
- EV battery demand is expected to increase lithium market share from 30% to 95% between 2015 and 2030.
- Spodumene ore will play significant role in meeting demand
- Spodumene processing relies on two pyrometallurgical thermal processes
- Both rely on wet scrubber technology

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Spodumene Ore Processing:
2 Step Pyrometallurgical Process

Alpha phase spodumene
Compact, low reactivity

Step 1 Calciner

Beta phase spodumene
Porous, higher reactivity
Allows lithium extraction via leaching process

Direct Fired Rotary Kiln > 900°C
Calcination is high temperature treatment of solid material below melting point

Beta phase spodumene mixed with 95% to 97% sulfuric acid

Step 2 Roaster

Roaster product allows lithium to be extracted as water soluble sulfate

Indirect Fired Rotary Kiln @ 250°C

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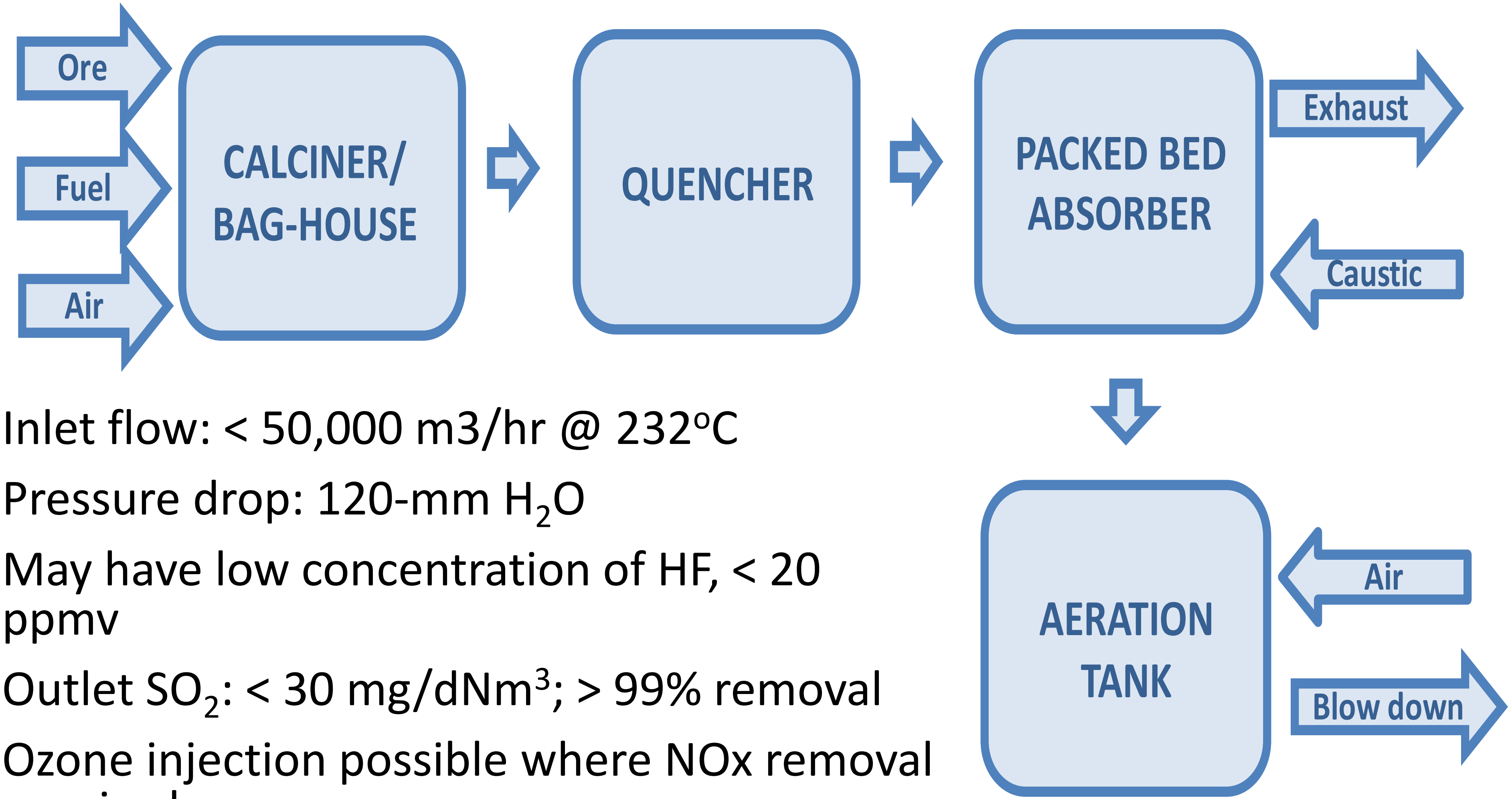
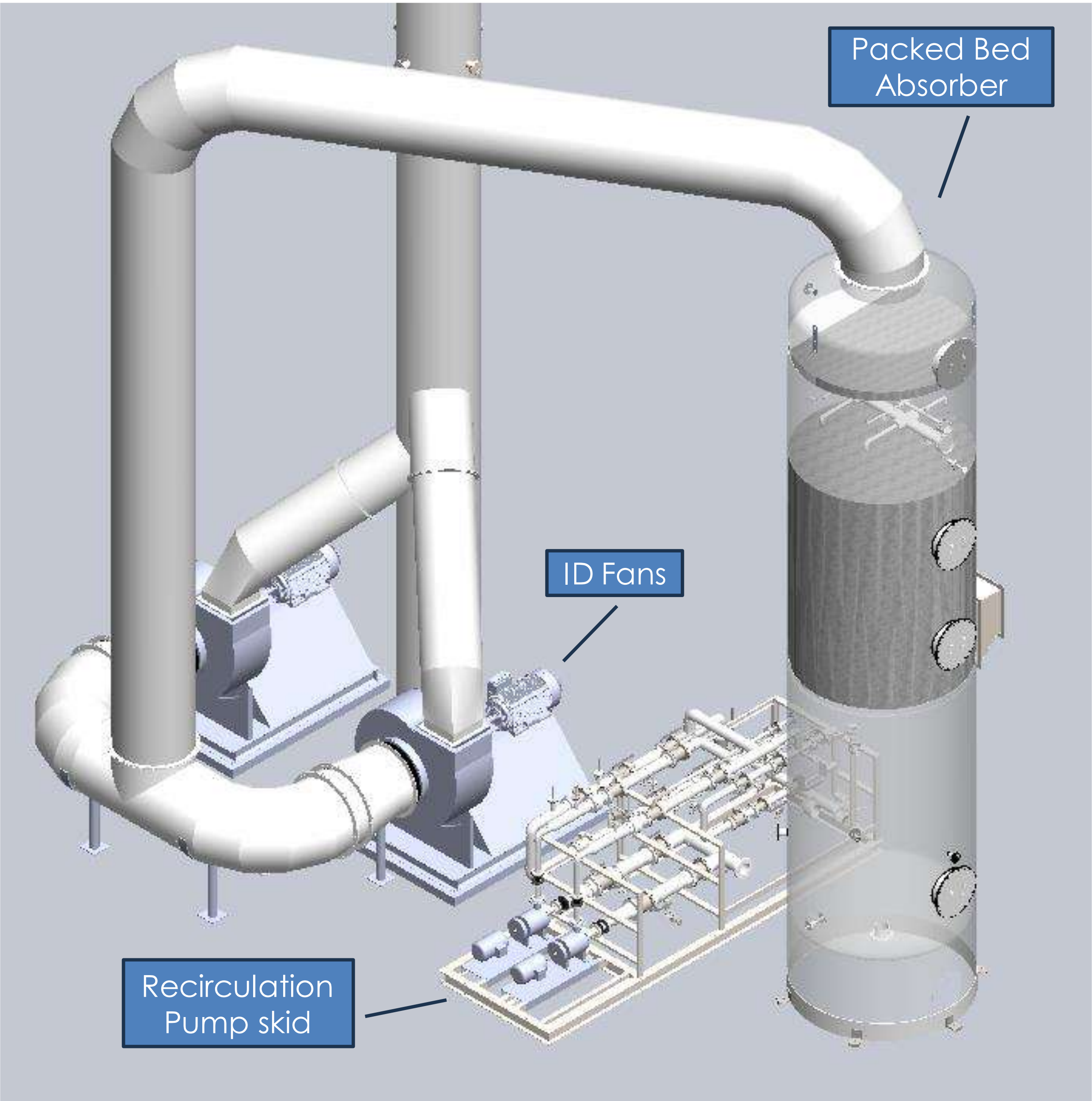
Typical Spodumene Calciner Wet Scrubber Block Diagram



