# USE OF ALTERNATIVE FUELS IN CEMENT PRODUCTION (continuing study)


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*Earth Engineering Center,*

*Columbia University and City College of New York*


*WTERT 2014 Meeting, October 20, 2014*

# Some of the more active GWC members

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**We welcome today our newest member: WTERT-Chile (Prof. Alex Godoy of Universidad del Desarollo, Santiago)**

# Objectives of WTERT Global Council (GWC)

- to identify the best available technologies for the treatment of various "waste" materials
- to recover materials and energy from "waste"materials
- to conduct academic research on sustainable waste management
- to disseminate this information by means of publications, the multilingual WTERT web pages, and periodic meetings and conferences, at the national and international levels
- to provide high level education on Sustainable Waste Management

**For example: This meeting!**

# At this meeting you heard papers on Reduction (South Korea), Recycling (VBWF), Landfill Gas utilization, waste-to-fuels and waste-to-energy

- **Energy can be recovered from wastes by:**
- **Combustion in WTE plants** (about 10% of the U.S, post-recycling MSW goes to WTE plants; but 90% still goes to landfills)

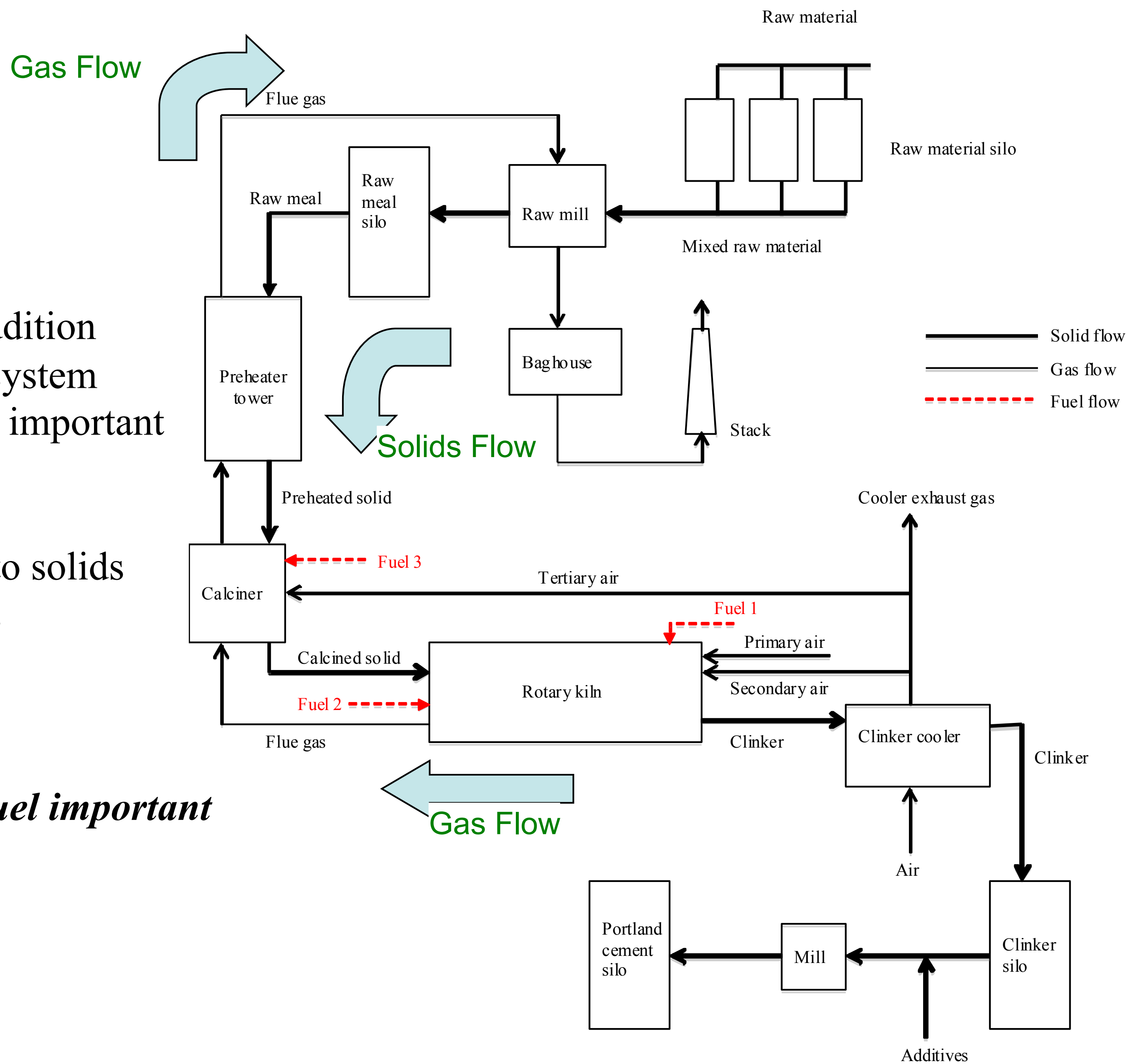
- **But: Energy can also be recovered by using "wastes" in industrial processes in place of fossil fuels**

