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Air Emissions Data Summary for Portland Cement Pyroprocessing Operations Firing Tire-Derived Fuels

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KEYWORDS

Air pollution, carbon monoxide, dioxins, furans, hydrocarbons, hydrogen chloride, metals, nitrogen oxides (NO_x), particulates, pyroprocessing, rotary kilns, sulfur dioxide (SO_2), tire-derived fuels (TDF).

ABSTRACT

This report highlights data concerning the impact of tire-derived fuel (TDF) firing on the emissions of a variety of air contaminants from pyroprocessing operations. The database includes emission test data applicable to thirty-one of the forty- three cement plants presently firing TDF. Dioxin-furan emission test results indicated that kilns firing TDF had emissions approximately one-third of those kilns firing conventional fuels – this difference was statistically significant. Emissions of particulate matter (PM) from TDF-firing kilns were 35% less than the levels reported for kilns firing conventional fuels (not statistically significant due to the low PM emissions reported for essentially all cement kilns). Nitrogen oxides, most metals, and sulfur dioxide emissions from TDF-firing kilns also exhibited lower levels than those from conventional fuel kilns. The emission values for carbon monoxide and total hydrocarbons were slightly higher in TDF versus non-TDF firing kilns. However, none of the differences in the emission data sets between TDF versus non-TDF firing kilns for sulfur dioxide, nitrogen oxides, total hydrocarbons, carbon monoxide, and metals were statistically significant. Previous air emission related TDF studies conducted by governmental agencies and consulting engineering firms have indicated that TDF firing either reduces or does not significantly affect emissions of various contaminants from cement kilns. This PCA TDF air emission study confirms these previous studies.

REFERENCE

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ACRONYMS

APCD	Air Pollution Control Device
CFR	Code of Federal Regulations
EDBS	Environmental Data Base System
EMPC	Estimated Maximum Pollutant Concentration
EPA	U.S. Environmental Protection Agency
ESP	Electrostatic Precipitator
NESHAPS	National Emission Standards for Hazardous Air Pollutants
MACT	Maximum Achievable Control Technology
QA	Quality Assurance
PCA	Portland Cement Association
PDF	Plastics Derived Fuel
POP	Persistent Organic Pollutants
TEQ	Toxic Equivalent Quantity
TDF	Tire-Derived Fuel

UNITS OF MEASURE

ng TEQ/NM^3 @ 7% O_2	Nanograms toxic equivalent quantity per normal cubic meter corrected to 7% oxygen
Lbs/ton of dry feed	Pounds of filterable particulate matter per ton of dry kiln feed (For convenience, the term “Lbs/ton” will be assumed to include the qualifying phrase “of dry kiln feed.)
ppmvd@7% O_2	Parts per million (volume, dry basis) corrected to 7% oxygen
μg/NM^3 @ 7% O_2	Micrograms per normal cubic meter corrected to 7% oxygen

AIR EMISSIONS DATA SUMMARY for PORTLAND CEMENT PYROPROCESSING OPERATIONS FIRING TIRE-DERIVED FUELS

John Richards, Ph.D., P.E.; David Goshaw, P.E.; Danny Speer, and Tom Holder, CHMM[1]

1. EXECUTIVE SUMMARY

The Portland Cement Association (PCA) has sponsored the compilation of air emission test data obtained at cement kilns firing tire-derived fuels (TDF) such as whole tires and chipped tires. Cement kilns provide an excellent environment for TDF combustion due to the extremely high gas temperatures and long gas stream residence times. The use of TDF reduces the quantities of coal, coke, and/or natural gas needed for kiln operation and reduces the quantity of iron that must be added with the raw materials. The purpose of this project is to provide up-to-date emissions data concerning the impact of TDF firing on the emissions of a variety of air contaminants from cement kilns.

Air emissions data applicable to seventy-one of the 109 cement plants in the U.S. were received and compiled. This database includes emission test data applicable to thirty-one of the forty- three cement plants presently firing TDF.

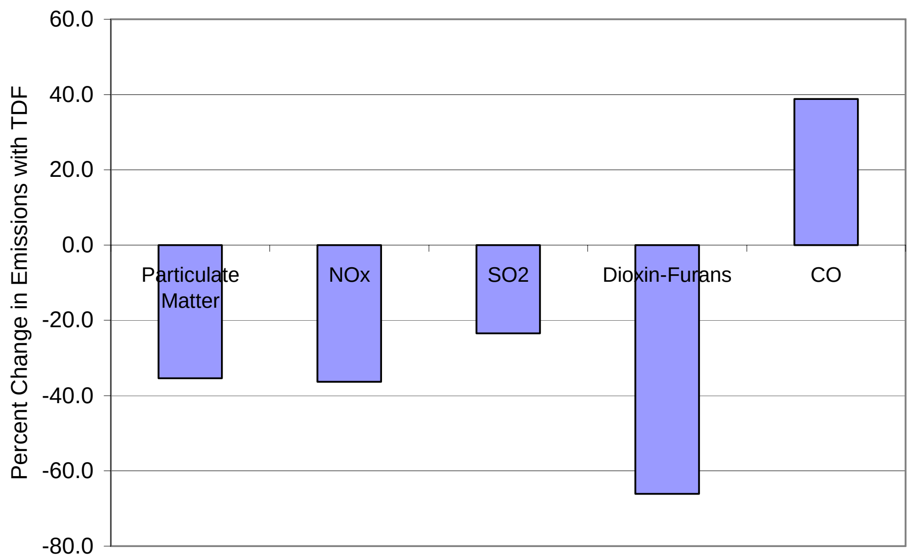

Figure 1-1. Emission changes associated with TDF firing.

PCA compiled a total of two hundred fifty-eight dioxin furan test reports as part of this project. The dioxin-furan emission test results shown in Figure 1-1 indicate that kilns firing TDF had emissions approximately one-third of those kilns firing conventional fuels such as coal, coke, and natural gas. This difference in emissions for kilns with and without TDF was statistically significant at more than the 99% confidence level. Research is needed to identify factors contributing to this significant difference.

[1] Air Control Techniques, P.C., Cary, North Carolina

Emissions of particulate matter from TDF-firing kilns were 35% less than the levels reported for kilns firing conventional fuels. Due to the low emissions reported for essentially all cement kilns, this difference in emissions was not statistically significant.

The number of emission test reports compiled in this project concerning nitrogen oxides, sulfur dioxide, total hydrocarbons, carbon monoxide, and metals were considerably smaller than those concerning dioxin-furans and particulate matter. The data that are available indicated that emissions from TDF-firing kilns had lower emissions of nitrogen oxides, sulfur dioxide, and most metals. The emission values for carbon monoxide and total hydrocarbons were slightly higher in TDF versus non-TDF firing kilns. None of the differences in the emission data sets for sulfur dioxide, nitrogen oxides, total hydrocarbons, carbon monoxide, and metals were statistically significant.

The available data for particulate matter, NOx, SO_2, dioxin-furans, and CO are summarized in Figure 1-1. Other analytes are not shown because the data sets consisted of less than 10 test reports for the non-TDF firing condition

Previous air emission related TDF studies conducted by governmental agencies and consulting engineering firms have indicated that TDF firing either reduces or does not significantly affect emissions of various contaminants from cement kilns. This PCA TDF air emission study confirms these previous studies and substantially expands the air emission data available to evaluate the relationship between TDF firing and air emissions.

2. INTRODUCTION

The Portland Cement Association (PCA) has sponsored the compilation of air emission test data obtained at cement plants firing tire-derived fuels (TDF). The purpose of this project is to provide up-to-date emissions data concerning the impact of TDF firing on the emissions of a variety of air contaminants from pyroprocessing operations.

The intended audience for this report includes technical and non-technical professionals in the cement industry. Background information concerning the operating characteristics of portland cement plants and the regulatory requirements applicable to portland cements are not included.

2.1 Sources of the Air Emissions Data

The PCA Energy and Environmental Committee sent letters to all member companies operating cement plants in the U.S. requesting copies of TDF-related air emission test reports. This request was limited to test reports submitted to state and/or local agencies. All but a few of the test reports received concerned test programs conducted during or after 1999.

Following the test report gathering effort, three hundred eighty four test reports were received and reviewed. All of the reports and test data included in these reports have been submitted to regulatory agencies. Data from research studies and other non-regulatory related studies have not been obtained, reviewed, or included.

