Lessons Learned Related to Dioxin Formation in Cement Kilns

Robert Schreiber - Schreiber, Yonley & Associates

Manufacturing Technical Committee
PC MACT Standard
Dioxins & Furans

- Two part standard
  1. Dioxin standard - 0.2 ng/dscm TEQ
     Temperature control - set during performance test
  2. Dioxin standard - 0.4 ng/dscm TEQ
     Temperature control - set during performance test and less than 400°F
Dioxin Molecule

2,3,7,8 Tetrachlorodibenzodioxin
Furan Molecule

2, 3, 7, 8 Tetrachlorodibenzofuran
Dioxin Versus Temperature

PCDD/PCDF = 4.96E-1 * exp(1.17E-2 * F)
R^2 = 0.73

Group 2:
O2%: 5.9
CO ppm: 621
THC ppm: 24
HCl ppm: 30

PCDD/PCDF = 3.96E-3 * exp(1.4E-2 * F)
R^2 = 0.75

Group 1:
O2%: 10.3
CO ppm: 117
THC ppm: 12.7
HCl ppm: 21

PCDD (ng/dscm @ 7% O2)
APCD Inlet Temperature (F)
Dry Process Preheater/ Precalciner System

There are still five jobs to be done

- Drying
- Preheating
- Calcining
- Sintering
- Cooling

Preheater Precalciner Kiln

60% Fuel Split
40%
Temperature Profile PH/PC Kiln
Wet Kiln Process Material and Gas Temperatures
Test Results - Dioxin TEQs

CONTINENTAL CEMENT COMPANY
MRI RUN
May 1992

Dioxin Equivalents

Fuel Combinations
Coal
HWF + Coal
HWF + Coal
Diesel + Coal
Distribution of Organic Mass in Kiln Emissions

DISTRIBUTION OF ORGANIC MASS

Concentration (ppmw, dry as propane)

Run Number

> C17
C7 - C17
C1 - C7

1
2
3
4
5
6
## Test Parameters for Historical Study

<table>
<thead>
<tr>
<th>Test Run</th>
<th>Kiln Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 - 3</td>
<td>Normal</td>
</tr>
<tr>
<td>4 - 6</td>
<td>Added Na$_2$Co$_3$</td>
</tr>
<tr>
<td>7 - 9</td>
<td>Added Na$_2$Co$_3$ + H$_2$O</td>
</tr>
<tr>
<td>10 - 12</td>
<td>Added H$_2$O</td>
</tr>
<tr>
<td>13 - 15</td>
<td>Coal Only</td>
</tr>
</tbody>
</table>
Test Results
Total Dioxin/ Furans in Waste Dust and Stack Gases

Waste Dust (ppt)  Stack Gas (ng/dscm at 7% O2)

Runs 4-9 had sodium carbonate added
Test Results
Comparison of Waste Dust Dioxin to Sodium in Waste Dust

Continental Cement 7/12/93 - 7/16/93
# Test Parameters for Historical Study

<table>
<thead>
<tr>
<th>Test Day</th>
<th>Kiln Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Normal</td>
</tr>
<tr>
<td>2</td>
<td>Addition of activated carbon (100 lb/hr) into duct work between kiln and ESP</td>
</tr>
<tr>
<td>3</td>
<td>Addition of atomized water (30 gal/min) into back end of kiln</td>
</tr>
<tr>
<td>4</td>
<td>Addition of atomized water (30 gal/min) into back end of kiln; set insufflation dust rate equal to zero</td>
</tr>
<tr>
<td>5</td>
<td>Addition to sulfur to raw mill (10 tons flake sulfur/4700 tons slurry)</td>
</tr>
</tbody>
</table>
Kiln Mass Balance

Total Dioxin
ND = 0
Test Day 2 Results:

- Dioxin concentration on Test Day 2 averaged 34.61 ppt TEQ compared to 0.52 ppt for Test Day 1
- Dioxin concentration on Test Day 2 averaged 1341.7 ppt total D/F compared to 25.27 ppt for Test Day 1

The addition of activated carbon increased the dioxin concentration in the CKD by two orders of magnitude.
Statistical Analysis of High and Low THC ITEQ Data

The prudent selection of raw materials has resulted in a dramatic decrease in dioxin emissions.
Statistical Analysis of High THC ITEQ Data

High Total Hydrocarbon (THC) ITEQ Data

Test Number

ITEQ (dg/dcs/m)

Series 1
Statistical Analysis of Low THC ITEQ Data

Low Total Hydrocarbon (THC) ITEQ Data

ITEQ (ng/dscm)

Test Number
Dioxin Considerations in Cement Kilns

- Temperature effects
- Raw material effects on dioxin concentration
- Alkali and chlorine effects
Dioxin Considerations in Cement Kilns

- Temperature effects: 450°F-750°F
- Accurate readings
- Stratification
- Downcomer and duct temperature
- Air inleakage
Dioxin Considerations in Cement Kilns

- Raw material effects
- Mill scale and fly ash
- Build up in raw mill
- Looking for sources of chlorinated aromatics
- Laboratory test methods are challenged
Dioxin Considerations in Cement Kilns

- Alkali and sulfur changes in kiln system
- Can affect formation mechanism
- Usually sufficient chlorine available for formation to occur
Questions?