- Inlet flow: < 50,000 m3/hr @ 232°C
- Pressure drop: 120-mm H_2O
- May have low concentration of HF, < 20 ppmv
- Outlet SO_2: < 30 mg/dNm^3; > 99% removal
- Ozone injection possible where NOx removal required

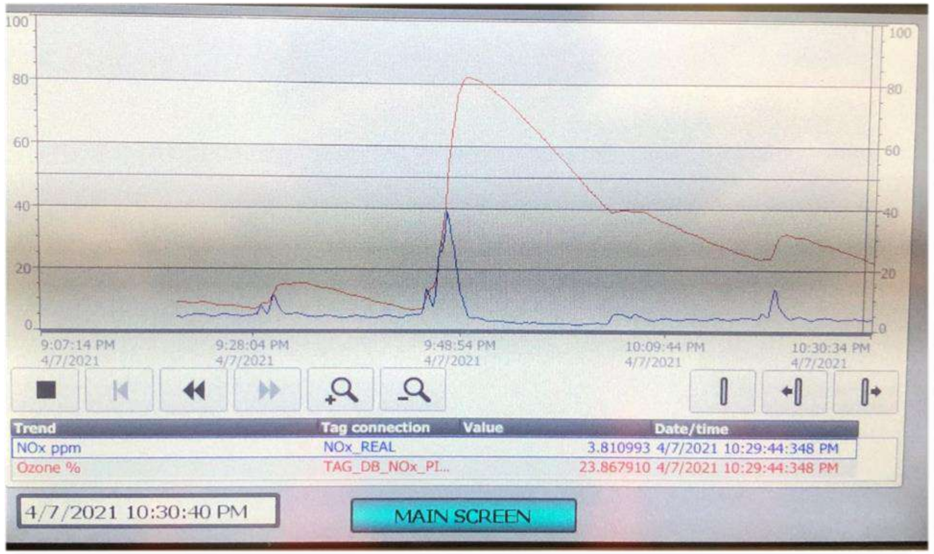
Typical Spodumene Calciner Scrubber Arrangement

- Evaporative quencher – Stainless or Alloy Steel
- Absorber vessel – FRP or Stainless Steel
- Sump – Forced oxidation to convert sulfite (SO_3) to sulfate (SO_4)
- Pump skid – Redundant pumps
- ID Fans – Redundant for increased uptime
- Ozone injection if required