2.2 Test Data Processing

The air emission test data provided in the reports were converted to a consistent format. All of the total filterable particulate matter data were converted to a form of pounds of particulate matter per ton of dry feed to the pyroprocessing system. All of the dioxin-furan emissions data were converted to a form of nanograms[2] toxic equivalent quantity per normal cubic meter corrected to seven percent oxygen (ng TEQ/NM^3 @ 7% O_2). Data concerning sulfur dioxide nitrogen oxides, carbon monoxide, hydrogen chloride, and total hydrocarbons were converted to ppm (dry basis) corrected to 7% oxygen. Data concerning metals, organic compounds, and semi-volatile compounds were converted to units of micrograms per cubic meter corrected to 7% oxygen.

In a few cases, it was necessary to recalculate the dioxin-furan emissions in reports in which the testing contractor included Estimated Maximum Pollutant Concentration (EMPC) values in the calculations. Inclusion of EMPC values is not included in EPA Reference Method 23. These corrections had a relatively small impact on the dioxin-furan emission rates.

The test data were excluded from the data set if the test results were not provided in the required format, and the necessary information to convert the data to the required format was not available. In a number of cases, filterable particulate matter data were excluded because kiln feed rate data were not available. In a few cases, it was necessary to exclude dioxin-furans, gaseous compounds, and metals emission test results because the oxygen data were not provided.

The emissions data were tabulated with a number of descriptive parameters useful for characterizing the emissions.

- Type of pyroprocessing system (wet kiln, long dry kiln, preheater kiln, and preheater-precalciner kiln)
- Use of tire-derived fuels, other alternative fuels, and conventional fossil fuels
- Type of air pollution control system (fabric filter or electrostatic precipitator)
- Status of in-line raw mill, if present (mill-on or mill-of)

The term “preheater kiln” was assumed to mean kilns having a minimum of four large diameter cyclones in a series arrangement for the recovery of heat. Other types of kilns with single stage or double stage cyclones were classified as long dry kilns.

Many of the test reports for plants with preheater kilns or preheater-precalciner kilns included data for a separate alkali bypass system stack and data applicable to periods when the in-line raw mill was and was not operating. All of the emissions data applicable to a specific pyroprocessing unit are usually combined to determine compliance with emission requirements. However, in this data summary, the emission values for each of these separate emission points and operating conditions of the pyroprocessing system were reported separately to ensure that information concerning these specific sources and operating conditions was not obscured by the regulation-required averaging calculations.[3]
All of the air emissions data have been rounded to three significant digits to be consistent with the precision and accuracy limits of the U.S. EPA reference test methods used in conducting the air emission test programs.

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[2] A nanogram is one billionth of a gram.

[3] The TDF emissions data summary that provides the support for this survey will be made available to PCA members upon request.

2.3 Quality Assurance Review

A quality assurance (QA) evaluation of each report was conducted to confirm that the data and information received for review were complete and accurate. A moderate number of test reports had to be set aside due to incomplete process data or due to missing information necessary to check the accuracy of the test results.

The scope of the QA review included, but was not necessarily limited to the following items. In most cases, the QA review was limited to one or two runs, rather than all of the test data. This was useful in identifying any problems in sample identification, emission calculations, or field testing procedures. If QA issues were identified during this review, the full report was evaluated. Overall, few QA problems were found in the emissions test data.

Dioxin-Furan Test Data QA Checks

- Proper sampling train temperatures
- Sampling train leak checks
- Conformance with Method 1 sampling location criteria and Method 2 traversing requirements
- Conformance with isokinetic sampling requirements
- Conformance with sampling volume minimum requirements
- Proper spike recovery procedures
- Proper sample recovery and analysis procedures
- Proper calculation of TEQ quantities

Filterable Particulate Matter, Hydrogen Chloride, and Metals QA Checks

- Proper sampling train temperatures
- Sampling train leak checks
- Conformance with Method 1 sampling location criteria and Method 2 traversing requirements
- Conformance with isokinetic sampling requirements
- Conformance with sampling volume minimum requirements

Sulfur Dioxide, Nitrogen Oxides, Carbon Monoxide, and Total Hydrocarbon QA Checks

- Proper sample acquisition
- Proper zero, span, and drift checks
- Proper data reduction

The few reports with suspected QA problems were deleted from the data set. No attempt was made to correct problems affecting data quality.

2.4 Data Base Summary

Air emission test reports prepared for seventy one cement plants[4] were received during this project. The air emissions data base compiled as part of this project includes data from sixty five cement plants. This is sixty two percent of the total number of U.S. cement plants. Thirty one of

[4] Many of the emission test reports concerned more than one kiln at the cement plant.

these sixty-two plants fire TDF. As indicated in Table 2-1, the emission test reports cover a very broad range of kiln types, kiln fuel types, and air pollution control systems.

Table 2-1. Emission Test Report Applicability

Category	Characteristic	Percentage
Kiln Type	Wet	18
	Long Dry	18
	Preheater	29
	Preheater-Precalciner	35
Kiln Fuel[5]	Coal	88
	Coke	48
	Natural Gas	45
	Oil	14
	Tire-Derived Fuel[1]	33
	Plastic Derived Fuel	0.3
	Biosolids	1
	Hazardous Waste	7
	Other	1
Air Pollution Control System	Fabric Filter	68
	Electrostatic Precipitator	32
In-Line Raw Mill Status	Mill On	27
	Mill Off	26

[1] Emission test values applicable to TDF firing conditions comprised 33 percent of the total number of test values and were obtained at thirty one separate cement plants.

Most of the TDF-related air emissions data concerns dioxin-furans and filterable particulate matter. The emissions data compiled concerning these two categories of contaminants are extensive and can be used to base definitive conclusions regarding the impact of TDF on emissions from cement kilns. The emissions data available for sulfur dioxide, nitrogen oxides, carbon monoxide, hydrogen chloride, and total hydrocarbons are relatively limited. The data available concerning metals emissions are also quite limited.

3. USE OF TDF AS AN ALTERNATIVE FUEL AT CEMENT KILNS

3.1 Applicability of TDF as a Cement Kiln Fuel

Portland cement kilns have operating characteristics that are especially well suited for the safe and efficient consumption of TDF. The efficiency of air contaminant destruction is extremely high because cement kilns operate at gas temperatures over 1,650 °C (3,000°F) and solid material temperatures up to 1,480°C (2,700°F). These temperatures are much higher than the operating temperatures of boilers and municipal waste incinerators.

The efficiency of air contaminant destruction is extremely high because the gas streams formed in cement kilns remain in the extremely high temperature areas of the kiln for 3 seconds

[5] Many plants burn multiple fuels.

above 1,200ºC (2,190ºF) and as much as 6 seconds above 1,000ºC (1,832ºF). These high temperature conditions are much are more intense than the 2 seconds at 1,000ºC (1,832ºF) common in waste incinerators.

The inorganic reactions generated at these operating temperatures result in the inclusion of most of the ash of the fuels (fossil fuels and alternative fuels) in the clinker. Very little of the ash from TDF combustion is carried out of the kiln to the particulate matter collection systems. There is very little impact of TDF firing on the quantities of dust that must be disposed in a landfill.

There continues to be a strong interest in the consumption of TDF in cement kilns due to the ideal combustion environment of the high temperature zones of the cement kiln. For these reasons, countries such as Japan, Germany, Switzerland, and Norway have been actively involved in tire firing in cement kilns for over thirty years [1]. The use of TDF as an alternative fuel began to be investigated in the U.S. and Canada in the late 1980s. Three kilns were firing TDF by 1991, and there has been a steady increase in TDF firing at U.S. cement kilns since the early 1990s as indicated in Figure 3-1.

Portland Cement Association (PCA) data suggest that 43 separate plants (some plants have multiple kilns) were firing TDF in 2004. This is approximately 40% of the clinker-producing cement plants in operation in the U.S.

This steady increase demonstrates that there continues to be an excess quantity of tires that can not be readily used in recycling applications. The TDF firing systems in service now benefit from the extensive development work that has been performed by operating companies and equipment vendors over an extended time period. TDF firing in cement kilns is a well established technology.

