

US EPA ARCHIVE DOCUMENT

CHAPTER THREE

CKD GENERATION AND CHARACTERISTICS

3.0 INTRODUCTION

Cement production processes in current use in the U.S. generate CKD as an intrinsic process residue. During cement production, kiln combustion gases flow countercurrent to the raw feed and exit the kiln under the influence of induced draft fans. The rapid gas flow and continuous raw feed agitation are turbulent processes that result in large quantities of particulate matter being entrained in the combustion gases. The entrained particulate matter (as well as various precipitates) is subsequently removed from the kiln exhaust gases by air pollution control equipment; this particulate matter constitutes CKD.

For purposes of this report, as discussed in greater detail later in this chapter, *gross CKD* constitutes the dust collected at the air pollution control device(s) (APCDs) associated with a kiln system. Gross CKD is generated as an inherent process residue at all cement plants, though the fate of this material varies by facility. After collection, gross CKD is either *recycled* back to the kiln system or removed from the kiln system as *net CKD*. Net CKD is either treated and returned to the kiln system, disposed in an on-site waste management unit, or sold or given away for beneficial use. Exhibit 3-1 illustrates the potential management pathways for gross CKD. Although a number of plants directly recycle all gross CKD back to the kiln system, most plants remove a significant quantity of CKD from the system, for subsequent treatment and recycle back into the kiln, disposal, or for beneficial use.

Although CKD generation is unavoidable, the amount and characteristics of the dust that is generated (and the degree to which it is recycled or reused) can be influenced by several factors. These factors include kiln type, cement production rate, raw feed material types and proportions, fuel type(s), and the types and numbers of APCDs employed. Through variations in these factors, many facilities recycle some portion of their generated dust back to the kiln. This chapter presents information on CKD generation rates and characteristics (including current recycling practices and limitations on CKD that is returned to the kiln system) and describes the physical and chemical characteristics of CKD. Finally, for the interest of the reader, this chapter also presents information on the characteristics of clinker materials.

3.1 CKD GENERATION

As mentioned above, gross CKD generation is defined in this report as the collection of dust via APCDs from cement kiln exhaust gases. This definition excludes that portion of generated CKD that passes the APCDs and exits the kiln system with the exhaust gases. Based on typical APCD efficiency standards, generally between 98 and 100 percent of all particulate matter is captured before exiting the kiln system.¹

¹ Engineering-Science, 1987. Background Information Document For The Development of Regulations To Control The Burning of Hazardous Wastes In Boilers and Industrial Furnaces. Vol. II: Industrial Furnaces. January, 1987. p. 3-47.

Exhibit 3-1

Flow Chart of Gross CKD Management Pathways

**Contains Data for
Postscript Only.**

Based on an extrapolation of the data supplied to EPA by respondents to the 1991 PCA Survey, which represents data from 64 percent of active U.S. cement kilns,² the U.S. cement industry generated an estimated 12.9 million metric tons (14.2 million tons) of gross CKD and 4.6 million metric tons of net CKD in 1990. Operators of U.S. kilns recycled about 8.3 million metric tons, or 64 percent, of the gross CKD. This section discusses how CKD is collected, provides information on plant level CKD generation rates, and finally, addresses factors that may affect gross CKD generation, recycling rates, and net CKD generation.

3.1.1 Dust Collection Devices

APCDs are used to limit dust emissions from the kiln system to the atmosphere. The combustion gases that exit the kiln consist primarily of carbon dioxide, water, fly ash (i.e., fine solid particles of ashes, dust, and soot from burning of fuels), sulfur, and nitrogen oxides. The components of these gases are derived from the combustion of fuels, contaminants (organic and inorganic) in the kiln solids, small particles of feed and clinker material, and (for wet kilns) slurry water. After passing through the air pollution control system, the remaining combustion gases, which are discharged through a stack, consist

² Operators of 144 kilns provide usable data in response to the PCA Survey; there are approximately 225 kilns in the U.S. industry.

primarily of carbon dioxide and water.³ Undesirable contaminants (in terms of clinker quality) may volatilize in the burning zone of the kiln and precipitate as alkalies, sulfates, and chlorine compounds to become part of the CKD.⁴

CKD as collected is a fine-grained, solid, highly alkaline material that is generated at a temperature near 1,482°C (2,700°F). These characteristics tend to limit the types of dust collection devices that can be used to control air pollutant emissions from cement kilns. For example, because its fine-grained nature (diameter ranging from near zero micrometers or microns [μm] to greater than 50 μm) allows CKD to be easily entrained in exhaust gases, settling chambers that rely on gravity to separate particulate matter from a gas stream can only be used as a primary dust collection device to remove coarse dust particles and, in general, must be combined with more complex devices such as fabric filters (i.e., baghouses) or electrostatic precipitators. Wet scrubbers, commonly used in many mineral processing industries, cannot be used in the cement industry because adding water to the captured CKD causes it to harden ("set up") due to its cementitious properties.

The predominant APCDs in use at cement plants are electrostatic precipitators (ESPs) and fabric filters arrayed in baghouses. Both are often preceded by one or more cyclones. Additional APCDs include gravity/inertial separators and granular bed filters. Dust collection systems at cement plants may involve a combination of the above units. These systems typically remove dust at an efficiency ranging from 98 to nearly 100 percent.⁵ Each of these technologies is described below in Exhibit 3-2 and is illustrated in Exhibit 3-3.

Dust collection systems are sensitive to the temperature of the inlet gases because very low or high temperatures may damage APCD components; the moisture and sulfur content of the gases require that the temperature be controlled within a set range. For example, moisture can condense in a baghouse or in an ESP when the temperature falls below the dewpoint of the gases. Such condensation can cause plugging problems and result in corrosion of the dust-collection equipment. A conservative minimum dust collector inlet temperature should be 176°C to allow for the additional temperature drop that may occur within a baghouse. At the other end of the range, the temperature of gases passing through most baghouses cannot exceed 299°C before damage to the filters occurs.⁶

Exhibit 3-4 summarizes the quantities of CKD collected in 1990 by APCD type among respondents to the 1991 PCA Survey. APCD types are characterized according to the four choices provided in the survey: baghouse, multiclone, ESP, or other APCD. Some respondents reported quantities for systems with two different APCD types. This exhibit shows that ESPs and baghouses in isolation are the predominant APCDs used by facilities. These two types of devices collected approximately 65 percent of the CKD generated by the 123 kilns for which survey responses are available. In contrast, 23 percent of the survey respondents collected CKD with a multiclone in combination with a baghouse in 1990. Other combinations accounted for the remaining 12 percent of the CKD collected. Very few survey respondents indicated "other" to describe their APC system.

³ Engineering-Science, 1987, *op. cit.*, p. 3-4.

⁴ Kohlhaas, B., *et al.*, 1983. *Cement Engineer's Handbook*. Bauverlag GMBH, Wiesbaden and Berlin. p. 624.

⁵ Engineering-Science, 1987, *op. cit.*, pp. 3-47 and 3-49.

⁶ Peray, Kurt E., 1986. *The Rotary Cement Kiln*. Chemical Publishing Co., Inc. New York, NY. p. 172.

Exhibit 3-2**Air Pollution Control Devices Used at Cement Kilns^{a,b}**

APCD	Description
<i>Electrostatic Precipitators</i>	One or more high intensity electrical fields are generated and cause particles to acquire an electrical charge. These charged particles migrate to a collecting surface that has the opposite electrical charge. The collecting surface may be wet or dry. Facility operators then retrieve the captured CKD. One advantage of this technology is that flow is not restricted during collection. Collection efficiencies can be as high as 99.75 percent.
<i>Fabric Filters</i>	Filters remove particulate matter from gas streams by retaining the particles in a porous structure, and are typically used in series to form a baghouse. The porous structure is generally a woven or felt fabric with a retention efficiency that improves as the interstices fill with captured dust, but with the negative effect of increased flow resistance. Thus, regular filter cleaning is required to maintain efficiency. Baghouse filters can also be constructed of siliconized glass fibers (i.e., fiberglass). Fabric filters can remove submicron-sized particles at collection efficiencies as high as 99.95 percent.
<i>Cyclones</i>	A vortex within a collector propels particles to deposition areas for removal. Cyclones may be operated either wet or dry. They deposit the collected particulate matter into a hopper for eventual collection. Cyclones have collection efficiencies that range from 58 to 97 percent. Multiple cyclones used as part of one unit are referred to as multiclones. Multiclones have collection efficiencies that range from 85 to 94 percent for dust particles with diameters of 15 to 20 microns.
<i>Gravity/Inertial Separators</i>	These devices collect particulate matter by gravity or centrifugal force, but do not depend upon a vortex as do cyclones. Examples include settling chambers, baffled chambers, louvered chambers, and devices in which the gas and particulate mixture passes through a fan. In general, collectors of this type are of relatively low collection efficiency and are frequently followed by other types of collectors. Gravity settling chambers remove coarse dust particles at collection efficiencies ranging from 30 to 70 percent.
<i>Granular Bed Filters</i>	Dust is captured and bound on a porous medium through the principle of adsorption. The most commonly used medium is granular activated carbon (GAC). Collection efficiencies have been reported to be as high as 99.9 percent.

^a Kohlhaas, B., *et al.*, 1983. *Cement Engineer's Handbook*. Bauverlag GMBH, Wiesbaden and Berlin. p. 635.

^b Duda, W.H., 1976. *Cement-Data-Book: International Process Engineering in the Cement Industry*. Bauverlag GMBH Wiesbaden and Berlin, pp. 403-417.

Exhibit 3-3

Schematic Diagrams of Common Types of Air Pollution Control Devices

Exhibit 3-3 (continued)

Schematic Diagrams of Common Types of Air Pollution Control Devices

Exhibit 3-4

1990 Gross CKD Collection by Different Types of Air Pollution Control Devices^a

APCD	No. of Facilities with APCD Type	Percent of Facilities	Gross CKD Generation ^b (Metric Tons)			
			CKD Collected	Cumulative CKD Collected	Percent of Total CKD Collected ^c	Cumulative Percent Collected
ESP	37	50.7	3,578,934	3,578,934	41.1	41.1
Baghouse	19	26.0	1,662,784	5,241,718	19.1	60.2
Multiclone with Baghouse	7	9.6	2,128,021	7,369,739	24.4	84.6
Baghouse with ESP	5	6.8	678,642	8,048,381	7.8	92.4
Multiclone with ESP	4	5.5	552,804	8,601,185	6.3	98.7
Baghouse and Other	1	1.4	112,945	8,714,130	1.3	100.0
Total	73	100.0	8,714,130	8,714,130	100.0	100.0

^a Based on the usable responses from 73 facilities reported in the PCA Surveys.

^b This exhibit presents only APCD collection quantities, while the remainder of this chapter considers only quantities of CKD reported as gross or generated CKD. A number of facilities reported gross CKD generation rates that were different than the associated CKD collection rates reported for the APCDs.

^c (Collected CKD by given APCD) ÷ (Total CKD Collected) × 100

Responses in this category are either variations on one of the previously discussed APCDs (e.g., cyclones as opposed to multiclones) or consist of uncommon APCDs (e.g., fallout chambers).

3.1.2 Plant-Level CKD Generation Rates

To better understand the nature of contemporary CKD practices, EPA has performed an extensive evaluation of plant-level gross and net CKD generation rates. Any significant patterns with respect to CKD generation and in-line recycling could have important implications with respect to EPA's analysis of the adequacy of current management practices and the feasibility of CKD management alternatives.

As stated previously, CKD generation rates vary widely among facilities on both a gross and net basis. These rates do not, however, necessarily vary in direct proportion with one another. A scatter plot of gross versus net CKD generation for plants responding to the 1991 PCA Survey is presented in Exhibit 3-5. As this exhibit demonstrates, there is no clear, apparent relationship between the amount of gross CKD generated and the amount of net CKD generated, even within a given process type. Facilities that generate large quantities of gross CKD do not necessarily generate large amounts of net CKD. Conversely, a facility may generate moderate quantities of CKD on a gross basis, but may be one of the larger net CKD generators by virtue of the fact that it recycles none of its

Exhibit 3-5

Relationship Between Net and Gross CKD Generated in 1990

**Contains Data for
Postscript Only.**

Source: 1991 PCA Survey Responses.

Note: For clarity of presentation, available data on the LaFarge Corporation, Alpena facility was excluded from the above exhibit because it was an outlier. In 1990, this facility generated about 650 thousand metric tons of gross CKD and about 430 thousand metric tons of net CKD.

CKD. Therefore, gross CKD generation rate is not an accurate indicator of the magnitude of waste management issues at individual cement facilities.

