

A decorative graphic consisting of a vertical blue line on the left side of the slide. A horizontal blue line branches off from this vertical line, extending to the right. At the end of this horizontal line is a solid red circle. Another solid red circle is located at the bottom of the vertical blue line.

Continuous Emissions Monitoring in Support of the Cement MACT

McIlvaine Webinar on Cement MACT

March 30, 2011

Topics Covered

- Overview of Portland Cement MACT
- Mercury monitoring on cement kilns
- PM CEMS
- HCl CEMS
- THC CEMS



Portland Cement MACT: Compliance by Oct 2013

All Cement Facilities (40 CFR Parts 60 & 63)

Existing sources
(before May 6, 2009)

New sources
(after or on May 6, 2009)

Raw mills

Kilns

Clinker
coolers

Raw material
dryers

Finish mills

PM

HCl

THC

Mercury

SO₂

NO_x

~~CO~~

~~CHG~~

PC MACT Limits for Top Pollutants

	PM (lb/ton clinker)	THC¹ (ppmv)	HCl (ppmvd)	Mercury (lb/ton clinker)
Existing kiln	0.04	24	3	55
New kiln	0.01	24	3	21
Existing clinker cooler	0.04			
New clinker cooler	0.01			
Existing or new raw material dryer		24		

Pollutant	Limit (lb/ton clinker)
SO ₂	0.4
NO _x	1.5

¹Any source subject to the 24 ppmvd THC limit may elect to meet an alternative limit of 9 ppmvd for total organic HAP. If the source demonstrates compliance with the total organic HAP under the requirements of § 63.1349 then the source's THC limit will be adjusted to equal the average THC emissions measured during the organic HAP compliance test.

Complete Portfolio to Support the Cement Industry

	PM	THC	HCl	Mercury	SO ₂	NO _x
Thermo Scientific Product	PM CEMS	51i	15i, 70i	Mercury Freedom System	43i Series	42i Series
PC MACT Limit	0.04 lb/ton clinker	24 ppmv	3 ppmvd	55 lb/ton clinker	0.4 lb/ton clinker	1.5 lb/ton clinker
Expected range	-	0-100 ppmv	0-10 ppmvd	0-500 ug/m3	0-1000 ppmv	0-1000 ppmv
Product status	Alpha	Active	15i-Active 70i-Beta	Active	Active	Active

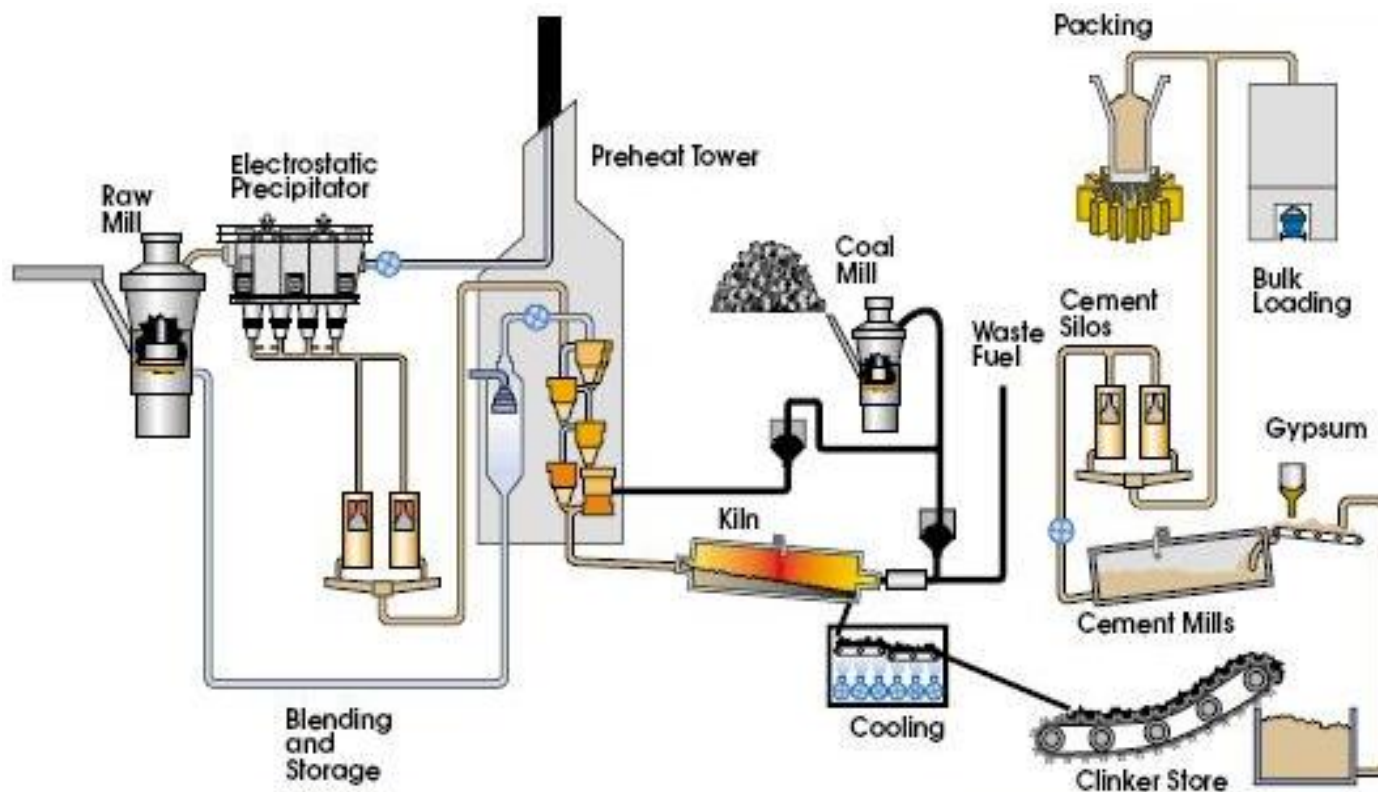
Industry needs a comprehensive package to meet new regulations

