Impact of Proposed MACT Limits for Mercury and Possible Solutions

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Background

<u>6/14/99 -</u>

- EPA promulgates MACT limits for Portland Cements Plant which did not include Hg emission limits

<u>12/20/06 -</u>

- In response to litigation EPA promulgated 41 $\mu g/m^3$ for new cement kilns commencing construction after 12/2/05. The rule announced reconsideration to obtain additional public comment and data.

Background (cont.)

12/20/06 -

- Petitions for review of the Hg limit and other issues (e.g., HCl) filed by states and environmental group

1/26/09 -

- Petitions consolidated and EPA published proposed settlement agreement in which EPA proposed new rules 4/22/09 (extended to June)
- Final rule to be promulgated by 6/22/201

Expected Hg Limits

Existing Plants

- Based on the average emission of the lowest emitting 12% of population
  - 11 plants in population
  - Average Hg emission 27.4 lb/MM ton KK
  - Expected limit with consideration of variability in data 43 lb/MM ton KK

New Plants

- Based on lowest emitting plant in population
  - Hg emissions 7.1 lb/MM ton KK
  - Expected limit considering variability in data 14 lb/MM ton KK

Impact on Cement Industry

Existing Plants

- 90% exceed limit expected to be proposed
- Compliance date expected to be 3 years from promulgation (~4/22/13)

Expected Impact

- Changes in new mix design may bring some into compliance

- Changes in Fuel supplier may bring some into compliance

Impact on Cement Industry

Expected Impact

- End-of-pipe controls may allow some to comply (unproven effectiveness)
- A few will be required to cease operations.

Impact on Cement Industry (cont.)

New Plants

- Expected to apply to new/reconstructed kilns commencing construction after date of proposal (i.e., ~4/22/09)
- Must meet emission limit upon start-up of facility
- Difficult to estimate emission and control effectiveness to certify compliance
- High cost of control
- Future variability in mix, fuels and operating conditions will impact operations and compliance.
- Compliance monitoring (e.g., CEMS)

Proposed MACT Limits/Changes

Pollutant	Current	Expected
PM_{10}	0.30 lb/ton KF[a,b]	0.080 lb/ton clinker[b] 0.085 lb/ton clinker[c]
Hg	none	43 lb/MM ton KF[c] 14 lb/MM ton KF[b]
THC	20 ppm[b]	6 ppmd(v) @ 7 %O2[b] 7 ppmd(v) @ 7 % O2[c]
HCl	none[b]	0.1 ppmd(v) @ 7% O2[b] 2.0 ppmd(v) @ 7 %O2[c]

[a]Kiln PM10 limit is surrogate for metals and other inorganic HAP pollutants
[b]Applicable for new plants
[c]Applicable to existing plants

NSPS Limits Proposed

Pollutant	Current	Expected
PM_{10}	0.30 lb/ton KF[a]	0.080 lb/ton CLK[a] 0.085 lb/ton CLK[b]
SO_2	none	1.30 lb/ton CLK[a]
NO_x	none	1.5 lb/ton CLK[a]

[a] Applicable new or modified plants
[b] Applicable existing plants

Path Forward

Regulations

- Comments taken on new proposed rules

Compliance Planning

- Develop Hg impact matrix (better detection limits)
- Stack tests (mill-in/mill-down)
- Develop Mix design options
- Alternative Fuel Considerations
- Evaluate End-of-pipe controls
- In-process Hg removal
- Evaluate meal desorption

Compliance Methods for MACT and NSPS Limits

SO_2

- Microfine lime injection to CT, down comer, or raw mill
- KF desorption system

HCl

- Microfine lime injection to CT, downcomer or raw mill
- KF desorption system

Hg

- Desorption of kiln feed or CKD with carbon capture

THC

- Desorption of kiln feed with oxidation in precalciner

$PM_{2.5}$

- Desorption of pre-cursor pollutants with oxidation in precalciner (NH3, semivolatiles, condensibles, etc.)