In comparison with the other kiln types, operators of preheater/precalciner kilns recycle higher percentages of the gross CKD that they generate; this difference is especially apparent at the higher gross CKD generation rates (i.e., more than 200,000 metric tons per year). Moreover, while there is a considerable amount of scatter in the data, it appears that at lower gross CKD generation rates (less than 200,000 metric tons per year), the distribution of points corresponding to both the wet and the preheater/precalciner plants follows one of two patterns: 1) the points fall along the X-axis (net CKD is zero or close to zero); or 2) the points fall along a diagonal line (net CKD equals or is close to gross CKD), meaning that recycled CKD is or is close to zero. Plants operating long dry kilns, in contrast, are more difficult to categorize with respect to CKD generation trends.

To further examine industry-wide CKD generation rates and trends, EPA analyzed CKD generation and management data comprising useable results from PCA Survey responses covering 79 active U.S. cement plants; the data obtained have been tabulated and, for purposes of presentation, split into ten groups of eight facilities.⁷ Exhibit 3-6 shows gross and net CKD generation for these groups arrayed in descending order, by net CKD generation. The top ten percent of facilities generated about 2.25 million metric tons of gross CKD in 1990, which was two to three times more than the gross CKD generated by any other group (except for the seventh decile), and was about 10 times higher than the gross CKD generated by the sixth decile. The gross CKD generation rates of the plants in the remaining groups do not differ markedly, with most generating between 0.5 and a little more than one million metric tons per year, with an average of about 700,000 metric tons per year.

It is apparent from the relative heights of the bars on the right half of the diagram that approximately one-half of all 79 plants in the sample directly recycle all, or almost all, of the gross CKD that they generate. In general, it also would appear, based upon an examination of the heights of the gross CKD bars of deciles 1-5 with those of deciles 6-10, that the gross CKD generation rates of the groups with very high aggregate recycling rates are comparable to those of the groups generating significant quantities of net CKD. Finally, it is clear that some facilities in all of these groups recycle significant quantities of CKD, due to the substantial differences in gross and net CKD generation rates in each group represented.

Plant-by-plant net CKD generation rates vary dramatically among facilities in the U.S. cement industry. The top ten facilities together accounted for over 50 percent of the total net CKD generated in 1990. In fact, the top three facilities alone accounted for close to 30 percent of the net CKD generated during this period. To determine whether the share of net CKD generated was simply a function of facility size or throughput, the Agency compared net CKD generation to clinker capacity. Exhibit 3-7 shows the share of total net CKD and clinker production capacity accounted for by each group of eight facilities. The top ten percent accounted for almost 47 percent of net CKD generated in 1990. Although as a group these facilities are also the top ten percent in terms of production capacity, they represent only about 15 percent of total industry capacity. In the remaining groups, no pattern with respect to net CKD generation and production capacity emerges. For example, the seventh decile represents close to 12 percent of capacity but only two percent of net CKD generation, whereas the second decile represents less capacity (9.4 percent) but accounts for a substantially larger share of net CKD generation (19.7 percent).

⁷ The last group contains only seven facilities.

Exhibit 3-6

Gross and Net CKD Generated (1990)

**Contains Data for
Postscript Only.**

Source: 1991 PCA Survey Responses.

Note 1: Data on gross CKD generated was not available for one data point in the fifth decile and one data point in the eighth decile. Therefore, the gross CKD indicated for these two deciles is the total generated at only seven of the eight facilities in each decile.

Note 2: The last decile contains only seven facilities.

Exhibit 3-7

Share of Net CKD Generated and Clinker Production Capacity (1990)

**Contains Data for
Postscript Only.**

Source: 1991 PCA Survey Responses.

Note 1: Data on clinker production capacity was not available for one data point in the third decile and one data point in the last decile.

Note 2: The last decile contains only seven facilities.

Exhibit 3-8 lists seven facilities whose share of net CKD generated in 1990 was three to four times higher than their share of clinker production capacity. All seven facilities, not surprisingly, fall in the top two deciles of net CKD generators. The facilities that display the sharpest difference between shares of clinker production capacity and net CKD generation are the LaFarge, Alpena, facility, which is also the largest generator of net and gross CKD, and the Holnam, Ada, facility. Five of the seven facilities in the exhibit have wet process kilns. With respect to fuel usage, there appears to be a fairly even distribution between hazardous and non-hazardous waste burners. Five of the seven facilities displayed in Exhibit 3-8 are Holnam facilities and the remaining two are owned by LaFarge Corporation.

Exhibit 3-8

Facilities With High Net CKD Generation Relative to Clinker Capacity

Facility	Share of Clinker Capacity (1)	Share of Net CKD Generated (2)	Ratio (2)/(1)	Fuel	Process
LaFarge, Alpena	3.28	13.50	4.12	H	Dry Long
Holnam, Holly Hill	2.15	8.11	3.77	H	Wet
Holnam, Clarksville	2.22	7.11	3.20	H	Wet
Holnam, Ada	1.06	4.50	4.25	N	Wet
Holnam, Florence	0.82	3.05	3.72	N	Wet
Holnam, Fort Collins	0.77	2.67	3.47	N	Dry PH/PC
LaFarge, Fredonia	0.65	2.11	3.25	H	Wet

Conversely, there are several facilities that generate little or no net CKD; however, these facilities account for a fairly large percentage (around two percent or more) of clinker capacity. The Kaiser Cement, Cupertino, facility accounted for 2.73 percent of total clinker capacity, yet generated almost zero percent of total net CKD in 1990. Most of these facilities operate dry kilns (usually preheater/precalciner kilns) and do not burn hazardous waste fuels.

Exhibit 3-9 provides information on the percentages of gross CKD that were recycled, sold, and wasted in 1990 for the ten groups of eight facilities, again arranged in descending order by net CKD generation rate. The percentage of gross CKD recycled in 1990 ranges from about 34 percent for the top net CKD generators all the way up to 100 percent. The percentage sold does not follow any discernible pattern and generally varies from zero to approximately 10 percent, with the marked exception of the sixth decile. The facilities in the sixth decile sold as much as 26.7 percent of the gross CKD they generated in 1990. The last three deciles, which consist of facilities that recycle large portions of their gross CKD, not surprisingly sell negligible quantities of CKD. Finally, the percentage of CKD wasted increased marginally from 53.7 percent in the top decile to 56.6 percent in the second decile and then decreased substantially in each decile, with the exception of the sixth, reaching zero in the tenth and final group.

Exhibit 3-9

Percentages of Gross CKD Recycled, Sold, and Wasted (1990)

**Contains Data for
Postscript Only.**

Source: 1991 PCA Survey Responses.

Note 1: Data on CKD recycled was not available for one data point in the fifth decile and one data point in the eighth decile.

Note 2: The last decile contains only seven facilities.

Finally, the Agency looked at percentages of CKD recycled at the plant level based on the individual kiln type and fuel usage. Of the 79 facilities for which PCA data are available, 48 operate dry kilns and the remaining 31 operate wet kilns. Of the 48 dry kiln facilities, 14 are equipped with dry long kilns and 34 with preheaters/precalciners (Ph/Pc).

Exhibit 3-10 summarizes recycling rates among the 48 facilities in EPA's data base that operate dry kilns. Hazardous waste burners in general do not appear to be recycling as much as non-hazardous waste burners, and operators of dry long kilns seem to recycle less than those operating Ph/Pc kilns. Low recycling rates, however, do not always imply that a large percentage of CKD is wasted. For example, the Heartland Cement Company's Independence facility, which operates a dry long kiln and burns hazardous waste, wastes only about 8.5 percent of the CKD it generates even though it recycles only around 37 percent. The facility sold close to 55 percent of the gross CKD it generated in 1990. Similarly, Southdown's Dixie facility, a hazardous waste burner operating a Ph/Pc kiln, sold 44 percent of its CKD in 1990 and wasted only 16 percent.

Exhibit 3-10

Recycling Rates Among Facilities That Operate Dry Kilns

Fuel Type	Number of facilities	Percent of CKD Recycled (Number of Facilities)		
		>50%	>90%	100%
Facilities That Operate Dry Long Kilns				
Hazardous Waste	5	2	1	0
Non-Hazardous Waste	9	6	3	1
All Fuels	14	8	4	1
Facilities That Operate Dry Ph/Pc Kilns				
Hazardous Waste	5	3	1	1
Non-Hazardous Waste	29	21	18	12
All Fuels	34	24	19	13
Facilities That Operate Dry Kilns (Long or Ph/Pc)				
Hazardous Waste	10	5	2	1
Non-Hazardous Waste	38	27	21	13
All Fuels	48	33	23	14

Note: Data are not available on one facility that operates dry long kilns and uses non-hazardous fuels and on one facility that operates dry Ph/Pc kilns and uses non-hazardous waste fuels.

Among facilities that burn non-hazardous waste fuels and operate Ph/Pc kilns, an interesting pattern can be observed. These facilities fall at one of two extremes -- they either recycle a large percentage or none of their gross CKD. In 1990, as shown in Exhibit 3-10 above, 18 of the 29 Ph/Pc plants for which data are available recycled over 90 percent of the gross CKD they generated, and three others recycled over 50 percent. In contrast, six of the remaining eight facilities recycled zero percent of the gross CKD they generated (though the operators of two facilities, LaFarge, Davenport and Monarch, Humboldt, each sold over 40 percent of their CKD).

Exhibit 3-11 summarizes recycling rates among the 31 facilities in EPA's data base that operate wet kilns. As shown in this exhibit, operators of facilities with wet kilns do not appear to recycle as much as dry kiln operators. The most glaring difference is the fact that no facilities that operate wet kilns recycle 100 percent of the CKD they generate. Among hazardous waste burners, only two of the eight facilities recycled over 50 percent of their CKD in 1990, and none recycled over 90 percent. The percentage of CKD wasted is high, with five of the eight facilities wasting over 50 percent of their CKD. Among the non-hazardous waste burners, 10 out of 23 recycled over 50 percent and three recycled over 90 percent. A total of six facilities sold over 40 percent of their CKD in 1990. The operator of the Holnam facility in Seattle recycled only about 51 percent of the CKD it generated, but sold the rest.

Exhibit 3-11

Recycling Rates Among Facilities That Operate Wet Kilns

Fuel Type	Number of facilities	Percent of CKD Recycled (Number of Facilities)		
		>50%	>90%	100%
Hazardous Waste	8	2	0	0
Non-Hazardous Waste	23	10	3	0
All Fuels	31	12	3	0

Finally, because of the observed wide variability in gross and net CKD generation rates, as well as the demographic characteristics (i.e., age distribution) of domestic cement kilns, EPA examined whether the age of individual cement kilns appears to influence the generation of CKD, on either a gross or net basis. The first step was to perform a simple linear correlation analysis of CKD generation and kiln age for the kilns within the sample of 79 cement plants providing useable data. The Agency conducted this test using all plants, then repeated the procedure separately for plants both burning and not burning hazardous waste fuels, and for wet and dry process kilns (i.e., the Agency conducted a set of five correlation analyses). Results of this exercise showed that for gross CKD generation, the correlation coefficients were negative and statistically significant at the 95 percent confidence level for all kilns, non-hazardous waste-burning kilns, wet process kilns, and dry process kilns; correlation coefficients for these groups ranged from -0.26 to -0.38. That is, the older kilns generate less gross CKD than the newer kilns, all else being equal. However, on a net CKD basis, no such relationship is apparent; no statistically significant correlation coefficients (at the 95 percent confidence level) were found within any of the five groups with respect to kiln age.

Because, as documented in Chapter 2, kiln capacity (and therefore, potential gross CKD generation) has increased over time, EPA proceeded to repeat the above analysis using CKD generation data that were normalized for clinker capacity. That is, we divided the per-kiln CKD generation rates by

reported kiln capacity to eliminate the potential effects of the trend toward larger cement kilns over the past few decades.⁸ Results of this exercise show that for both gross and net CKD, the normalized CKD generation rates are not related to kiln age for any of the five groups (i.e., none of the correlation coefficients are significantly different than zero). EPA therefore concludes that CKD generation is not related to kiln age, even if adjusted for fuel type or processing technology.

3.1.3 Quantities and Fate of CKD Generated

In an effort to further characterize the highly variable gross and net CKD generation rates described above, EPA conducted an analysis of potentially significant cement kiln design and operating variables. The two primary factors that are identified and examined in this section are kiln process type (wet or dry), and fuel type (i.e., whether the kiln is or is not fired with hazardous waste). As discussed earlier in this chapter, U.S. cement plants generated a total of about 12.9 million metric tons of gross CKD in 1990, and 4.6 million metric tons of net CKD, that is, material removed from the kiln system. As discussed further in Chapter 8, few practical process modifications can alter gross CKD generation rates. Nonetheless, it is important to look at differences between kiln types and operating practices to identify the process factors that may influence the gross quantity of dust generated.