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Cement Process has Distinct Hg Monitoring Needs



- Large swings in Hg levels when raw mill switches states
- Wide array of raw materials and fuels contribute to mercury emissions
- High particulate levels and moisture can affect mercury content

Mercury Freedom[®] System Overview

Model 82i Probe Controller

Model 80i Mercury Analyzer

Model 81i Mercury Calibrator

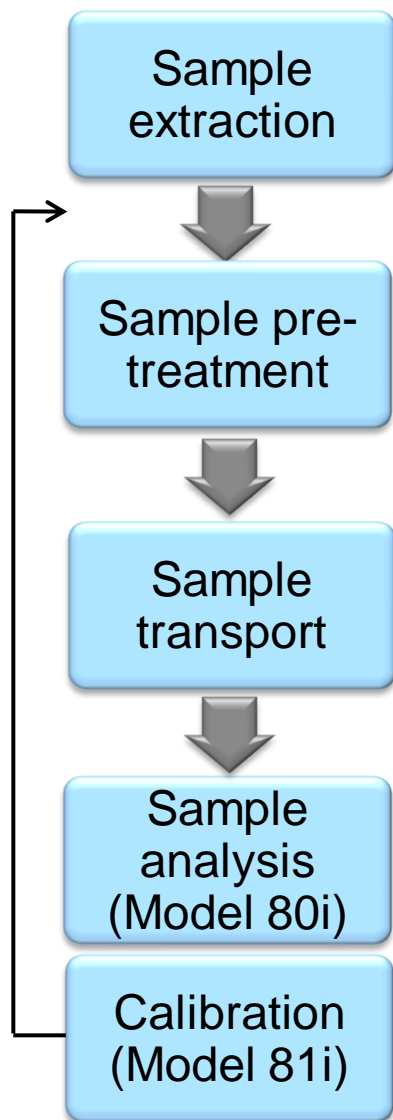
Zero air supply
Optional Nitrogen Generator



Model 83i Inertial Probe

Proven performance in multiple CEMS applications

Combining Performance with Ease of Use



- Probe with high flow inertial filter is proven to work in high dust applications
- Dry conversion at stack avoids potential loss or chemistry changes of oxidized mercury in the sample line
- Dry conversion requires no wet chemistry or water supply
- Direct measurement CVAF ensures linearity over broad range and avoids interferences with SO₂
- High bench sensitivity eliminates need for expensive carrier gas and gold trap replacements
- Real-time monitoring with 10 second response time over entire range is ideal for process control
- *i*-Series platform offers modular design, enhanced interface capabilities with seamless integration into plant data flow

