



# Heavy metal outputs from a cement kiln co-fired with hazardous waste fuels

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Received 1 February 1996; accepted 15 April 1996

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## Abstract

Measured data from a kiln equilibration test are analyzed for heavy metal outputs from a cement kiln co-fired with hazardous waste fuels. Metal outputs from stack emissions, cement kiln dust and cement clinker are considered. Equations are derived for predicting all three metal outputs at any hazardous waste feed rate under steady state conditions. Through analysis of two steady state conditions, at the beginning and end of the equilibration test, essentially the same ratios of metal feed rates are found to be distributed to the kiln dust at either high or low metal feed rates. Applying the same distribution ratios in the derived equations, metal concentrations of wasted kiln dust are predicted when the kiln is not using hazardous waste fuels. Measured concentrations of arsenic, beryllium, cadmium, chromium, and lead in wasted kiln dust, at the highest intended hazardous waste feed rates to the kiln, are 68, 10, 72, 18, and 68 times those predicted for feed rates with no hazardous waste. In addition, the intermediate, non-steady state segment of the equilibration test is analyzed. If metals are assumed not to accumulate in the kiln, the intermediate metal concentrations in cement clinker are predicted to be substantially higher than those at the final steady state.

*Keywords:* Arsenic; Beryllium; Cadmium; Cement clinker; Cement kiln; Cement kiln dust; Chromium; Hazardous waste fuel; Heavy metal; Lead

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## 1. Introduction

The combustion of hazardous waste fuels (HWF) in cement kilns offers an alternative to disposal or incineration of certain waste streams. This practice is intended to

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decompose hazardous organic compounds. However, some HWF contain not only toxic organic compounds but also toxic heavy metals. Heavy metals in fuels may be discharged through three separate streams. These include emissions from a kiln through exhaust stacks and incorporation into cement kiln dust (CKD) and cement clinker; these latter two solids are continuously withdrawn from the kiln. A portion of the CKD may be recirculated back to the kiln. Some environmental concerns have been raised regarding the metal outputs. Among these concerns are: air pollution by stack emissions, groundwater pollution by disposal of CKD in existing quarries, and leaching of heavy metals in drinking-water conveyance systems made or lined with cement produced in these kilns.

The high alkali content in cement kilns and the scrubbing action of the high solids content favor the retention of metal compounds in the clinker and collected particulate matter (including CKD) [1,2]. Emissions of refractory metals (such as arsenic, beryllium, and chromium) are generally below 0.1% of the input feed rates, and emissions of semi-volatile metals (such as cadmium and lead) are generally below 0.5% [1,2].

The cement industry [3,4] and the U.S. Environmental Protection Agency [5] have collected and analyzed CKD samples for acid-soluble and leachable amounts of metals. However, since the operating conditions under which individual CKD samples were taken (e.g., waste burning vs. non-waste burning) were not reported in those data sets, assessing in detail the impacts on metal outputs of burning HWF is precluded.

In this paper, analysis of a relatively complete set of measured data from a cement kiln is presented. Data for all three outputs of metals, in stack emissions, CKD, and cement clinker, are evaluated.

## 2. Availability and selection of data for analysis

For a cement kiln burning HWF, the operator is required, under the Boiler and Industrial Furnace (BIF) regulations (40 CFR Part 266), to submit a Certification of Compliance (CoC) Report. The objective of the CoC test is to demonstrate that emissions from the kiln, although burning HWF at the maximum rate intended for future operation, do not exceed regulatory limits. Prior to the CoC test, the operator is required to conduct an equilibration test to demonstrate that the kiln reaches equilibrium (steady state) with regard to inputs and outputs of metals within a certain time interval after HWF addition to the kiln begins. Therefore, a complete CoC test report provides information not only at steady state (during the CoC test) but also at non-steady state (during the equilibration test).

During an equilibration test for metals, metal solutions are spiked (pumped) into the kiln and the spiking (pumping) rate is changed from zero to a higher level. Thus, the total metal feed rate (sum of the pre-existing metal feed and the metal spike) is increased from one, lower level to another higher, constant level (a step rise). During the test, samples of metal outputs (either stack emissions or wasted CKD) are taken at least every hour and measured until concentrations no longer show a distinct increase. The time interval for the sample metal concentration to increase from a lower, constant value to a higher, asymptotically constant value is defined as the time interval of equilibration.

All CoC test reports are required to provide information on stack emissions, one of the three metal outputs from the kiln. During some CoC tests, wasted CKD samples were also collected and analyzed to verify their Bevill status. Under current regulations, as long as the criteria outlined in BIF 40 CFR 266.112 are met, CKD generated from the processing of HWF is excluded from being considered a hazardous waste, which is regulated under RCRA Subtitle C. This is known as the Bevill Exclusion.

Among eight CoC reports examined, the most complete CoC test data available were found in the report submitted by the Continental Cement Company (CCC), Hannibal, MO [6]. This CCC report provides information on all three metal outputs from stack emissions, CKD and clinker during steady state operation. CKD concentrations during the equilibration test (non-steady state) were also reported. Therefore, the data of CCC were chosen for the present analysis.

### 3. Continental cement kiln processing

CCC produces Portland cement in a wet process rotary kiln in which hazardous waste, both liquid and solid, is used as part of the fuel [6]. Fig. 1 depicts a simplified process flow diagram of the CCC manufacturing process. The overall length of the kiln is 190 m with two distinct zones. Raw materials (clay, shale, limestone, silica) are fed as a slurry (32% water) into the cold zone of the kiln. This cold zone (64 m in length by 5.5 m in diameter) dries the slurry. As raw materials traverse the length of the kiln toward the burning zone (126 m in length by 4.9 m in diameter), a series of chemical and physical reactions occurs which is critical to clinker production [3,7]. Clinker, after cooling, is discharged to holding silos until it is ground. The clinker cooling system is not shown in Fig. 1. Clinker is ground in a ball mill with a small amount of gypsum added to produce commercial cement.

