Cement Manufacturing Mercury Emissions

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Outline

- Overview of cement sector and manufacturing process
- Sources, fate of mercury in the cement manufacturing process and estimated emissions of mercury from Canadian cement kilns
- Approaches to mercury emissions from cement kilns in other jurisdictions
- Available techniques for reduction of emissions
- Implications of using available techniques

Cement manufacturing in Canada

The Canadian cement industry consists of 16 facilities owned by 7 companies located in 5 provinces (BC, AB, ON, QC, NS)

Province	Number of Plants	Number of Kilns	Clinker Production Capacity (Mt/year)	% of Total
British Columbia	3	3	2.35	15
Alberta	2	3	2.16	14
Ontario	7	12	8.15	51
Québec	3	7	2.69	17
Nova Scotia	1	2	0.48	3
Total	16	27	15.83	

Canadian cement production is relatively low on a global scale, estimated at 14.1 megatonnes (Mt) for 2003 compared to world production estimated at 1860 Mt for the same year

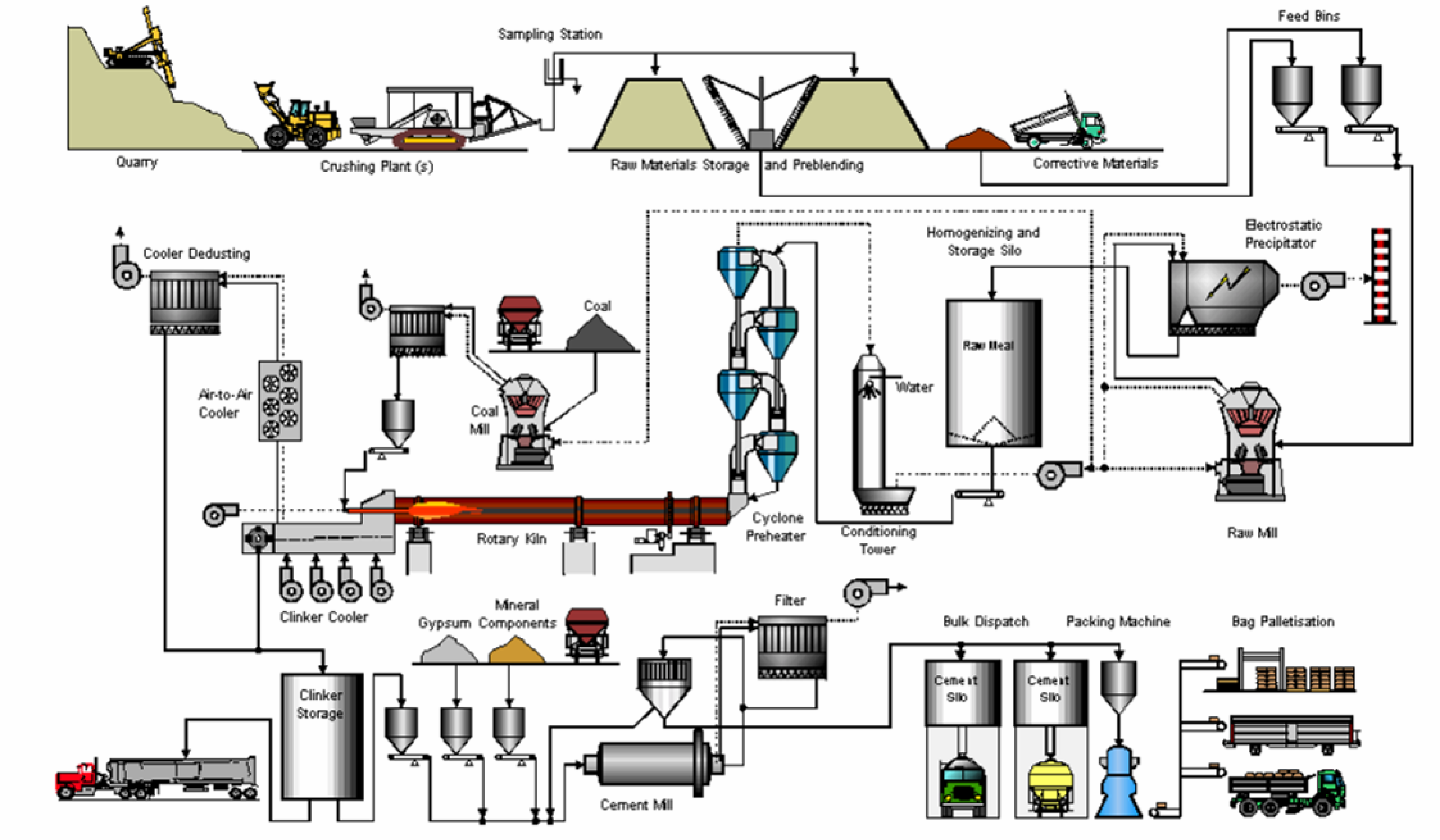
The top five producing countries were estimated as producing 750 Mt (China), 110 Mt (India), 92.6 Mt (United States), 72.0 Mt (Japan) and 56.0 Mt (South Korea)