- **With the help of CEMEX, an international cement company headquartered in Monterey, Mexico, GWC is examining the use of "waste" fuels in cement production**

# CEMEX Corporation

- Presence in 50 countries
- 43,000 employees
- 94 million tons of cement/year
- New York City office
- Cement plant visited by authors: Balcones (San Antonio, Texas)
- Cement production is, by far, the largest worldwide high temperature process
  - Use of fossil fuels: Typically, 3.6 MJ/kg of cement "clinker"

# The Cement Process (Jiao Zhang Thesis, Columbia, 2013)




**Best integrated process**

- Multiple places for fuel addition
  - Determined by feed system
- Chemical content of AF is important
- Thermal integration helps

- Gas flow counter-current to solids
  - Self-cleaning process

- ***Size and preparation of fuel important***

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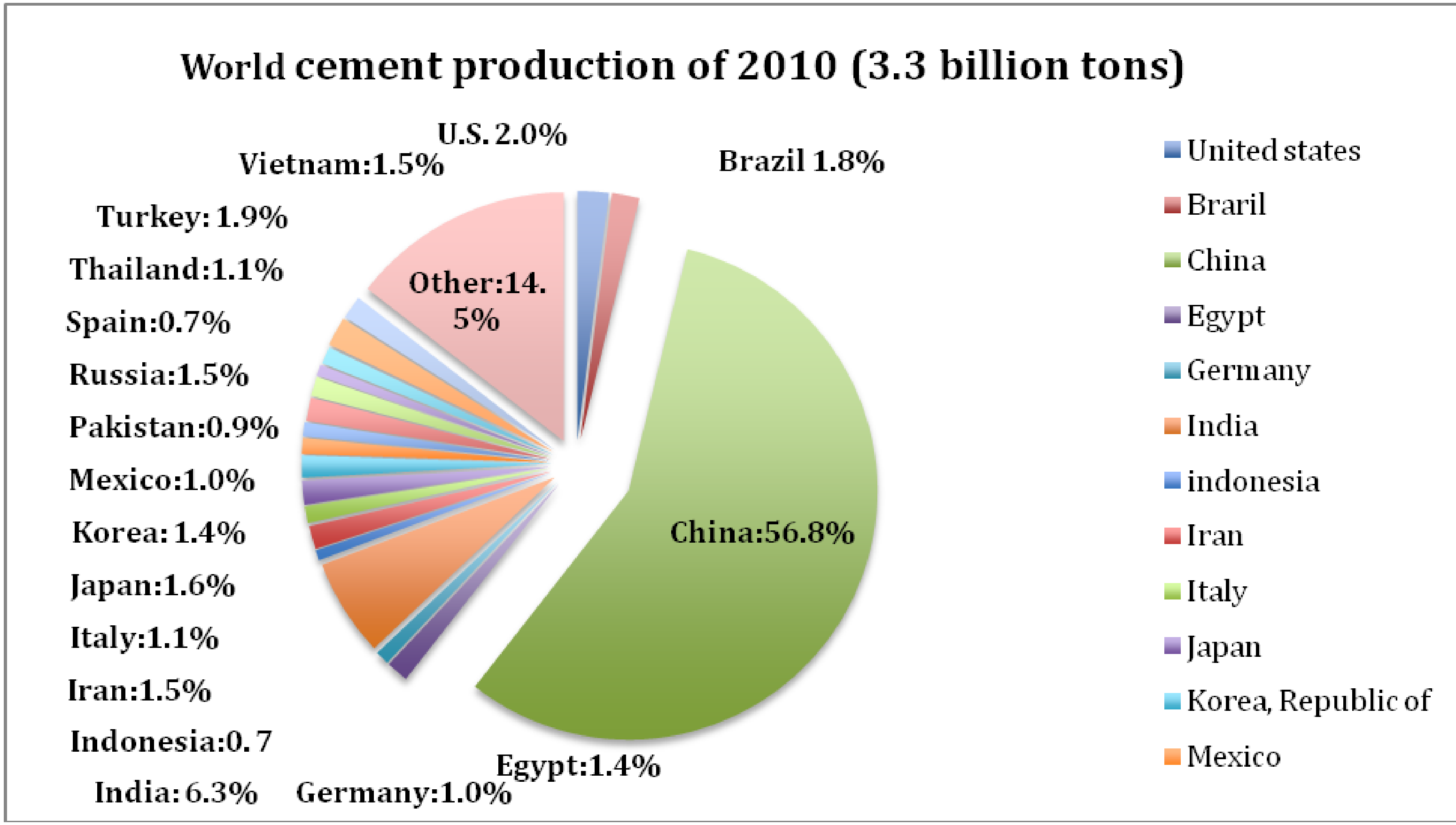
# Cement Production Worldwide