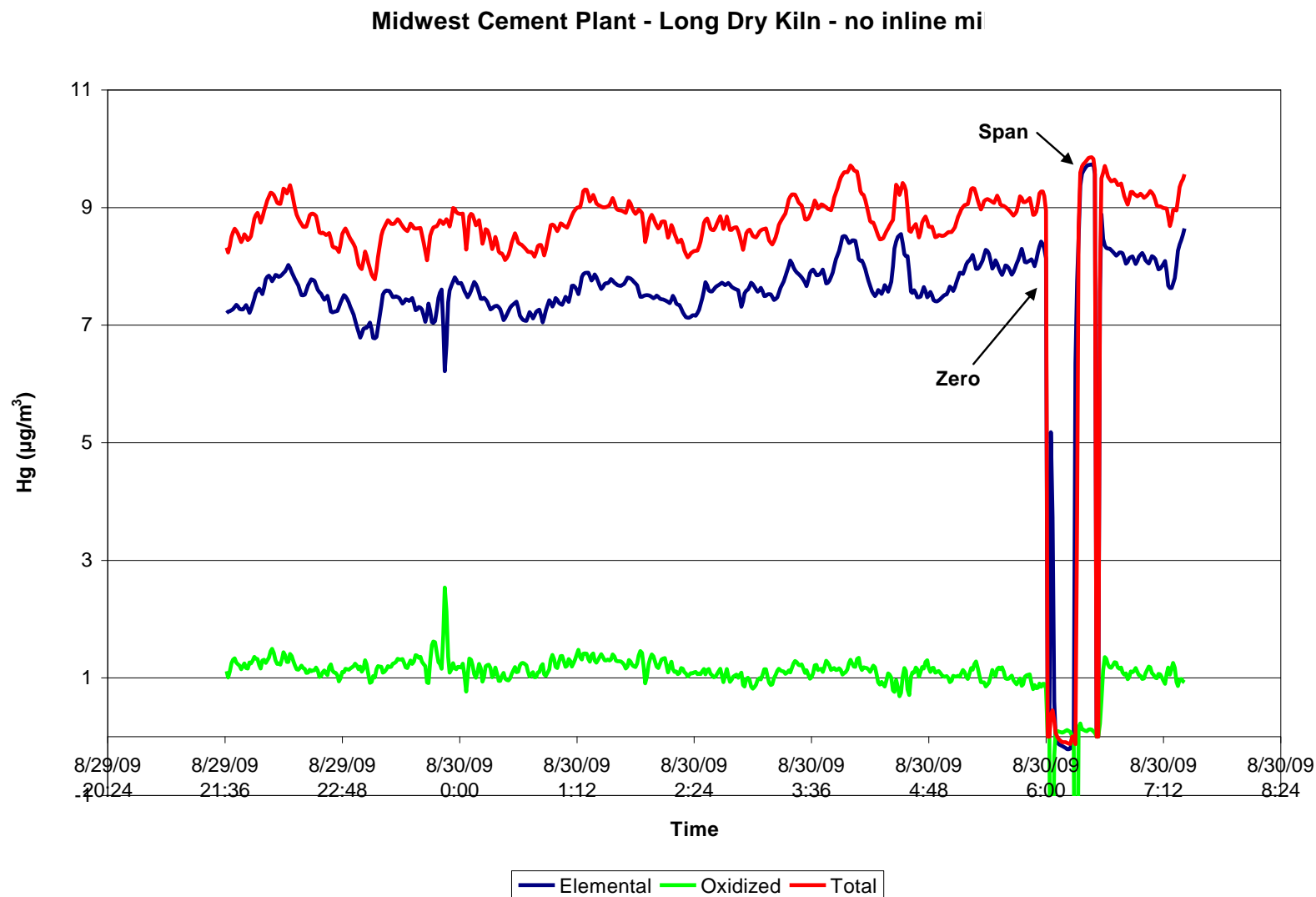
Midwest Plant - Dry, Horizontal Kiln without inline mill



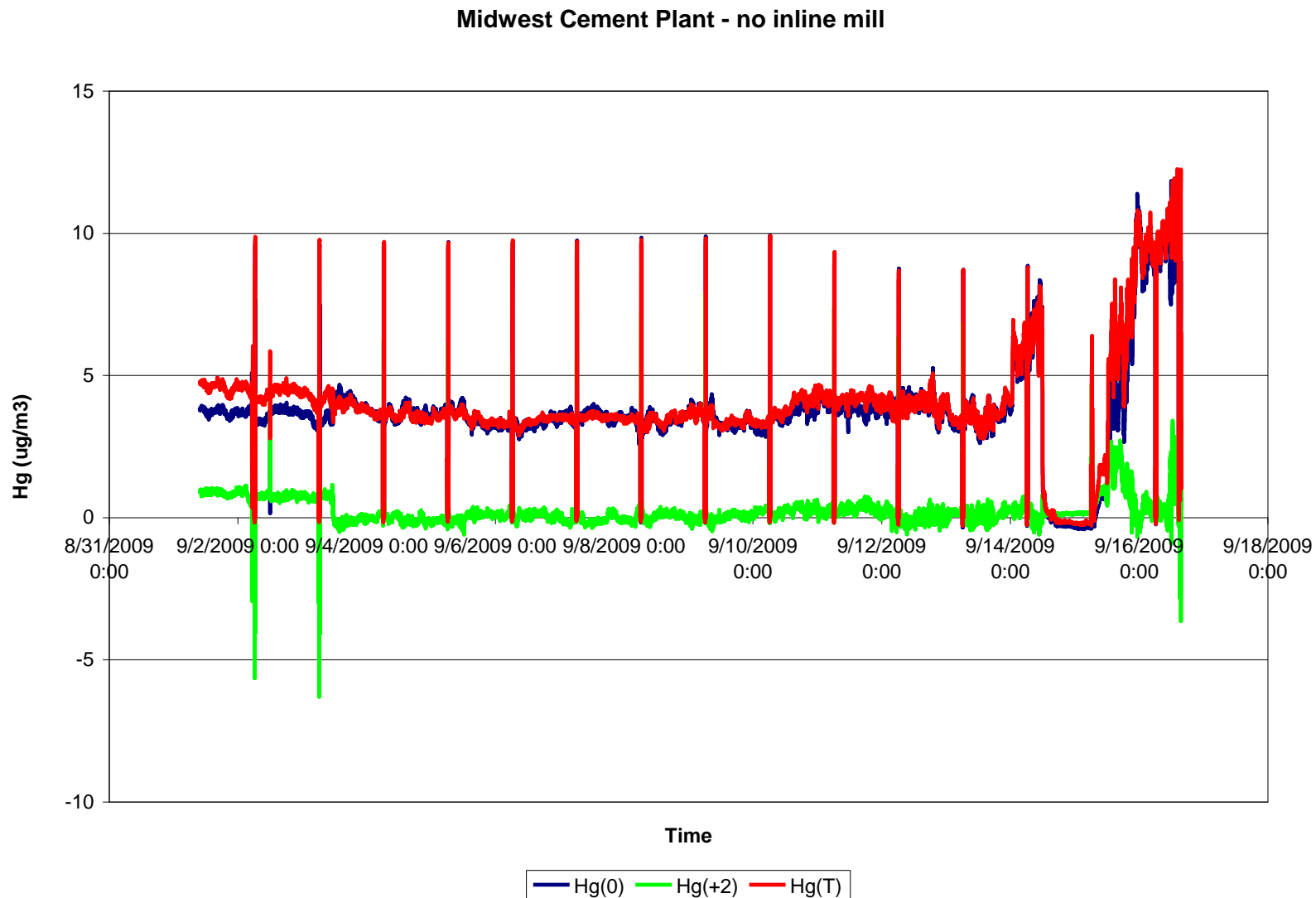
Midwest Plant – Installed Mercury Freedom® System