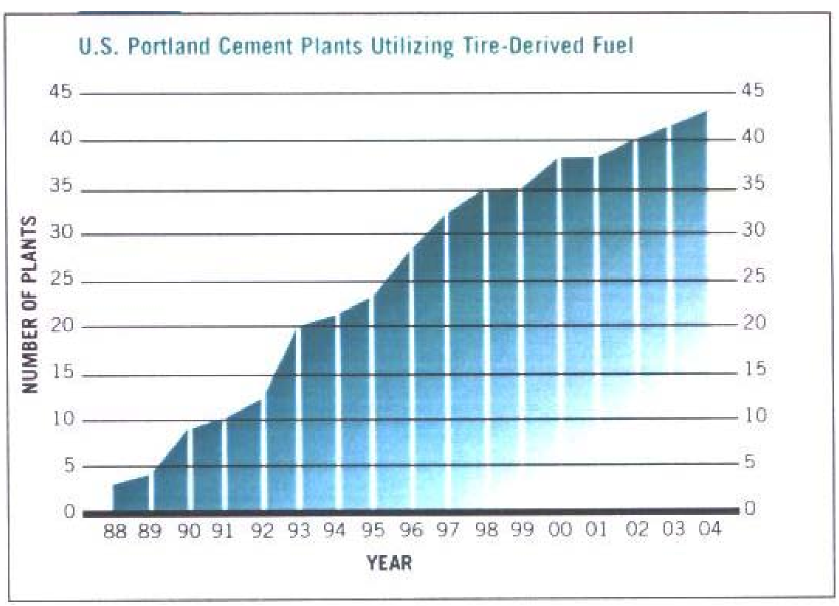

Figure 3-1. U.S. cement plants firing TDF (PCA IS325).

Superimposed over this trend of increasing TDF use has been the development of stringent air emission regulations for U.S. cement kilns. In the U.S., cement kilns are subject to Maximum Achievable Control Technology (MACT) standards. These standards differ with respect to the requirements applicable to kilns fired with conventional fuels only and those that include hazardous wastes as a portion of the kiln fuel. In response to the MACT standards, all cement kilns in the U.S. have conducted dioxin-furan emission tests, and many kiln operators have found it necessary to reduce the inlet temperature to the air pollution control systems to suppress formation of dioxin-furan compounds. Due to this important change in operating conditions, dioxin-furan emissions in the U.S. cement industry have decreased significantly since the 2002 compliance date of the MACT standard for kilns subject to Subpart LLL. Dioxin-furan emission data obtained prior to 2002 for cement kilns are not necessarily representative of the lower, post-MACT emission rates with and without TDF firing.

The initial air emission tests during TDF firing in the cement industry in the late 1980s and early 1990s provided favorable results and encouraged the expanded use of TDF as an alternative fuel. There were a few tests during the initial studies in the late 1980s and early 1990s that showed increases in the emission rates of some analytes during TDF firing. These early studies are often cited by advocacy groups concerned about the air quality impact of TDF firing. As more experience is accumulated with respect to TDF firing, the tests during the earliest period of TDF use should receive less weight than the more recent data.

3.2 Agency Review of Previously Published Emissions Data

Tire derived fuel firing in cement kilns has been approved and encouraged by public health officials for over fifteen years in Canada and the U.S. as an environmentally sound means to minimize (1) health problems relating to mosquito breeding in the water trapped in tires dumped in tire stockpiles, (2) air emissions from intentional and accidental tire stockpile fires, and (3) the tire disposal impact on the limited capacity of landfills. These significant public health and environmental problems continue to exist throughout Canada and the U.S.

As part of the permit evaluation process and the development of overall public health programs, regulatory agencies have reviewed the available data and reached their own conclusions regarding the impact of TDF firing in cement kilns on air emissions and air quality. Some of the published statements from regulatory agencies regarding this question are reproduced below.

- Based on over 15 years of experience with more than 80 individual facilities, EPA [*U.S. EPA]* recognizes that the use of tire-derived fuels is a viable alternative to the use of fossil fuels. EPA testing shows that TDF has a higher BTU value than coal. The Agency supports the responsible use of tires in portland cement kilns and other industrial facilities, so long as the candidate facilities (1) have a tire storage and handling plan; (2) have secured a permit for all applicable state and federal environmental programs; and (3) are in compliance with all the requirement of that permit. U.S. Environmental Protection Agency, 2005 [3].
- Cement kilns provide a good environment for the combustion of tire derived fuels. "A cement kiln provides an environment conducive to the use of many fuel substances, such as tires, not normally included in the fuel mix." U.S. Environmental Protection Agency, 1991[5], Page 4-1.
- "The long residence time and high operating temperatures of cement kilns provide an ideal environment to burn tires as supplemental fuel. Results of several tests conducted on cement kilns while burning tires or TDF indicate the emissions are not adversely affected, but in many cases improve when burning tires. U.S. Environmental Protection Agency, 1991[5], Page 4-36.

- "When tires burn in the open, as in the Hagersville tire fire, the temperature of combustion is not high enough for complete incineration and toxic compounds are released into the air and soil. On the other hand, complete combustion to inorganic gases and ash can be achieved through high-temperature incineration, as is practiced in cement kilns and coal-fired thermal-electric generating stations. Very little is mentioned of research efforts showing that tires can be safely incinerated at high temperatures and the released energy used for industrial applications; consequently, concerned citizens and environmental groups tend to oppose all tire incineration on the grounds that it might pose a health hazard. <u>Murray. W. Science and Technology Division, Government of Canada. [6].</u>
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A variety of State agencies and other organizations in the U.S. have reached similar conclusions regarding TDF firing based on the review of the emissions data.

- "The Board has concluded that, under the right conditions, tires can be safety burned as a fuel supplement. Use of tires in cement kilns displaces coal … Emissions tests at two California cement kilns burning waste tires with coal fuel showed no appreciable difference in toxic air contaminant emissions when compared to burning coal fuel only. The use of tires by cement kilns is a method with existing technology that could be quickly implemented, and has the potential to eliminate all of the waste tires stockpiled and generated. ... The Board recommends that support be provided for the use of tires as fuel in cement kilns." <u>California Integrated Waste Management Board [7], Pages 59 and 60, 1992.</u>
- "TCEQ also used funds appropriated by the 77th Legislature to award grants to two cement kilns for retrofit of their facilities to use TDF. One of the two cement kilns completed the retrofit and burned a total of 1.4 million whole scrap tires in 2003 and an estimated 2.5 million whole scrap tires in 2004. The second cement kiln is anticipated to completed its facility retrofit and initiate TDF burning operations in mid-2005. The facilities should consume a combined total of three to five million whole scrap tires as TDF annually. <u>Texas Commission on Environmental Quality (TCEQ) and the Texas Department of Transportation (TxDOT). 2005 [8].</u>
- "To date, the TNRCC has permitted the combustion of TDF at seventeen facilities, most of them cement kilns, in Texas. Although public concern has been expressed about the use of TDF at these facilities, the TNRCC believes that scientific evidence has demonstrated that tires can be safely burned for fuel provided proper emission control devices are used. The United States Environmental Protection Agency (USEPA) and other state environmental programs have reviewed the available data, and have reached the same conclusion." <u>Texas Natural Resources Conservation Commission[6] March 2001 [9].</u>
- "Support for the burning of TDF is provided by extensive reviews of data from pilot studies and emissions monitoring efforts nationwide. Independent of these studies, the TNRCC has also required smokestack testing for several facilities proposing to use tires as a fuel supplement in Texas. In addition, in order to address the concerns of local citizens, air and soil monitoring has been conducted in Texas communities located near facilities which burn TDF<u>." Texas Natural Resources Conservation Commission, [9].</u>

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[6] TNRCC is now known as the Texas Council of Environmental Quality ("TCEQ")

- “In examining all of the data, an overall picture emerges of no discernable pattern of impact on emissions through the use of TDF. Good combustion practices and proper operation of effective air pollution control systems seem to maintain emissions within a normal ‘error band’ of process and measurement methodology variation.” California Integrated Waste Management Board, June 1997 (Draft) [10].
- “Although there were some initial concerns regarding the burning of tires, studies have shown the health risks associated with burning a mixture of tires and coal are actually lower than the health risks of burning coal alone.” Pennsylvania Department of Environmental Protection, Undated [11].
- “Based on the risk assessment approach used and the theoretical health risks projected for the tire burning facility, Alberta Health supported the position that a properly operated cement kiln should not pose significant long-term exposures and health risks when a portion of its natural gas fuel is replaced with scrap tires. Alberta Health and the Edmonton Board of Health. 1994 [12].