Emission Profile

- Hg emitted in three species
  - Elemental (Hg)
  - Oxide (HgO)
  - Salts ($HgCl_2$, $HgSO_4$)
- Species weighting is kiln specific and site specific
- Rate of emissions variable based on system operation
  - Dust wasting (CKD)
  - Direct/compound operating mode
  - Main filter temperature
  - Oxidation of Hg in the process

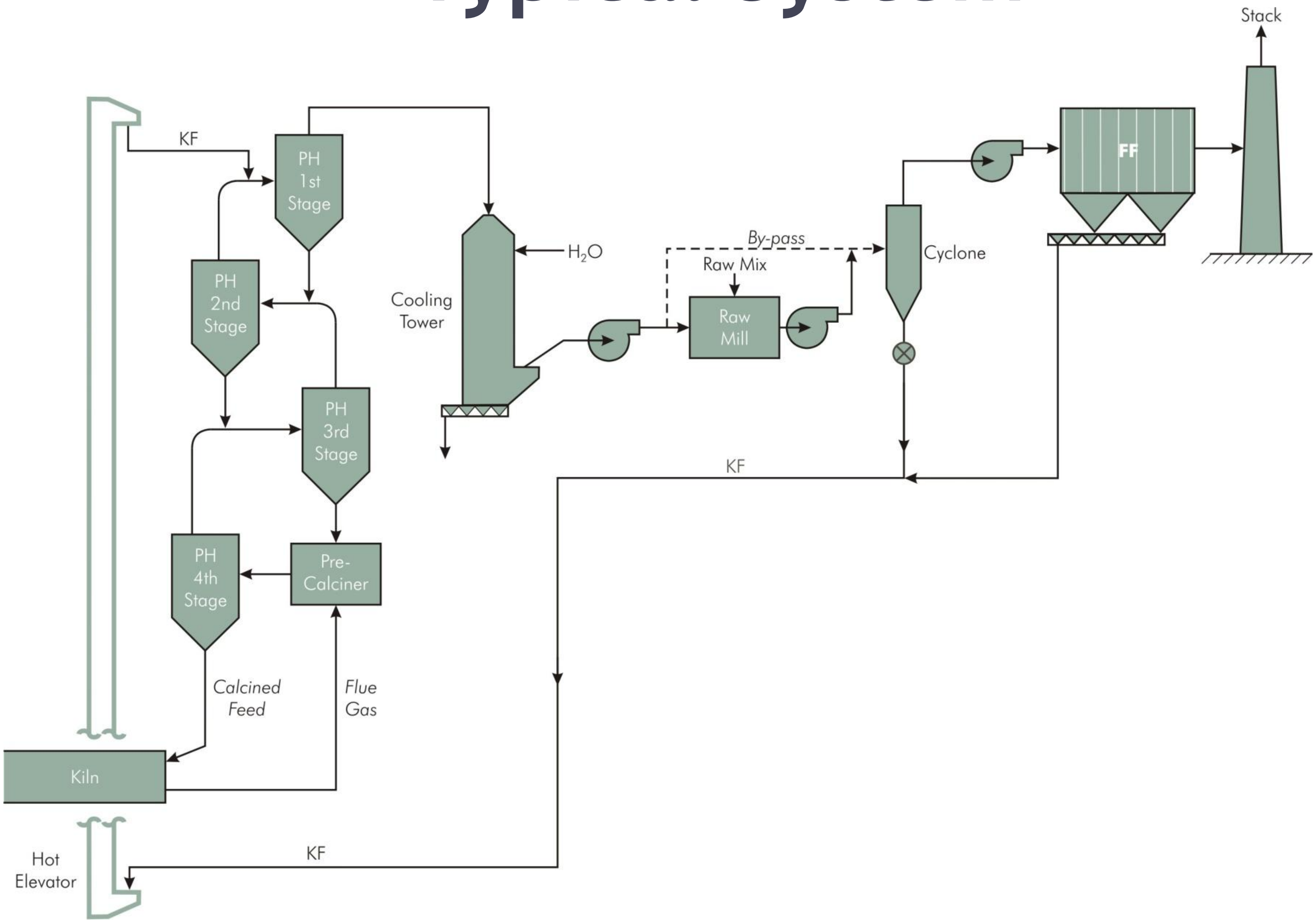
Species Present in Cement Kiln Operations

Temperature	Compounds
2200°C	Hg (elemental, vapor)
480-590°C	HgCl2
<350°C	HgO, $HgCl_2$
<325°C	$HgSO_4$
225-325°C	$HgSiO_3$

General Observations

- Long dry/wet kilns generally emit elemental Hg as predominate species
- Preheater/precalciner operating with in-line grinding have a high fraction emitted as oxide and/or salts
- Hg can be captured on kiln dust surface (condensed) as gas stream cools.

Typical System



Preheater/Precalciner Operations

- Hg enters via raw materials and as contamiant in the kiln and precalciner fuels.
- Hg is present as elemental in vapor phase due to elevated temperatures
- Hg entering via mix is released as kiln feed temperature is elevated in the preheater
- Hg is condensed onto the meal in the raw mill as gases are cooled during grinding.
- As meal is injected to the preheater, Hg is volatilized and a fraction oxidized depending on preheater temperature and oxygen content.

