



EMERGENCY PLANNING AND COMMUNITY RIGHT-TO-KNOW ACT - SECTION 313: Guidance for Reporting Toxic Chemicals within the Dioxin and Dioxin-like Compounds Category

Section 313 of the Emergency Planning and Community Right-to-Know Act of 1986 (EPCRA) requires certain facilities manufacturing, processing, or otherwise using listed toxic chemicals to report the annual quantity of such chemicals entering each environmental medium. Such facilities must also report pollution prevention and recycling data for such chemicals, pursuant to section 6607 of the Pollution Prevention Act, 42 U.S.C. 13106.

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LIST OF ABBREVIATIONS AND ACRONYMS

| | |
|----------------|--|
| BACT | Best Available Control Technology |
| BADT | Best Available Demonstrated Technology |
| CAAA | Clean Air Act Amendments |
| CAS | Chemical Abstract Service |
| CDDs | Chlorinated dibenzo-p-dioxins |
| CDFs | Chlorinated dibenzofurans |
| dscf | dry standard cubic foot |
| dscm | dry standard cubic meter |
| EPCRA | Emergency Planning and Community Right-to-Know Act of 1986 |
| ESP | Electrostatic precipitator |
| g | gram |
| kg | kilogram |
| L | liter |
| lb | pounds (avoir) |
| m ³ | cubic meter |
| MACT | Maximum Achievable Control Technology |
| ng | nanogram. 1 E-09 gram |
| °C | Temperature in Celsius |
| °F | Temperature in Fahrenheit |
| pg | picogram. 1 E-12 gram |
| s | seconds |
| SIC | Standard Industrial Classification Code |
| yr | year |

Table 4-6. This is because the state-of-the-art involved in secondary copper smelting calls for the mechanical removal of plastic material prior to smelting and refining, and to use copper-laden scrap that is relatively free of organic contamination. Therefore, if your facility processes copper scrap containing a relatively high amount of plastics, then the emission factors listed in Table 4-6 are not appropriate to use as default emission factors.

Section 4.3. Cement Kilns

Section 4.3.1. Applicability

Kilns used in the pyroprocessing of Portland Cement clinker as defined in SIC Code 3241.

Section 4.3.2. Summary Description / Air Emission Factors

In the United States, the primary cement product is called Portland cement. Portland cement is a fine, grayish powder consisting of a mixture of four basic materials: limestone, silica, alumina, and iron compounds. Cement production involves heating (pyroprocessing) the raw materials (known as raw meal) to a very high temperature in a rotary (rotating) kiln to induce chemical reactions that produce a fused material called clinker. The cement clinker is further ground into a fine powder and mixed with gypsum to form the Portland cement.

The cement kiln is a large, rotating steel cylindrical furnace lined with refractory material. The kiln is aligned on a slight angle, usually a slope of 3E - 6E. This allows for the materials to pass through the kiln by gravity. The upper end of the kiln is known as the cold or back end and this is where the raw materials, or meal, is generally fed into the kiln. The lower end of the kiln is known as the "hot" end. The hot end is where the combustion of primary fuels (coal, petroleum coke, natural gas, etc.) transpires to produce a high temperature.

The cement kiln is operated in a counter-current configuration. This means that the hot combustion gases are convected up through the kiln while the raw materials are passing down toward the lower end. The rotation of the kiln induces mixing and the forward progress of mixed materials. As the meal moves through the cement kiln and is heated by the hot combustion gases, water is vaporized and pyroprocessing of materials occurs.

When operating, the cement kiln can be viewed as consisting of three temperature zones necessary to produce clinker. Zone 1 is at the upper end of the kiln where the raw meal is added. Temperatures in this zone typically range from ambient up to 600EC. In this area of the kiln, moisture is evaporated from the raw meal. The second thermal zone is known as the calcining zone. Calcining occurs when the hot combustion gases from the combustion of primary fuels dissociates calcium carbonate from the limestone to form calcium oxide. In this region of the kiln, temperatures are in a range of 600EC to 900EC. The third region of the kiln is known as the burning or sintering zone. The burning zone is the hottest region of the kiln. In this region, temperatures in excess of 1,500EC induce

the calcium oxide to react with silicates, iron and aluminum in the raw materials to form clinker. The formation of clinker actually occurs near the lower end of the kiln (close to the combustion of primary fuel) where temperatures are the hottest. The chemical reactions that occur here are referred to as pyroprocessing.