It is apparent from the excerpts provided above that the issue of changing air emissions as a result of TDF firing has been addressed by regulatory agencies throughout the U.S. and Canada for more than fifteen years. In reaching these conclusions, the regulatory agencies have relied primarily upon emissions data compiled and published from 1989 through 1997. The emphasis in this project concerns TDF-related emissions data obtained from 1999 through 2006.

4. AIR EMISSIONS DATA

Section 4 presents two complimentary approaches for evaluating the impact of TDF-firing on air emissions. Kiln-specific data from a small number of plants provide a direct indication of the changes in emissions resulting from the substitution of the fraction of conventional fuels with TDF. However, the interpretation of site-specific data gathered over relatively short time periods at a small number of plants can be confounded by routine variations in emissions due to numerous factors unrelated to TDF firing. Also, due to the cost of air emission testing, most facilities that fire TDF only test when TDF is being used. There are very little directly comparable data. For this reason, kiln-specific comparison data are limited.

Comparison of emissions from those kilns firing TDF with those that do not fire TDF provides another useful means to evaluate the impact of TDF firing conditions. Due to the large number of sources included in this type of evaluation, there is less vulnerability to misinterpretation due to routine, short term variability at a single kiln. However, this multiple kiln approach provides a less direct indication of the impact of TDF firing.

4.1 Kiln-Specific Test Programs With and Without TDF

The emissions data compiled for this project include paired TDF and Non-TDF emissions data applicable to seven cement kilns. In these seven data sets, at least one and as many as ten separate analytes were measured. The multiple analyte data are especially helpful in evaluating the impact of TDF firing.

Plant 77 includes a long dry cement kiln fired with coal. Tests conducted in December 2003 and summarized in Table 4-1 indicated that two of the analytes tested increased slightly and another two decreased slightly. With these limited data, it is not possible to determine if these modest changes have any dependence on TDF firing or are simply due to routine variability of the emissions over a several day period.

Table 4-1. Effect of TDF Firing, Plant 77

Analyte	Emission Concentration, TDF Firing	Emission Concentration, without TDF	Percent Difference Due to TDF Firing
Nitrogen Oxides, ppmvd @7% O_2	444	380	16.8
Sulfur Oxides, ppmvd @7% O_2	207	293	-29.4
Carbon Monoxide, ppmvd @7% O_2	656	559	17.4
Total Hydrocarbons, ppmvd @7% O_2	104	127	-18.1

Plant 256 operates a Humboldt kiln controlled by an electrostatic precipitator. The kiln is fired with coal and coke. The plant operator conducted air emission tests without TDF and with TDF. During sets of tests conducted in 2005, the dioxin-furan emissions decreased by 76.8%; however, both the TDF and non-TDF firing conditions had near-negligible emission concentrations. The nitrogen oxide concentrations increased by 54% while the sulfur oxides concentrations increased 31.8%. The carbon monoxide concentrations decreased 11% during TDF firing. It is possible that none of these changes presented in Table 4-2 are strongly related to the TDF firing condition.

Table 4-2. Effect of TDF Firing, Plant 256

Analyte	Emission Concentration, TDF Firing	Emission Concentration without TDF	Percent Difference Due to TDF Firing
Dioxin-Furans, ng TEQ/NM^3	0.0019	0.0082	-76.8
Nitrogen Oxides, ppmvd @7% O_2	271	591	-54.1
Sulfur Oxides, ppmvd @7% O_2	257	377	-31.8
Carbon Monoxide, ppmvd @7% O_2	1247	1123	11.0

Plant 266 has a preheater-precalciner kiln fired with coal. TDF in the form of whole tires was fired up to a substitution rate of 15%. During air emission tests conducted in 1992, the nitrogen oxides concentrations decreased by 26%, while the sulfur dioxide concentrations decreased by 9.3%. There were also decreases in the filterable particulate matter and carbon monoxide concentrations as indicated in Table 4-3. The concentrations of four of the five metals increased by factors of 7.8 to 50%.

Table 4-3. Effect of TDF Firing, Plant 266

Analyte	Emission Concentration, TDF Firing	Emission Concentration without TDF	Percent Difference Due to TDF Firing
Filterable Particulate, lbs/ton of dry feed	0.139	0.12	15.8
Nitrogen Oxides, ppmvd @7% O_2	318	252	26.2
Sulfur Oxides, ppmvd @7% O_2	165	151	9.3
Carbon Monoxide, ppmvd @7% O_2	1525	1234	23.6
Total Hydrocarbons, ppmvd @7% O_2	58	87	-33.3
Arsenic, $\mu g/M^3$@7%O_2	0.99	0.88	12.5
Chromium, $\mu g/M^3$@7%O_2	2.6	5.2	-50.0
Mercury, $\mu g/M^3$@7%O_2	5.9	6.4	-7.8
Nickel, $\mu g/M^3$@7%O_2	3.4	5.1	-33.3
Zinc, $\mu g/M^3$@7%O_2	5.8	9.8	-40.8

Plant 276 has a wet kiln fired with coal and coke. The test data summarized in Table 4-4, indicates a substantial increase in the nitrogen oxides levels from 644 ppm to 990 ppm. Sulfur dioxides levels were similar with and without TDF. Carbon monoxide levels were also similar and extremely low with and without TDF. Concentrations of chromium and zinc increased substantially, while the concentration of mercury decreased substantially. All of these changes were due to short term routine variations in emissions that were probably unrelated to TDF firing.

Table 4-4. Effect of TDF Firing, Plant 276

Analyte	Emission Concentration, TDF Firing	Emission Concentration without TDF	Percent Difference Due to TDF Firing
Nitrogen Oxides, ppmvd@7%O_2	644	990	-34.9
Sulfur Oxides, ppmvd@7%O_2	27	27	0.0
Carbon Monoxide, ppmvd@7%O_2	14	13	7.7
Arsenic, $\mu g/M^3$@7%O_2	2.7	2.7	0.0
Chromium, $\mu g/M^3$@7%O_2	9.7	30.6	-68.3
Mercury, $\mu g/M^3$@7%O_2	53.2	4.4	1109.1
Zinc, $\mu g/M^3$@7%O_2	23.1	76.2	-69.7

Site specific test data obtained with and without the use of TDF fuels are summarized in Table 4-5. Plant 11 operates a long dry kiln using coal and coke as the primary fuels. Plant 90 has a wet kiln fired with coal. All of the measured dioxin-furan concentrations were extremely low, and any differences in the emission concentrations were well within the precision of Method 23. _Conclusions regarding the impact of TDF firing cannot be based on dioxin-furan concentration values in the very low range of Table 4-5.

Table 4-5. Effect of TDF Firing on Dioxin-Furan Emissions, Plants 11 and 90

Plant	Emission Concentration, TDF Firing ng TEQ/NM^3	Emission Concentration without TDF ng TEQ/NM^3	Percent Difference Due to TDF Firing
11	0.0173	0.023	-25.4
90	0.0005	0.0003	80.0

[1] Percentage values calculated using the "Without TDF" value as the basis.

Four of the kiln-specific emission data sets included nitrogen oxides data with and without TDF. Two of the data sets include slightly increased nitrogen oxides emissions during TDF firing. Two of the data sets have large decreases in nitrogen oxide emissions. Due to the short term variations in nitrogen oxide emissions, none of these four site specific data sets conclusively demonstrate that nitrogen oxides are affected by TDF firing. The large decreases in emissions included in Reports 256 and 276 suggest that additional site specific data will probably indicate that TDF reduces NOx emissions.

Four of the data sets had sulfur dioxide emission data with and without TDF firing. Two of the data sets indicated moderate reductions in sulfur dioxide with TDF firing, and two of the data sets indicated essentially no change due to TDF firing. None of these differences provide a conclusive demonstration that TDF firing has a positive or negative impact on emissions. The short term variability in sulfur dioxide emissions at a specific kiln and the kiln-to-kiln differences in sulfur dioxide emissions are too large to allow for meaningful conclusions based on the limited kiln-specific data compiled during this project.

Four of the site-specific emission data sets included carbon monoxide emissions data with and without TDF. Three of the four data sets indicate slightly increased carbon monoxide emissions during TDF firing.

Two of the site-specific emission data sets included decreased total hydrocarbon emissions data with TDF. These differences are probably caused by routine variations in kiln feed stream organic levels.

The site specific data suggest that TDF firing does not have a major impact on the emissions of any of the metals evaluated, including zinc. However, there is insufficient information to base conclusions for a broad population of cement kilns.