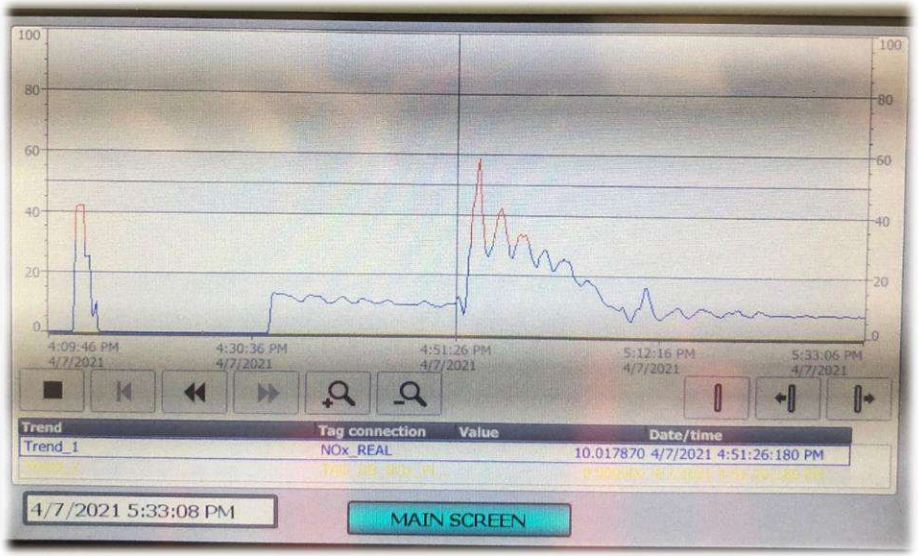
Design Considerations

- Design life and material of construction
  - Presence of HF
  - Tolerance for replacement intervals (quencher, fans, pumps)
- Uptime/reliability - Redundancy
- Performance
  - Chemical oxygen demand (COD) – Need for forced oxidation
  - NOx – Need for NOx control
- Water balance – Automation and feedback control
- Capital cost – MOC, redundancy



Trend	Tag connection	Value	Date/time
NOx ppm	NOx_REAL	3.810993	4/7/2021 10:29:44:348 PM
Ozone %	TAG_DB_NOx_PI...	23.867910	4/7/2021 10:29:44:348 PM