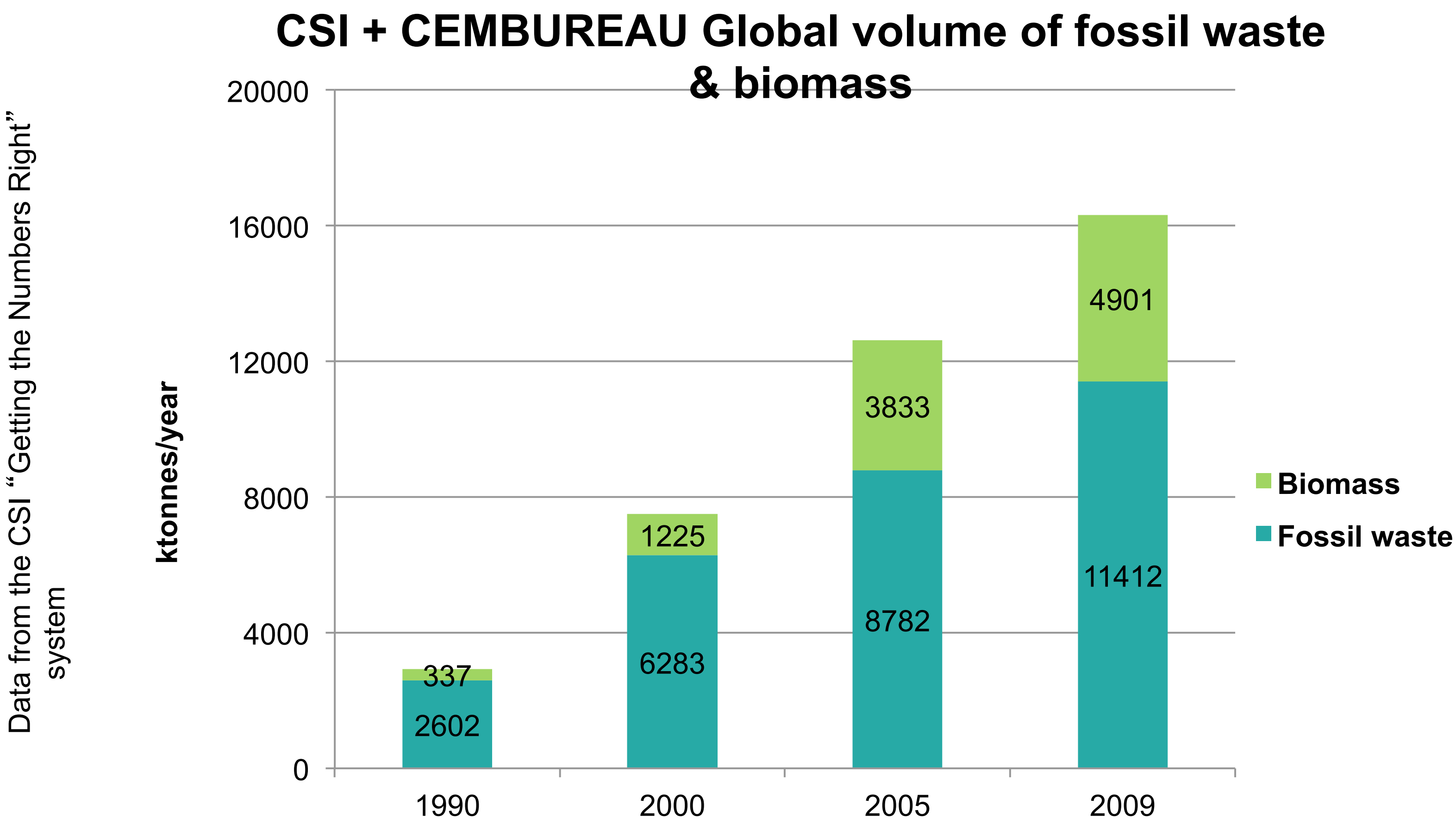

Source: Cement" in U.S. Geological Survey, 2012, Mineral Commodity summaries 2012: U.S. Geological Survey, 198p.

# Impacts of Cement Production

- $CO_2$, CO, NOx & $SO_2$
  - 200 kg of coal per tonne of cement
  - 900-1000 kg $CO_2$ per tonne of clinker (~5% of total GHG emissions)
    - 60 % is related to calcination of $CaCO_3$, remainder is fuel combustion.
- NOx emissions amount to ~0.3-4.7 kg/tonne of clinker
- US cement clinker production 78 million tons in 2010