Exhibit 3-12 presents tabulated data that summarize CKD generation rates per ton of clinker produced as a function of fuel usage (i.e., burning or not burning hazardous waste) and process type (i.e., wet, dry long, dry with preheater/precalciner). CKD generation data per ton of product eliminate differences in generation rates that are a function of differences in kiln size; this allowed the Agency to examine whether there are differences in generation rates that appear to be directly related to process types and/or fuel usage.

Differences in CKD Generation Rates Across Process Types

Exhibit 3-12 reveals the following relationships with respect to CKD generation across different process types:

- Wet kilns, which comprise 36 percent of all kilns in Exhibit 3-12, on average generate less gross CKD per ton of product than dry kilns. The data indicate that wet kilns generate about 24 percent less CKD per ton of product than dry long kilns and about eight percent less than Ph/Pc kilns.
- Operators of wet kilns, however, recycle a lower percentage of CKD than operators of dry kilns; on average, they generate more net CKD per ton of product (9.5 percent more than dry long kilns and 167 percent more than Ph/Pc kilns).
- With respect to dry kilns, Ph/Pc kilns generate about 17 percent less gross CKD and about 60 percent less net CKD per ton of product than dry long kilns.

⁸ Ideally, the data would have normalized using kiln-specific clinker production data. Because, as discussed above, such data are unavailable, EPA used clinker capacity data as the best available proxy.

Exhibit 3-12**Average CKD Generation Rates Per Ton of Product (1990)^a**

Kiln Type	No. of Kilns	CKD Per Ton of Product Ratio ^b		
		Gross CKD	Net CKD	CKD Recycled ^c
Wet Kilns				
Burning Hazardous Waste	13	0.219	0.163	0.056
No Hazardous Waste	28	0.179	0.093	0.086
All Fuels	41	0.192	0.115	0.077
Dry Long Kilns				
Burning Hazardous Waste	13	0.236	0.131	0.105
No Hazardous Waste	19	0.264	0.087	0.177
All Fuels	32	0.253 ^c	0.105 ^c	0.148
Dry Preheater/Precalciner Kilns				
Burning Hazardous Waste	6	0.175	0.071	0.104
No Hazardous Waste	34	0.215	0.038	0.177
All Fuels	40	0.209 ^c	0.043 ^c	0.166
All Dry Kilns				
Burning Hazardous Waste	19	0.217	0.112	0.105
No Hazardous Waste	53	0.233	0.055	0.178
All Fuels	72	0.228	0.070	0.158
All Kilns				
Burning Hazardous Waste	32	0.218 ^c	0.133 ^c	0.085
No Hazardous Waste	81	0.214 ^c	0.068 ^c	0.146
All Fuels	113	0.215	0.087	0.128

^a Source: Bureau of Mines.^b In general, Gross CKD = Net CKD + CKD Recycled.^c Computed from Bureau of Mines data.

EPA has evaluated the significance of these data further by performing pair-wise t-test comparisons of the average waste-to-product ratio value (means) provided in Exhibit 3-12. The results of this exercise demonstrate that there are no statistically significant differences (at a 95 percent confidence level) in the normalized gross CKD generation rates between any of the groups identified in the exhibit. That is, despite the apparent differences in average gross CKD generation rates per unit of product between, for example, hazardous waste-burning wet kilns and non-hazardous waste burning wet kilns, these differences are not sufficient, on a statistical basis, to indicate that these two groups are fundamentally different with respect to this variable.

In marked contrast, a number of statistically significant differences are apparent between various groups with respect to net CKD generation relative to production. Looking at the sample as a whole, the 32 kilns burning hazardous waste generate substantially more net CKD per unit of product, on average, than the 81 kilns that are not fired with this alternative fuel. The difference (average of 0.113 versus 0.068 tons of net CKD per ton of product, respectively) is significant at the 99 percent confidence level. A similar pattern is observed within kiln type groups: both wet and dry kilns burning hazardous waste fuels have significantly higher (at a 95 percent confidence level) average net CKD generation rates than kilns of the same technology type that do not burn hazardous waste fuels. Interestingly, the differences within the dry process kiln type category diminish when considering dry long and dry Ph/Pc kilns individually; although average net CKD generation rates are higher for the hazardous waste burners within each of these technology type sub-groups, the differences between these rates and those of the non-hazardous waste burning kilns within their respective sub-groups are not statistically significant at a 95 percent confidence level.

Average normalized net CKD generation rates also appear to vary significantly by kiln technology type alone. Wet process kilns have average net dust generation rates that are significantly higher than those of dry process kilns, and within the dry process kiln type, dry long kilns generate significantly more net CKD per unit of product, on average, than Ph/Pc kilns. The significance levels for EPA's comparisons between these groups approach or exceed 99 percent.

Differences in CKD Generation Rates Across Process Types and Fuel Usage

Further examination of the data in Exhibit 3-12 reveals the following findings:

- Wet kilns that burn hazardous waste fuels generate about 22 percent more gross CKD per ton of product than those that do not burn hazardous wastes. In the case of dry kilns, the data suggest the opposite -- dry kilns that burn hazardous waste generate about 7 percent less gross CKD per ton of product.
- The inverse relationship between hazardous waste burning and gross CKD generation in dry kilns becomes more marked with increasing technological sophistication. Dry long kilns burning hazardous waste generate close to 11 percent less gross CKD per ton of product than dry long kilns not burning hazardous waste; Ph/Pc kilns that burn hazardous waste generate almost 20 percent less gross CKD per ton of product.
- Across all process types, operators of kilns that burn hazardous waste (representing almost 30 percent of all kilns), recycle significantly less CKD per ton of product than non-hazardous waste burners. The result is that hazardous waste burners generate almost twice as much net CKD per unit of product as non-hazardous waste burners, though they generate only about two percent more gross CKD.
- In the case of dry kilns, lower recycling rates (per ton of product) can be partly attributed to the fact that kilns burning hazardous waste generate lower quantities of gross CKD per ton of product than kilns that do not burn hazardous waste. Operators of dry kilns that burn hazardous waste, however, recycle a lower percentage of the gross CKD they generate than kilns that do not burn hazardous waste -- 48 percent compared with 70 percent, respectively.

Differences in Gross CKD Generation Rates

The observations highlighted above reveal that for the wet and dry kilns overall (i.e., regardless of which kilns burn hazardous waste), gross CKD generation rates per ton of product appear to be slightly lower in wet kilns (19.2 percent) than in dry kilns (22.8 percent). This finding supports at least one source that states wet kilns generate less gross CKD than dry kilns.⁹

Gross CKD generation rates per unit of product, when all kilns are considered together, are slightly higher for hazardous waste burners than for kilns not burning hazardous waste. When different process types are considered, this relationship holds true only for wet kilns. Therefore, there is no conclusive evidence indicating that burning hazardous waste results in increased gross CKD generation, though such a finding was indicated in an early EPA study on this topic.¹⁰ One argument against this conclusion is that kilns that burn hazardous waste should generate less ash per unit of energy consumed than kilns that burn coal. Burning hazardous waste fuels, however, may allow the facility operator to burn a lower grade of coal (i.e., with a higher ash content) than it could otherwise, thus maintaining a relatively high overall ash content.

Differences in Net CKD Generation Rates

Based on observations from Exhibit 3-12, net CKD generation rates are higher in kilns burning hazardous waste. Although EPA has not found definitive evidence that burning hazardous waste causes increased net CKD generation rates, limited documentation suggests a link between the two variables. In one early study conducted by EPA in 1981, trial burns were conducted at three dry process cement kilns and two wet process kilns to compare results when coal was burned alone and when coal was co-fired with hazardous waste at unspecified rates. (None of these kilns was identified in the study.) In one of the dry process kilns, normal coal-fired operations generated approximately 91 metric tons per month of net CKD. When hazardous waste was co-fired, this figure increased to 1,800 metric tons per month, reportedly to keep system chloride levels within prescribed limits. Information on changes in the amount of dust generated at the other four facilities was not reported.¹¹

More recent data are not adequate to support conclusions regarding any cause-and-effect relationship(s) between combustion of hazardous waste fuels and net CKD generation rates, because the available data were not collected over time and do not include observations obtained during both hazardous waste fuel burning and the absence of this practice at the same plants. Nonetheless, the data analyzed and presented in this report reflect the actual operating experience of the majority of active cement plants in the U.S. and do allow the Agency to make some interesting comparisons. These data show that within each kiln type group, on average, kilns fired with hazardous waste fuels have net CKD generation rates that are substantially higher than those of kilns not fired with hazardous wastes. In each of the three basic kiln type groups, net CKD generation, normalized for actual production rates, was from 50 to 87 percent higher in kilns burning hazardous wastes than in kilns not burning these alternative fuels. In addition, net CKD generation rates are substantially higher for wet kilns than for preheater/precalciner kilns, and are somewhat higher than for dry long kilns. This pattern is apparent in both fuel type groups.

CKD Recycling

⁹ Engineering-Science, 1987, *op. cit.*, p. 3-12.

¹⁰ *Ibid.*

¹¹ Engineering-Science, 1987, *op. cit.*, p. 4-18.

Although net CKD may be viewed as a waste, its nature as essentially an "off-spec clinker," or intermediate product, makes direct return to the kiln, or recycling, a desirable option for cement plant operators. If more CKD could be returned to the kiln system via recycling, less net CKD would be generated. Decreasing net CKD quantities reduces the quantity of dust that must be managed in some other manner. Moreover, reduced net CKD generation saves energy and raw materials through minimizing raw feed demand and heat lost to materials that are removed from the system and not productively used.

A variety of methods are currently used to directly return CKD to the kiln system. First, dust is injected, or insufflated, through or near the flame at the hot end of the kiln. Second, CKD is conveyed to a shroud, or sleeve, that embraces the middle of the kiln near the material inlet to the calcining zone. In both of these cases, CKD is mechanically conveyed by a screw conveyor from the APCD to the point of re-introduction to the kiln. Third, operators introduce CKD at the front end along with the raw feed. Alternatively, CKD can be returned to the kiln after first treating it for removal of undesirable contaminants (e.g., through leaching, volatilization, or recovery scrubbing). These approaches to returning CKD to the kiln are the subject of further elaboration in Chapter 8.

Conceptually, the ideal strategy for any cement plant operator would be to return all of the gross CKD to the process, which would eliminate any need to dispose of or find alternative uses for waste CKD. Returning CKD to the kiln system, however, involves balancing savings in resources, energy, and waste management costs with the costs of increased concentrations of certain CKD constituents and the capital and operating costs of the necessary equipment. While cement plant operators do typically recycle some portion of the gross CKD, the gradual accumulation of alkalis in the dust usually necessitates that some CKD be removed from the system as a net waste. Through recycling, chlorine and alkalis tend to accumulate in the gross CKD that is generated. These constituents can continue to build up in the kiln system as alkalis and alkali salts, which may impair the cement production process in three primary ways:

- Increased particulate matter emissions. As discussed in Sections 3.2.1 and 3.2.2, below, alkalis and chlorides may decrease the efficiency of ESPs, resulting in increased particulate matter emissions.¹²
- Kiln damage and/or preheater plugging. Alkali chlorides, which can damage kiln linings, condense more readily in the kiln than oxides, which help to protect kiln linings. Alkali chloride condensation can also lead to preheater plugging and ultimately to increased alkali recirculation.
- Inferior quality cement product. Alkali levels also affect the quality of the cement product. The American Society for Testing and Materials (ASTM) sets specific limits on alkali levels in portland cement. ASTM C 150 mandates that cement contain no more than 0.6 percent alkali.¹³ This standard was created to minimize a detrimental phenomenon in concrete called alkali-aggregate reactivity.¹⁴ Through this phenomenon, chemical

¹² Beers, A., 1987. New York State Legislature, Legislative Commission on Toxic Substances and Hazardous Wastes. Hazardous Waste Incineration: The Cement Kiln Option. December. p. 11.

¹³ American Society for Testing and Materials, 1987. ASTM C150-86, Vol. 04.02. *Concrete and Aggregates*. p. 91.

¹⁴ Kosmatka, S. and Panarese, W., 1990. *Design and Control of Concrete Mixtures*. Portland Cement Association. Skokie, Illinois. pp. 42-43.

reactions between the cement gel and the aggregates (i.e., gravel that is mixed with the cement to form concrete) cause the concrete to expand and may result in cracking or other structural defects. To limit alkali concentrations in the cement product, some CKD must typically be removed from the system.