The CCC kiln is primarily fueled by coal; however, solid and liquid waste fuels are fired at up to a 100% replacement level. Liquid waste fuels are fired at rates up to 11 000 kg h<sup>-1</sup> through an axial pipe within the coal pipe or through a separate pipe

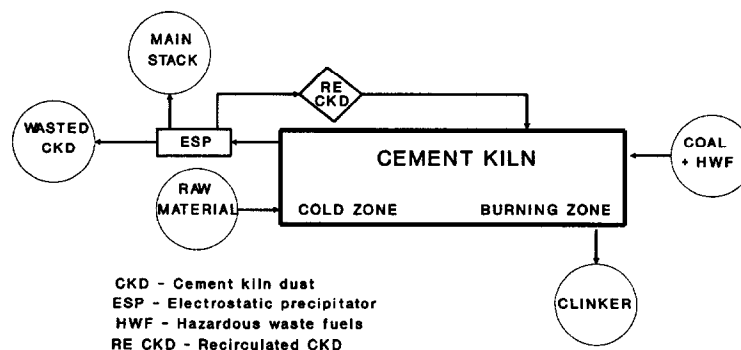


Fig. 1. Simplified process diagram of the Continental Cement Company kiln.

mounted outside the coal pipe. Solid waste fuels are conveyed with the coal through the coal pipe.

An induced-draft fan pulls a countercurrent air stream through the CCC kiln and maintains a negative pressure in the kiln. Combustion gases are drawn through an electrostatic precipitator (ESP) for particulate control and exhausted to the atmosphere through a 46 m stack. Dust collected by the ESP is defined as CKD. CKD from the first two ESP compartments is blown into the burning zone of the kiln; this is recirculated CKD. The remaining CKD is the wasted CKD. Temperatures in the kiln are typically in the ranges 1400–1650°C in the burning zone, 870–980°C in the chain section and 260–315°C at the inlet to the ESP. Overall, gas-residence time in the kiln is 5–10 s.

#### 4. Metal outputs under steady state conditions

##### 4.1. Governing equations for mass balance under steady state conditions

The principle of conservation of mass requires that, under steady state conditions, the sum of inputs to a system equals the sum of outputs. Governing equations for the mass balance are listed below. In these equations,  $m$  stands for the mass input or output rate;  $ME$  stands for the input or output rate for each individual metal; the subscripts hwf, coa, raw, emi, clk, ckd, ckdr, and ckdw stand for HWF, coal, raw material, stack emissions, clinker, total CKD, recirculated CKD and wasted CKD, respectively.

The global mass balance for the kiln system (Fig. 1) is governed by the following equation

$$m_{\text{hwf}} + m_{\text{coa}} + m_{\text{raw}} = m_{\text{ckdw}} + m_{\text{emi}} + m_{\text{clk}} \quad (1)$$

The global mass balance for each individual metal is

$$ME_{\text{hwf}} + ME_{\text{coa}} + ME_{\text{raw}} = ME_{\text{ckdw}} + ME_{\text{emi}} + ME_{\text{clk}} \quad (2)$$

The local mass balance for CKD about the ESP (Fig. 1) is

$$m_{\text{ckd}} = m_{\text{ckdw}} + m_{\text{ckdr}} \quad (3)$$

The local mass balance for each individual metal in CKD is

$$ME_{\text{ckd}} = ME_{\text{ckdw}} + ME_{\text{ckdr}} \quad (4)$$

##### 4.2. Definitions of process and operational parameters

Dellinger et al. [2] developed empirical models, based on the principle of mass conservation, to examine the influence of several process and operational parameters on the emissions of metals from two different kiln types. However, some process and operational parameters in their models, such as those measuring the entrainment rate of solids and the extent of vaporization, cannot be defined with the data available in the CoC reports. Therefore, simplified process and operational parameters are defined herein.

The distribution ratio for metal output to total CKD is defined as

$$R_{\text{ckd}} = \frac{ME_{\text{ckd}}}{ME_{\text{hwf}} + ME_{\text{coa}} + ME_{\text{raw}} + ME_{\text{ckdr}}} \quad (5)$$

The denominator is the total, local feed rate of each metal to the cement kiln (Fig. 1) and the numerator is the collection rate of each metal in the total CKD.

The distribution ratio for metal output to stack emissions is defined as

$$R_{\text{emi}} = \frac{ME_{\text{emi}}}{ME_{\text{hwf}} + ME_{\text{coa}} + ME_{\text{raw}} + ME_{\text{ckdr}}} \quad (6)$$

The distribution ratio for metal output to clinker is defined as

$$R_{\text{clk}} = \frac{ME_{\text{clk}}}{ME_{\text{hwf}} + ME_{\text{coa}} + ME_{\text{raw}} + ME_{\text{ckdr}}} \quad (7)$$

The CKD mass recirculation ratio is defined as

$$rm_{\text{ckdr}} = \frac{m_{\text{ckdr}}}{m_{\text{ckd}}} \quad (8)$$

The CKD metal recirculation ratio is defined as

$$RC_{\text{ckdr}} = \frac{ME_{\text{ckdr}}}{ME_{\text{ckd}}} \quad (9)$$

#### 4.3. Equations for predicting metal outputs under steady state conditions

If the distribution ratios and the CKD mass and metal recirculation ratios for a kiln are constant, explicit equations can be derived to predict all three metal outputs for any HWF feed rate. Combining Eqs. (4) and (5) and solving for  $ME_{\text{ckdw}}$  gives

$$ME_{\text{ckdw}} = R_{\text{ckd}}(ME_{\text{hwf}} + ME_{\text{coa}} + ME_{\text{raw}}) - (1 - R_{\text{ckd}})M_{\text{ckdr}} \quad (10)$$

Combining Eqs. (5) and (9) and solving for  $ME_{\text{ckdr}}$  give

$$ME_{\text{ckdr}} = (ME_{\text{hwf}} + ME_{\text{coa}} + ME_{\text{raw}}) \frac{RC_{\text{ckdr}}R_{\text{ckd}}}{1 - RC_{\text{ckdr}}R_{\text{ckd}}} \quad (11)$$

Substituting Eq. (11) into Eq. (10) and collecting terms, a predictive equation for wasted CKD is obtained

$$ME_{\text{ckdw}} = (ME_{\text{hwf}} + ME_{\text{coa}} + ME_{\text{raw}}) \frac{(1 - RC_{\text{ckdr}})R_{\text{ckd}}}{1 - RC_{\text{ckdr}}R_{\text{ckd}}} \quad (12)$$

If  $ME_{\text{ckdw}}$  and the mass output rate of wasted CKD ( $m_{\text{ckdw}}$ ) are known, the concentration of each metal in wasted CKD is

$$C_{\text{ckdw}} = \frac{ME_{\text{ckdw}}}{m_{\text{ckdw}}} \quad (13)$$

Substituting Eq. (11) into Eq. (6) the following equation is obtained to predict the output rate of each metal from stack emissions

$$ME_{emi} = (ME_{hwf} + ME_{coa} + ME_{raw}) \frac{R_{emi}}{1 - R_{ckd}RC_{ckr}} \quad (14)$$

If  $ME_{emi}$  and the gas flow rate are known, the concentration of each metal can be computed.