The clinker that leaves the hot end of the kiln is a gray-colored, glass-hard material comprised of dicalcium silicate, tricalcium silicate, calcium aluminate, and tetracalcium aluminoferrite. At this point, the clinker has a temperature of about 1,100°C. The hot clinker is then transferred into the clinker cooler. Once cooled, the clinker is ground into a fine powder and mixed with gypsum to produce Portland cement.

Cement kilns are either wet or dry processes. In the wet process, the raw materials are ground and mixed with water to form a slurry. The meal-water slurry is fed into the kiln through a pump. A greater amount of heat energy is needed in the wet process to evaporate the additional water.

In the dry process, the raw meal is ground to a fine, dry powder prior to entering the kiln. There are three types of dry processes: long-dry, preheater, and preheater/precalciner. Long dry kilns are similar to wet kilns, with the exception of the dry state of the raw materials. In preheater kilns, the raw material is heated prior to entering the kiln. This allows for a shorter kiln and lower combustion fuel use. Precalciners take this a step further by heating the raw feed to a level at which partial calcination takes place prior to entering the kiln. A typical preheater/precalciner kiln consists of a vertical tower containing a series of cyclone-type vessels. Raw meal is added at the top of the tower, and hot kiln exhaust flue gases from the kiln operation are used to preheat the meal prior to being introduced into the kiln. Preheating and precalcining the meal has the advantage of lowering fuel consumption of the kiln.

There are also two primary types of air pollution control devices (APCDs) for the kiln: fabric filters and electrostatic precipitators (ESPs). Either of these can be used on any of the four process types.

Cement manufacturing is an energy intensive manufacturing process. Fossil fuels are the primary sources of fuel. In addition, 15 cement plants in the U.S. currently supplement their fuel needs through the use of energy-bearing hazardous waste. For the last ten years, these facilities have been regulated by the Resource Conservation and Recovery Act's (RCRA) Boiler and Industrial Furnace (BIF) rules. As a result, a database has been developed characterizing emissions from these facilities. Testing and additional studies have contributed significantly to our understanding of dioxin formation in cement plants.

In developing Maximum Achievable Control Technology (MACT) standards for cement plants, EPA "considered both hazardous waste burning cement kiln and non-hazardous waste burning cement kiln data together because both data sets are adequately representative of general dioxin/furan behavior and control in either type of kiln. This similarity is based on our engineering judgement that

hazardous waste burning does not have an impact on dioxin/furan formation, dioxin/furan is formed post-combustion.” (See 64 FR 52876) APCD air inlet temperature (and the time that the air takes to enter the device) in conjunction with other site-specific elements is the determining factor.

On June 14, 1999, EPA published a National Emission Standard for Hazardous Air Pollutants (NESHAP) for the Portland cement industry in the Federal Register (64 FR 31898). In addition, on September 30, 2000, EPA published a National Emission Standard for Hazardous Air Pollutants (NESHAP) for hazardous waste combustors (including cement kilns that recover energy from hazardous wastes) in the Federal Register (64 FR 52828). These rules require, among other things, that all cement plants periodically conduct dioxin/furan testing.

The EPA source emissions data base contains test reports of CDD/CDF emissions from 15 cement kilns not burning hazardous waste. The average CDD/CDF emission factors displayed in Table 4-7 are derived as an average from these test data. These default emission factors are more appropriate for facilities tested in 1998, and do not reflect changes that have occurred since that time. As an operator/owner of a facility, you may elect to use more current information in the development of an emission factor, or you may elect to use the EPA default. If you elect to use more current emission factors, then you will be using Approach 2 (Section 2.1.2) to derive your emission estimate appropriate for your facility.