Recycling Differences

To help identify some of the factors influencing recycling rates, it is useful to compare a facility that recycles all of its gross CKD to a facility that recycles none of its gross CKD. The operator of the active kiln at the Kaiser Cement Company in Cupertino, California, for example, recycles almost all (99.97%) of the gross CKD back to the raw feed. The unit is a dry process kiln with a preheater and precalciner, and is fired primarily with low-sulfur coal, and to a lesser extent, petroleum coke. The facility operators attribute the high recycling rate to the inherently low alkali, chloride, and sulfate levels in the raw material and fuel inputs.¹⁵

In contrast to the Kaiser Cupertino plant, the operator of the four active wet process kiln systems at Texas Industries, Inc., in Midlothian, Texas, recycles none of the gross CKD. Each kiln is fired with a mixture of coal, natural gas, petroleum coke, and liquid hazardous waste. According to the facility operator, the raw feed is high in alkalies, and because Texas Industries produces low-alkali cement, the operator believes that as generated CKD cannot be recycled back to the kiln.¹⁶

The idea that recycling rates are solely dependent on raw feed yields a simple generalization. Generally, higher alkalies should result in reduced recycling for a given cement grade. However, process and fuel differences can also significantly influence recycling rates. The remainder of this section discusses these differences in greater depth by examining the PCA Survey data for recycling rate differences across process type and fuel type. The influence of raw feed cannot be assessed in this analysis because appropriate raw feed characterization data are not readily available.

Exhibit 3-13 presents summary data that express CKD going to the various management pathways as a weight percent of gross CKD, as a function of whether they burn or do not burn hazardous waste, and process type (i.e., wet, dry long, and dry with preheater/precalciner). The data in Exhibit 3-13 demonstrate a number of interesting relationships that are outlined below. This discussion enhances the discussion relating to Exhibit 3-12, particularly with respect to the percentage of gross CKD that is disposed and sold.

Differences in Fate of CKD Across Process Types

Exhibit 3-13 reveals the following relationships with respect to CKD fate across different process types:

- Wet kilns generate, on average, 59 thousand metric tons of gross CKD, compared with about 69 thousand metric tons generated in dry long kilns and 60 thousand metric tons generated in Ph/Pc kilns. As previously noted, however, operators of wet kilns recycle a lower percentage of their gross CKD -- 45 percent in contrast with 65 percent in the case of dry long kilns, and 82 percent in the case of Ph/Pc kilns.

¹⁵ U.S. EPA, 1992. Sampling Trip Reports.

¹⁶ *Ibid.*

- The percentage of gross CKD that is sold is about five times higher for wet kilns than it is for dry kilns. Operators of wet kilns sell 13 percent of all the gross CKD they generate, compared with less than three percent for either category of dry kiln (though operators of hazardous waste-burning Ph/Pc kilns sold about 9.5 percent of their gross CKD in 1990).
- Despite the relatively large percentage of gross CKD that is sold by wet kilns, the lower percentage of CKD recycled by the operators of such kilns results in them wasting the highest percentage of gross CKD. In 1990, operators of wet kilns disposed of over 40 percent of all the CKD they generated. In the same year, dry long kiln operators disposed of about one-third of the CKD they generated, while the operators of Ph/Pc kilns disposed of only about 15 percent.

Differences in Fate of CKD Across Process Types and Fuel Usage

Examination of the fuel usage data in Exhibit 3-13 reveals the following relationships:

- Across all process types, hazardous waste-burning kilns generate, on average, more gross CKD than those not burning hazardous wastes. The difference is the greatest in the case of wet and Ph/Pc kilns, where hazardous waste burners generate almost twice as much gross CKD as non-hazardous waste burners. Part of this phenomenon is explained by the fact that kilns burning hazardous waste fuels tend to be larger than those not burning such fuels. The difference in size is apparent when Exhibit 3-13 is compared with Exhibit 3-12, where CKD generation rates have been normalized by production rates. For example, gross CKD per ton of product for wet kilns is only 1.2 times higher for hazardous waste burners than it is for non-hazardous waste burners (see Exhibit 3-12), though the former generate almost twice as much gross CKD as the latter in terms of absolute quantity (see Exhibit 3-13). In the case of dry kilns, gross CKD generated per ton of product is less for hazardous waste burners than it is for non-hazardous waste burners (see Exhibit 3-12), though the former generate larger average quantities of gross CKD (see Exhibit 3-13).
- Across all process types, operators of hazardous waste-burning kilns recycle a lower percentage of their gross CKD than those operating non-hazardous waste-burning kilns. Operators of wet kilns, as well as dry kilns that burn hazardous waste fuels, recycle almost 35 percent less of their gross CKD than those who do not burn hazardous waste fuels (34 percent compared with 52 percent in the case of wet kilns, and 55 percent compared with 83 percent in the case of dry kilns). Overall, kilns burning hazardous wastes generate about twice as much net CKD as a weight percentage of gross CKD than do kilns not burning hazardous wastes.
- This difference in recycling rates based on fuel usage is the most marked in the case of dry long kilns, where the percentage of gross CKD recycled by hazardous waste burners is only about half that of non-hazardous waste burners. Hazardous waste burners in this process type generate almost three times as much net CKD as a percentage of gross CKD -- 54 percent, compared with 20 percent in the case of non-hazardous waste burners.

Exhibit 3-13

Fate of CKD as a Percent of Gross CKD (1990)^a

Fate of CKD as a Percent of Gross CKD (Averages)							
Kiln Type	No. of Plants	No. of Kilns	Average Gross CKD per kiln (metric tons)	Weight Percent of Gross CKD			
				Net	Recycled	Disposed	Sold ^b
Wet							
Burning Hazardous Waste	8	14	84,724	65.96	34.04	54.32	11.64
No Hazardous Waste	23	39	49,944	47.90	52.19	33.34	14.56
All Fuels	31	53	59,131	54.74	45.32	41.28	13.45
Dry Long							
Burning Hazardous Waste	5	15	69,081	54.35	45.65	53.05	1.31
No Hazardous Waste	8	19	68,707	19.65	80.39	17.28	2.37
All Fuels	13	34	68,872	35.01	65.01	33.11	1.90
Dry PH/PC							
Burning Hazardous Waste	5	6	94,253	29.02	70.98	19.53	9.49
No Hazardous Waste	28	51	56,389	17.06	83.73	14.97	2.09
All Fuels	33	57	60,374	19.03	81.63	15.72	3.31
All Dry Kilns							
Burning Hazardous Waste	10	21	76,273	45.41	54.59	41.21	4.20
No Hazardous Waste	36	70	59,732	17.87	82.69	15.69	2.18
All Fuels	46	91	63,549	25.50	74.90	22.76	2.74
All Kilns							
Burning Hazardous Waste	18	35	79,653	54.15	45.85	46.79	7.36
No Hazardous Waste	59	109	56,230	27.41	72.99	21.30	6.11
All fuels	77	144	61,923	35.77	64.51	29.27	6.50

^a Based on usable responses from 1991 PCA Survey.^b "CKD Sold" quantities may also include CKD that was given away.

- No patterns emerge from the data in Exhibit 3-13 with respect to the percentage of gross CKD sold by operators of hazardous versus non-hazardous waste-burning cement kilns. In the case of wet kilns, hazardous waste burners sell a lower percentage of their CKD than non-hazardous waste burners, though the difference is not striking. In the case of dry kilns, however, hazardous waste burners sold a higher percentage of the CKD they generated in 1990 than non-hazardous waste burners. Operators of Ph/Pc kilns that burned hazardous waste fuels sold over four times more, as a percentage of gross CKD, than did the operators of the Ph/Pc kilns that do not burn hazardous waste fuels.
- Hazardous waste burners across all process types dispose of a larger percentage of the gross CKD they generated as compared with non-hazardous waste burners. This result is consistent with the earlier observation with respect to recycling rates. Although no pattern emerged in the case of CKD sold, the percentages of CKD sold are generally low relative to CKD recycled and it is not surprising that the percentages of CKD sold did not significantly influence the outcome with respect to CKD wasted.
- Across the entire sample of 144 kilns and 77 plants, close to 65 percent of the gross CKD generated was internally recycled in 1990, and of the more than 35 percent comprising net CKD, approximately 82 percent was disposed and 18 percent was sold or given away.

The data contained in Exhibits 3-12 and 3-13 show that recycling rates do differ between process type and between fuel type. Although some CKD must be removed from the system to reduce alkali levels, it is possible that some facility operators recycle none of their CKD to reduce the complexities of clinker quality control. Any explanation for the greatly reduced recycling rates observed among wet kilns compared to dry kilns is probably based on economics, because full recycling (in some cases with treatment of CKD) could probably be achieved for any process if cost were not an issue. Possible recycling technologies are discussed in greater depth in Chapters 8 and 9. Nonetheless, three potential explanations are presented here for the finding that wet kilns recycle less CKD than dry kilns.

One reason that wet kilns recycle less CKD than dry kilns is apparently because, relative to the number of kilns in each process type, a larger proportion of wet kilns burn hazardous waste than dry kilns. As discussed above, decreased CKD recycling rates are associated with hazardous waste burning. According to the 1991 PCA Survey, 13 of 43 wet kilns (30 percent) burn hazardous waste while only 19 of 82 dry kilns (23 percent) burn hazardous waste. This practice is probably driven by economics. Because of the higher water content of the raw feed, which must be dried, wet process kilns are inherently less energy efficient than dry kilns.¹⁷ To supplement the large energy demands required by wet process kilns in a cost-competitive manner, wet kiln operators have presumably looked to hazardous waste as an inexpensive source of fuel with high heat content.¹⁸

Another possible explanation is the fact that wet kilns generally represent older systems than dry kilns, and that perhaps these kilns also represent a sector of the cement industry where any system modifications are not projected to be cost-effective. Hence, operators of wet kilns may be wasting a greater proportion of dust to simplify their process operations. Rather than installing recycling process equipment and constantly monitoring CKD constituents to determine appropriate recycling rates, such operators may find it easier and more economical to waste the dust.

¹⁷ Beers, A., 1987, *op. cit.*

¹⁸ Gossman, D., 1992. The Reuse of Petroleum and Petrochemical Waste in Cement Kilns. *Environmental Progress* (Vol. 11, No. 1). February. p. 5.

As mentioned previously, observed recycling differences between kiln systems may owe to plant-specific differences in raw feed inputs, where the raw feed inputs may typically be higher in alkalies for wet kilns than for kilns not burning hazardous waste, or for dry process kilns. Due to a general paucity of raw feed data, the only relevant comparison that can readily be made to explore this possibility is to compare the geographic distribution of kilns based on recycling rate, which can indicate regional differences in the geology and chemistry of raw materials. If regional trends were noted, EPA could infer an influence from raw feed inputs. In reviewing the geographic distribution of recycling rates (through mapping), however, EPA noted no recycling patterns by region for process type or for fuel type.

The most plausible explanation for decreased recycling rates among kilns burning hazardous waste is that chloride, alkali, and/or sulfate levels in some hazardous wastes may significantly increase the loading rates of these contaminants in the dust. To maintain acceptable levels of chloride, alkali, and sulfate in the system, more CKD may need to be removed from the system than if the kiln had not been burning hazardous waste as fuel. Some facility operators report that the burning of hazardous waste with high chlorine levels can induce the precipitation of alkali chlorides in the kiln. Bleeding of CKD then removes these alkali chlorides from the system.¹⁹ This idea is supported in the co-firing study cited above, where net CKD in one kiln was increased from 91 metric tons per month to 1,800 metric tons per month to control chloride levels.²⁰

3.2 CKD GROSS CHARACTERISTICS

CKD is comprised of thermally unchanged raw materials, dehydrated clay, decarbonated (calcined) limestone, ash from fuel, and newly formed minerals corresponding to all stages of processing up through the formation of the clinker.^{21,22} An unusual feature of CKD is that, unlike typical process wastes that are substantially different than the product, CKD is essentially cement clinker that does not quite meet commercial specifications.

3.2.1 Physical Characteristics

Although the relative constituent concentrations in CKD can vary significantly, CKD has certain physical characteristics that are relatively consistent. When stored fresh, CKD is a fine, dry, alkaline dust that readily absorbs water. When managed on site in a waste pile, CKD can retain these characteristics within the pile while developing an externally weathered crust, due to absorption of moisture and subsequent cementation of dust particles on the surface of the pile.