Preheater/Precalciner Operations (cont.)

- A portion of the Hg species (elemental, oxide, and salts) are recaptured in mill and fabric filter forming a recirculating load similar to alkali, ammonia, and sulfur species.
- When kiln is operating in direct mode, the fabric filter captures Hg but generally it is operating at a higher temperature and Hg ions reaches the stack.

Control Options

- Coal cleaning/fuel selection
- Mix design changes
- Combustion additives ($CaCl_2$, NaCl)*
- Oxidation processes (SCR, ozone, UV)*
- Fixed adsorption (noble metals)**
- Meal desorption (EQM/ECI)
- Flue gas desulfurization (wet scrubber)
- Sorbent injection (Carbon)***

*Must be combined with end-of-pipe controls (fabric filter or wet scrubber)

**Must be combined with a desorption/capture system

***Using fabric filter

Combustion Additives

$CaCl_2$ or NaCl injection into kiln system

- Increases oxidation
- End of pipe removal in wet scrubber or fabric filter

Sorbent Capture

Metalsaolinite and Calcium

- Captures Hg^{o} and Hg^{++}
- Effective at 800°F (15%) to 1200°F (100%)
- Desorbed at > 1700°F for Hg recovery

Sorbent Injection

Activated Carbon

- Chemical treatment to operate about 300°F
- Brominated activated carbon up to about 800°F
- Injection rates 1 lb/MM ACF of flue gases
- Residence time < 1 sec
- SO_3 is an interference

Oxidation Processes

- SCR
- UV radiation
- Ozone
- Requires end of pipe Hg removal after oxidation (wet scrubber or fabric filter)

Fixed Adsorption

- Noble metals are used capture Hg in flue gases (gold)
- Desorption thermally to recover Hg
- Final removal in secondary device

Wet Scrubber for Hg Control

- Wet scrubber reduces flue gas temperature and condenses Hg.
- Effective only on oxidized forms
- Capture is via particulate (impaction, absorption, and adsorption).
- Removal is highly variable depending on species (elemental, oxide, salts) and is site specific. Efficiencies of 50-98% reported for mill down operation.
- Power plants report higher capture if scrubber is operated in alkaline pH conditions (pH 7.5-8.0)
- Alkaline pH causes fouling in scrubbers when operating with carbonates as reagents.