The following equation can be derived, by substituting Eq. (11) into Eq. (7) and the definition of concentration, to predict the concentration of each metal in clinker ( $C_{clk}$ )

$$C_{clk} = \left( \frac{ME_{hwf} + ME_{coa} + ME_{raw}}{m_{clk}} \right) \left( \frac{R_{clk}}{1 - R_{ckd}RC_{ckdr}} \right) \quad (15)$$

#### 4.4. Analysis of data at the final steady state of an equilibration test

Feed and output rates of mass and metals for the kiln were not explicitly given for the final steady state of the equilibration test in the report [6]. However, according to the compliance-test protocol, they should be the same as those during the CoC test. Table 1 lists all relevant values either reported directly in the original CoC test data sheets or computed from the data sheets. Specific locations of CoC data are also given in Table 1. Those CoC test data, except the output rate of metal in wasted CKD (Table 1, column 6, rows 4–8), were used for the analysis of the final steady state of the equilibration test.

The output rate of metal in wasted CKD ( $ME_{ckdw}$ ) can be calculated by rearranging Eq. (13) if  $C_{ckdw}$  and  $m_{ckdw}$  are known. For the final steady state of the equilibration test, the mass output rate of wasted CKD from the CoC test and the metal concentration of wasted CKD from the final steady state of the equilibration test are used. Thus

$$ME_{ckdw}^{equ} = m_{ckdw}^{coc} C_{ckdw}^{equ} \quad (16)$$

where  $ME_{ckdw}^{equ}$  is the calculated output rate of metal which is wasted through CKD at the final steady state of the equilibration test (Table 1, column 6, rows 4–8 in parentheses),  $m_{ckdw}^{coc}$  is the mass rate of wasted CKD during the CoC test (Table 1, column 6, row 2), and  $C_{ckdw}^{equ}$  is the measured concentration of wasted CKD at the final steady state of the equilibration test (Table 2, right-hand column).

The output rate of metal in wasted CKD calculated for the final steady state of the equilibration test ( $ME_{ckdw}^{equ}$ ) is different from that reported for the CoC test because metal concentrations in wasted CKD reported in the two tests are not identical, although in theory they should be the same. The concentrations of each metal in wasted CKD from the CoC test (steady state) and from the final steady state of the equilibration test are listed in Table 2. The disagreement might have been caused by differences in metal feed rates; however, the differences are not consistent with the operation of the mechanical metal feed systems. Arsenic and cadmium solutions were spiked together through one pump, and chromium and lead solutions were spiked together through another pump. If the reason for the difference is contrasting feed rates, the As concentration from the equilibration test should not be smaller than that from the CoC test, where the Cd concentration from the equilibration test exceeds the CoC test value. Furthermore, if

Table 1  
Measured data from certification of compliance test (steady state) on May 5, 1992, Continental Cement Company, Hannibal, MO

(1)	HWF (2)	Coal(3)	Raw material(4)	Recirculated CKD(5)	Wasted CKD(6)	Stack emissions(7)	Clinker(8)
Mass feed or production rate/(Mg h <sup>-1</sup> )(2)	14.5 <sup>b</sup>	5.23 <sup>a,c</sup>	132 (dry) <sup>b</sup>	10.9 <sup>b</sup>	16.3 <sup>a,c</sup>	N/A	69.6 <sup>a,c</sup>
Thermal feed rate/(10 <sup>9</sup> J h <sup>-1</sup> )(3)	383 <sup>a,b</sup>	106 <sup>a,c</sup>	N/A (small)	N/A	N/A	N/A	N/A
As/(g h <sup>-1</sup> )(4)	9430 <sup>c</sup>	19.8 <sup>c</sup>	54.9 <sup>c</sup>	1230 <sup>a,b</sup>	2150 <sup>c</sup> (1460 <sup>d</sup> )	0.622 <sup>c</sup>	7040 <sup>c</sup>
Be/(g h <sup>-1</sup> )(5)	1190 <sup>c</sup>	11.9 <sup>c</sup>	79.0 <sup>c</sup>	56.8 <sup>a,b</sup>	117 <sup>c</sup> (140 <sup>d</sup> )	0.403	611 <sup>c</sup>
Cd/(g h <sup>-1</sup> )(6)	7120 <sup>c</sup>	0.654 <sup>c</sup>	97.2 <sup>c</sup>	1950 <sup>a,b</sup>	4570 <sup>c</sup> (6400 <sup>d</sup> )	41.5 <sup>c</sup>	120 <sup>c</sup>
Cr/(g h <sup>-1</sup> )(7)	43700 <sup>c</sup>	87.6 <sup>c</sup>	2130 <sup>c</sup>	3600 <sup>a,b</sup>	6220 <sup>c</sup> (6650 <sup>d</sup> )	19.6 <sup>c</sup>	33600 <sup>c</sup>
Pb/(g h <sup>-1</sup> )(8)	46300 <sup>c</sup>	54.0 <sup>c</sup>	468 <sup>c</sup>	15500 <sup>a,b</sup>	33000 <sup>c</sup> (44500 <sup>d</sup> )	283 <sup>c</sup>	855 <sup>c</sup>

N/A: not available.

<sup>a</sup> From Table 2.1 in CoC report [6].

<sup>b</sup> From Table 7.1 in CoC report [6].

<sup>c</sup> From Table 8.2.1 in CoC report [6] (medium values are used).

<sup>d</sup> Computed for final steady state of the equilibration test (see text).

Table 2

Measured metal concentrations of wasted CKD from certification of compliance test (steady state) on May 5, 1992 and equilibration test (final steady state) on May 4, 1992, Continental Cement Company, Hannibal, MO

Metal	CoC test (steady state) <sup>a</sup>	Equilibration test (final steady state) <sup>b</sup>
arsenic/ppm	132	90
beryllium/ppm	7.21	8.6
cadmium/ppm	281	394
chromium/ppm	383	409
lead/ppm	2030	2740

<sup>a</sup> From Table 2.1 in CoC report [6].

<sup>b</sup> From Table 7.2 and associated graphs in CoC report [6].

caused by a feed rate difference, Cr and Pb concentrations should increase proportionately. Thus, the concentration differences cannot be reconciled.