Data – Midwest Cement Plant – no inline mill



Data – Midwest Cement Plant – no inline mill



RATA Results at Midwest Plant

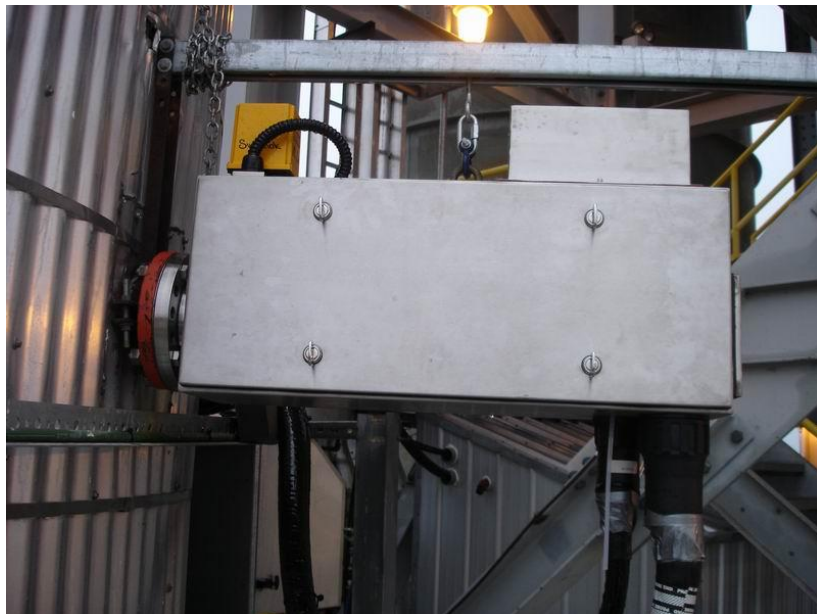
	Test Run	Date	Start Time	End Time	Reference Method Hg μg/scm	CEM Output Hg μg/scm	(RM-CEM) Difference (di)	Difference^2 (di^2)
1	1	09/22/09	0945	1015	12.1	11.7	0.35	0.13
1	2	09/22/09	1053	1123	11.2	11.4	-0.23	0.05
0	3	09/22/09	1148	1218	12.5	11.5	1.01	1.02
1	4	09/22/09	1251	1321	12.1	11.3	0.82	0.67
1	5	09/22/09	1354	1424	10.3	10.8	-0.47	0.22
1	6	09/22/09	1446	1516	11.7	11.8	-0.05	0.00
1	7	09/22/09	1545	1615	12.0	12.0	0.03	0.00
1	8	09/22/09	1638	1708	11.4	12.1	-0.73	0.53
1	9	09/22/09	1730	1800	12.1	11.9	0.19	0.03
1	10	9/23/2009	0855	0925	9.7	9.6	0.06	0.00

n	9
t(0.025)	2.306
Mean RM Value	11.396 RM
Mean CEM Value	11.400 CEM avg
Sum of Differences	-0.035 di
Mean Difference	-0.004 d avg
Sum of Differences ²	1.638 di^2
Standard Deviation	0.452 sd
Confidence Coefficient	0.348 CC
Relative Accuracy based on % of RM Value	3.1 %
Relative Accuracy based on difference	0.0 Mean Difference