4/7/2021 10:30:40 PM



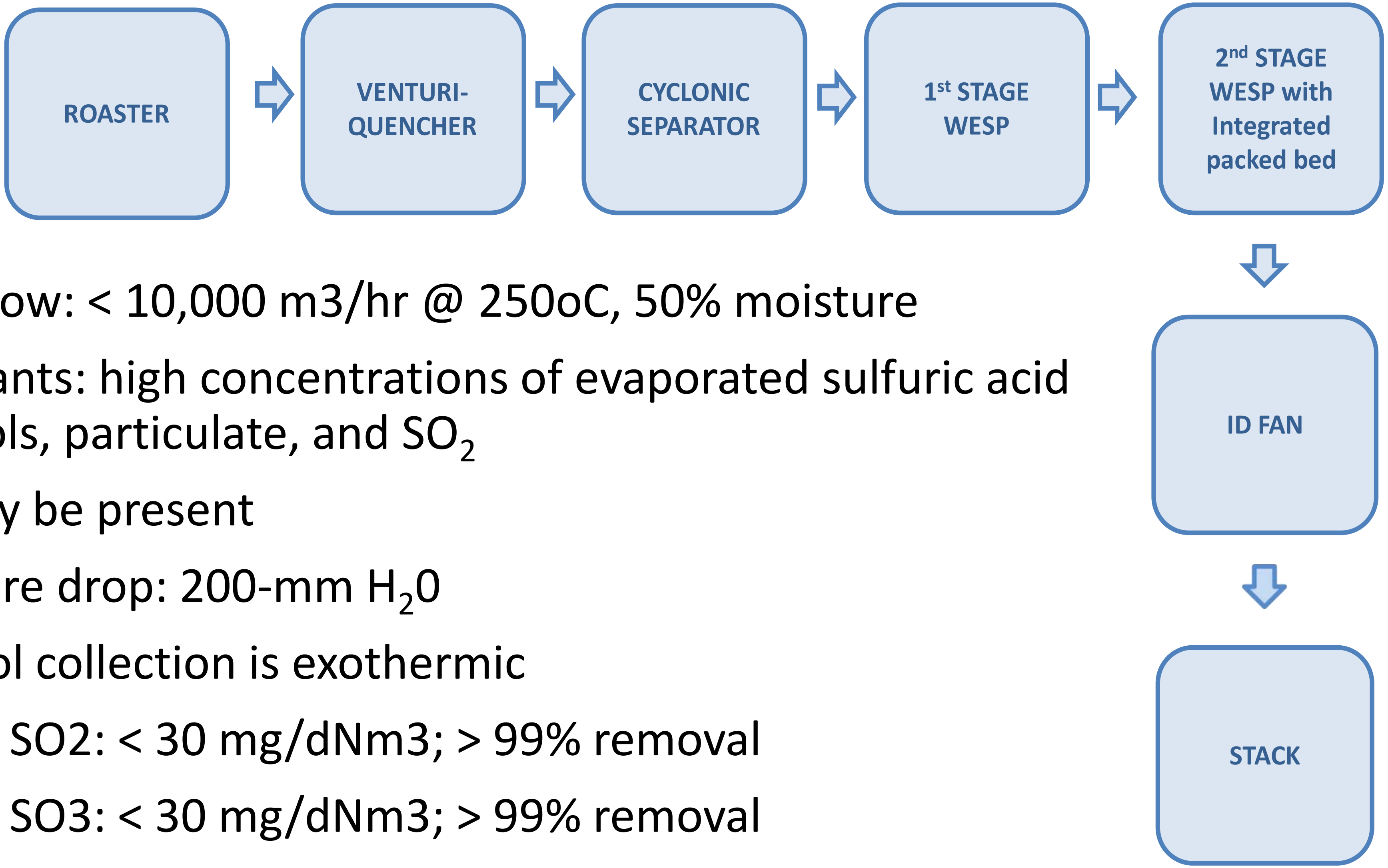
Trend	Tag connection	Value	Date/time
Trend_1	NOx_REAL	10.017870	4/7/2021 4:51:26:180 PM
[illegible]	[illegible]	[illegible]	[illegible]

4/7/2021 5:33:08 PM

- 10,700 Am3/hr @980^{o}C
- Inlet/outlet NOx 130/67 ppm
- US EPA HMIWI MACT Standard

Two (2) medical waste incinerators for Department of Homeland Security using ozone injection for NOx control

Typical Spodumene Roaster Scrubber Block Diagram



- Inlet flow: < 10,000 m3/hr @ 250oC, 50% moisture
- Pollutants: high concentrations of evaporated sulfuric acid aerosols, particulate, and SO_2
- HF may be present
- Pressure drop: 200-mm H_20
- Aerosol collection is exothermic
- Outlet SO2: < 30 mg/dNm3; > 99% removal
- Outlet SO3: < 30 mg/dNm3; > 99% removal