Table 4-7. Average Emission Factors (ng/kg of cement clinker produced) for Estimating Air Releases of Dioxin and Dioxin-like Compounds from Cement Kilns Not Combusting Hazardous Waste as Supplemental Fuel

| CDD Congener | Emission Factor (ng/kg clinker) | CDF Congener | Emission Factor (ng/kg clinker) |
|--|--|----------------------|--|
| 2,3,7,8-TCDD | 0.012 | 2,3,7,8-TCDF | 0.729 |
| 1,2,3,7,8-PeCDD | 0.034 | 1,2,3,7,8-PeCDF | 0.102 |
| 1,2,3,4,7,8-HxCDD | 0.028 | 2,3,4,7,8-PeCDF | 0.224 |
| 1,2,3,6,7,8-HxCDD | 0.042 | 1,2,3,4,7,8-HxCDF | 0.185 |
| 1,2,3,7,8,9-HxCDD | 0.048 | 1,2,3,6,7,8-HxCDF | 0.054 |
| 1,2,3,4,6,7,8-HpCDD | 0.426 | 1,2,3,7,8,9-HxCDF | 0.007 |
| 1,2,3,4,6,7,8,9-OCDD | 0.692 | 2,3,4,6,7,8-HxCDF | 0.082 |
| | | 1,2,3,4,6,7,8-HpCDF | 0.146 |
| | | 1,2,3,4,7,8,9-HpCDF | 0.005 |
| | | 1,2,3,4,6,7,8,9-OCDF | 0.234 |
| 3 CDDs | 1.28 | 3 CDFs | 1.77 |
| 3 Dioxin and dioxin-like compounds* | 3.05 | | |

* 3 Dioxin and dioxin-like compounds = 3 CDDs + 3 CDFs

Section 4.4. Utilities

Section 4.4.1. Applicability

This applies to SIC Codes 4911, 4931, and 4939 Electric Services. This guidance is for electric power utility boilers burning coal, wood and oil for the expressed purpose of producing steam to operate a steam generator, which, in turn, generates electricity.

Section 4.4.2. Description/Emissions Factors for Coal-Fired Electric Utility Boilers

In 1993, the U.S. Department of Energy (DOE) and the Electric Power Research Institute (EPRI) collaborated on assessing stack emissions of hazardous air pollutants at coal-fired power plants. As part of this project, CDD/CDF stack emissions were measured at seven U.S. coal-fired power plants (utility boilers). The levels reported for individual 2,3,7,8-substituted congeners were typically not detected or very low (i.e., #0.033 ng/Nm³). In general, CDF levels were higher than CDD levels. OCDF and 2,3,7,8-TCDF were the most frequently detected congeners. Variation in emissions between plants could not be attributed by Riggs et al. (1995) to any specific fuel or operational characteristic. The Electric Power Research Institute (EPRI) has published the results of the DOE/EPRI

Table 4-11 Average Emission Factors (ng/kg waste feed) for Estimating Air Releases of Dioxin and Dioxin-like Compounds from Boilers and Industrial Furnaces Burning Hazardous Waste (other than cement kilns)

| CDD Congener | Emission Factor (ng/kg waste feed) | CDF Congener | Emission Factor (ng/kg waste feed) |
|--|------------------------------------|----------------------|------------------------------------|
| 2,3,7,8-TCDD | 0.00 | 2,3,7,8-TCDF | 0.81 |
| 1,2,3,7,8-PeCDD | 0.04 | 1,2,3,7,8-PeCDF | 0.38 |
| 1,2,3,4,7,8-HxCDD | 0.08 | 2,3,4,7,8-PeCDF | 0.52 |
| 1,2,3,6,7,8-HxCDD | 0.18 | 1,2,3,4,7,8-HxCDF | 0.83 |
| 1,2,3,7,8,9-HxCDD | 0.20 | 1,2,3,6,7,8-HxCDF | 0.37 |
| 1,2,3,4,6,7,8-HpCDD | 1.17 | 1,2,3,7,8,9-HxCDF | 0.02 |
| 1,2,3,4,6,7,8,9-OCDD | 5.24 | 2,3,4,6,7,8-HxCDF | 0.56 |
| | | 1,2,3,4,6,7,8-HpCDF | 0.93 |
| | | 1,2,3,4,7,8,9-HpCDF | 0.16 |
| | | 1,2,3,4,6,7,8,9-OCDF | 0.70 |
| 3 CDD | 6.91 | 3 CDF | 5.28 |
| 3 Dioxin and dioxin-like compounds* | 12.2 | | |