Midwest plant: Relatively Stable Mercury Levels

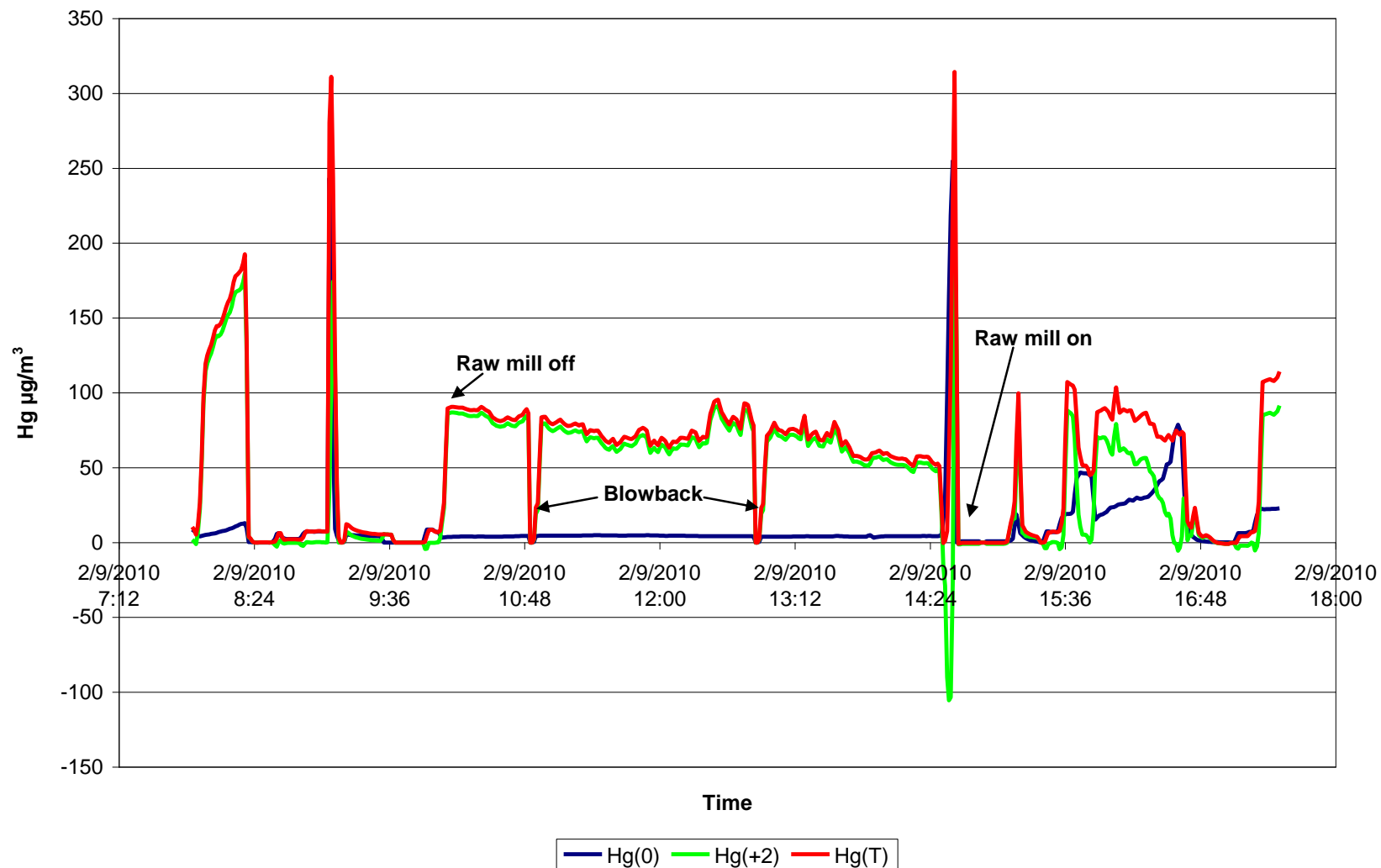
- Observed mercury concentrations were consistently in the range 3 to 15 $\mu\text{g}/\text{m}^3$ in the absence of an inline raw mill
- Current Model 81i Calibrator is adequate for this type of application
- Elemental Hg formed more than 90% of the total reading
- Mercury Freedom System passed RATA @ 3.1% and performed very well in this application
- This was the first known instance of 30B traps tested against a real-time, continuous mercury CEMS on a cement kiln

Southeast Cement Plant – with inline Raw-mill



Data – Southeast Cement Plant – with inline mill

Souteast Cement Plant - with inline mill



Southeast plant: Raw Mill Impacts Mercury levels

- Observed mercury concentrations wildly varied from <1 to $> 300 \mu\text{g}/\text{m}^3$
 - Variability of readings clearly correlated to raw mill status
- Results confirm need for high-level Hg calibrator ($0\text{-}500+ \mu\text{g}/\text{m}^3$)
 - Mass Flow Controller changes
 - Hg reservoir temperature increase
- Planning NIST certified Vendor Prime at calibration point of $353 \mu\text{g}/\text{m}^3$
- Oxidized mercury formed more than 90% of total reading
- Mercury Freedom CEMS performed well over a broad range

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- PM CEMS
- HCl CEMS
- THC CEMS



Common Technologies for PM CEMS

- Light scattering

f (scattered light)

- Beta attenuation

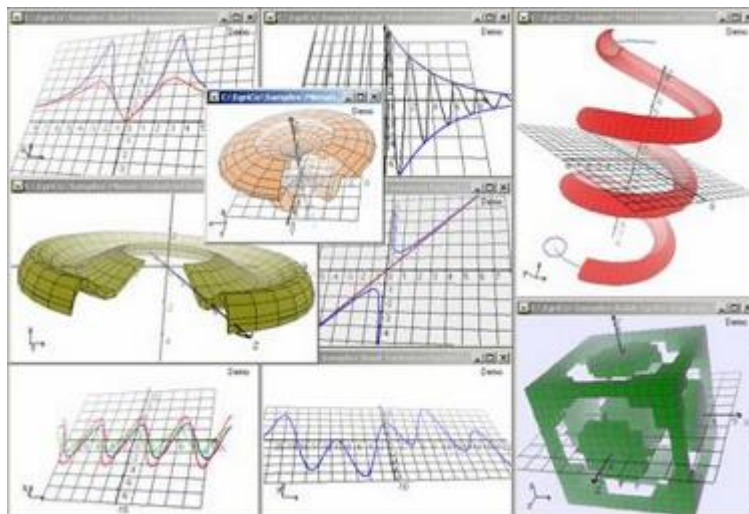
f (beta reduction)