4.2 Analyte Specific Industry-Wide Data

4.2.1 Dioxin-Furan Emissions. The MACT standards promulgated in 1999 for the U.S. Cement Industry strictly limit dioxin-furans based on the Toxic Equivalent Quantity (TEQ). This regulatory approach uses a set of toxic weighting factors to adjust the quantities of seventeen different dioxin-furan congeners to a single value based on the most toxic compound, 2,3,7,8 dibenzo-p-dioxin. The MACT emission limit is now 0.200 nanograms (as TEQ) per normal cubic meter adjusted to 7% O_2 to correct for stack dilution.

Prior to 1990, only limited data were available concerning dioxin-furan emissions from cement pyroprocessing systems. Since 1995, the industry has conducted numerous dioxin-furan emission tests in preparation for and to demonstrate compliance with the MACT standard. These intensive test programs have supported very successful efforts to reduce dioxin-furan emissions. The U.S. EPA requires that cement plants maintain control system inlet gas temperatures below those demonstrated during the compliance test as being adequate to maintain emissions below the 0.200 nanogram TEQ limit. Accordingly, the control system inlet gas temperature provides a useful surrogate for continuously monitoring dioxin-furan emissions.

Dioxin-furan emissions should be slightly lower during TDF firing due to the reduction in the amount of kiln feed additives used. These emissions are due almost exclusively to the quantities and characteristics of organic compounds present in the kiln feed stream. The pyrolysis and volatilization of organic compounds in the feed stream provide organic precursors. These organic precursors form dioxin-furan compounds at a rate that is dependent primarily on the effluent gas stream temperature and, to a lesser extent, on the concentrations of catalysts (i.e. copper) and chlorine gas (Cl_2). In kilns with high alkali (sodium and potassium), the concentration of Cl_2 that can form in the gas stream is low, which reduces the vulnerability of the kiln to dioxin-furan formation.

It is important to note that dioxin-furan formation is not believed to be related to the total chlorine (present as chlorides) in the solids and gases processed in the pyroprocessing system. The quantities of chlorides available in a pyroprocessing system are substantially in excess of the organic compound precursors and particle surfaces needed to facilitate the reactions [25]. Accordingly, any increase or decrease in total chlorides due to TDF firing has little impact on dioxin-furan emissions.

Dioxin-Furan Emission Literature Review. The California Integrated Waste Management Board [10] compiled dioxin-furan emission data for seven cement plants. Based on that data compiled prior to 1997, they concluded that“ ...there were no statistically significant trends in either increases or decreases of emissions when the facilities were using tires or TDF as compared to baseline results. The World Business Council for Sustainable Development [13] has concluded that “Co-processing of alternative fuels and raw materials fed to the main burner, kiln inlet, or the precalciner does not seem to influence or change the emissions of POPs.”[7] [13]

The study conducted by Giugliano et al [14] for the Barletto, Italy plant indicated that there was no change in the observed low dioxin-furan emission rates. Tests at baseline conditions and with 36% heat replacement with TDF were both at less than 0.100 ng TEQ/M^3 @ 11% O_2. These emissions are well below the U.S. MACT limit of 0.200 ng TEQ/M^3 @ 7% O_2.

Dioxin-Furan Air Emission Data Summary. Two hundred fifty eight dioxin-furan emission test values have been included in the project database. Each one of these test values was the result of a U.S. EPA reference method test consisting of a minimum of three test runs of three hours duration. A summary of the emission test results is provided in Table 4-6.

Table 4-6. Dioxin-Furan Emission Data Summary for Kilns With and Without TDF

Parameter	With TDF	Without TDF
Number of Emission Test Values	97	161
Average Concentration, ng TEQ/NM^3@ 7% O_2	0.021	0.062
Median Concentration, ng TEQ/NM^3@ 7% O_2	0.004	0.013
Standard Deviation, ng TEQ/NM^3@ 7% O_2	0.054	0.119
Minimum Concentration, ng TEQ/NM^3@ 7% O_2	0.000	0.000
Maximum Concentration, ng TEQ/NM^3@ 7% O_2	0.380	0.644

[7] POPs are persistent organic pollutants

The average emission rate of 0.021 ng TEQ/NM^3@ 7% O_2 for TDF-firing kilns is substantially lower than the 0.062 ng TEQ/NM^3@ 7% O_2 value for non-TDF firing kilns. The difference in the average values for these two categories is due, in part, to several higher-than-normal dioxin-furan emission test values in three reports (7, 16, 68) at plants not firing TDF. Deletion of these eight test values decreases average concentration during non-TDF firing to 0.045 ng TEQ/NM^3@ 7% O_2, a value that is still well above the average value for TDF-firing tests. Mann-Whitney analysis of these two categories of dioxin-furan emissions indicates that the lower emissions measured during TDF firing conditions are significant at more than the 99% level ($Z=-4.664$, $\sigma=0.000$).

The reduction in dioxin-furan emissions associated with the use of TDF fuels is applicable to all three major categories of kilns. As indicated in Tables 4-7 through 4-9, the average and median dioxin-furan emissions were lower for all three major categories of kilns firing TDF.

Table 4-7. Dioxin-Furan Emission Data Summary, Wet Kilns With and Without TDF

Parameter	With TDF	Without TDF
Number of Emission Test Values	12	31
Average Concentration, ng TEQ/NM^3@ 7% O_2	0.036	0.056
Median Concentration, ng TEQ/NM^3@ 7% O_2	0.011	0.021
Standard Deviation, ng TEQ/NM^3@ 7% O_2	0.058	0.120
Minimum Concentration, ng TEQ/NM^3@ 7% O_2	0.0003	0.0003
Maximum Concentration, ng TEQ/NM^3@ 7% O_2	0.189	0.644

Table 4-8. Dioxin-Furan Emission Data Summary, Long Dry Kilns With and Without TDF

Parameter	With TDF	Without TDF
Number of Emission Test Values	9	34
Average Concentration, ng TEQ/NM^3@ 7% O_2	0.029	0.060
Median Concentration, ng TEQ/NM^3@ 7% O_2	0.013	0.020
Standard Deviation, ng TEQ/NM^3@ 7% O_2	0.038	0.112
Minimum Concentration, ng TEQ/NM^3@ 7% O_2	0.005	0.0009
Maximum Concentration, ng TEQ/NM^3@ 7% O_2	0.122	0.579

Table 4-9. Dioxin-Furan Emission Data Summary, Preheater and Preheater-Precalciner Kilns With and Without TDF

Parameter	With TDF	Without TDF
Number of Emission Test Values	76	90
Average Concentration, ng TEQ/NM^3@ 7% O_2	0.018	0.068
Median Concentration, ng TEQ/NM^3@ 7% O_2	0.002	0.012
Standard Deviation, ng TEQ/NM^3@ 7% O_2	0.054	0.125
Minimum Concentration, ng TEQ/NM^3@ 7% O_2	0.000	0.000
Maximum Concentration, ng TEQ/NM^3@ 7% O_2	0.380	0.616

Mann-Whitney nonparametric tests indicate that the differences in the dioxin-furan emissions for wet kilns and long dry kilns were not statistically significant. The results for preheater and preheater-precalciner kilns indicate that the dioxin-furan emissions are significantly lower at the 99% confidence level for TDF firing conditions (Z=-4.23, σ=0.000). Some preheater and preheater-precalciner kilns are equipped with in-line raw mills. A comparison of dioxin-furan emissions with and without the in-line raw mill operating is provided in Table 4-10. As indicated in this table, all of the dioxin-furan emissions are low. The variations in the emissions are not statistically significant (Mann Whitney Z=-1.204, σ = 0.229) and are probably unrelated to the in-line raw mill operating status.

Table 4-10. Dioxin-Furan Emission Data Summary, Preheater and Preheater-Precalciner Kilns Firing TDF, With and Without In-Line Raw Mill

Parameter	In-Line Raw Mill Operating	In-Line Raw Mill Offline
Number of Emission Test Values	35	34
Average Concentration, ng TEQ/NM^3@ 7% O_2	0.008	0.005
Median Concentration, ng TEQ/NM^3@ 7% O_2	0.0004	0.002
Standard Deviation, ng TEQ/NM^3@ 7% O_2	0.023	0.009
Minimum Concentration, ng TEQ/NM^3@ 7% O_2	0.000	0.000
Maximum Concentration, ng TEQ/NM^3@ 7% O_2	0.124	0.045

Impact of TDF Firing on Dioxin-Furan Emissions. The air emissions data compiled in this project indicate that dioxin-furan emissions from wet kilns, long dry kilns, and preheater-precalciner kilns firing TDF are all at or below the levels of kilns not firing TDF. These lower emissions associated with TDF firing were statistically significant for the preheater-precalciner kilns. Research is needed to identify the possible reasons for the significantly reduced dioxin-furan emissions during TDF firing. Site specific tests with and without TDF would be especially useful for further evaluating the impact of TDF on dioxin-furan emissions.