* 3 Dioxin and dioxin-like compounds = 3 CDDs + 3 CDFs

Section 4.5.3. Cement Kilns Burning Hazardous Waste as Supplemental Fuel

The high temperatures achieved in cement kilns make cement kilns an efficient technology for combusting hazardous waste as supplemental fuel. Sustaining the relatively high combustion temperatures (1,100EC to 1,500EC) that are needed to form cement clinker requires the burning of a fuel with a high energy output. Therefore, coal or petroleum coke is typically used as the primary fuel source. Because much of the cost of operating the cement kiln at high temperatures is associated with the consumption of fossil fuels, some cement kiln operators have elected to burn hazardous liquid and solid waste as supplemental fuel. Facilities that burn hazardous waste for energy recovery must comply with both RCRA and CAA regulations that specifically regulate this practice. Currently about 75 percent of the primary fuel is coal. Organic hazardous waste may have a similar energy output as coal (9,000 to 12,000 Btu/lb for coal). The strategy of combusting the waste as supplemental fuel is to offset the amount of coal/coke that is purchased and burned by the kiln. Much of the high energy and ignitable wastes are primarily comprised of such diverse substances as waste oils, spent organic solvents, sludges from the paint and coatings industry, waste paints and coatings from the auto and truck assembly plants, and sludges from the petroleum refining industry (Greer et al., 1992). The conditions inherent in the cement kiln mimic conditions of hazardous waste incineration. For example, the gas residence time in the burning zone is typically three seconds while at temperatures in excess of 1,500EC (Greer et al.,

1992). In addition, trial burns have consistently shown that 99.99 to 99.9999 percent destruction and removal efficiencies for the very stable organic wastes can be achieved in cement kilns (Greer et al., 1992). Although the combustion of hazardous waste as supplemental or substitute fuel does have apparent advantages, only 16 percent of the Portland cement kilns (34 of the 212 kilns) combusted hazardous waste in 1995 (Federal Register, 1996b), as of 2000 only 15 plants (32 kilns) were burning hazardous waste. Other types of supplemental fuel used by these facilities include automobile tires, used motor oil, and sawdust, and scrap wood chips. The method of introducing liquid and solid hazardous waste into the kiln is a key factor to the complete consumption of the waste during the combustion of the primary fuel. Liquid hazardous waste is either injected separately or blended with the primary fuel (coal). Solid waste is mixed and burned along with the primary fuel. The pyroprocessing of raw meal in a cement kiln produces cement as fine particulates. At some facilities, cement kiln dust, which is an even finer particulate, is collected and controlled with fabric filters and/or electrostatic precipitators. Acid gases such as SO₂ can be formed during pyroprocessing of the sulfur-laden minerals, but the minerals have high alkalinity which neutralizes SO₂ gases.

Emission factors (ng/kg clinker produced) for Portland cement kilns burning hazardous waste as supplemental fuel are displayed in Table 4-12. These emission factors were developed from stack testing of CDD/CDF emissions from eleven cement kilns burning hazardous waste. The majority of stack emissions data from cement kilns burning hazardous waste were derived during trial burns, and may overestimate the CDD/CDF emissions that most kilns achieve during normal operations.