- **Global cement production: 3.5 billion tons**
- **Hypothetically, 50% use of Alternative Fuels would utilize 350 million tons (175% of current WTE capacity)**

# Use of Alternative Fuels in cement industry




- In 2009 the cement industry recovered 16.3 million tonnes of waste
- The use of fossil waste grew fast between 1990 and 2000, whereas biomass grew fast since 2000 and continues

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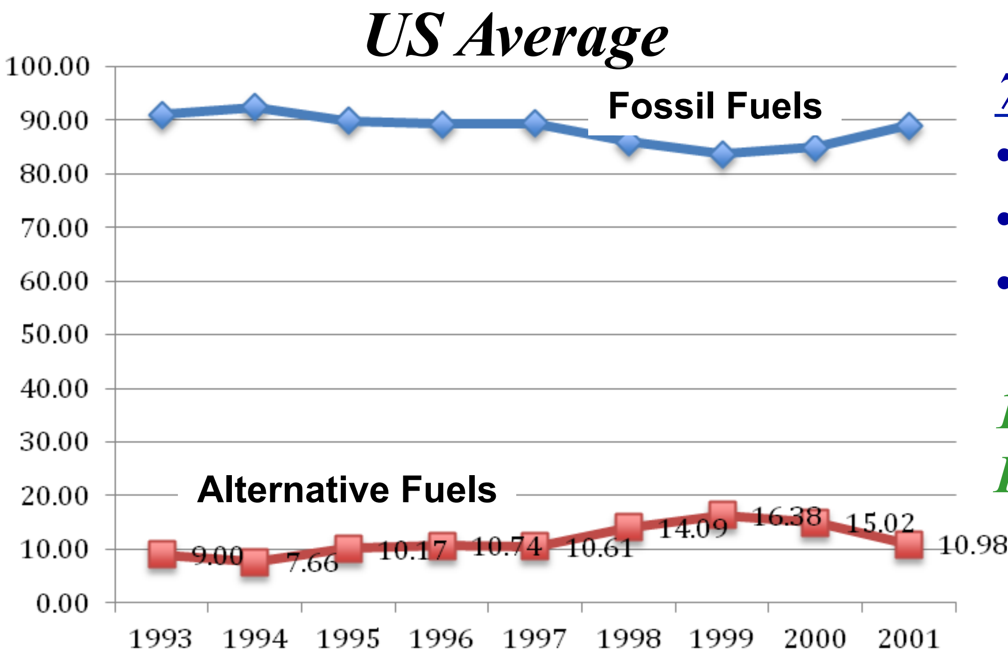
Source: CEMBUREAU March 2012 – Global Fuels Conference & Exhibition