- Light extinction

f (attenuation of light)

- Inertial microbalance

f (frequency)



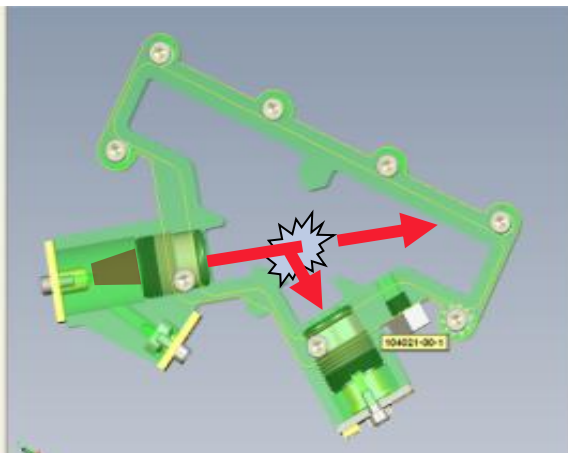
Most measurements are surrogate

Hybrid PM CEMS Technologies

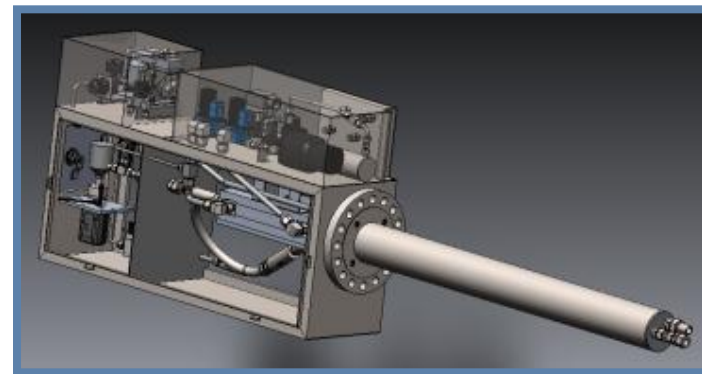
- Hybrid PM CEMS combines desirable features from parent technologies:
 - Inertial microbalance (TEOM)
 - Light scattering



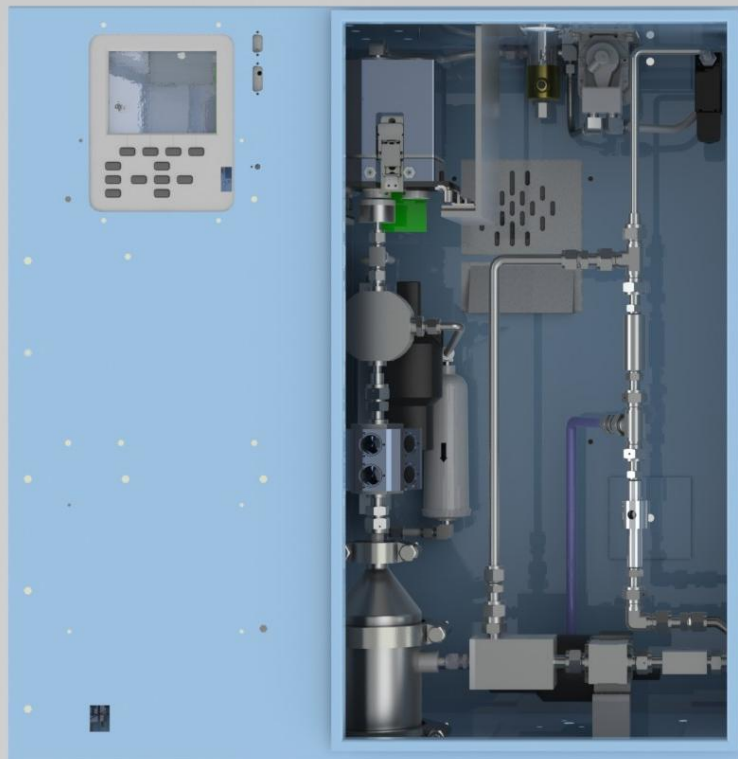
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CEMS Design – Early Prototype



- In-stack dilution followed by mixing, transport and analysis
- 16:1 nominal dilution ratio
- Transport at stack temp + 10 deg C
- Light scattering module
- TEOM mass transducer module
- System zero, blow back



PM CEMS Summary

- Hybrid PM CEMS uses light scattering and TEOM
- TEOM offers NIST traceability to mass
- Dual scattering captures dynamic changes in particulate characteristics and can be a diagnostic tool
- Technology expected to support market trends
- Need more collocated data as alpha design evolves

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- THC CEMS



Multiple Options for Monitoring HCl??

Fourier Transform
Infra Red
Spectroscopy

Current rule states an HCl CEMS must follow PS 15 (FTIR)

Will EPA relax this requirement and allow other CEMS methods for HCl be accepted?