The data in Table 1 are used to evaluate the global mass balance for each individual metal as expressed by Eq. (2). Total input rates (the sum of values in columns 2, 3, and 4) of As, Be, Cd, Cr, and Pb are 9500, 1280, 7220, 45 900, and 46 800 g h<sup>-1</sup>, respectively. These are in comparison with the total output rates (the sum of values in columns 6, 7, and 8), 8500, 751, 6560, 40 300, and 45 600 g h<sup>-1</sup>, respectively. Total input rates for As, Be, Cd, Cr, and Pb exceed output rates by 11.8%, 70.4%, 10.1%, 13.9%, and 3.0%, respectively. These discrepancies may result in part from the chemical analytical methods used. The acid digestion method used to determine the metal content of solids (EPA SW-846, method 3050 or 3051) is not aggressive enough to extract all metals from certain solids [8]. In contrast, the metals are spiked to the kiln in solution, whereby they will be bound much less strongly. X-ray fluorescence (XRF) spectrometry is probably a more accurate method for determining total metal contents of silica-rich solids.

Nevertheless, the data in Table 1 can be used to calculate the process and operational parameters defined above. All three computed distribution ratios (Eqs. (5)–(7)) for As, Be, Cd, Cr, and Pb are listed in Table 3. The variations of these distribution ratios are in agreement with the contrasting volatilities of the metals considered. Cd and Pb exhibit intermediate volatility, and thus are distributed strongly to the CKD. As, Be, and Cr are refractory, and are thus distributed strongly to the clinker. The smallest portion of each metal is discharged from stack emissions, because none of them are highly volatile. The sum of the three distribution ratios in Table 3 is not equal to one, as the measured metal input and output are not balanced, as discussed above. The CKD mass recirculation ratio (Eq. (8)) and the CKD metal recirculation ratios (Eq. (9)) for each metal are listed in Table 3. The distribution ratios calculated herein are relevant to the kiln considered with the fixed metal recirculation ratio.

#### 4.5. Verification of predicted metal concentrations of wasted CKD at the initial steady state of the equilibration test.

The available data can be used to evaluate the constancy of CKD distribution ratios at different metal feed rates. This constancy is critical to predictions of CKD metal



Table 3

Distribution ratios for metal outputs from CKD, stack emissions and clinker and CKD recirculation ratios at final steady state of equilibration test on May 4, 1992, Continental Cement Company, Hannibal, MO

Metal	Relative volatility	CKD distribution ratio	Stack emission distribution ratio	Clinker distribution ratio	CKD metal recirculation ratio <sup>a</sup>
arsenic	refractory	0.251	0.0000620	0.656	0.457
beryllium	refractory	0.147	0.000301	0.457	0.290
cadmium	intermediate	0.911	0.00452	0.0131	0.233
chromium	refractory	0.206	0.000395	0.679	0.351
lead	intermediate	0.956	0.00451	0.0137	0.258

<sup>a</sup> CKD mass recirculation ratio (Eq. 8) is 0.402.

concentrations at alternative feed rates. Eqs. (12) and (13) are applied to predict metal concentrations in wasted CKD at the initial steady state of the equilibration test. The distribution ratios and the metal recirculation ratio of CKD at the initial steady state are assumed to be the same as those at the final steady state (Table 3). Metal feed rates at the initial steady state of the equilibration test (Table 4) are equal to those at the final steady state (Table 1, column 2, rows 4–8) minus the metal spike rates. The metal feed rates from coal and raw material at the initial steady state (Table 4) are assumed to be the same as those in the CoC test (Table 1, columns 3 and 4), since they should be equivalent. Eqs. (12) and (13) are used to predict the metal output rates and concentrations, respectively, in wasted CKD. The mass production rate of wasted CKD at the initial steady state is assumed to be the same as that at the final steady state (Table 1, column 6, row 2); this assumption appears reasonable, as the mass of CKD wasted is dependent primarily on the raw material mass feed rate, which is expected to remain the same.

Predicted metal concentrations of wasted CKD at the initial steady state of the equilibration test, along with measured values, are given in Table 4. The predicted and measured metal concentrations of wasted CKD are similar, especially for metals of intermediate volatility (cadmium and lead). This comparison supports the assumption

Table 4

Predicted and measured metal concentrations of wasted CKD at the initial steady state of the equilibration test on May 4, 1992, Continental Cement Company, Hannibal, MO

Metal	HWF metal feed rate/ (g h <sup>-1</sup> ) <sup>b</sup>	Coal metal feed rate/ (g h <sup>-1</sup> ) <sup>b</sup>	Raw material metal feed rate/(g h <sup>-1</sup> ) <sup>b</sup>	Predicted metal concentration of wasted CKD (ppm)	Measured metal concentration of wasted CKD (ppm) <sup>a</sup>
arsenic	84.0	19.8	54.9	1.51	2.30
beryllium	13.0	11.9	79.0	0.697	0.852
cadmium	73.0	0.654	97.2	9.32	8.84
chromium	3890	87.6	2130	54.3	38.6
lead	5810	54.0	468	368	386

<sup>a</sup> From Table 7.2 and associated graphs in CoC report [6].

<sup>b</sup> From Table 8.2.1 in CoC report [6].

that distribution ratios are constant at widely varying HWF feed rates, for this particular kiln at a fixed metal recirculation ratio. Thus, Eqs. (12) and (13) are verified to predict accurately metal concentrations of wasted CKD at widely varying HWF feed rates.

#### 4.6. Prediction of wasted CKD metal concentrations for burning fossil fuel only

Wasted CKD metal concentrations also can be predicted for a case in which only fossil fuel is used to fire the kiln. Eqs. (12) and (13) are used for these predictive calculations. In Eq. (12), the metal feed rates from HWF ( $ME_{\text{hwf}}$ ) are set equal to zero; the metal feed rates of raw materials ( $ME_{\text{raw}}$ ) are assumed equal to those at the initial steady state (Table 4). However, the metal feed rates from coal ( $ME_{\text{coa}}$ ) must be increased. Additional coal is required to create a thermal input to the kiln identical to that at the initial steady state of the equilibration test, conditions near which the kiln is normally operated [6].

The following equation is used to compute the required increase in the coal mass feed rate

$$\Delta m_{\text{coa}} = \Delta m_{\text{hwf}} \frac{\text{Thermal energy per unit mass of HWF}}{\text{Thermal energy per unit mass of Coal}} \quad (17)$$

Here,  $\Delta m_{\text{coa}}$  is the required increase in coal mass feed rate to maintain an equivalent thermal feed rate with a reduction in the HWF mass feed rate ( $\Delta m_{\text{hwf}}$ ). For the case considered, the mass feed of HWF is completely eliminated; thus, the mass feed reduction ( $\Delta m_{\text{hwf}}$ ) is the same as the HWF mass feed rate at the initial steady state. The HWF mass feed rate at the initial steady state is assumed to be the same as that at the final steady state (Table 1, column 2, row 2), as the metal spiking solution of the equilibration test contributed minimal additional mass. Thermal energy per unit mass of HWF and thermal energy per unit mass of coal are computed from values in Table 1.