# Alternative fuel usage in Cement Kilns




***<u>700,000 tons of EF utilized</u>***

- ***reduced GHG by 1% in US***
- ***5.2% increase in WTE capacity***
- ***280,000 tons of ash used***

***14.6 MMtonnes estimated US max***
***Increases WTE capacity by 110%***

**<u>CEMEX Alternative Fuel Usage</u>**

•Engineered fuel, tires and biomass
•38.9% Jan – April 2013
• Avg US from 1993-2001, → 10%-15%

***Representation of the AF mixture***
***High Pet Coke replacement achieved***

| | Eng.Fuel | Wood | Tires | Bottom Ash | Pecan Shells | Other | Sum |
|---|---|---|---|---|---|---|---|
| **Apr-13** | 19.6% | 18.5% | 12.8% | 1.9% | 0.7% | 0.0% | 53.5% |
| **Feb-13** | 15.2% | 18.3% | 12.2% | 2.3% | 0.6% | 0.1% | 48.7% |

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# "Engineered Fuel": Non-marketable residue of Materials Recovery Facilities (MRF) consisting of a mixture of plastics and paper

*Engineered Fuel (EF) Fluff*

*Engineered Fuel (EF) extruded pellet*

**Samples of EF collected by Themelis and Castaldi at Balcones Plant**

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# Emissions

- *Hg emission was 0.000014 $mg/Nm^3$*
- *Dioxin ~0.01 ng $TEQ/Nm^3$ (an order of magnitude below E,U./U.S. standard)*
- *Inherent advantage: Presence of CaO makes cement production a self-scrubbing process that sequesters chlorine.*
- *The chlorine input in the fuel is limited only by possible operational problems (chloride accretions in calciner or pre-heater)*

| | **EU standard after conversion to 7% O2 in stack gas** | |
|---|---|---|
| **Emissions** | Combustion plants | kilns |
| | mg/Nm3 | mg/Nm3 |
| **Total dust** | 23.32 | 38.19 |
| **HCl** | 10.0 | 12.73 |
| **HF** | 1.0 | 1.273 |
| **NOx** | 187 | 636.5 |
| **Cd+Tl** | 0.05 | 0.06365 |
| **Hg** | 0.05 | 0.06365 |
| **Sb+As+Pb+Cr+Co +Cu+Mn+Ni+V** | 0.05 | 0.6365 |
| **SO2** | 233 | 63.65 |
| **TOC** | 10 | 12.73 |
| **CO** | 50.0 | 89.0 |

# Modeling Effort of Gases

- Development of reaction mechanism (GRI modification)
- Simulate different fuels and scenarios
- Find a suitable mixture minimizing emissions

$$\text{Rate} = k\, C_{fuel} C_{ox} \qquad k = AT^n \exp\left(\frac{-E}{RT}\right)$$