Gas Filter
Correlation

Our Model 15i Analyzer and CEMS is a viable alternative method for HCl measurement

FTIR is the reference method but other methods will likely be added as alternate methods

FTIR Based CEMS: System Architecture

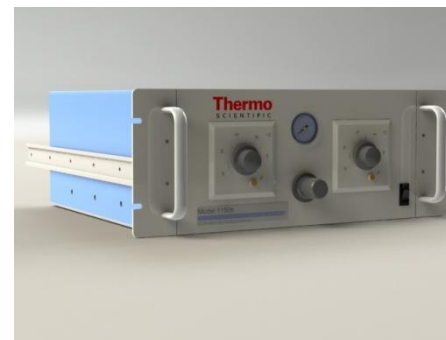
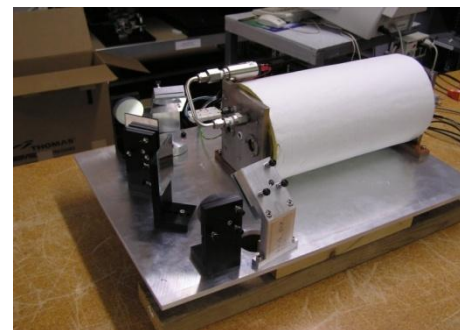
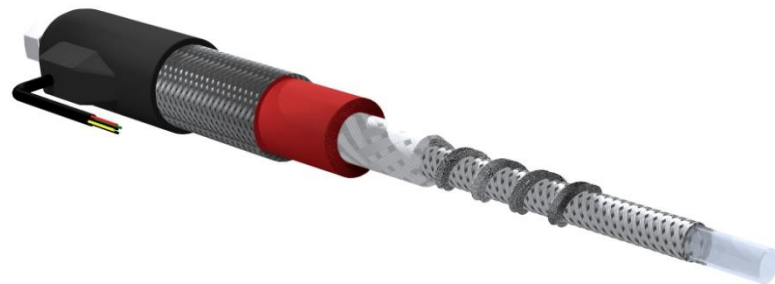
- Power System
 - 240 VAC 50/60 Hz
 - Two 25 Amp Circuits
 - Master ON/OFF switches and individual circuit breakers at front of rack (EN requirement)

2' Rittal power box, 19"



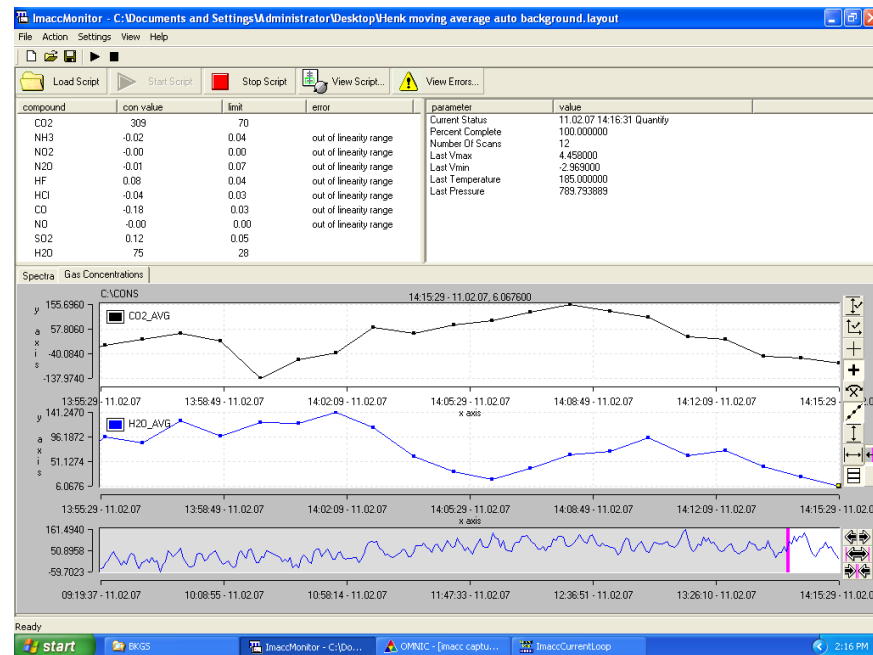
FTIR Based CEMS: System Architecture

- Sampling System
 - Full Extractive Sample Probe
 - Winkler Heated Lines
 - Heated Air Driven Ejector pump
- Optical System
 - Hot and wet sample gas at 185 ° C temperature
 - Materials that are highly resistant against corrosive compounds
 - Multi-pass fixed path length: 5.2m
- Support System
 - Zero Air Conditioning System
 - Parker FT-IR Purge Gas Generator
 - McLean Air Conditioner



FTIR Based CEMS: Operation

- IMACC Monitor Software
 - Controls FTIR
 - Gathers data from temperature controllers and pressure sensor
 - All concentrations displayed on screen, updated once per minute
 - Historical data may be graphed for any compound
 - Concentration, temperature, and pressure data stored in space-delimited text files
- Thermo Scientific OMNIC
 - Interface to FTIR
- IMACC Current Loop Server
- IMACC MODBUS Server