Exhibit 3-14 provides particle size distributions for CKD generated by various process types. It demonstrates that the size distribution of CKD can vary significantly, with diameters ranging from near zero to greater than 50 μm . (The lack of statistical information from the sources of these figures necessitates that only qualitative conclusions about particle size distributions be drawn.) The data show that from 15 to 90 percent of CKD has a diameter below 10 μm , within the respirable range for humans. Moreover, Exhibit 3-14 suggests that at least 55 percent of CKD measures less than 30 μm in diameter,

¹⁹ *Ibid.*

²⁰ Engineering-Science, 1987, *op. cit.*, p. 4-18.

²¹ Kohlhaas, B., *et al.*, 1983, *op. cit.*, pp. 624.

²² Engineering-Science, 1987, *op. cit.*, pp. 3-4, 3-12, 4-18.

while a nearly uniform 82 percent falls below 50 μm . Although the data contained in Exhibit 3-14 are limited in scope and therefore inconclusive, it appears that dry precalciner kilns generate larger CKD particles than wet kilns or dry long kilns, while dry long kilns may produce the smallest CKD particles. Dry long kilns appear to generate nearly all (90 percent) of their CKD in the respirable range, while only 17 percent of CKD from dry kilns with precalciners is in this size range. Median sizes also suggest that dry, long kilns may have the smallest CKD particles, at 3 μm , followed by wet kilns at 9.3 μm , and finally dry kilns with precalciners at 22.2 μm .

Exhibit 3-14

Particle Size Distribution of CKD by Process Type

Particle Size (μm)	SOURCE 1 ^a	SOURCE 2 ^b		
	Unspecified Process Type (weight percent)	Wet Kilns (weight percent)	Long Dry Kilns (weight percent)	Dry Kilns with Precalciner (weight percent)
0-5	5	26	45	6
5-10	10	19	45	11
10-20	30	20	5	15
20-30	17	9	1	23
30-40	13	8	1	18
40-50	7	1	0	9
>50	18	17	3	18
Median Particle Size	No Data	9.3	3.0	22.2

^a Kohlhaas, *et al.*, 1983, *op. cit.*, p. 640. The number of samples used to develop data was not specified.

^b Todres, H., A. Mishulovich, and J. Ahmed, 1992. CKD Management: Permeability. Research and Development Bulletin RD103T, Portland Cement Association, Skokie, Illinois, p. 2. It appears that one sample per process type was analyzed to develop the data presented above.

Exhibit 3-15 presents particle size data submitted by Midwest Portland Cement Company in Zanesville, Ohio, in response to a request for data by EPA under Section 3007 of RCRA. This facility operates two wet process kilns. These data show that "peaks" in the particle size distribution occur at diameters of 22 μm (approximately 13 percent of total dust volume) and 3.9 μm (about 11 percent of the total dust volume). Thirty percent or more of the CKD examined in this analysis had an aerodynamic diameter of less than 10 μm , which is the respirable range for humans.

Coplay (ESSROC Materials) Cement Company of Frederick, Maryland, in response to the same RCRA Section 3007 request, submitted particle-size screen analysis data on "typical stack dust."²³ These data were similar to those submitted by Midwest Portland, showing 99.9 percent of dust passing a screen size of approximately 185 μm , 99.4 percent passing 130 μm , 88.8 passing 110 μm , and 72.4 percent passing 72 μm . (These screen sizes were converted from screen sizes of #20 mesh, #50 mesh, #100 mesh, and #200 mesh, respectively.)

Exhibit 3-15

Particle Size Distribution of CKD Midwest Portland Cement Company, Zanesville, Ohio^a

Particle Size (μm)	Percent Volume Passing	Cumulative Percent Volume Passing
176.0	1.6	100.0
125.0	7.0	98.4
88.0	9.3	91.4
62.0	9.1	82.1
44.0	8.0	73.0
31.0	8.5	64.9
22.0	12.8	56.5
16.0	5.7	43.7
11.0	9.6	38.0
7.8	6.7	28.4
5.5	7.4	21.7
3.9	11.4	14.3
2.8	2.5	2.9
1.9	0.4	0.4
1.4	0.0	0.0

^a Midwest Portland Cement Company, 1992. Particle size distribution of kiln dust laboratory sample, February 14, 1992. Submitted on September 2, 1992 in response to RCRA Section 3007 request for information by U.S. EPA, August 18, 1992.

²³ ESSROC Materials, Inc., 1992. Particle size distribution of "typical stack dust," February 14, 1992. Submitted on November 3, 1992 in response to RCRA Section 3007 request for information by U.S. EPA, August 18, 1992.

The fine-grained nature of CKD makes it easily transportable in air, a factor that necessitates the use of effective air pollution control devices to remove this material from kiln exhaust gases. The smallest particles may not be fully captured by air pollution control devices, and may instead be released into the atmosphere. Particles smaller than 75 μm can be suspended in the air and tend to follow air currents. At 30 μm or less, these particles can travel long distances before settling.

The ability of CKD to absorb water stems from its chemically dehydrated nature, which results from the thermal treatment it receives in the kiln system. The action of absorbing water (rehydrating) releases a significant amount of heat from non-weathered dust, a phenomenon that can be exploited in beneficially using CKD. For example, CKD can be used to dewater municipal sewage sludge, while the heat of hydration can be used to sterilize the blended material. Such uses are discussed further at the end of this chapter and in more detail in Chapter 8.

Hydraulic conductivity represents a physical characteristic of particular interest for CKD managed in piles or beneficially used in applications such as bulk fill. If, for example, CKD were to conduct water fairly well, it could be used as a bulk fill without concern about ponding and structurally unstable saturated material. Disposal of CKD in a waste management unit that readily conducted water might, however, require controls to prevent release of leachate to the environment.

EPA's data on CKD hydraulic conductivity are limited to two sources. Source 1 is a report on CKD pile characteristics by General Portland (now National Cement), in Los Robles, California.²⁴ The report presents test results comparing fresh CKD to CKD that had been placed in a waste pile. In a laboratory experiment, the two dust types were compacted to varying degrees under an empirically determined optimum compacting moisture content, and their hydraulic conductivities were measured. Source 2 is a conductivity study conducted by researchers for PCA.²⁵ In this study, investigators compared the conductivity of CKD from three process types: wet, dry long, and dry with precalciner. Exhibit 3-16 summarizes the results of these studies.

As shown in Exhibit 3-16, the hydraulic conductivity of CKD is inherently low, at least compared to typical soil types. Compacted CKD conductivities are as low as 1×10^{-10} cm/sec, an extremely low value compared to the typical conductivity of a compacted clay landfill liner, which is about 1×10^{-7} cm/sec. The highest conductivity was 3×10^{-3} cm/sec, which indicates moderate permeability. Making solely qualitative comparisons because additional data were not provided, no clear pattern was observed between process types from Source 2. For example, although dust from the wet process exhibited lower permeabilities at medium and high compactions, this same dust had the highest conductivity under light compaction. For Source 1, the waste pile dust appeared to exhibit a lower conductivity than the fresh dust. The authors of Source 1 attributed the lower conductivity of the waste pile dust to its "setting" during prolonged weathering. Although all or most of the cemented aggregations that might have formed during weathering would most likely be broken down during compaction in the test, the disaggregated particles in the managed dust appear to more readily bind and reduce conductive pore space than in the generated dust. The data from this test suggest that, although CKD hydraulic conductivity appears to be inherently low, this property appears to decrease even further with time, especially when CKD is exposed to atmospheric influences such as humidity and rain.

²⁴ Chadbourne, J. and E. Bouse, General Portland, 1985. Los Robles Cement Plant CKD Waste Classification Report. August. p. 5.

²⁵ Todres, H., A. Mishulovich, and J. Ahmed, 1992. *CKD Management: Permeability*. Research and Development Bulletin RD103T, Portland Cement Association, Skokie, Illinois, p.7.

Exhibit 3-16

Hydraulic Conductivity of Freshly Generated and Managed CKD

SOURCE 1 ^a			SOURCE 2 ^b			
Percent of Maximum Compacted Density	Hydraulic Conductivity (cm/sec) ^c		Degree of Compaction ^d	Hydraulic Conductivity (cm/sec)		
	Waste Pile	Fresh		Wet Process	Dry Process	Dry Process with Precalciner
85	6.5×10^{-6}	3.5×10^{-5}	Light	1.5×10^{-3}	3.0×10^{-3}	5.1×10^{-4}
90	5.5×10^{-6}	1.3×10^{-5}	Medium	7.6×10^{-6}	7.0×10^{-6}	2.1×10^{-5}
95	1.9×10^{-6}	4.7×10^{-6}	Heavy	1×10^{-10}	4.9×10^{-8}	1.6×10^{-6}

^a Chadbourne, J., and E. Bouse, 1985, *op. cit.*, p. 5.

^b Todres, H., *et al.*, 1992, *op. cit.*, p. 7.

^c Relative hydraulic conductivities between soil/rock types (Todres *et al.*, 1992, p. 5):

Relative Permeability	Hydraulic Conductivity	Typical Soil/Rock Type
High	$>10^{-1}$ (cm/sec)	Coarse gravel
Medium	10^{-1} to 10^{-3} (cm/sec)	Sand, fine sand
Low	10^{-3} to 10^{-5} (cm/sec)	Silty sand, dirty sand
Very Low	10^{-5} to 10^{-7} (cm/sec)	Silt, fine sandstone
Near Impervious	$<10^{-7}$ (cm/sec)	Clay

^d Degrees of compaction were designed to simulate the following treatments: Light Compaction = "as dumped", with little or no compactive effort; Medium Compaction (Standard Proctor) = Compaction in the field at appropriate moisture content, using moderate equipment on thin lifts; Heavy Compaction (Modified Proctor) = Compaction in the field at appropriate moisture content, using heavy equipment on controlled lift thicknesses.

3.2.2 Bulk Chemical Characteristics

An analysis of the chemical composition of CKD can be conducted on two levels: 1) the major, or "bulk" constituents of the material, and 2) minor, or "trace" constituents that may comprise very small percentages of total CKD mass but nonetheless be important from an operational and/or environmental standpoint. Bulk constituents are defined herein as those that exceed 0.05 percent by weight in the CKD. Bulk constituents are primarily those found in clinker, though they also may be present at levels in CKD that are unacceptable in the cement product. Although the types of bulk constituents found in CKD do not vary significantly among samples from different plants and over time, the relative proportions of these constituents vary widely. Trace CKD characteristics are presented in Section 3.3 and clinker characteristics are presented in Section 3.5.

Exhibit 3-17 summarizes some of the data on bulk constituents available for comparison, which suggest that significant CKD variability can occur even between kilns with relatively minor process differences. The first two columns of data show ranges for data provided by respondents to the 1991 PCA Survey, divided between all wet kilns and all dry kilns for which there are data. The third and fourth columns contain analytical data representing two types of dry preheater kilns: dry with cyclone preheater and dry with grate preheater.

Although wide concentration ranges exist for most constituents, Exhibit 3-17 generally shows that the primary bulk constituents in CKD are silicates, calcium oxide, carbonates (expressed as loss of CO_2 and H_2O on ignition), potassium oxide, sulfates, chlorides, various metal oxides, and sodium oxide. The information presented in Exhibit 3-17 suggests that few inferences can be drawn from these data regarding process influences on CKD chemical composition. That is, variability in CKD composition appears to be without trend among the process types, based upon this limited sample. The chloride content of the wet kiln CKD may exceed that of the dry kiln CKD by a factor of about two. Exhibit 3-17 does serve to demonstrate that factors other than process type (e.g., fuels, feed, product specifications) may be influencing CKD chemical characteristics, because of the high degree of constituent concentration variability within each process type.

As an additional measure of chemical characteristics, Exhibit 3-17 shows that CKD is inherently alkaline. This characteristic is a clear function of the large quantity of CaO and other alkaline compounds, such as K_2O , NaOH , Na_2CO_3 , and Na_2SO_4 , that comprise CKD. Again, however, conclusions based on process differences are tenuous using the available data. In general, the pH of CKD leachates (using standard EPA leachate procedures) falls between 11 and 13.²⁶ The significance of these leachate levels with respect to environmental risk is discussed in detail in Chapter 6.

3.3 CKD TRACE CHARACTERISTICS

Trace constituents are generally found in concentrations of less than 0.05 percent by weight and are typically expressed as milligrams per kilogram (mg/Kg), or parts per million. These constituents include certain organic chemicals, metals such as cadmium, lead, and selenium, and radionuclides. Trace constituents are important to an analysis of the chemical characteristics of CKD because some of these elements and compounds are toxic or otherwise harmful at low concentrations, and as discussed below in Chapter 5, CKD has been managed in a way that may release these trace constituents to the environment. Furthermore, the use of hazardous waste and other wastes (e.g., slag) and raw materials as fuel and raw material inputs in cement kilns has raised concerns regarding the concentrations of certain heavy metals in CKD generated by plants that use these alternative materials.