The emission factors in Table 4-12 were derived from facilities that were stack tested in 1998 and may not reflect current regulatory requirements. In 1999, EPA promulgated final standards for the stack emission limits of dioxin and dioxin-like compounds from hazardous waste combustion facilities (64 FR 52828 - 53077; Final Standards for Hazardous Air Pollutants For Hazardous Waste Combustors; Final Rule; September 30, 1999). The promulgated regulations require periodic stack sampling for dioxin-like compounds for all cement kilns burning hazardous waste. The owner/operator of such facilities is encouraged to use actual facility-specific emissions data (i.e., Approach 1) in lieu of EPA's default emission factors. Such data are the most representative and best data to use in estimating annual releases of dioxin-like compounds.

Table 4-12. Average Emission Factors (ng per dscm) for Estimating Air Releases of Dioxin and Dioxin-Like Compounds from cement Kilns Combusting Hazardous Waste as Supplemental Fuel

| Facility | 2378-TCDD | 12378-PeCDD | 123478-HxCDD | 123678-HxCDD | 123789-HxCDD | 1234678-HPCDD | OCDD | | | |
|--|-----------|-------------|---|--------------|--------------|---------------|--------------|---------------|---------------|-------|
| A | 0.096 | 0.089 | 0.144 | 0.258 | 0.206 | 2.162 | 0.461 | | | |
| B | 0.028 | 0.014 | 0.009 | 0.008 | 0.010 | 0.043 | 0.459 | | | |
| C | 0.005 | 0.011 | 0.014 | 0.016 | 0.559 | 0.155 | 3.325 | | | |
| D | 0.310 | 0.496 | 0.709 | 1.381 | 1.893 | 6.011 | 0.784 | | | |
| E | 0.005 | 0.010 | 0.010 | 0.012 | 0.006 | 0.068 | 0.033 | | | |
| F | 0.007 | 0.009 | 0.006 | 0.012 | 0.013 | 0.057 | 0.201 | | | |
| G | 0.053 | 0.327 | 0.536 | 0.832 | 0.812 | 5.366 | 1.752 | | | |
| H | 0.026 | 0.039 | 0.054 | 0.078 | 0.048 | 0.430 | 0.140 | | | |
| I | 0.067 | 1.191 | 1.385 | 1.875 | 2.697 | 9.971 | 1.542 | | | |
| J | 0.035 | 0.041 | 0.048 | 0.047 | 0.044 | 0.216 | 0.091 | | | |
| K | 0.016 | 0.019 | 0.022 | 0.023 | 0.018 | 0.064 | 0.154 | | | |
| Mean emission factor | 0.059 | 0.204 | 0.267 | 0.413 | 0.573 | 2.231 | 0.813 | | | |
| Facility | 2378-TCDF | 12378-PeDF | 23478-PeCDF | 123478-HxCDF | 123678-HxCDF | 123789-HxCDF | 234678-HxCDF | 1234678-HPCDF | 1234789-HpCDF | OCDF |
| A | 1.080 | 0.078 | 0.183 | 0.098 | 0.043 | 0.031 | 0.065 | 0.051 | 0.048 | 0.116 |
| B | 0.755 | 0.070 | 0.093 | 0.034 | 0.019 | 0.007 | 0.025 | 0.006 | 0.008 | 0.029 |
| C | 0.380 | 0.035 | 0.067 | 0.039 | 0.017 | 0.003 | 0.027 | 0.026 | 0.006 | 0.021 |
| D | 1.604 | 1.050 | 2.353 | 2.024 | 1.029 | 0.316 | 1.441 | 0.946 | 0.256 | 0.141 |
| E | 0.111 | 0.005 | 0.012 | 0.008 | 0.004 | 0.005 | 0.006 | 0.009 | 0.010 | 0.039 |
| F | 0.011 | 0.005 | 0.010 | 0.011 | 0.005 | 0.002 | 0.006 | 0.010 | 0.003 | 0.008 |
| G | 0.562 | 0.654 | 1.790 | 1.366 | 0.533 | 0.115 | 1.168 | 0.609 | 0.192 | 0.119 |
| H | 0.072 | 0.014 | 0.054 | 0.022 | 0.015 | 0.003 | 0.011 | 0.009 | 0.006 | 0.008 |
| I | 0.572 | 0.239 | 0.570 | 0.450 | 0.208 | 0.060 | 0.344 | 0.208 | 0.066 | 0.060 |
| J | 0.239 | 0.223 | 0.226 | 0.182 | 0.103 | 0.023 | 0.085 | 0.185 | 0.043 | 0.095 |
| K | 0.462 | 0.121 | 0.133 | 0.078 | 0.031 | 0.017 | 0.032 | 0.050 | 0.024 | 0.106 |
| Mean emission factor | 0.532 | 0.227 | 0.499 | 0.392 | 0.182 | 0.053 | 0.292 | 0.192 | 0.060 | 0.067 |
| Dioxin and dioxin-like compounds: | | | 7.06 per dry standard cubic meter of stack gas | | | | | | | |