Example of sulfur reactions

| | $A$ | $n$ | $E_{act}$ |
|---|---|---|---|
| $S + O_2 \leftrightarrow SO + O$ | $6.30 \times 10^{11}$ | 0.5 | 0 |
| $O + S_2 \leftrightarrow SO + S$ | $6.30 \times 10^{1}$ | 0.5 | 0 |
| $SO + O_2 \leftrightarrow SO_2 + O$ | $1.80 \times 10^{11}$ | 0 | 0 |
| $SO + SO \leftrightarrow SO_2 + S$ | $3.30 \times 10^{11}$ | 0 | 2250 |
| $S_2 + H \leftrightarrow S_2O + H$ | $1.80 \times 10^{13}$ | 0 | 0 |

Chlorine reactions

| | | | |
|---|---|---|---|
| $Cl + H_2 = HCl + H$ | 2.88E+08 | 1.58 | 3,199 |
| $H + Cl_2 = HCl + Cl$ | 9.64E+13 | 0 | 1,680 |
| $H + Cl_2 = HCl + Cl$ | 9.64E+08 | 0 | 1,680 |

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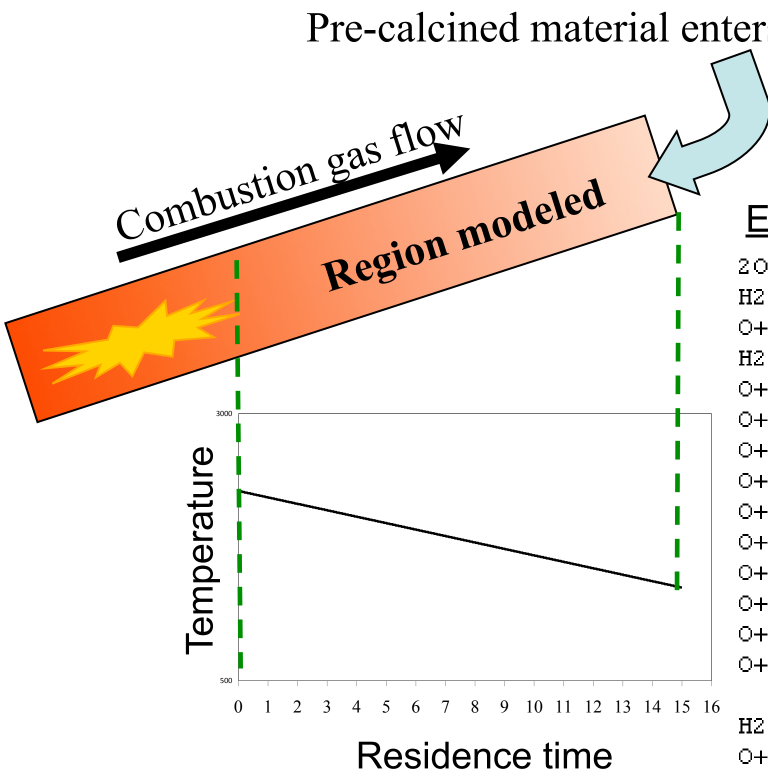
# Modeling Effort of Gases




Elementary step mechanism anchored by combustion gas residence time (15 seconds)