4.2.2 Filterable Particulate Matter Emissions*.* Particulate matter emitted from cement kilns consists of (1) feed solids reentrained from the kiln feed stream moving in a countercurrent direction toward the kiln and (2) flyash formed by fuels fired in the kiln. This material is collected at high efficiency in the electrostatic precipitator serving the kiln.

The use of TDF should not have a significant impact on particulate matter emissions. The low ash content of the TDF should slightly reduce the flyash concentrations in the kiln effluent gas stream; however, this change has little impact because the flyash is a very small part of the particulate matter loading.

Particulate matter emissions from cement kilns are governed primarily by the efficiency of the air pollution control system. Emissions are not a strong function of the ash content of the fuels or the mix of fuels used in kilns. Nevertheless, the possible impact of TDF firing on the total particulate matter emissions has been evaluated. The particulate matter emissions have been measured by U.S. EPA Method 5.

Filterable Particulate Matter Emission Literature Review. Studies conducted by PES for EPA [5] and by the California Integrated Waste Management Board [10] have not found any significant impact of TDF on particulate matter emissions. The data provided by Giugliano et al [14] for the Barletta, Italy plant indicated no significant increase in total particulate matter emissions. The emission rate during baseline conditions was 2.1 mg/M^3, while the rate during TDF firing (36% heat replacement) was 2.2 mg/M^3. Both of these values are extremely low, and the difference in emissions is well within the precision limits of the particulate matter test methods.

Filterable Particulate Matter Air Emissions Data Summary. One hundred fifty nine filterable particulate matter emission test values have been included in the project database. Each one of these test values is the result of a U.S. EPA Reference Method 5 test consisting of a minimum of three test runs of at least one hour duration. A summary of the emission test results is provided in Table 4-11.

Table 4-11. Particulate Matter Data Summary for Kilns With and Without TDF

Parameter	With TDF	Without TDF
Number of Emission Test Values	59	100
Average Concentration, Lbs. per ton of dry kiln feed	0.064	0.099
Median Concentration, Lbs. per ton of dry kiln feed	0.047	0.065
Standard Deviation, Lbs. per ton of dry kiln feed	0.059	0.113
Minimum Concentration, Lbs. per ton of dry kiln feed	0.002	0.000
Maximum Concentration, Lbs. per ton of dry kiln feed	0.262	0.658

The average emission rate of 0.064 pounds per ton of dry kiln feed for TDF-firing kilns is slightly lower than the 0.099 pounds per ton of dry kiln feed value for non-TDF firing kilns. Mann-Whitney analysis of these two categories of filterable particulate matter emissions indicates that the lower emissions measured during TDF firing conditions are not significant at the 90% confidence level ($Z=-1.230$, $\sigma=0.219$).

Impact of TDF firing on Filterable Particulate Matter Emissions. Overall, the impact of TDF firing on total particulate matter emissions appears to be negligible. There are no indications that TDF firing results in an increase in filterable particulate matter emissions.

4.2.3 Nitrogen Oxides Emissions. Nitrogen oxides (NOx) include nitric oxide (NO) and nitrogen dioxide (NO_2). In cement kilns, NOx is formed due primarily to the high temperature chemical reactions that are generally described by the Zeldovich Mechanism. The quantity of NOx generated is strongly related to the peak gas temperature, the peak oxygen concentrations at the point of maximum gas temperature, the gas residence time in the high temperature portion of the processes, and the amount of combustion gas in this portion of the process. This NOx formation mechanism is generally described as “thermal NOx.” The NOx emissions from long dry-single stage preheater kilns are due primarily to thermal NOx formation in the flame of the kiln burner. The amount of gas moving through the portion of the kiln especially subject to thermal NOx is reduced by the use of TDF. Due to the high sensitivity of thermal NOx formation to the intensity of combustion in the kiln burner flame, it is reasonable to expect moderate-to-substantial NOx emission reductions due to even moderate TDF usage rates. The considerably lower nitrogen content of TDF as compared to coal reduces the amount of nitrogen from the kiln feed that can also participate in chemical reactions to form NOx. Substantial reductions in NOx emissions are one of the reasons that many regulatory agencies have encouraged the use of TDF as an alternative fuel in cement kilns.

Nitrogen Oxides Emission Literature Review. Most previous studies [5, 7, 15, 16, 17, 18] of a single kiln or a group of kilns have indicated that firing TDF in place of a portion of the fossil fuel results in either (1) no significant difference in NOx emissions or (2) a decrease in NOx emissions.

EPA has concluded that mid-kiln firing of TDF in dry kilns results in an average reduction of 33.3% in NOx emissions.[24] An example of the extent of NOx reduction related to TDF firing is described by Giugliano et. al. [14] with respect to a kiln in Italy. He observed NOx reductions from 360 ppmvd @11% O_2 to 210 ppmvd @11% O_2 during firing of TDF chips into the preheater tower of a preheater-precalciner kiln fired with petroleum coke.
Rosenhoj et al [19] have observed that NOx is reduced 10% to 50% with various forms of TDF firing in European kilns. Syverud [20] reports that NOx reductions up to 40% have been observed in preheater-precalciner kilns. He attributes these reductions to reburning reactions. Miller et al. [21] have also demonstrated decreased NOx emissions of 20% to 63% due to the use of TDF as a reburn fuel in a pilot scale combustion facility. Carrasco et al [22] observed an 11% reduction in NOx during TDF firing at a cement kiln in Canada.

Nitrogen Oxides Air Emissions Data Summary. Thirty nitrogen oxides emission test values have been included in the project database. Each one of these test values is the result of a U.S. EPA Reference Method 7E test. A summary of the emission test results is provided in Table 4-12.

Table 4-12. Nitrogen Oxides Emissions Data Summary for Kilns With and Without TDF

Parameter	With TDF	Without TDF
Number of Emission Test Values	20	10
Average Concentration, ppmvd @ 7% O_2	443	696
Median Concentration, ppmvd @ 7% O_2	409	707
Standard Deviation, ppmvd @ 7% O_2	189	408
Minimum Concentration, ppmvd @ 7% O_2	252	240
Maximum Concentration, ppmvd @ 7% O_2	1,055	1,563

The average emission rate of 443 ppmvd @7% O_2 for TDF-firing kilns is lower than the 696 ppmvd @7% O_2 value for non-TDF firing kilns. Mann-Whitney analysis of these emissions with and without TDF indicates that the lower emissions measured during TDF firing conditions are not significant at the 90% level ($Z=-1.452$, $\sigma=0.155$). The kiln-to-kiln differences are too large to identify the effect of TDF on nitrogen oxide emissions in the relatively small data set available.

Impact of TDF Firing on Nitrogen Oxides Emissions. The available air emissions data suggest that TDF firing reduces nitrogen oxides emissions. However, nitrogen oxides emissions are highly variable over short time periods and from kiln-to-kiln due to factors unrelated to TDF firing or other fuel firing conditions. The presently available data are not sufficient to confirm that conclusions reached by others that nitrogen oxide emissions are reduced through the use of TDF.

4.2.4 Sulfur Dioxide Emissions. Sulfur dioxide (SO_2) emissions from cement kilns are formed due to mechanisms that differ substantially from coal-fired boilers and other industrial processes. In cement kilns, the main source of SO_2 is the oxidation of pyritic sulfur present in the limestone in the kiln feed. In long dry kilns, the SO_2 forms at the back end (feed inlet) of the kiln and enters the effluent gas stream. This SO_2 will be termed "feed SO_2" for the purpose of this document.

SO_2 emissions from cement kilns can also form due to the oxidation of organic, pyritic, and sulfate sulfur present in the pulverized coal and petroleum coke fuels used in the kiln burner. This SO_2 will be termed "fuel SO_2" for the purposes of this document. The large majority of the fuel SO_2 is adsorbed by clinker and kiln feed materials in the kiln and in the single stage preheater tower. Accordingly, the SO_2 concentrations approach very low levels except for kilns operating with unusually low oxygen concentrations.