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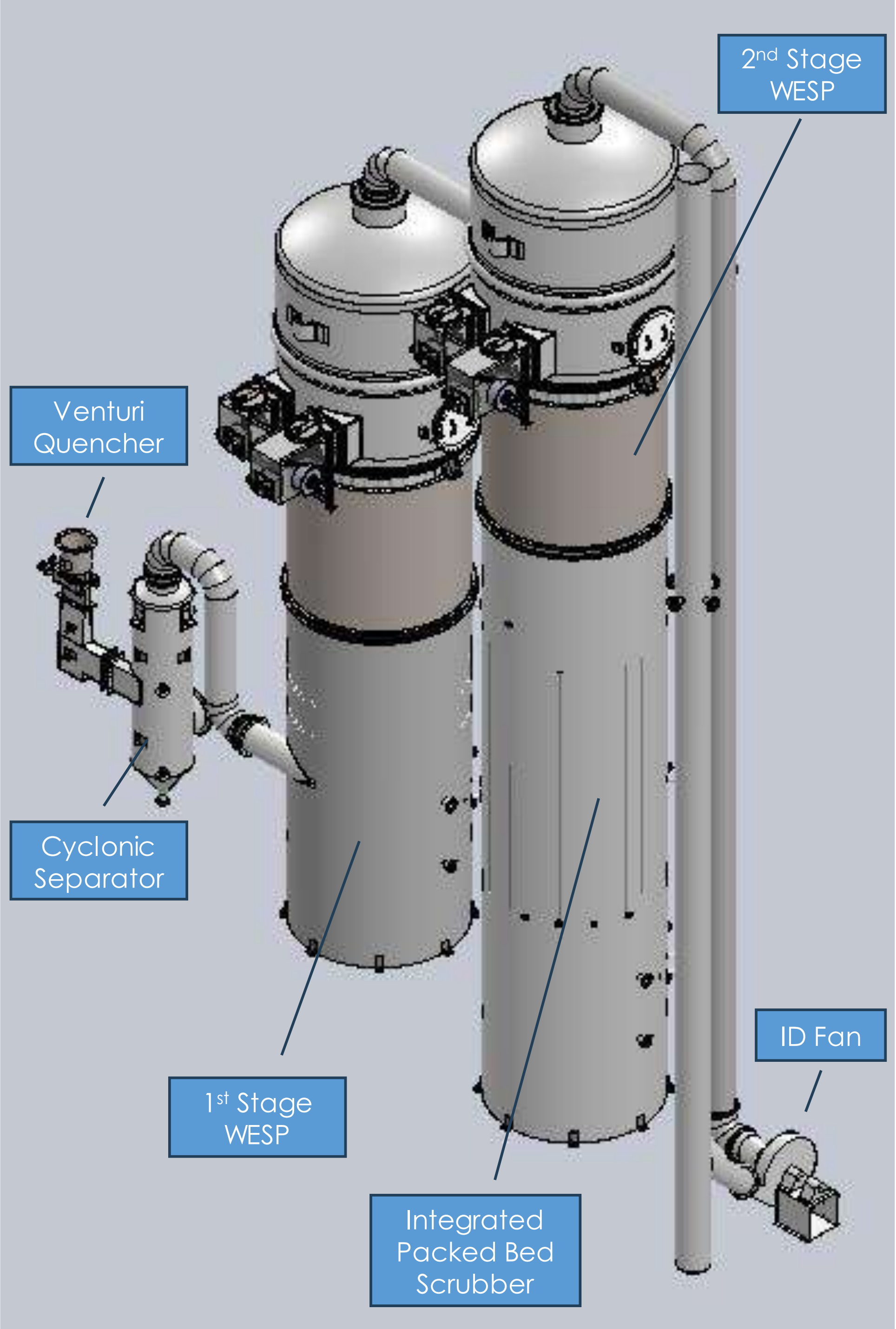
Typical Spodumene Roaster Scrubber Arrangement

- Venturi quencher – Alloy Steel
- Cyclonic separator - FRP
- WESP Shells – FRP
- 1st Stage WESP collector – Alloy steel
- 2nd stage WESP collector – alloy steel or stainless
- 2nd stage WESP – Integrated packed bed absorber for SO_2 removal



Design Considerations

- Design life and material of construction
  - FRP vessels due to corrosive nature of the gas
  - Presence of HF drives MOC decisions on metallic components
- Uptime/reliability
  - Redundancy
- Performance
  - Collector area may be impacted by heavy metals in the ore and local regulatory requirements.
- Water balance – Automation and feedback control
- Capital cost – MOC, redundancy
- Sub-cooling improves reliability, performance, and CapX, but impacts water balance

Summary

- Global warming is driving demand for lithium
- Thermal processing of spodumene ore plays a significance role in meeting demand.
- Advanced wet scrubber technology needed to meet environmental requirements
- Importance to partner with an experienced technology provider that can optimize solutions to meet facility specific needs.