The increases in metal feed rates from coal ( $\Delta ME_{\text{coa}}$ ) are equal to the product of the required increase in the coal mass feed rate ( $\Delta m_{\text{coa}}$ ) and the concentration of the metal

Table 5

Predicted metal concentrations of wasted CKD if kiln is not using hazardous waste fuels, Continental Cement Company, Hannibal, MO

Metal	HWF metal feed rate/(g h <sup>-1</sup> )	Coal metal feed rate/(g h <sup>-1</sup> ) <sup>a</sup>	Raw material feed rate/(g h <sup>-1</sup> ) <sup>b</sup>	Predicted metal concentration of wasted CKD at zero HWF feed rate for the considered test period (ppm)	Range of measured metal concentration of wasted CKD at zero HWF feed rate for other two test periods (ppm) <sup>c</sup>
arsenic	0	91.0	54.9	1.32	ND–8.0
beryllium	0	54.6	79.0	0.868	0.27–0.70
cadmium	0	3.00	97.2	5.47	3.7–15.4
chromium	0	402	2130	22.3	14.8–39.0
lead	0	248	468	40.3	44.0–192

<sup>a</sup> Sum of that in Table 8.2.1 of CoC report [6] and that derived from additional coal feeds required for thermal input (see the text).

<sup>b</sup> From Table 8.2.1. of CoC report [6].

<sup>c</sup> From Appendix F of [7] for two five day test periods (August 30 to September 3, 1991 and July 3–7, 1992).

Table 6  
Comparisons of metal concentrations of wasted CKD at three different HWF feed rates to Continental Cement Company kiln, Hannibal, MO

Metal	Concentration at zero HWF feed rate (predicted)/ppm	Concentration at normal HWF feed rate (measured)/ppm	Concentration at maximum intended HWF feed rate (measured)/ppm	Concentration ratio (3)/(2)	Concentration ratio (4)/(2)
(1)	(2)	(3)	(4)	(5)	(6)
arsenic	1.32	2.30	90.0	1.7	68
beryllium	0.868	0.852	8.6	0.98	10
cadmium	5.47	8.84	394	1.6	72
chromium	22.3	38.6	409	1.7	18
lead	40.3	386	2740	9.6	68

in coal. The concentration of each metal in coal is calculated as  $ME_{\text{coa}}/m_{\text{coa}}$  from the values given in Table 1 (column 3, rows 2 and 4–8). The total thermal adjusted metal feed rates from coal are equal to the sum of the coal metal feed rate at the initial steady state (Table 4) and  $\Delta ME_{\text{coa}}$ . The CKD distribution ratios and metal recirculation ratios are assumed to remain the same; these assumptions are validated in Section 4.5. In Eq. (13), the mass production rate of wasted CKD is assumed to remain constant.

Predicted metal concentrations of wasted CKD, along with all external metal feed rates, are given in Table 5. These are obtained assuming the kiln is not burning HWF during the period considered: May 5–27, 1992. Wasted CKD was sampled and analyzed for metal concentrations during two other five day test periods (August 30–September 3, 1991 and July 3–7, 1992) during which no hazardous waste was burned [9]; the reported concentrations for these two other test periods are also given in Table 5. Predicted metal concentrations of wasted CKD fall either within or close to the range of measured values.

To illustrate the effect of burning HWF, metal concentrations of wasted CKD at three different HWF feed rates are listed together in Table 6. Also listed are ratios of wasted CKD metal concentrations at the two HWF burning levels over that for the coal-only burning condition. At the normal level of HWF feed, concentrations of As, Be, Cd, Cr, and Pb in wasted CKD are up to 9.6 times those when only coal is burned. When the kiln is burning the maximum intended amount of HWF, concentrations of As, Be, Cd, Cr, and Pb in wasted CKD are up to 68 times those when only coal is burned.

## 5. Metal outputs under non-steady state conditions

### 5.1. Governing equation for metal balance under non-steady state conditions

Metal balance for the kiln system under unsteady state conditions is governed by the following equation

$$\frac{dA_{\text{kiln}}}{dt} = ME_{\text{hwf}} + ME_{\text{coa}} + ME_{\text{raw}} - ME_{\text{ckdw}} - ME_{\text{emi}} - ME_{\text{clk}} \quad (18)$$

where  $A_{\text{kiln}}$  is the total amount of each metal in the kiln system (kiln, ESP, CKD

recirculation pipe, etc.) at any time,  $t$  is the time, and terms on the right-hand side are defined above. The left-hand side represents the time rate of change of the total amount of each metal in the kiln system, and the right-hand side represents the difference between the metal feed and the output rates for the kiln system. The same definitions of process and operational parameters apply for non-steady state conditions.

### 5.2. Solutions to the governing equation

The process of kiln equilibration is a non-steady state process when the HWF feed rate is increased from a lower level to a higher level within some time interval. This produces CKD concentrations that, overall, increase with time (e.g., Fig. 2). The HWF feed rate is assumed to increase linearly from a low level to a high level as expressed by the following functions

$$ME_{\text{hwf}} = ME_{\text{hwf1}}, \text{ for } 0 \leq t \leq t_1 \quad (19)$$

$$ME_{\text{hwf}} = ME_{\text{hwf1}} + \frac{\Delta ME_{\text{hwf}}}{\Delta T} (t - t_1), \text{ for } t_1 < t < (t_1 + \Delta T) \quad (20)$$

$$ME_{\text{hwf}} = ME_{\text{hwf2}}, \text{ for } t \geq (t_1 + \Delta T) \quad (21)$$

where  $ME_{\text{hwf}}$  is the HWF metal feed rate at any time,  $ME_{\text{hwf1}}$  is the HWF metal feed rate at the initial steady state of the equilibration test,  $ME_{\text{hwf2}}$  is the HWF metal feed rate at the final steady state of the equilibration test,  $t$  is the time, and  $\Delta T$  is the time interval during which the HWF feed rate is increasing (step rising) from one constant level,  $M_{\text{hwf1}}$ , to another constant level,  $M_{\text{hwf2}}$ . A time variation of the lead external