TDF has sulfur levels that are similar to those in most coals and below most petroleum coke fuels; however, the absorption of essentially all fuel SO_2 in the kiln and preheater tower makes these differences relatively unimportant. For most cement kilns, TDF firing should have little, if any, positive or negative impact on SO_2 emissions.

Sulfur Dioxide Emission Literature Review. The sulfur content of TDF and other alternative fuels is lower than the sulfur content of most eastern and midwestern coals and lower than some types of coke fuel. Accordingly, the substitution of TDF for a portion of these fuels has the potential for slightly reducing sulfur dioxide emissions. A number of previous studies have indicated either unchanged SO_2 emissions or reductions of SO_2 emissions of up to 25%. [20, 21] The study by Carrasco et al [22] found a 24% increase in SO_2 emissions with TDF; however, the measured concentrations were relatively low.

The emissions of sulfur dioxide from cement kilns are complicated by chemical reactions in preheaters and in the feed ends of kilns. These reactions can result in "scrubbing" of sulfur dioxide and in reactions in the calcining and clinkering zones. Considering that SO_2 scrubbing is at a maximum in the kiln, TDF firing in the kiln probably has less beneficial impact on SO_2 emissions than TDF firing in a precalciner. Furthermore, the benefits of TDF firing in both the kiln and the precalciner depend on the sulfur content of the fuel being replaced by TDF.
TDF firing can result in increased SO_2 emissions during some unusual kiln operating conditions. If TDF firing contributes to chemically reducing conditions in the kiln due to inadequate oxygen levels, the extent of SO_2 scrubbing in the kiln can be reduced from baseline (non-TDF firing) conditions. This could result in an increase in SO_2 emissions.

Sulfur Dioxide Air Emission Data Summary. Thirty sulfur dioxide emission test values have been included in the project database. Each one of these test values is the result of a U.S. EPA Reference Method 6C test. A summary of the emission test results is provided in Table 4-13.

Table 4-13. Sulfur Dioxide Emissions Data Summary for Kilns With and Without TDF

Parameter	With TDF	Without TDF
Number of Emission Test Values	19	10
Average Concentration, ppmvd @ 7% O_2	153	200
Median Concentration, ppmvd @ 7% O_2	165	89
Standard Deviation, ppmvd @ 7% O_2	127	239
Minimum Concentration, ppmvd @ 7% O_2	1.5	0.0
Maximum Concentration, ppmvd @ 7% O_2	397	587

The average emission rate of 153 ppmvd @7% O_2 for TDF-firing kilns is lower than the 200 ppmvd @ 7%O_2 value for non-TDF firing kilns. However, the averages for both categories presented in Table 4-13 are subject to influences caused by several large values. The variability of sulfur dioxide emissions from kiln-to-kiln due to factors unrelated to fuel firing conditions is too large to allow for meaningful comparisons of emissions with and without TDF firing.

Impact of TDF Firing on SO_2 Emissions. The published air emissions data concerning SO_2 emissions indicate that TDF firing usually has a slight beneficial impact. The data compiled during this study generally support this conclusion. However, the variability of sulfur dioxide emissions is too large to conclusively demonstrate the benefits of TDF firing on emissions.

4.2.5 Carbon Monoxide Emissions. Carbon monoxide (CO) is formed due to incomplete oxidation of organic compounds. It is especially difficult to oxidize CO to CO_2; therefore, CO is often a good surrogate for the overall adequacy of oxidation conditions. If the CO is low, then all the total hydrocarbon (THC) compounds are also low because they are substantially easier to oxidize. High CO levels are often, but not always, associated with increased concentrations of THC.

CO emissions from cement pyroprocessing operations result from both the kiln feed (feed CO) and the pyroprocessing fuels (fuel CO). As with THC emissions, feed CO is the dominant source of CO; however, non-optimum combustion conditions can result in fuel CO. Operators of cement kilns may require some time to learn how to adjust kiln operating conditions to include the use of TDF up to 30% of the system fuel input. Accordingly, any long-term evaluation of the impact of TDF on CO emissions should be conducted only after the operators have optimized kiln operating conditions.

TDF firing could have both positive and negative impacts on CO emissions from cement kilns. The positive (emission reduction) impact is usually small and difficult to identify with the routine variations in CO concentrations. The possible negative impact of CO emissions during TDF firing is often the result of emission testing prior to operator adjustment to the revised kiln operating characteristics.

Carbon Monoxide Emission Literature Review. Carbon monoxide emissions from combustion sources are related to the adequacy of oxidation conditions. One previous study [5] indicated that TDF firing caused a slight increase in carbon monoxide emissions, while others [5, 18, 20] indicated either a decrease or no effect of TDF firing on emissions.

The study by Giugliano et al [14] at a cement plant in Italy indicated that the CO was not affected by the rate of TDF firing. As indicated in Table 4-14, the CO concentrations remained at approximately 200 ppmvd as the TDF firing rate increased from 0% to 36% of the total kiln heat input.

Table 4-14. CO Emissions at Barletta, Italy [14]

Parameter	TDF Addition (% total heat input)			
	Baseline	16%	22%	36%
CO at ESP Inlet (ppmvd @ 6% O_2)	204	227	197	196
Clinker Cooler Air Temperature (°C)	1050-1130	1140-1150	1200-1220	1100
Kiln Inlet Temperature (°C)	995-1050	950-990	950-980	980
Cyclone Tower Flue Gas Discharge Temperature (°C)	330-335	320-330	320-325	325
Raw Feed Temperature Difference Across Preheater (°C)	110-105	110-112	110-115	100

Carbon Monoxide Air Emission Data Summary. Thirty one carbon monoxide emission test values have been included in the project database. Each one of these test values is the result of a U.S. EPA Reference Method 10 test. A summary of the emission test results are provided in Table 4-15.

Table 4-15. Carbon Monoxide Emissions Data Summary for Kilns With and Without TDF

Parameter	With TDF	Without TDF
Number of Emission Test Values	20	11
Average Concentration, ppmvd @ 7% O_2	604	435
Median Concentration, ppmvd @ 7% O_2	409	182
Standard Deviation, ppmvd @ 7% O_2	565	494
Minimum Concentration, ppmvd @ 7% O_2	0.0	5.1
Maximum Concentration, ppmvd @ 7% O_2	1,525	1,234

The average emission rate of 604 ppmvd @7% O_2 for TDF-firing kilns is higher than the 435 ppmvd @7% O_2 value for non-TDF firing kilns. Mann-Whitney analysis of these two categories of carbon monoxide emissions indicates that the higher emissions measured during TDF firing conditions are not significantly different at the 90% level ($Z=-0.743$, $\sigma=0.457$). The kiln-to-kiln variability in carbon monoxide emissions appears to be large to allow for the identification of an impact on emissions due to TDF.

Impact of TDF Firing on CO Emissions. The air emission test results for CO are mixed. The overall data set indicates that there is no significant difference in carbon monoxide emissions from kilns with or without TDF firing.

4.2.6 *Total Hydrocarbon Emissions*. Total hydrocarbon emissions (THC) include all organic compounds that are in a gaseous or vapor state at the temperature that exists in the stack. There are two sources of THC at cement plants: (1) feed THC and (2) fuel THC. Feed THC results from the pyrolysis and/or volatilization of organic compounds in the kiln feed as it is gradually heated while passing through the drying zone and the calcination zone of the kiln. Feed THC is by far the dominant source of emissions in cement pyroprocessing operations.

Fuel THC results from incomplete combustion of fossil fuels and/or TDF in the kiln. Due to the extremely high gas temperatures and gas residence times in cement kilns, the concentrations of fuel THC are usually extremely low and often undetectable. Due to the high efficiency oxidation conditions, TDF firing in mid-kiln areas of wet and long dry kilns and other forms of TDF firing should not have a substantial impact on overall THC emissions.

There are considerable plant-to-plant differences in the levels of feed THC. There can also be considerable differences at a specific plant over time due to (1) changes in the organics levels in the portion of the quarry providing limestone, (2) the organics content of mill scale often used as a source of iron for the kiln, and (3) the organics content of boiler flyash or bottom ash used as a source of aluminum for the kiln. These concentration variations must be taken into account when evaluating the impact of TDF on emissions.