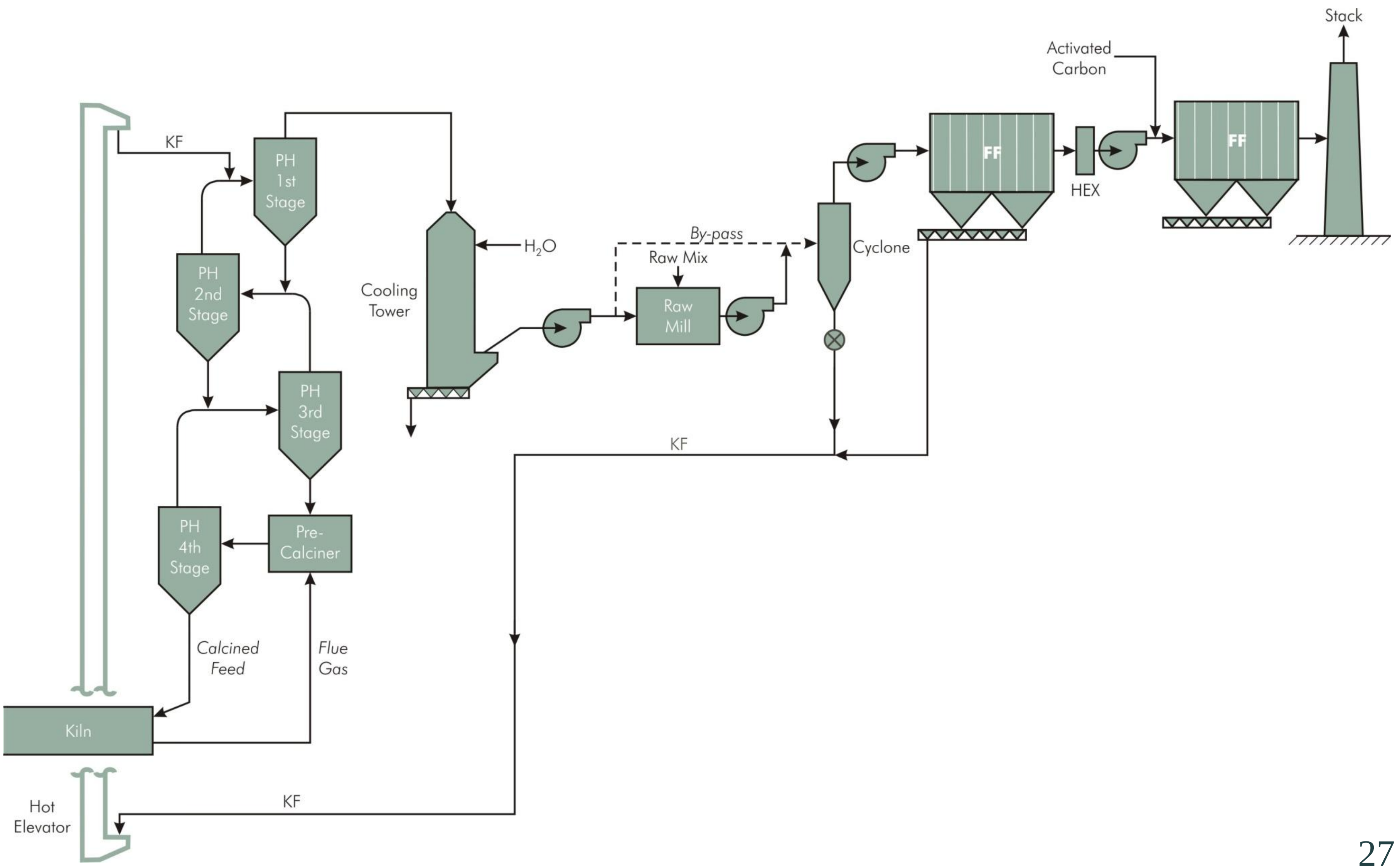
Problems in Using Wet Scrubber

- Variability in capture with species
- Hg will partition into blow down liquor creating disposal issues.
- High SO_2 in flue gases may be inconsistent with required operating conditions to remove Hg.
- High capital and operating costs ($12-$20 MM installed)
- Additives may be needed (hydrogen peroxide) to form non-volatile salts)
- Upstream processes may be required to favor oxidation of elemental Hg.

Carbon Capture (ACI End of Pipe)

- Requires second fabric filter after main baghouse (combined gases, coal mill, and pyroprocessor).
- Filter temperature must be 120-150°F to be effective requiring heat exchange to reduce temperature.
- Carbon injections of 1-2 lb/MM acf for Hg capture
- Carbon cost $4.00/lb plus disposal $2.50/lb (hazardous)
- Increased static pressure losses (~ 10 in. wg)
- High capital cost $20MM for 1,000,000 acfm

Mercury Removal Using Activated Carbon



Carbon Disposal

- Carbon disposal depends on TCLP (0.2 ppm) and Hg concentration
- Subtitle D landfill (non-hazardous)
- Stabilization (if hazardous and below 260 ppm total Hg)
- Retort (if hazardous and above 260 ppm total Hg)

Problems in Using Carbon

- Elemental Hg vapor not captured by carbon
- Br and Cl^- can be impregnated into carbon to oxidize elemental to oxide.
- Full scale applications not proven
- Variability in kiln Hg emissions and species fractions

EQM Proposed Hg Abatement System

- EQM and ECI have been issued a patents for a method and operation for thermally removing Hg and other volatile species from kiln feed.
- In existing preheater kiln designs volatile species are released into the full volume of combustion gases. The resulting flue gases therefore have a low concentration of pollutants and require a high volume of gases to be processed.

EQM Proposed Hg Abatement System (cont.)

- EQM method is to heat kiln feed (mill product or fabric filter dust) in a closed system through indirect heating to release the pollutants into a small carrier gas volume.
- Treatment of this volume of gases is at higher concentration at lower cost.

Kiln Feed Indirect Heating

- The kiln feed is combined with a portion of calcined meal in a reaction vessel which is indirectly heated using by-pass gases from the kiln.
- The combined thermal heating of flue gas and calcined meal raises the kiln feed temperature to >350°F which releases organic material, ammonia species, volatile organic compounds and mercury.
- The reaction is ventilated and purged using a small carrier gas volume then filtered, Hg oxidized, and captured using activated carbon.

Kiln Feed Indirect Heating (cont.)

- Treated gases are returned to the precalciner for heat recovery and destruction of VOC, THC, CO, D/F and ammonia.
- Heated and cleaned kiln feed is transferred to first stage preheater where stored heat is recovered.
- Generated dust from vent gas fabric filter is returned to the inlet of the thermal treatment and the activated carbon containing Hg is recovered for disposal.

Thermal Desorption Mercury Removal System