(Portland) Cement manufacturing process in brief

- Cement production requires pyroprocessing (drying/heating raw materials, calcination/sintering of feed to form “clinker”)
- Raw materials for Portland cement:
  - lime (calcareous) – from limestone
  - silica (siliceous) and alumina (argillaceous) – from clay, shale
  - iron (ferriferous) – from pyrite, steel mill slag
- Limestone becomes lime by calcination ($CaCO_3 \longrightarrow CaO + CO_2$)
- “Clinkers” -- hard, gray, spherical nodules 0.32 - 5.0 cm (1/8 - 2") in diameter created from chemical reactions between the raw materials during sintering or “burning” (mainly calcium silicates, aluminates)
- Clinker is then cooled, ground and combined with gypsum and other materials to form various types of cement
- Pyroprocessing requires large amounts of heat (1450 °C needed to burn clinker); energy use is a major cost of production
  - built-in incentive for energy conservation; newer kiln technologies more energy-efficient

A typical dry process kiln system

(Source: CEMBUREAU. Best Available Techniques for the Cement Industry, December 1999; http://www.cembureau.be/

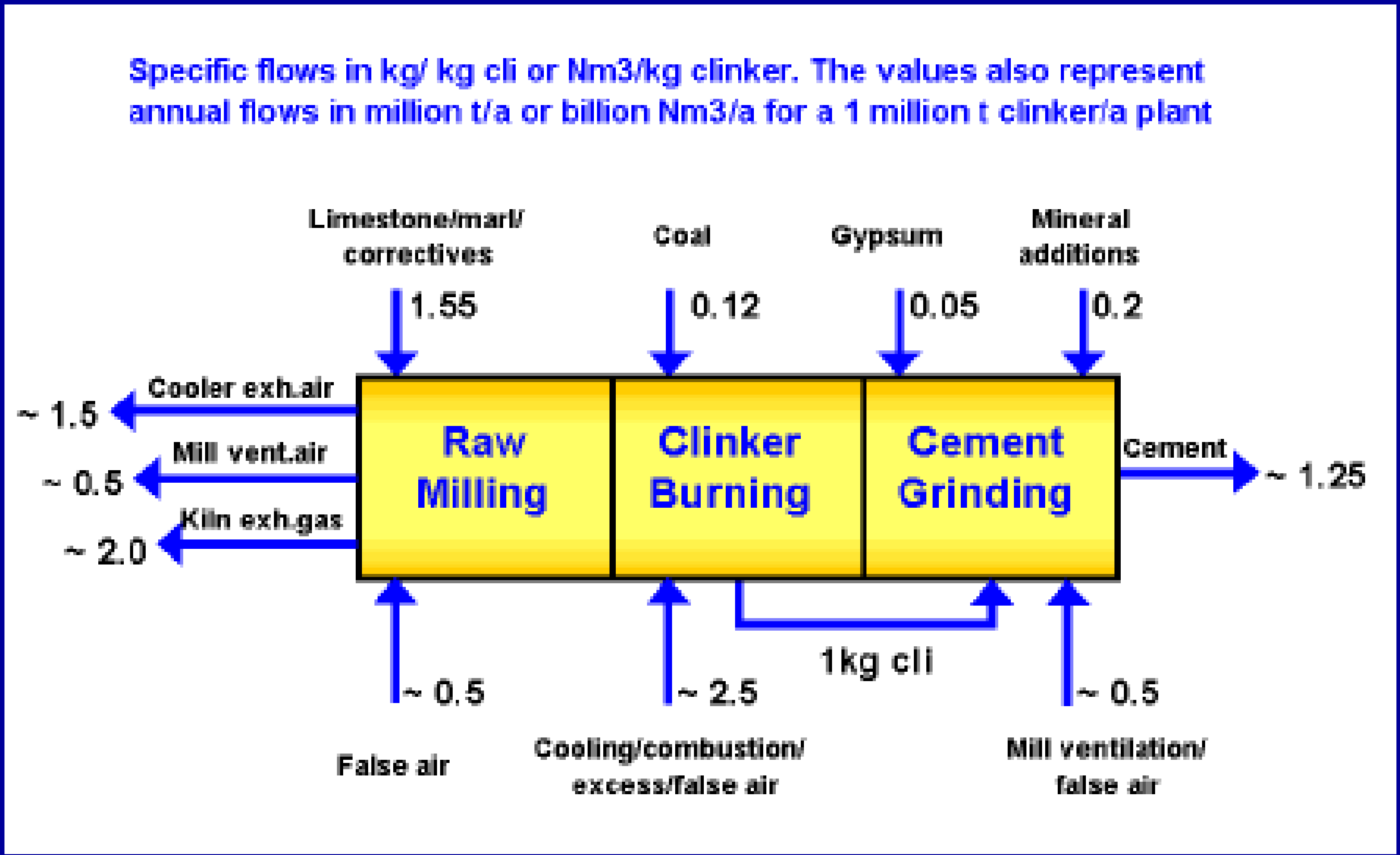


Mercury in the cement process

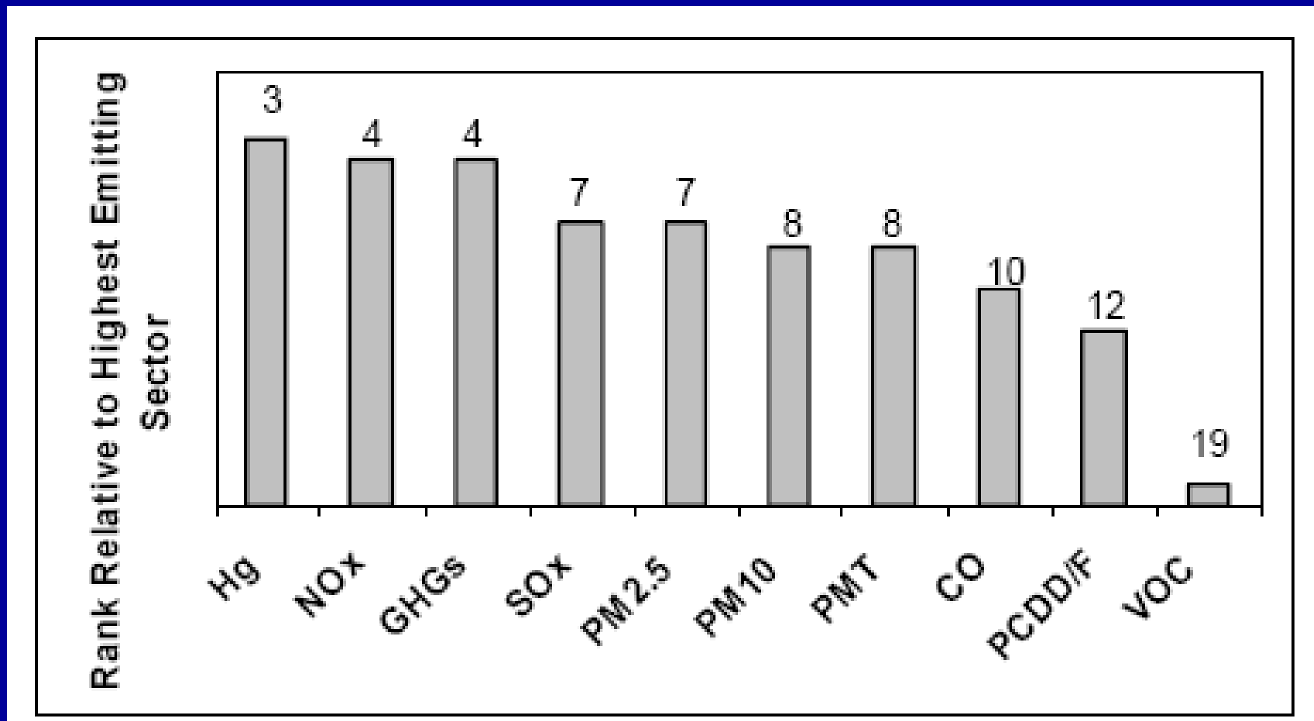
- Present in raw materials; both natural and recycled inputs
- Limestone, shale can contain mercury; due to volume of limestone used, can be significant
- Recycled streams such as fly ash from electric power generation often also contribute significantly
- Fuels (coal, waste-derived fuels) also contribute varying, sometimes significant amounts
- A significant fraction of the mercury present in the feed is not retained in the product; the fraction of that which escapes and is a solid is collected in the particulate air pollution control system, but mercury also exists in the exhaust as a gas

Material flows in a cement plant

(Source: CEMBUREAU. Best Available Techniques for the Cement Industry, December 1999; http://www.cembureau.be/



Mercury emissions' relative importance in cement plant exhaust



Source: Environment Canada National Emissions Inventories - 2000
Note: PCDD/F emissions are for calendar year 1999
Cement Sector Emissions Ranking to Other Industrial Sectors – 2000