Total Hydrocarbon Emission Literature Review. Hydrocarbons are emitted due to volatilization of organic compounds present in the raw materials entering the pyroprocessing system and due to incomplete combustion of fuels in the kilns and/or precalciner. Due to the high temperatures and long gas stream residence times, the contribution of hydrocarbons caused by incomplete combustion is small compared to volatilization of organic compounds in the limestone, clay, shale, and sand raw materials.

TDF would impact hydrocarbon emissions only if combustion were incomplete. Total hydrocarbon emission data obtained primarily by U.S. EPA Reference Method 25A were evaluated to identify the impact on TDF firing on total hydrocarbon emissions.

Total Hydrocarbons Air Emissions Data Summary. Twenty nine total hydrocarbon emission test values have been included in the project database. Each one of these test values is the result of a U.S. EPA Reference Method 25A test. A summary of the emission test results is provided in Table 4-16.

Table 4-16. Total Hydrocarbons Emissions Data Summary for Kilns With and Without TDF

Parameter	With TDF	Without TDF
Number of Emission Test Values	22	7
Average Concentration, ppmvd as propane @ 7% O_2	48	37
Median Concentration, ppmvd as propane @ 7% O_2	38	17
Standard Deviation, ppmvd as propane @ 7% O_2	74	50
Minimum Concentration, ppmvd as propane @ 7% O_2	0.4	1.1
Maximum Concentration, ppmvd as propane @ 7% O_2	355	127

The average emission rate of 48 ppmvd as propane @7% O_2 TDF-firing kilns is slightly higher than the 37 ppmvd as propane @7% O_2 value for non-TDF firing kilns. Mann-Whitney analysis of these two categories of total hydrocarbon emissions indicates that the higher emissions measured during TDF firing conditions are not significant at the 90% level ($Z=-0.819$, $\sigma=0.415$).

Impact of TDF Firing on Total Hydrocarbon Emissions. The data compiled during this project and published emissions data indicate that TDF firing does not significantly affect the emissions of total hydrocarbons. Any differences reported are probably due primarily to the precision of the emission testing method and to routine variability in the organic content of the kiln raw materials.

4.2.7 Metals Emissions*.* The scope of this study includes the five separate metals listed below. These metals were chosen to represent a variety of different metals potentially present in coal and in TDF. They were also chosen to address metals having distinctly different volatilities and, therefore, having different modes of emission from cement kilns.

- Arsenic
- Chromium (Total)
- Nickel
- Mercury
- Zinc

Numerous factors affect the emissions of these metals from cement kilns. The quantities of metals entering as trace constituents in the limestone and clay/shale raw materials can vary substantially on a routine basis. TDF has significantly lower concentrations of certain metals such as arsenic and mercury. Zinc can be present in higher concentrations in TDF than in the coal and coke baseline fuels. Zinc concentrations can be up to 2.0% by weight of the TDF.

The emissions of metals are not controlled entirely by the input quantities in the fuels and raw materials. Due to the volatilities of the metals and their chemical reactions in the kiln, some of the metals are partitioned to the clinker, while others are partitioned primarily to the gas stream going to the air pollution control system. Previous studies of metal behavior in cement kilns indicate that partitioning occurs mainly in accordance with the groups listed below.

Metals Primarily Captured by the Clinker in the Kiln

- Arsenic
- Chromium
- Nickel
- Zinc

Metals Primarily Exiting the Kiln in the Gas Stream

- Mercury

Considering the general partitioning characteristics, changes in the input quantities of metals that primarily become part of the clinker should be relatively small. Changes in the input quantities of metals that are partitioned primarily to the gas stream entering air pollution control systems may be more important.

The fuels input material balance calculations for TDF firing facilities will show an increased input level due to the higher levels of zinc in tires as compared to conventional fossil fuels. The particulate matter control devices used for high efficiency particulate matter removal will remain highly effective for zinc-containing particles despite a possible increase in the input loading of zinc.

Metals Emission Literature Review. The data compiled by PES for EPA [5], by the California Waste Management Board [7, 10], and by Marechal [16] indicated that essentially all of the cement kilns firing TDF experienced no increase in the measured emissions of zinc and other metals.

The comprehensive emission testing programs conducted by Giugliano et al [14] at the Barletta, Italy plant indicated that firing TDF at a rate equivalent to 36% of the total kiln heat input rate did not result in increased metals emissions (Table 4-17).

Table 4-17. Metals Emissions at Barletta, Italy Cement Plant [14]

Analyte	Baseline Test, Emissions in $\mu g/M^3$ @ 11% O_2	TDF Test, (36% Btu replacement) Emissions in $\mu g/M^3$ @ 11% O_2
Arsenic	<0.2	<0.2
Chromium (Total)	0.2	0.7
Nickel	0.4	0.4
Mercury	4	4
Zinc	10	10

Emissions data for Florida Crushed Stone provided by Gray [23] indicate that the emission rates of metals were essentially unchanged when whole tires were introduced into the riser ducts of the preheater kiln. Emissions were measured while using 14% TDF. It is important to note that this plant shares a fabric filter with a coal-fired boiler; therefore, the metals emissions are related to the performance of these two separate sources. The zinc concentration decreased by approximately 50%; however, this is probably not a statistically significant change. All other metals stayed at the same concentrations in the baseline and 14% TDF tests. The levels of metals were consistently low (0.02 to 8.13 pounds per hour, 3.12. pound per hour of zinc).

Metals Air Emissions Data Summary. Only a few of the emission test reports received during this project included metals emissions data. The data received for arsenic, chromium (total), nickel, mercury, and zinc are summarized in Table 4-18. Considering the plant-to-plant differences and temporal variations at specific plants, there are insufficient data to evaluate the impact of TDF firing on metals emissions.

Table 4-18. Metals Data Summary for Kilns With and Without TDF

Metal	Parameter	With TDF	Without TDF
Arsenic	Number of Emission Test Reports	15.0	2.0
	Average Concentration, µg/M^3 @ 7% O_2	1.8	1.8
	Median Concentration, µg/M^3 @ 7% O_2	1.3	1.8
	Standard Deviation, µg/M^3 @ 7% O_2	2.2	1.3
	Minimum Concentration, µg/M^3 @ 7% O_2	0.0	0.9
	Maximum Concentration, µg/M^3 @ 7% O_2	7.6	2.7
Chromium	Number of Emission Test Reports	11	2
	Average Concentration, µg/M^3 @ 7% O_2	4.3	17.9
	Median Concentration, µg/M^3 @ 7% O_2	3.1	17.9
	Standard Deviation, µg/M^3 @ 7% O_2	3.8	18.0
	Minimum Concentration, µg/M^3 @ 7% O_2	0.0	5.2
	Maximum Concentration, µg/M^3 @ 7% O_2	12.3	30.6
Nickel	Number of Emission Test Reports	18.0	1.0
	Average Concentration, µg/M^3 @ 7% O_2	5.9	5.1
	Median Concentration, µg/M^3 @ 7% O_2	1.9	5.1
	Standard Deviation, µg/M^3 @ 7% O_2	10.6	
	Minimum Concentration, µg/M^3 @ 7% O_2	0.0	5.1
	Maximum Concentration, µg/M^3 @ 7% O_2	41.4	5.1
Mercury	Number of Emission Test Reports	11.0	2.0
	Average Concentration, µg/M^3 @ 7% O_2	18.0	5.5
	Median Concentration, µg/M^3 @ 7% O_2	10.1	5.5
	Standard Deviation, µg/M^3 @ 7% O_2	18.7	1.3
	Minimum Concentration, µg/M^3 @ 7% O_2	0.4	4.5
	Maximum Concentration, µg/M^3 @ 7% O_2	53.2	6.4
Zinc	Number of Emission Test Reports	8.0	2.0
	Average Concentration, µg/M^3 @ 7% O_2	10.8	42.9
	Median Concentration, µg/M^3 @ 7% O_2	7.8	42.9
	Standard Deviation, µg/M^3 @ 7% O_2	9.8	47.1
	Minimum Concentration, µg/M^3 @ 7% O_2	0.1	9.6
	Maximum Concentration, µg/M^3 @ 7% O_2	23.2	76.2

Impact of TDF Firing on Metals Emissions. There is insufficient information to evaluate the impact of TDF firing on the emissions of metals such as arsenic, total chromium, mercury, nickel, and zinc.

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