The emission factors in Table 4-12 are in units of nanogram dioxin-like compound per dry standard cubic meter (at standard temperature and pressure and adjusted to 7% oxygen) of stack gas flow. This unit is a concentration of dioxin-like compounds measured in the stack gases. The facilities listed in Table 4-12 are cement kilns burning hazardous waste, and the emission factors (expressed on a concentration basis) are the average of multiple “runs” at the same facility. A “run” is defined as a single stack sampling episode to determine the amount of dioxin-like compounds present in the gases leaving the stack. These data can be found in a database maintained by EPA’s Office of Solid Waste as documented in: Final Technical Support Document for Hazardous Waste Combustors (HWC) MACT Standards; HWC Emissions Database, Volume II; Appendix A: Cement Kilns; In: Final Standards for Hazardous Air Pollutants For Hazardous Waste Combustors; Final Rule; September 30, 1999. This cement kiln dioxin/furan database may be accessed on the Internet at the following URL: <http://www.epa.gov/epaoswer/hazwaste/comust/>.

In order to estimate annual air emissions of dioxin-like compounds using the EPA default emission factors, the owner/operator are advised to follow the calculation steps given in section 3.1.1. Please note that the EPA default emission factors are generally applicable to all Portland cement kilns burning hazardous waste regardless of primary fuel type; constituents of hazardous waste burned as supplemental fuel; air pollution control equipment installed at the kiln; temperature of the kiln and whether or not the kiln is a wet or dry process. However, the emissions of dioxin-like compounds in Table 4-12 are more representative of cement kilns that operate the air pollution control equipment at temperatures of 204° Celsius (400° F) or less. Such temperatures are known to suppress the post combustion formation of dioxins and furans, and result in lower emissions of dioxin-like compounds than if the temperatures were more elevated.

Section 4.5.4. Hazardous Waste Incineration (HWI) Facilities

The four principal furnace designs employed for the combustion of hazardous waste in the United States are: liquid injection, rotary kiln, fixed hearth, and fluidized-bed incinerators (Dempsey and Oppelt, 1993). The majority of commercial operations are of the rotary kiln incinerator type. On-site (noncommercial) HWI technologies are an equal mix of rotary kiln and liquid injection facilities, with a few additional fixed hearths and fluidized bed operations (U.S. EPA, 1996h). Each of these HWI technologies is discussed below:

Rotary Kiln HWI: Rotary kiln incinerators consist of a rotating kiln, coupled with a high temperature afterburner. Because these are excess air units designed to combust hazardous waste in any physical form (i.e., liquid, semi-solid, or solid), rotary kilns are the most common type of hazardous waste incinerator used by commercial “off-site” operators. The rotary kiln is a horizontal cylinder lined with refractory material. Rotation of the cylinder on a slight slope provides for gravitational transport of the hazardous waste through the kiln (Buonicore, 1992a). The tumbling action of the rotating kiln causes mixing and exposure of the waste to the heat of combustion, thereby enhancing burnout. Solid and semi-solid wastes are loaded into the top of the kiln by an auger or rotating screw. Fluid and pumpable sludges and wastes are typically introduced into the kiln through a water-cooled tube. Liquid hazardous waste is fed directly into the kiln through a burner nozzle. Auxiliary fuel (natural gas or oil) is burned in

Section 7.0 REFERENCES

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