3.3.1 EPA Sampling Program

With the exception of metals and general chemistry data,²⁷ the Agency found that existing chemical characterization data on CKD was insufficient for the purpose of determining what organic and

²⁶ Although some leachate pH values from dry kiln-derived CKD have been measured below 9.0, the Agency does not believe that kiln type exerts a significant influence on the alkalinity of CKD, and believes that the validity of some reported data is questionable. For example, results from EPA's 1992 field sampling and analysis yielded several as generated and as managed CKD samples with reported laboratory leachate values below pH 9.0. The Agency believes these pH levels may not be representative of typical CKD leachate characteristics.

²⁷ General chemistry analytes are also referred to as "major ions" and "wet chemistry" in this document. This class of analytes includes chlorides, sulfates, sulfides, fluorides, cyanide, and total organic carbon.

inorganic constituents may be present in CKD. Therefore, the Agency decided to undertake a sampling program in order to characterize CKD more fully for this Report to Congress. During the spring of 1992 and spring of 1993, EPA visited a total of 20 cement manufacturing facilities for the

Exhibit 3-17

Typical CKD Bulk Constituents

Constituent	Concentration Ranges (weight percent)			
	Long Dry Kilns, Dry Kilns with Preheaters, and/or Calciners ^a	Wet Kilns ^b	Rotary Kiln with Cyclone Preheater ^c	Rotary Kiln with Grate Preheater ^c
SiO ₂	4.3-10.1	4.1-7.7	7-11	2-19
Al ₂ O ₃	1.0-3.3	1.3-3.3	3-6 ^d	0.5-8 ^d
TiO ₂	0.07-0.2	0.08-0.2		
Fe ₂ O ₃	0.7-2.3	0.8-2.0	1-3 ^d	0.5-4 ^d
Mn ₂ O ₃	0.01-0.2	0.02-0.04		
CaO	11.0-45.0	15.9-38.0	41-51	6-26
MgO	0.4-2.0	0.4-1.9	0.5-2	0-2
SO ₃	0.1-7.7	0.1-6.0	0.5-4	7-41
K ₂ O	0.2-9.7	0.2-12.1	0.5-4	14-40
Cl ⁻	0.08-2.7	4.2-6.3	0-0.3	0.9-4.5
Na ₂ O	0.07-1.2	0.1-4.1	0-0.5	0.5-3
LOI (CO ₂ +H ₂ O)	Not Available	22-25 ^e	29-38	4-24
pH	6.11 - 12.83 ^f (s.u.)	11.64-12.98 ^g (s.u.)	No Data	No Data

^a Based on 28 tests from 12 facilities responding to 1991 PCA Survey.

^b Based on 19 tests from 9 facilities responding to 1991 PCA Survey.

^c Kohlhaas, B, *et al.*, 1983, *op. cit.*, p. 623. No information was provided on the size of the population samples or operational characteristics.

^d The responses for the corresponding constituents are aggregated.

^e Range based on (1) a Dragon Products Company memorandum (December 6, 1991) from Steve Wallace to John Bangeman regarding typical analyses of several Dragon Products materials; and (2) a typical analysis of Stable Sorb at Keystone Cement Company (February 18, 1991).

^f Based on EPA sampling data for TCLP and SPLP leachate tests on as generated CKD from seven facilities. These leachate samples are obtained using an acid solution, so that actual CKD pH values may be higher than indicated here.

^g Based on EPA sampling data for TCLP and SPLP tests on as generated CKD from eight facilities. These leachate samples are obtained using an acid solution, so that actual CKD pH values may be higher than indicated here.

primary purpose of obtaining samples of cement kiln dust to determine its composition.²⁸ Fifteen of the facilities were selected at random from the population of U.S. facilities. The other five were selected for individual characteristics such as kiln type (e.g., wet or dry), use of hazardous waste as kiln fuel, and geographic location, so that these factors would be represented in the final data set. Then, the Agency collected samples of "as generated" and "as managed" CKD from each of the visited facilities and subjected them to chemical analysis.²⁹

The Agency selected the following classes of analytes to characterize cement kiln dust: volatile organic compounds, semi-volatile organic compounds, dioxins, furans, pesticides, polychlorinated biphenyls (PCB), metals, radionuclides, and general chemistry. The individual target compounds that were determined are identified in the respective sampling project plans. The project plans are available in the EPA docket for this Report to Congress.³⁰ The organic analytes were selected primarily from EPA's list of RCRA Hazardous Constituents, which is presented in Appendix VIII of 40 CFR Part 261.

Because CKD is typically managed in open piles outdoors, the Agency believed it necessary to also examine the potential for constituents to leach from CKD into the surrounding environment. Therefore, the Agency also prepared TCLP and SPLP leachates from subsamples of selected CKD samples and subjected them to analysis for certain of the analytes identified above, including metals, dioxins, furans, pesticides, radionuclides, and general chemistry.³¹ TCLP is a laboratory method that simulates the generation and release of leachate from an improperly disposed solid waste (i.e., a mis-management scenario). In certain cases, EPA uses an analogous method, SPLP, to simulate land disposal of inorganic wastes in monofills, a situation that commonly occurs at domestic cement plants.³² Under both leaching procedures, the analyte concentrations that are measured in the leached extract are compared with a set of EPA regulatory standards, which are based on 100 times the respective EPA primary drinking water standards (i.e., toxicity characteristic).

3.3.2 Total Concentrations

The total concentrations (i.e., mass of a particular constituent per mass of CKD) of trace constituents found in CKD are presented below by the following classes: metals, dioxins and furans, general chemistry, volatile organic compounds, semi-volatile organic compounds, pesticides, polychlorinated biphenyls (PCB), and radionuclides.

Metals

²⁸ The EPA sampling efforts conducted in 1992 and 1993 are also referred to as the Phase I and Phase II sampling efforts, respectively. Also, one of the 20 facilities was re-visited and sampled a second time for analysis verification purposes. The re-visit is not included in the facility counts presented in this document.

²⁹ As generated refers to newly generated CKD that was obtained from the air pollution control device at the kiln. As managed refers to CKD that was obtained from the facilities' on-site CKD storage or disposal piles. The as-managed CKD samples were obtained from storage or disposal pile areas containing dust that had typically been in storage or disposal status for up to six months.

³⁰ The sampling project plans are entitled *Cement Kiln Industry Sampling and Analysis and Quality Assurance Project Plan*, dated March 1992, and *Cement Kiln Industry Sampling and Analysis and Quality Assurance Project Plan - Phase 2*, dated May 1993.

³¹ TCLP stands for Toxicity Characteristic Leaching Procedure. SPLP stands for Synthetic Precipitation Leaching Procedure. The protocols for these procedures are found in SW-846 analytical methods numbered 1311 and 1312, respectively.

³² Only the TCLP test and its results have regulatory significance; though the SPLP is an official EPA method, it is not used for identifying hazardous wastes under 40 CFR Part 261.

EPA collected as generated CKD samples from the 15 facilities that were sampled by EPA in 1992 and as managed CKD samples from 13 of these facilities.³³ EPA analyzed these samples for the following metals: antimony, arsenic, barium, beryllium, cadmium, chromium, lead, mercury, nickel, selenium, silver, thallium, and vanadium. With a few exceptions, all of the metals were detected in all of the as generated and as managed CKD samples. As discussed below, these data were used to supplement the metals data made available to the Agency by the cement manufacturing industry and in literature published by the U.S. Bureau of Mines.

Upon conducting several assessments of the types and concentrations of trace metal constituents in as generated and as managed CKD, the Agency has concluded that a number of trace metal constituents occur in CKD at highly variable concentrations. Exhibits 3-18 and 3-19 present basic univariate statistics (number of samples, number of non-detected values, and mean, minimum, maximum, and median concentrations) describing the occurrence of several trace metal constituents in as generated and as managed CKD, respectively. These data were generated by separate studies conducted by the Portland Cement Association, the U.S. Bureau of Mines, and EPA in its 1992 sampling and analysis effort.

Data on the total constituent concentrations of trace metals found in both the as generated and as managed CKD show that the eight Toxicity Characteristic (TC) metals listed in 40 CFR §261.24 and nine other metals are consistently present (although at variable concentrations) in CKD. In general, the predominant trace metals include antimony, barium, lead, manganese, strontium, thallium, and zinc, and the minor trace metals include beryllium, copper, hexavalent chromium, mercury, nickel, silver, and thallium. A comparison of the data characterizing the as generated and as managed CKD suggests that the total constituent concentrations of trace metals found in the as generated CKD are greater by as much as an order of magnitude; however, the apparent differences may be attributable to changes in composition of materials charged to the kiln over time.

Intuitively, one would expect a mineral production waste such as CKD to contain the same types of constituents naturally present in the parent material. The concentration of the constituents found in such a waste, however, is likely dependent on whether the operator utilized a concentrating or extracting processing procedure. To help assess whether CKD contains elevated levels of any specific trace metal, the Agency compared the highest of the average concentrations of each trace metal observed in the five studies presented in Exhibit 3-18 for the as generated CKD and the two studies presented in Exhibit 3-19 for the as managed CKD to the range of trace metals commonly found in native soils. As shown in Exhibit 3-20, the levels of several of the trace metals found in CKD are within the range commonly found in native soils. Interestingly, these data suggest that CKD contains seven trace metals (antimony, cadmium, lead, mercury, selenium, silver, and zinc) at levels outside the range commonly found in native soils. These data also show that CKD may have arsenic and strontium at levels that are within the range of naturally occurring soils but that exceed the average

³³ One additional set of metals data was generated too late for consideration during the development of this report. This data set includes EPA's analysis for the 14 metals in as managed CKD from the six facilities that were sampled by EPA in 1993 (Phase 2). These data have been included in the EPA RCRA docket for this report for access by interested parties, and they will be considered by the Agency during its formulation of the final regulatory determination for CKD.

Exhibit 3-18
Trace Metal Concentrations in As Generated CKD
(parts per million)

Data Source	Analyte	Number of Samples	Number of Non-Detected Values	Mean	Minimum	Maximum	Median
EPA SAMPLING ^a	Antimony	17	1	7.7	1.77	27.2	6.2
	Arsenic	17	0	6.9	2.1	20.3	4.9
	Barium	17	0	172.1	11.0	779.0	103.0
	Beryllium	17	1	0.71	0.158	1.6	0.59
	Cadmium	17	0	13.2	0.89	80.7	4.6
	Chromium	17	0	26.6	11.5	81.7	18.1
	Lead	17	0	388.4	5.1	1,490.0	287.0
	Mercury	17	3	1.0	0.005	14.4	0.11
	Nickel	17	0	19.0	6.9	39.0	15.9
	Selenium	17	0	17.5	2.5	109.0	11.3
	Silver	17	0	6.9	1.1	22.6	3.7
	Thallium	17	0	17.1	0.99	108.0	3.5
	Vanadium	17	0	41.6	6.6	204.0	25.9
PCA SURVEY ^b	Antimony	1	1	0.53	0.53	0.53	0.53
	Arsenic	3	0	34.3	3.7	53.0	46.2
	Barium	1	0	150.0	150.0	150.0	150.0
	Beryllium	3	3	0.517	0.509	0.523	0.521
	Cadmium	3	0	8.05	3.0	12.1	9.05
	Chromium	3	0	39.0	32.7	49.0	35.2
	Chromium(VI)	2	0	7.82	7.05	8.59	7.82
	Copper	2	0	28.4	28.2	28.7	28.4
	Lead	3	0	210.3	151.0	270.0	210.0
	Manganese	5	0	211.2	200.0	222.0	212.0
	Mercury	3	3	0.104	0.100	0.107	0.106
	Nickel	3	0	18.3	10.0	23.8	21.1
	Selenium	1	0	6.5	6.5	6.5	6.5
	Silver	1	1	0.504	0.504	0.504	0.504
	Thallium	1	1	4.616	4.616	4.616	4.616
	Vanadium	3	0	33.5	23.0	39.2	38.3
	Zinc	3	0	104.3	86.0	116.0	111.0
PCA REPORT 1 ^c	Antimony	6	0	112.8	37.8	161.0	142.5
	Arsenic	6	2	20.4	3.726	80.7	8.86
	Barium	6	0	183.5	101.0	323.0	141.5
	Beryllium	6	0	3.88	2.86	4.64	3.81

	Cadmium	6	0	18.6	4.73	44.0	13.5
	Chromium	6	0	35.9	18.1	58.5	36.2
	Lead	6	0	283.7	53.2	819.0	171.0
	Mercury	6	3	0.062	0.003	0.305	0.015
	Silver	6	0	9.17	5.71	12.7	9.33
	Thallium	6	0	88.0	68.6	146.0	79.0