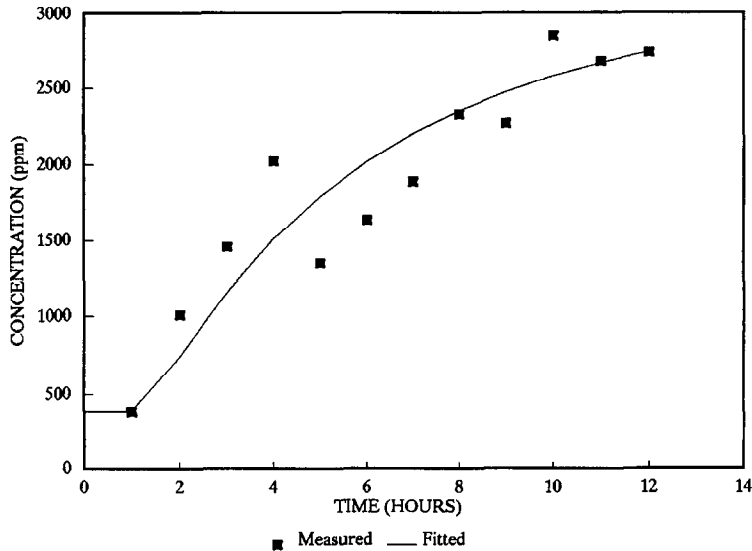


Fig. 2. Measured and fitted time variation of lead concentration in wasted CKD; May 4, 1992 kiln equilibration test.

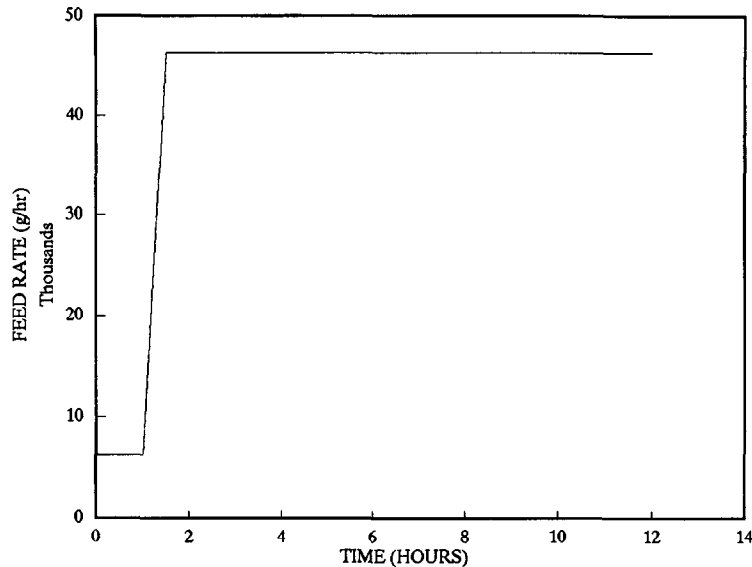


Fig. 3. Time variation of lead external feed rate (HWF, coal, and raw material) to cement kiln with an assumed step rise time interval of 0.5 h. The feed rate increase represents the process of introducing the metal spike.

(global) feed rate is shown in Fig. 3, in which the external feed rate of lead is assumed to increase from a lower to a higher level linearly within one half hour. The two constant external feed rates of lead shown in Fig. 3, at the initial and final steady states of the equilibration test, include all external sources: HWF, coal, and raw material.

The complete solution to Eq. (18) will give the time variations of all metal output rates from the kiln system and the time change of the amounts of metals which are accumulated in the kiln system. For the complete solution, either the metal input and output rates during the non-steady state process (right-hand side of Eq. (18)) or the rates at which metals accumulate in the kiln system (left-hand side of Eq. (18)) are needed. Information sufficient to define uniquely either side of Eq. (18) is not available; thus, a complete solution to Eq. (18) is not possible. To obtain a solution to Eq. (18), metals in the kiln are assumed not to accumulate, i.e., the left-hand side of Eq. (18) is equal to zero. Under this assumption, the total metal output from the kiln is equal to the total metal input to the kiln at any instant, even though the external metal feed rate is changing with time.

The lead concentrations in wasted CKD measured during the equilibration test are shown in Fig. 2. The time variation of the lead concentration of wasted CKD is fitted as follows

$$C_{\text{ckdw}} = C_1, \text{ for } t \leq 1.0 \text{ h} \quad (22)$$

$$C_{\text{ckdw}} = C_0 + (C_{\text{max}} - C_0)e^{-k/t}, \text{ for } t > 1.0 \text{ h} \quad (23)$$

where  $C_1$  is set to be the same as that at the initial steady state of the equilibration test (= 386 ppm, the first measured data point in Fig. 2);  $C_0$ ,  $C_{\text{max}}$ , and  $k$  are fitted to be

340 ppm, 3790 ppm, and 4.32 h, respectively. This form of regression function typically is used by kiln operators during an equilibration test to determine the ultimate, equilibrium concentration of CKD. By visually inspecting the measured lead concentrations in Fig. 2 (especially the last three measured data points), the lead concentration of wasted CKD at the final steady state of the equilibration test is estimated to be 2740 ppm (the last measured data point in Fig. 2 and listed in Table 2, right-hand column). This value is smaller than that of the fitted ultimate concentration ( $C_{\max}$ ). However, the values of fitted parameters ( $C_0$ ,  $C_{\max}$ , and  $k$ ) are dependent on the type of function chosen for the fitting. Thus, values of fitted parameters may not have unambiguous physical meanings.

Under the above no-accumulation assumption, Eq. (18) is simplified by setting the left-hand side equal to zero. If the very small output from stack emissions is neglected and the fitted metal output rate of wasted CKD is used, the metal incorporated into clinker can be predicted using the simplified Eq. (18) for the case of no metal accumulation in the kiln. For the lead external feed rate in Fig. 3, the predicted clinker concentration is shown in Fig. 4. For another lead external feed rate (Fig. 5), the predicted clinker concentration is shown in Fig. 6. The difference between these two lead external feed rates is the assumed step rise time interval ( $\Delta T$ ) over which the HWF spiking rate increases from one level to another; the assumed time intervals are 0.5 h and 6 h, respectively. For both time intervals used, the predicted lead concentrations of clinker in the intermediate, non-steady state process are much greater (17 and 4 times, respectively) than those at the final steady state.