Current emissions & requirements

- From Canada's *National Emissions Inventories for Criteria Air Contaminants and Greenhouse Gases* for 2000:
  - Cement sector emissions were estimated at 313 kg/year;
  - Taken together, all industrial sectors emitted 3,797 kg/year; thus
  - The cement sector emits 8.2% of industrial mercury emissions
- No national mercury rules for kilns not firing wastes; however, CCME has published *Guidelines for the Use of Hazardous and Non-Hazardous Wastes as Supplementary Fuels in Cement Kilns* (March, 1996)
  - Apply to kilns using more than 50 % fuel substitution with hazardous or non-hazardous wastes
  - Emission limit: 0.15 mg/Rm^3 for sum of "Class 3 metals" (Cd, Hg, Tl) [Reference conditions 25 °C, 1 atm, dry basis, 11 %O_2]
  - Based on German *TA Luft* air pollution regulation as written in the early-mid 1990s

Future emission trend

- Sector activity (production) is forecast to grow for the foreseeable future, increasing emissions of all air pollutants proportionally
- Increased utilization of recycled materials from other sectors also expected to continue, particularly waste-derived fuels due to energy pricing trends
- Barring new efforts to address emissions, significant growth is possible in loadings from this sector

US Developments

- US EPA decided not to set emission limits for mercury in cement kiln exhausts where hazardous waste is not fired with its most recent proposed MACT rules
  - Decision under reconsideration; comment period closed February 2006
  - STAPPA/ALAPCO stated disagreement with decision (comment letter dated February 23, 2006)
- Emission limits for mercury have been set in the NESHAP Final Rule (October 2005) for Hazardous Waste Combustors (which includes cement kilns)
  - Combination of feed concentration limits and/or emission limit
    - Emission limit for new or existing plants is 120 µg/dscm (84 µg/Rm^3)
    - Facilities may elect to use a combined feed restriction and MTEC of 120 µg/dscm instead; feed limit is 3 ppm(wt) for existing plants, 1.9 ppm(wt) for new or reconstructed sources
      - MTEC means ``maximum theoretical emission concentration'', and is equivalent to the mercury feed rate divided by the exhaust gas flow rate for the combustor
  - Existing emission data (n = 70) ranged between 0.2 ~ 1,240 µg/dscm; the mean was ~66 µg/dscm (0.14 – 866 µg/Rm^3; mean ~46 µg/Rm^3)

Emission control practice

- From CEMBUREAU's *Best Available Techniques for the Cement Industry:*
  - *The HM emissions of cement kilns are usually significantly below a total of 0.5 mg/Nm3 and therefore in compliance with most regulations.*
  - *The most common HM emission reduction measures are reduction of HM input and efficient dedusting. To avoid accumulation of HM in the kiln system a portion of the filter dust should continuously or periodically be extracted from the dedusting system. Additional secondary reduction measures like the adsorption on activated coke are only required if the content of the volatile HM (e.g. Hg) is very high.*
- Note that for mercury, particulate removal efficiency is not always a major factor in determining emissions and so "efficient dedusting" is not an effective option unless the mercury can be converted to a solid form, and even then a bleed stream must be used to avoid adding continually to the circulating mercury load in the kiln system

Summary of approaches

- Pollution Prevention Approach:
  - The most effective pollution prevention approach to addressing mercury emissions from cement kilns is to avoid using raw materials with elevated mercury content
    - No established benchmark value for each material, however, except U.S. Final Rule values for kilns firing hazardous waste
- Pollution Abatement Approaches:
  - An activated carbon filter bed system is being used successfully at one Swiss cement kiln to control mercury emissions;
  - Activated carbon injection upstream of a fabric filter is also used with success on incinerators to control mercury emissions, but has not been demonstrated for cement kiln applications
    - Exhaust gas cooling (usually by evaporative cooling) to <150 °C is also needed when activated carbon injection is used at incinerators; likely also required here

Implications

- Activated carbon injection could have impacts on cement kiln dust (CKD; dust caught in the particulate control system normally returned to the kiln as part of the feed mix) recirculation to kilns
  - A bleed stream must be provided to take mercury out of the system
  - The percentage recycled could be changed as a result of this option, resulting in more waste CKD for disposal
- Capital costs for activated carbon bed mercury abatement are significant but demonstrated technology exists and is effective
  - As bed carbon is sent to the kiln for destruction also, a bleed stream to take mercury out for disposal is still needed as above
- Carbon-based technologies will also collect UPOPs and other organic compounds as a co-benefit
- Minimizing mercury content in raw materials could affect ability to utilize certain waste-derived fuels (e.g., liquid or solid hazardous wastes contaminated with mercury), recycled materials (e.g., electric utility fly ash), and even some specific limestone deposits, in the cement process
  - Due to the limestone volume used, even low levels of contamination can lead to significant emissions due to limestone; also, kilns tend to be within convenient range of their committed limestone source to minimize transportation costs