| Elementary Reaction step | A | n | $E_{act}$ |
|---|---|---|---|
| 2O+M<=>O2+M | 1.200E+17 | -1.000 | .00 |
| H2/ 2.40/ H2O/15.40/ CH4/ 2.00/ CO/ 1.75/ CO2/ 3.60/ C2H6/ 3.00/ AR/ .83/ | | | |
| O+H+M<=>OH+M | 5.000E+17 | -1.000 | .00 |
| H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/ | | | |
| O+H2<=>H+OH | 3.870E+04 | 2.700 | 6260.00 |
| O+HO2<=>OH+O2 | 2.000E+13 | .000 | .00 |
| O+H2O2<=>OH+HO2 | 9.630E+06 | 2.000 | 4000.00 |
| O+CH<=>H+CO | 5.700E+13 | .000 | .00 |
| O+CH2<=>H+HCO | 8.000E+13 | .000 | .00 |
| O+CH2(S)<=>H2+CO | 1.500E+13 | .000 | .00 |
| O+CH2(S)<=>H+HCO | 1.500E+13 | .000 | .00 |
| O+CH3<=>H+CH2O | 5.060E+13 | .000 | .00 |
| O+CH4<=>OH+CH3 | 1.020E+09 | 1.500 | 8600.00 |
| O+CO(+M)<=>CO2(+M) | 1.800E+10 | .000 | 2385.00 |
| LOW/ 6.020E+14 .000 3000.00/ | | | |
| H2/2.00/ O2/6.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/3.50/ C2H6/3.00/ AR/ .50/ | | | |
| O+HCO<=>OH+CO | 3.000E+13 | .000 | .00 |
| O+HCO<=>H+CO2 | 3.000E+13 | .000 | .00 |
| O+CH2O<=>OH+HCO | 3.900E+13 | .000 | 3540.00 |
| O+CH2OH<=>OH+CH2O | 1.000E+13 | .000 | .00 |
| O+CH3O<=>OH+CH2O | 1.000E+13 | .000 | .00 |
| O+CH3OH<=>OH+CH2OH | 3.880E+05 | 2.500 | 3100.00 |
| O+CH3OH<=>OH+CH3O | 1.300E+05 | 2.500 | 5000.00 |
| O+C2H<=>CH+CO | 5.000E+13 | .000 | .00 |
| O+C2H2<=>H+HCCO | 1.350E+07 | 2.000 | 1900.00 |

CEMEX → Kiln outlet temperature
Calc → adiabatic flame temperature

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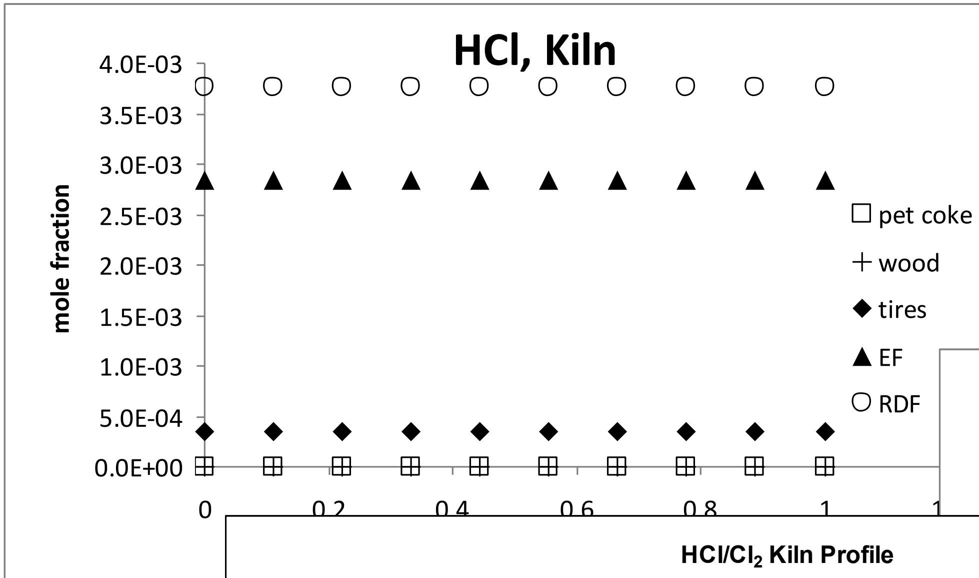
# Chlorine