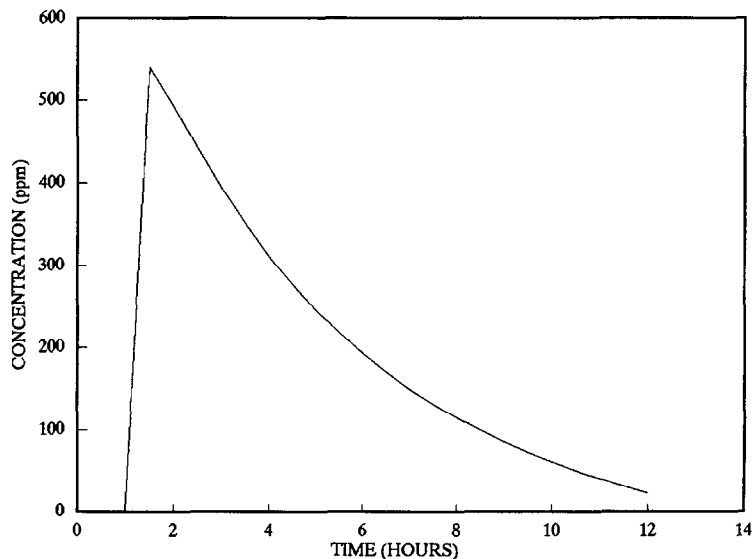


Fig. 4. Predicted time variation of lead concentration in clinker based on the lead external feed rate with an assumed step rise time interval of 0.5 h (Fig. 3) and on the fitted curve for wasted CKD concentrations in Fig. 2.

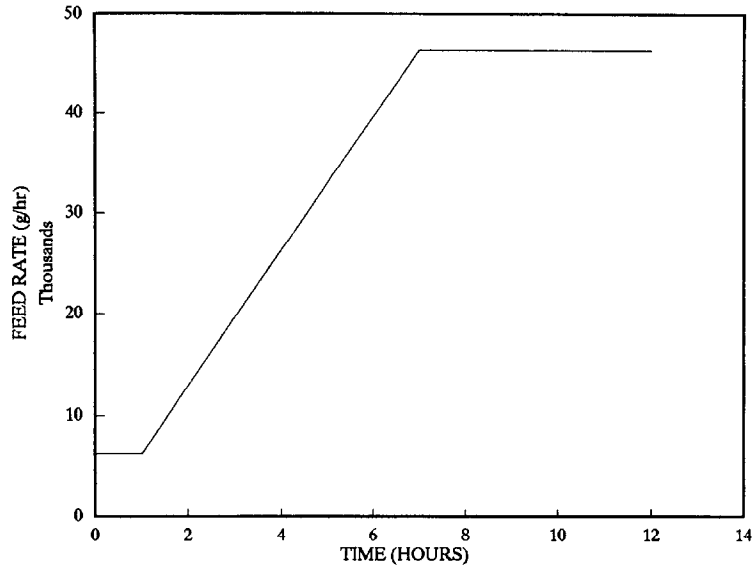


Fig. 5. Time variation of lead external feed rate (HWF, coal, raw material) to cement kiln with an assumed step rise time interval of 6 h. The feed rate increase represents the process of introducing the metal spike.

The assumed 0.5 h step rise time interval intuitively seems more realistic than the 6 h interval for the metal spiking operation. The assumed 6 h interval is used herein to compensate for the metal accumulation in the kiln. Metals fed into the kiln will either be

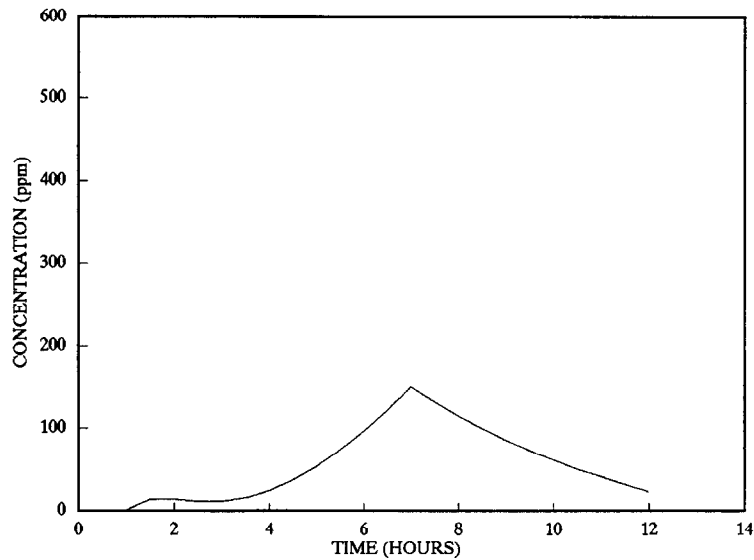


Fig. 6. Predicted time variation of lead concentration in clinker based on the lead external feed rate with an assumed step rise time interval of 6 h (Fig. 5) and on the fitted curve for wasted CKD concentrations in Fig. 2.

discharged directly (through stack emissions, CKD, and clinker) or accumulated (stored) in the kiln system (kiln, ESP, CKD recirculation pipe, etc.) for later discharge. As the discharge (output) through stack emissions is negligible and the output through wasted CKD is known, if the rest of metal that is fed into the kiln does not accumulate, it must be discharged into the clinker. If the metal is fed into the kiln too rapidly for the kiln system to store, the metal may be discharged through the nearest exit, the clinker exit, rather than distributed for discharge to stack emissions and wasted CKD. This could be a physical explanation for the higher metal concentration in clinker at intermediate times. No measured data are available to verify the predicted higher intermediate metal concentration. This result suggests that, during the equilibration test, metal outputs through not only stack emissions and wasted CKD, but also through clinker, should be monitored.

## 6. Discussion

For the Continental cement kiln considered in this study, using HWF is demonstrated to increase the contents of arsenic, cadmium, chromium, and lead in wasted CKD over those when the kiln is firing with only coal (Table 6). This results from the higher metal content per unit of thermal energy in HWF relative to fossil fuel. Based on the fuel information reported by CCC (Tables 1 and 4), for one billion joules (0.95 million BTUs), this HWF contains 0.22 g As, 0.034 g Be, 0.19 g Cd, 10 g Cr, and 15 g Pb, and this coal contains 0.19 g As, 0.11 g Be, 0.0062 g Cd, 0.83 g Cr, and 0.51 g Pb.