Exhibit 3-18 (continued)
Trace Metal Concentrations in As Generated CKD
(parts per million)

Data Source	Analyte	Number of Samples	Number of Non-Detected Values	Mean	Minimum	Maximum	Median
PCA REPORT 2 ^d	Antimony	95	86	0.395	0.083	3.43	0.21
	Arsenic	95	45	13.0	1.323	159.0	9.07
	Barium	95	0	185.8	35.0	1,402.0	133.0
	Beryllium	95	1	0.645	0.032	3.54	0.539
	Cadmium	95	14	8.83	0.008	59.6	3.27
	Chromium	95	0	40.8	8.25	293.0	29.1
	Lead	95	0	434.5	33.5	7,390.0	188.0
	Lithium	0	0	0	0	0	0
	Mercury	95	30	17.3	1.0	60.0	14.0
	Nickel	95	27	0.49	0.001	25.5	0.045
	Selenium	94	40	18.3	0.227	307.0	7.23
	Silver	95	3	10.3	3.549	40.7	9.28
	Thallium	95	6	40.6	0.109	776.0	8.96
BOM IC 8885 ^c	Antimony	113	71	3.3	0.701	70.0	0.83
	Arsenic	113	0	23.8	1.3	518.0	10.0
	Cadmium	113	17	20.0	0.687	352.0	7.6
	Chromium	113	0	41.6	11.0	172.0	35.0
	Copper	113	0	30.1	7.0	206.0	24.0
	Lead	113	5	252.9	11.335	1,750.0	148.0
	Lithium	113	15	18.0	1.754	76.0	16.0
	Manganese	113	0	385.6	63.0	2,410.0	284.0
	Nickel	113	51	19.3	5.421	91.0	16.0
	Silver	113	54	5.1	1.291	17.0	4.7
	Strontium	113	0	669.0	100.0	8,800.0	400.0
	Zinc	113	0	462.0	32.0	8,660.0	167.0

^a Data from EPA's 1992 sampling effort.

^b Data from the 1991 PCA Survey of U.S. cement plants.

^c Portland Cement Association, 1992. *An Analysis of Selected Trace Metals in Cement and Kiln Dust (Draft)*. PCA Report SP109T, Skokie, IL.

^d Portland Cement Association, 1992. *An Analysis of Selected Trace Metals in Cement and Kiln Dust*. PCA Report SP109T, Skokie, IL, 56 pages.

^e Haynes, B., and G. Kramer, 1982. *Characterization of U.S. CKD*. Bureau of Mines Information Circular (IC) 8885, U.S. Department of Interior. Bureau of Mines. Office of Assistant Director. Minerals and Materials Research, Washington, D.C.

Exhibit 3-19

**Trace Metal Concentrations in As Managed CKD
(parts per million)**

Data Source	Analyte	Number of Samples	Number of Non-Detected Values	Mean	Minimum	Maximum	Median
EPA SAMPLING ^a	Antimony	14	2	6.5	1.581	10.9	6.6
	Arsenic	14	0	7.7	2.1	19.8	6.4
	Barium	14	0	144.5	39.8	360.0	136.5
	Beryllium	14	2	0.68	0.175	1.5	.52
	Cadmium	14	0	11.8	0.62	27.4	10.1
	Chromium	14	0	35.0	9.6	110.0	21.4
	Lead	14	0	359.1	40.6	863.0	380.5
	Mercury	14	3	0.121	0.009	0.830	0.075
	Nickel	14	0	19.4	6.3	54.7	14.9
	Selenium	14	0	10.7	1.4	43.9	7.7
	Silver	14	2	4.2	0.348	17.2	1.95
	Thallium	14	0	4.1	1.1	14.6	2.3
	Vanadium	14	0	33.3	7.6	120.0	19.6
PCA SURVEY ^b	Antimony	37	13	27.7	0.099	360.0	7.2
	Arsenic	44	11	16.0	0.514	82.1	9.7
	Barium	42	0	235.2	2.0	635.0	207.0
	Beryllium	34	5	1.1	0.141	6.7	0.69
	Cadmium	44	0	24.3	0.41	85.7	17.3
	Chromium	44	0	40.1	3.3	132.0	34.8
	Chromium(VI)	7	1	0.11	0.02	0.23	0.13
	Copper	1	0	7.15	7.15	7.15	7.15
	Lead	44	0	857.9	3.12	4,230.0	441.0
	Manganese	2	0	165.9	123.0	208.8	165.9
	Mercury	42	24	1.0	0.002	4.7	1.1
	Nickel	11	0	22.4	3.6	46.3	16.0
	Selenium	34	9	15.0	0.518	103.0	7.5
	Silver	41	2	7.4	0.187	57.9	3.0
	Strontium	1	0	422.8	422.8	422.8	422.8
	Thallium	36	18	9.7	2.0	68.6	5.7
	Vanadium	1	0	30.0	30.0	30.0	30.0
	Zinc	2	0	128.6	37.2	220.0	128.6

^a Data from EPA's 1992 sampling effort.

^b Data from the 1991 PCA Survey of U.S. cement plants.

Exhibit 3-20**Trace Elements Commonly Found in Native Soils (mg/Kg)**

Trace Elements	Common Ranges	Average Concentrations	As Generated (Highest Average) ^a	As Managed (Highest Average) ^a
Antimony	2 - 10	NA	112.8	27.7
Arsenic	1 - 50	5	34.3	16
Barium	100 - 3,000	430	185.8	235.2
Beryllium	0.1 - 40	6	3.8	1.1
Cadmium	0.01 - 0.7	0.06	20	24.3
Chromium	1 - 1,000	100	41.6	40.1
Copper	2 - 100	30	30.1	7.1
Lead	2 - 200	10	434.5	857.8
Manganese	20 - 3,000	600	385.6	165.9
Mercury	0.01 - 0.3	0.03	17.3	1
Nickel	5 - 500	40	19.3	22.4
Selenium	0.1 - 2	0.3	18.3	15
Silver	0.01 - 5	0.05	10.3	7.4
Thallium	NA	NA	40.6	9.7
Vanadium	20 - 500	100	41.6	33.3
Zinc	10 - 300	50	462	128.6
Strontium	50 - 1,000	200	669	422.8

Source: Hazardous Waste Land Treatment, Table 6.46 - Trace Elements of Soils, U.S. Environmental Protection Agency, Cincinnati, Ohio, PB89-179014, April 1983, page 273.

^a EPA used the highest of the average concentrations of each trace metal observed in the five studies presented in Exhibit 3-18 for the as generated CKD and the two studies presented in Exhibit 3-19 for the as managed CKD.

native soil concentration by a factor of two or more. CKD, therefore, could be a potential contributor of these metals at higher than natural levels to the environment. For some metals (e.g., arsenic), the high end of the naturally occurring range of concentrations in native soils may present risk to human health and the environment. The potential risks to human health and the environment posed by these metals are identified and discussed in Chapters 5 and 6.

Dioxins and Furans

EPA analyzed dioxins and furans in as generated and as managed CKD samples from 11 facilities. A number of the dioxin and furan target compounds were detected in both as generated and as

managed CKD. Because these compounds were detected rather consistently in CKD, the Agency continued with analysis of the analytical data. Analyses were performed to determine whether the data from the 1992 EPA sampling could be pooled with the data from the 1992 sampling, and to determine whether there are relationships between dioxin and furan levels in CKD and two important operating factors: (1) use of hazardous waste as a fuel; and (2) use of wet process kilns versus dry process kilns.

One facility that was sampled during the Phase I sampling effort, River Cement Company, was re-sampled as part of the Phase II effort. This was done in part to conduct confirmatory analyses on the levels of dioxins that were reported from the Phase I effort at this facility. The CKD from this facility exhibited, by far, the highest levels of dioxins observed during the EPA sampling program. The results of the Phase II sampling did confirm the presence of dioxins in CKD at this facility, although the Phase II results showed dioxin levels generally three to four times lower than those measured during the Phase I sampling effort. As such, the Agency considers this facility to be non-typical of the industry in this respect. The Agency believes that the production of dioxins and furans in processes such as these may be heavily influenced by the incinerator or kiln exhaust gas temperatures, specifically at the inlet to the air pollution control devices (APCD) (e.g., baghouses, electrostatic precipitators). The levels of these organic constituents of CKD may be controllable through relatively minor process modifications to reduce exhaust gas or APCD inlet temperatures.

Exhibits 3-21 through 3-24 provide dioxins and dibenzofurans data resulting from sampling by EPA of as generated and as managed dust at six cement plants in 1993. It is worthy of note that dioxins and dibenzofurans were found in CKD samples collected from both facilities burning hazardous waste fuels and those not burning hazardous waste fuels.

Exhibit 3-21 presents total constituent concentration data for dioxins and dibenzofurans obtained from analyses of as generated CKD produced by both hazardous waste burning and non-hazardous waste burning facilities. These data indicate that dioxins and dibenzofurans (HpCDD, HpCDF, HxCDD, HxCDF, OCDD, OCDF, PeCDD, PeCDF, TCDD (including 2,3,7,8-TCDD) and TCDF are present at very low concentrations in CKD generated by both hazardous and non-hazardous waste fuel burning facilities. Most of the homologs, however, were detected at concentrations below 100 ppt, while several samples had homolog concentrations approaching one ppb. Only one homolog was detected at a concentration exceeding one ppb (total HxCDD at 1.5 ppb). These results correspond with the results obtained from EPA's Phase I analyses of dioxins and dibenzofurans, with the exception of one of seven samples where total HpCDD, HxCDD, HxCDF, PeCDD, PeCDF, TCDD, and TCDF were all detected at concentrations exceeding one ppb.

DIOXINS AND DIBENZOFURANS

- ◆ Tetrachlorinated dibenzo-p-dioxins (TCDD)
- ◆ Tetrachlorinated dibenzofurans (TCDF)
- ◆ Pentachlorinated dibenzo-p-dioxins (PeCDD)
- ◆ Pentachlorinated dibenzofurans (PeCDF)
- ◆ Hexachlorinated dibenzo-p-dioxins (HxCDD)
- ◆ Hexachlorinated dibenzofurans (HxCDF)
- ◆ Heptachlorinated dibenzo-p-dioxins (HpCDD)
- ◆ Heptachlorinated dibenzofurans (HpCDF)
- ◆ Octachlorinated dibenzo-p-dioxins (OCDD)
- ◆ Octachlorinated dibenzofurans (OCDF)

Exhibit 3-22 presents total constituent concentration data for dioxins and dibenzofurans obtained from analyses of as managed CKD generated by both hazardous waste burning and non-hazardous waste

burning facilities. These data show that dioxins and dibenzofurans (HpCDD, HpCDF, HxCDD, HxCDF, OCDD, OCDF, PeCDD, PeCDF, TCDD (including 2,3,7,8-TCDD) and TCDF also

Exhibit 3-21

Total Concentrations of Dioxins and Dibenzofurans in As Generated CKD (µg/Kg)