FTIR Based CEMS: Specifications

Compound	ppm → mg/m ³	Minimum measuring range		Required MDL = 2% of range (1σ)		MDL [ppm]
		[mg/m ³]	[ppm]	[mg/m ³]	[ppm]	
Carbon monoxide CO	1.249	0 - 75	0 – 0.0	1.5	1.2	0.15
Nitric oxide (gas turbine) NO	1.338	0 - 200 0 - 70	0 – 149.4 0 – 52.3	1.4	1.05	0.40
Sulphur dioxide SO ₂	2.854	0 - 75	0 – 6.3	1.5	0.53	0.50
Hydrogen chloride HCl	1.628	0 - 15	0 – 9.2	0.30	0.18	0.10
Ammonia NH ₃	0.758	0 - 5	0 – 6.6	0.10	0.13	0.10
Water H ₂ O	-	0 - 30 vol%	0 - 30 vol%	0.6 vol%	0.6 vol%	0.01 vol%
Nitrogen dioxide NO ₂	2.052	0 - 50	0 – 4.4	1.0	0.49	0.10
Nitrous oxide N ₂ O	1.962	0 - 100	0 – 0.9	2.0	1.02	0.10
Hydrogen fluoride HF	0.892	0 - 10	0 – 11.2	0.20	0.22	0.15
Carbon dioxide CO ₂	-	0 - 30 vol%	0 - 30 vol%	0.6 vol%	0.6 vol%	0.01 vol%

Topics Covered

- Overview of Portland Cement MACT
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- HCl CEMS
- Total Hydrocarbon



Model 51i Total Hydrocarbon Analyzer

- Pictured is a THC analyzer as part of an FTIR based CEMS
- Sampling System
 - Full Extractive Sample Probe
 - Heated Sample Umbilical
 - Hot / Wet measurement
- Analyzer
 - Heated at up to 200 ° C to avoid condensation
 - Based on the flame ionization technique (FID)

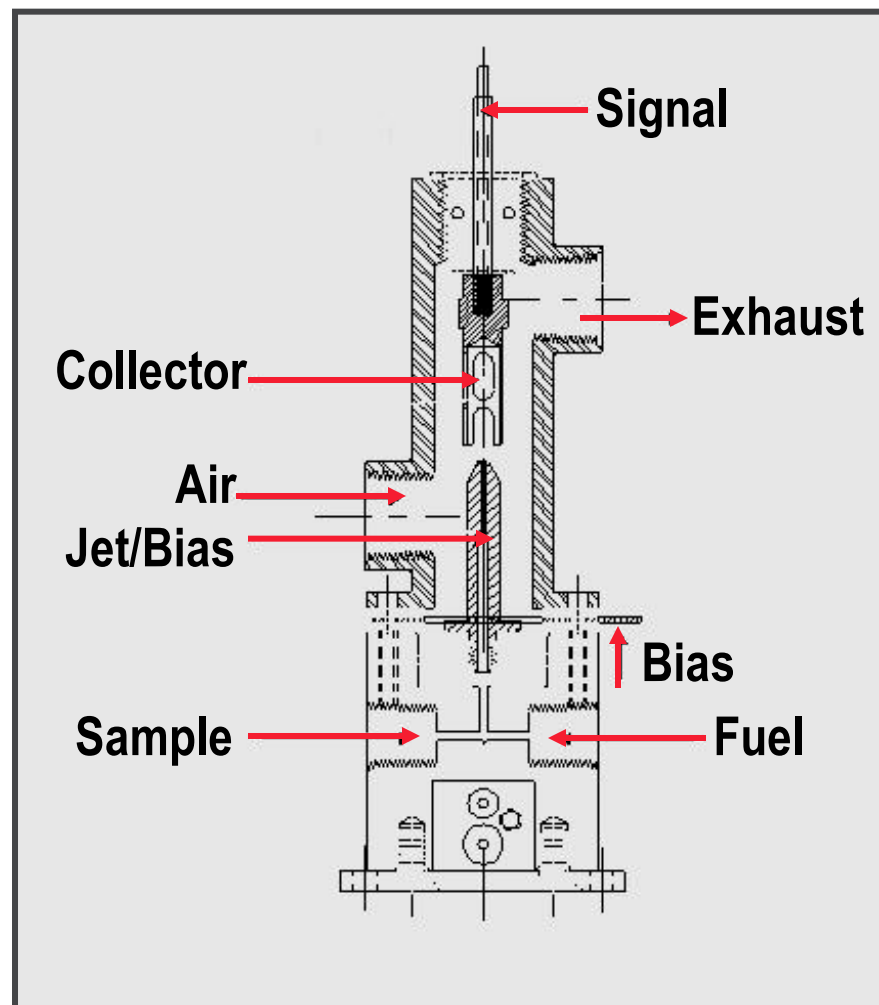


THC Analyzer

FID Detector Assembly

FID Operation:

- Ionizing organic compounds with a hydrogen flame
- Oxidizes organic compounds to generate CO₂ and H₂O
- Ions are formed in electrical field between polarized jet and cylindrical collector
- Negatively charged ions migrate to the collector
- Creates a current proportional to the concentration of carbon atoms



Summary

- Portland Cement MACT requires continuous monitoring by October 2013
- There may be some changes in monitoring requirements, i.e., HCl relaxed to include other technologies
- Thermo Fisher will have solutions for all required parameters well before required date
- Our HCl solution via FTIR later this year – GFC available now
- PM CEMS in alpha stage – will soon be looking for beta sites
- Updates expected by the IEEE conference in May
- Stay tuned.

Questions?



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