The Toxicity Characteristic Leaching Procedure (TCLP) is currently used to extract metal from wasted CKD to assess possible classification as a hazardous material, which would be regulated under RCRA Subtitle C. At the maximum HWF feed rate intended for future operation, the "total" acid-soluble concentrations of As, Be, Cd, Cr, and Pb in wasted CKD were measured to be 90 ppm, 8.6 ppm, 394 ppm, 409 ppm, and 2740 ppm, respectively (Table 2, right-hand column). No definitive correlation between the acid-soluble concentrations and the TCLP concentrations of these metals has been

Table 7

Projected TCLP concentrations of wasted CKD when kiln is using the maximum intended amount of HWF for future operation, Continental Cement Company, Hannibal, MO

Metal	Measured total conc. (acid-sol.)/ppm <sup>a</sup>	Mean ratio between TCLP and total conc. <sup>b</sup>	Projected mean TCLP conc./ppm	Maximum ratio between TCLP and total conc. <sup>b</sup>	Projected maximum TCLP conc./ppm	RCRA limit/ppm
arsenic	90	0.0037	0.33	0.01	0.90	5.0
beryllium	8.6	0.00062	0.0053	0.0028	0.024	0.007
cadmium	394	0.0028	1.1	0.014	5.5	1.0
chromium	409	0.0024	0.98	0.022	9.0	5.0
lead	2740	0.0008	2.2	0.0051	14	5.0

<sup>a</sup> From Table 7.2 and associated graphs in CoC report [6].

<sup>b</sup> Calculated from data in Ref. [3].



published previously [3]. However, the mean and maximum ratios of TCLP values to acid-soluble concentrations may be used to project TCLP concentrations of wasted CKD. This approach is intended, not as a rigorously supported method, but as an illustration to place the measured acid-soluble concentrations into a regulatory framework. These two ratios for each metal are based on an existing data set for CKD [3]; they are shown in Table 7. The maximum ratio for lead (0.0051 in Table 7) is obtained by dividing a measured TCLP concentration of 9.72 ppm by the corresponding measured acid-soluble concentration of 1910 ppm [3]. This maximum ratio is similar to the value of 0.0039 obtained by dividing 4.85 ppm (TCLP) by 1250 ppm (acid-soluble), values which are available from a separate data set [10].

None of the projected mean TCLP concentrations of metals in wasted CKD exceeds significantly the RCRA limits. However, the projected maximum TCLP concentrations of Be, Cd, Cr, and Pb would exceed significantly the RCRA limits. This behavior is in agreement with relative metal volatilities, whereby those metals of intermediate volatility would concentrate more strongly in the CKD. In addition, the TCLP may not be adequate for determining the maximum amounts of leachable metals from certain solids, especially from alkaline solids [8], and case-specific leaching procedures may be required [11]. Thus, these projected maximum TCLP concentrations could be of environmental concern regarding the disposal of wasted CKD in existing quarries or unlined landfills.

The very limited USEPA data [5] appear to indicate that using HWF in cement kilns increases not only metal contents, but also leachable amounts of metals in cement clinker. USEPA collected and analyzed seven clinker samples from kilns using HWF and nine samples from kilns using no HWF. More cement clinker samples must be collected and analyzed before any conclusions can be drawn about the impacts on clinker. In addition, in the present study, the possibility is raised that intermediate heavy metal concentrations in clinker might be much higher than those at the final steady state if metals are assumed not to accumulate in the kiln. Cement is widely used in applications that impact daily life. A number of concerns have been raised about the incorporation of heavy metals in clinker [12]. Of special concern is the use of cement with elevated heavy metal contents in drinking-water pipes. Case-specific leaching studies are also recommended for the use of cement products.

## 7. Conclusions

A set of measured data from a kiln equilibration test is analyzed for heavy metal outputs from a cement kiln co-fired with HWF. All three metal outputs, from stack emissions, CKD, and cement clinker, are considered. Distribution ratios for these three outputs are found to follow generally the relative volatilities of the individual metals. Furthermore, through analysis of two steady state conditions, the CKD distribution ratios for each metal, at either high or low HWF feed rates, are found to be essentially the same. Consequently, equations are derived for predicting heavy metal outputs at various HWF feed rates. The derived equations are applied to predict metal concentrations of wasted CKD when the kiln is using, no HWF, but a thermally equivalent amount of coal. Measured concentrations of arsenic, beryllium, cadmium, chromium, and lead in

wasted CKD, at the highest intended HWF feed rate to the kiln, are 68, 10, 72, 18, and 68 times those predicted for using no HWF.

In addition, the metal balance in the kiln under non-steady state conditions is analyzed. If metals are assumed not to accumulate in the kiln, the intermediate metal concentrations in cement clinker are predicted to be substantially higher than those at the final steady state. In conjunction with further studies of metal behavior in cement kilns, research is recommended on the leachability of heavy metals from CKD and from concrete products made with cement produced in HWF co-fired kilns.

## 8. Nomenclature

$A_{\text{kiln}}$	total amount of each metal in the kiln at any time
$C_{\text{ckdw}}$	concentration of each metal in wasted CKD
$C_{\text{clk}}$	concentration of each metal in clinker
$m_{\text{emi}}$	mass emission rate from stack
$m_{\text{ckd}}$	rate of total CKD mass which is collected by the ESP
$m_{\text{ckdr}}$	mass output rate of recirculated CKD
$m_{\text{ckdw}}$	mass output rate of wasted CKD
$m_{\text{clk}}$	mass production rate of clinker
$m_{\text{coa}}$	mass feed rate of coal
$m_{\text{hwf}}$	mass feed rate of HWF
$m_{\text{raw}}$	mass feed rate of raw material
$ME_{\text{emi}}$	output rate of each metal from the air emission stack
$ME_{\text{ckd}}$	collection rate of each metal in the total CKD by the ESP
$ME_{\text{ckdr}}$	recirculation rate of each metal in CKD to the kiln
$ME_{\text{ckdw}}$	output rate of each metal which is contained in wasted CKD
$ME_{\text{clk}}$	output rate of each metal which is contained in clinker
$ME_{\text{coa}}$	feed rate of each metal which is contained in coal
$ME_{\text{hwf}}$	feed rate of each metal which is contained in HWF
$ME_{\text{raw}}$	feed rate of each metal which is contained in raw materials
$R_{\text{emi}}$	distribution ratio for metal output from stack emissions
$R_{\text{ckd}}$	distribution ratio for metal output from CKD
$R_{\text{clk}}$	distribution ratio for metal output from clinker
$RC_{\text{ckdr}}$	CKD metal recirculation ratio
$rm_{\text{ckdr}}$	CKD mass recirculation ratio
$d$	differential
$T$	time
$t$	time
$\Delta$	variation

## Acknowledgements

This work was financially supported in part by the Association for Responsible Thermal Treatment (ARTT), Washington, DC. The authors acknowledge the assistance

of A.F. Moscati, Jr., who provided valuable discussions and all the CoC reports used in this study. Although the study was funded by ARTT, it does not necessarily reflect the views of ARTT and no official endorsement should be inferred.

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