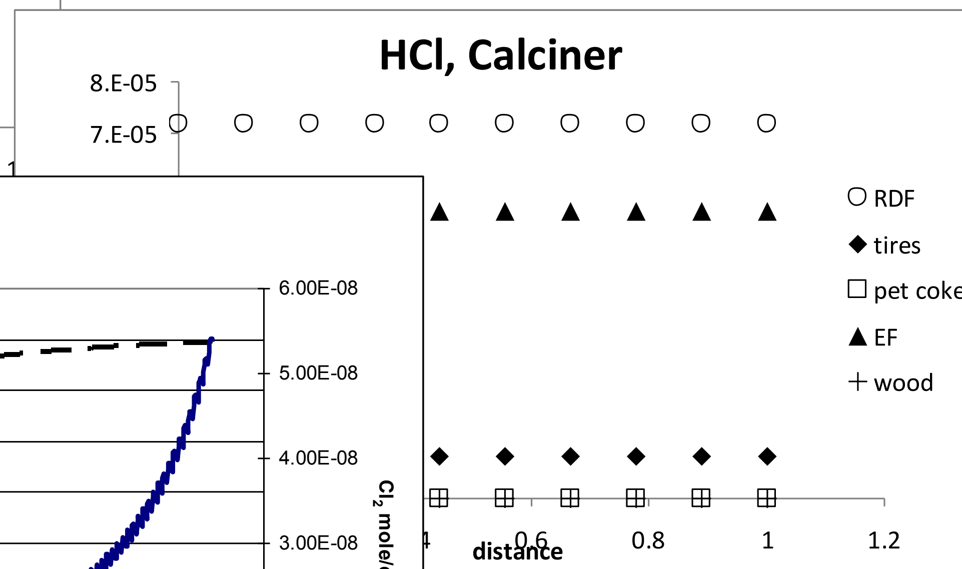


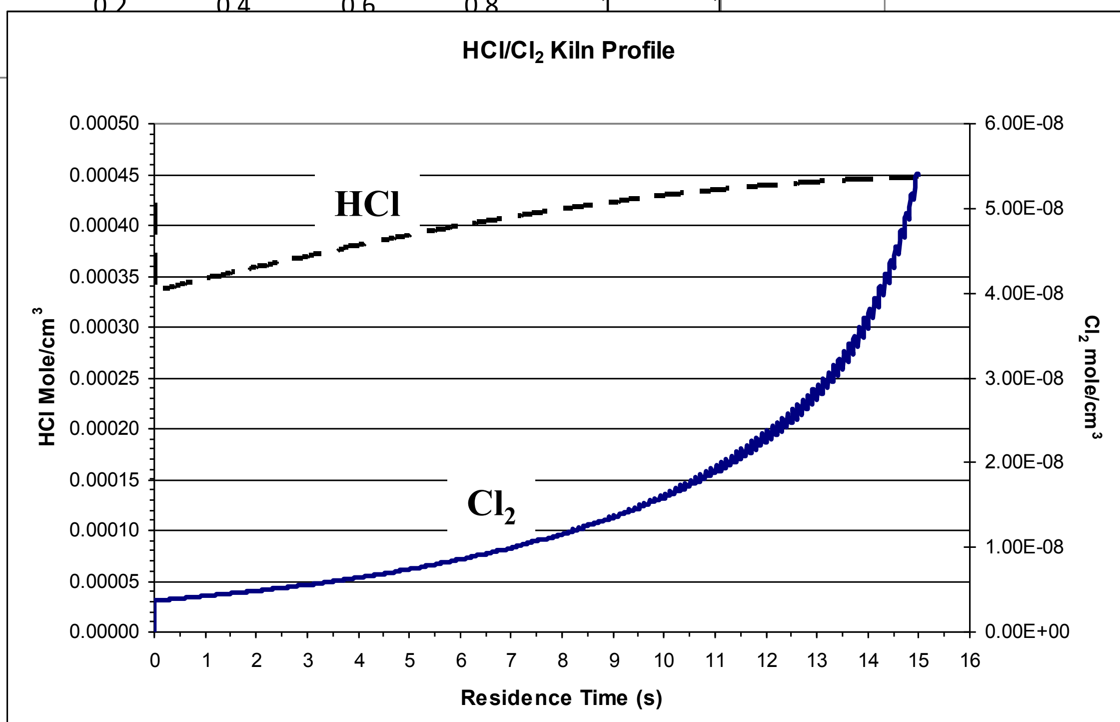

**Higher concentrations in Kiln**

Once formed, remains constant

$Cl_2$ increase toward exit end

- cement kiln dust
- corrosion

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