ANALYTE	HW-1 Sample 1	HW-1 Sample 2	HW-2	HW-3	NH-1	NH-2	NH-3	MAXIMUM	AVERAGE	AVERAGE DETECTED
1,2,3,4,6,7,8-HpCDD	0.0019	0.0018	B 0.25	B 0.0048	B 0.0051	J 0.0011	< 0.003	0.25	0.03824	0.04412
Total HpCDD	0.0037	0.0037	B 0.55	B 0.011	B 0.0098	0.0026	0.0079	0.55	0.08410	0.08410
1,2,3,4,6,7,8-HpCDF	< 0.00056	< 0.001	0.037	0.0024	< 0.0013	J 0.00028	< 0.0076	0.037	0.00716	0.01323
1,2,3,4,7,8,9-HpCDF	< 0.00052	< 0.001	0.0074	< 0.0017	< 0.0013	< 0.00069	< 0.00079	0.0074	0.00191	0.00740
Total HpCDF	0.0043	N.A.	B 0.067	B 0.0024	0.00047	B 0.0013	N.A.	0.067	0.01509	0.01509
1,2,3,4,7,8-HxCDD	< 0.00079	< 0.0014	0.025	< 0.0014	< 0.0012	< 0.00083	< 0.0012	0.025	0.00455	0.02500
1,2,3,6,7,8-HxCDD	< 0.00064	< 0.0021	0.049	< 0.0017	< 0.0018	< 0.00066	< 0.00096	0.049	0.00812	0.04900
1,2,3,7,8,9-HxCDD	< 0.00095	< 0.0019	0.041	< 0.00093	< 0.0014	< 0.001	< 0.0015	0.041	0.00695	0.04100
Total HxCDD	0.012	0.0076	1.5	0.00059	N.A.	N.A.	0.012	1.5	0.30644	0.30644
1,2,3,4,7,8-HxCDF	< 0.00073	< 0.0023	0.024	0.0028	< 0.0011	< 0.0007	< 0.00096	0.024	0.00466	0.01340
1,2,3,6,7,8-HxCDF	< 0.00044	< 0.0016	0.025	0.0028	< 0.00076	< 0.00049	< 0.00099	0.025	0.00458	0.01390
1,2,3,7,8,9-HxCDF	< 0.00044	< 0.0017	0.014	0.00096	< 0.00073	< 0.00085	< 0.0012	0.014	0.00284	0.00748
2,3,4,6,7,8-HxCDF	J 0.0004	< 0.0015	< 0.037	0.0023	< 0.00076	J 0.00057	< 0.00074	0.037	0.00618	0.00109
Total HxCDF	J 0.0004	N.A.	0.23	0.024	N.A.	0.00089	0.0019	0.23	0.05144	0.05144
OCDD	0.0036	0.0036	B 0.1	B 0.034	B 0.018	B 0.0046	B 0.0079	0.1	0.02453	0.02453
OCDF	< 0.001	< 0.0019	0.01	0.0017	< 0.0032	< 0.001	< 0.0014	0.01	0.00289	0.00585
1,2,3,7,8-PeCDD	< 0.0005	< 0.0012	0.03	< 0.0012	< 0.0015	< 0.00057	< 0.0021	0.03	0.00530	0.03000
Total PeCDD	0.0021	N.A.	0.85	N.A.	N.A.	N.A.	0.01	0.85	0.28737	0.28737
1,2,3,7,8-PeCDF	< 0.00046	< 0.00089	0.033	0.0061	0.00052	< 0.00051	< 0.00058	0.033	0.00601	0.01321
2,3,4,7,8-PeCDF	< 0.00053	< 0.00072	0.064	0.0038	< 0.00046	< 0.00033	< 0.00057	0.064	0.01006	0.03390
Total PeCDF	0.00039	N.A.	0.53	0.063	0.00052	0.00071	N.A.	0.53	0.11892	0.11892
2,3,7,8-TCDD	< 0.00031	< 0.0011	0.0056	< 0.00088	< 0.0013	< 0.00037	< 0.0016	0.0056	0.00159	0.00560
Total TCDD	0.0054	0.0035	B 0.44	N.A.	N.A.	N.A.	0.0091	0.44	0.11450	0.11450
2,3,7,8-TCDF	0.0005	< 0.00065	0.038	0.0044	0.00039	< 0.00087	< 0.00099	0.038	0.00654	0.01082
Total TCDF	0.0028	N.A.	0.96	0.076	0.00039	0.014	N.A.	0.96	0.21064	0.21064

"<" =Not Detected, the Associated Value is the Detection Limit.

N.A. =Detection limits are not available for total concentrations.

"B" =The Constituent was Detected in an Associated Blank.

"J" =The Concentration is an Estimate. The Constituent Was Positively Identified at a Trace Value

HW-1 -- Keystone Cement Co., Bath, PA

HW-2 -- River Cement Co., Festus, MO

HW-3 -- Heartland Cement Co., Independence, KS

NH-1 -- Ash Grove West, Inc., Inkom, ID

or is a Nontarget Constituent for which no Calibration was Performed.

Average

Detected =The average of the samples, excluding those that were not detected.

NH-2 -- Calaveras Cement Co., Tehachapi, CA

NH-3 -- Holnam, Inc., Artesia, MS

Exhibit 3-22

Total Concentrations of Dioxins and Dibenzofurans in As Managed CKD (µg/Kg)

ANALYTE	HW-1 Sample 1	HW-1 Sample 2	HW-2	HW-3	NH-1	NH-2	NH-3	MAXIMUM	AVERAGE	AVERAGE DETECTED
1,2,3,4,6,7,8-HpCDD	0.012	0.012	B 0.24	B 0.014	J 0.00067	< 0.0021	0.0039	0.24	0.040667	0.047095
Total HpCDD	0.023	0.023	B 0.54	B 0.027	J 0.00067	N.A.	0.014	0.54	0.104612	0.104612
1,2,3,4,6,7,8-HpCDF	< 0.0012	< 0.00082	0.1	0.0014	< 0.00047	< 0.00039	< 0.00087	0.1	0.015021	0.050700
1,2,3,4,7,8,9-HpCDF	< 0.00063	< 0.00062	0.012	< 0.00077	< 0.00078	< 0.00068	< 0.0014	0.012	0.002411	0.012000
Total HpCDF	N.A.	N.A.	B 0.15	B 0.0025	N.A.	N.A.	N.A.	0.15	0.076250	0.076250
1,2,3,4,7,8-HxCDD	< 0.0011	< 0.0027	0.022	< 0.00054	< 0.00052	< 0.00095	< 0.0016	0.022	0.004201	0.022000
1,2,3,6,7,8-HxCDD	0.0018	0.0023	0.038	< 0.00088	< 0.00085	< 0.00068	< 0.0016	0.038	0.006587	0.014033
1,2,3,7,8,9-HxCDD	< 0.0016	< 0.0015	0.026	< 0.00057	< 0.00062	< 0.00081	< 0.0018	0.026	0.004700	0.026000
Total HxCDD	0.057	0.06	0.86	0.0081	N.A.	N.A.	0.02	0.86	0.201020	0.201020
1,2,3,4,7,8-HxCDF	< 0.00089	< 0.0016	0.045	0.00048	< 0.00035	< 0.00033	< 0.00063	0.045	0.007040	0.022740
1,2,3,6,7,8-HxCDF	< 0.00049	< 0.00077	0.042	0.00046	< 0.0003	< 0.00027	< 0.00021	0.042	0.006357	0.021230
1,2,3,7,8,9-HxCDF	< 0.00035	< 0.00083	0.016	< 0.00033	< 0.00065	< 0.00063	< 0.0011	0.016	0.002841	0.016000
2,3,4,6,7,8-HxCDF	< 0.00065	J 0.00045	0.067	0.00074	J 0.00043	J 0.00042	< 0.0012	0.067	0.010127	0.013808
Total HxCDF	N.A.	J 0.0045	0.46	0.0027	J 0.00043	J 0.00042	N.A.	0.46	0.093610	0.093610
OCDD	0.009	0.008	B 0.19	B 0.046	B 0.0035	B 0.0027	B 0.011	0.19	0.038600	0.038600
OCDF	< 0.0024	< 0.0023	0.022	0.0016	< 0.0011	< 0.0029	< 0.0032	0.022	0.005071	0.011800
1,2,3,7,8-PeCDD	< 0.00076	< 0.0019	0.021	< 0.00057	< 0.00045	< 0.00043	< 0.0017	0.021	0.003830	0.021000
Total PeCDD	0.032	0.029	0.55	N.A.	N.A.	N.A.	0.0071	0.55	0.154525	0.154525
1,2,3,7,8-PeCDF	< 0.0012	< 0.0015	0.038	0.00048	< 0.00029	< 0.00047	< 0.00078	0.038	0.006103	0.019240
2,3,4,7,8-PeCDF	< 0.0006	< 0.0011	0.085	0.00044	< 0.00031	< 0.00041	< 0.00096	0.085	0.012689	0.042720
Total PeCDF	N.A.	N.A.	0.97	0.0054	N.A.	N.A.	0.00084	0.97	0.325413	0.325413
2,3,7,8-TCDD	< 0.001	< 0.0011	0.0034	< 0.00054	< 0.00059	< 0.0011	< 0.0013	0.0034	0.001290	0.003400
Total TCDD	0.036	0.035	B 0.24	B 0.002	N.A.	N.A.	0.0094	0.24	0.064480	0.064480
2,3,7,8-TCDF	< 0.00033	< 0.0015	0.029	0.00068	< 0.00037	< 0.00073	< 0.0012	0.029	0.004830	0.014840
Total TCDF	N.A.	0.0006	1.1	0.0091	N.A.	N.A.	N.A.	1.1	0.369900	0.369900

"<" = Not Detected, the Associated Value is the Detection Limit.

N.A. = Detection limits are not available for total concentrations.

"B" = The Constituent was Detected in an Associated Blank.

"J" = The Concentration is an Estimate. The Constituent Was Positively Identified at a Trace Value

HW-1 -- Keystone Cement Co., Bath, PA

HW-2 -- River Cement Co., Festus, MO

HW-3 -- Heartland Cement Co., Independence, KS

NH-1 -- Ash Grove West, Inc., Inkom, ID

Average
Detected = or is a Nontarget Constituent for which no Calibration was Performed.
The average of the samples, excluding those that were not detected.

NH-2 -- Calaveras Cement Co., Tehachapi, CA
NH-3 -- Holnam, Inc., Artesia, MS

are present at very low concentrations in the as managed CKD generated by both hazardous and non-hazardous waste fuel burning facilities. As was the case in the analyses of the as generated CKD, the majority of the dioxins and dibenzofurans were detected at concentrations below 100 ppt, while several samples had homolog concentrations approaching one ppb. Only one homolog was detected at a concentration exceeding one ppb (this time, total TCDF was detected at 1.1 ppb). These results also correspond with the results obtained from EPA's Phase I analyses of dioxins and dibenzofurans, with the exception of one of seven samples where total HpCDD, HxCDD, HxCDF, PeCDF, and TCDF were detected at concentrations exceeding one ppb. As summarized in Exhibit 3-23, the levels of dioxins and dibenzofurans detected in CKD appear to be slightly higher than those levels detected in samples of the as managed CKD, with the exception of total HxCDD, PeCDD, and TCDD homologs. The significance of this difference is not known; however, it is likely explained by both sample and analytical variation.

Finally, Exhibit 3-24 presents a summary of EPA's dioxin and furan analytical data collected in 1992 and 1993 that have been normalized to 2,3,7,8-TCDD equivalence.

Because dioxins and furans were detected in CKD from all 11 sampled facilities, the Agency believes it appropriate to carry consideration of these compounds through the risk assessment and decision rationale components of this report, which means that the presence of these compounds in CKD will influence the Agency's decisionmaking on the RCRA regulatory status of CKD.

General Chemistry

The following general chemistry target analytes were analyzed in all of the samples of as generated and as managed CKD obtained at 15 of the facilities sampled by EPA: chloride, fluoride, sulfate, sulfide, total organic carbon, total cyanide, and moisture content (or percent solids). Except for sulfide and sulfate, the same target analytes were also analyzed in all of the CKD samples obtained at the other five facilities sampled by EPA. Except for cyanide, the general chemistry target compounds were analyzed for general information, such as comparison with similar basic composition data supplied by the industry.

With one exception, total cyanide was not detected in any of the CKD samples. At one facility, cyanide was reported as detected in the as generated and as managed CKD samples. However, the reported levels were less than the method detection limit.

The Agency believes that no further consideration should be given to total cyanide for the purposes of this report because it does not appear to be present in CKD on an industry-wide basis. All of the analytical data from this effort are available in the docket for this Report to Congress.

Volatile Organics

Because of the nature of as generated CKD (i.e., temperature of 300° F or more, very dry matrix), the Agency considered it unlikely that volatile organic compounds would be present in this material. To confirm this, volatile organic compounds were analyzed in as generated CKD samples from 11 facilities.

The chemical analysis of the as generated CKD samples revealed a number of instances in which volatile organics were detected. The following discussion identifies those instances and presents the Agency's conclusions regarding their validity and implications.

Exhibit 3-23

Summary of Dioxin and Dibenzofuran Concentrations in CKD

ANALYTE	AS GENERATED - TOTAL (ug/Kg)			AS GENERATED - TCLP (ug/L)			AS MANAGED - TOTAL (ug/Kg)		
	MAXIMUM	AVERAGE	AVERAGE DETECTED	MAXIMUM	AVERAGE	AVERAGE DETECTED	MAXIMUM	AVERAGE	AVERAGE DETECTED
1,2,3,4,6,7,8-HpCDD	0.25	0.03824	0.04412	0.00003	0.000021	0.000019	0.24	0.040667	0.047095
Total HpCDD	0.55	0.08410	0.08410	0.000032	0.000018	0.000024	0.54	0.104612	0.104612
1,2,3,4,6,7,8-HpCDF	0.037	0.00716	0.01323	< 0.000017	< 0.000011		0.1	0.015021	0.050700
1,2,3,4,7,8,9-HpCDF	0.0074	0.00191	0.00740	< 0.000019	< 0.000014		0.012	0.002411	0.012000
Total HpCDF	0.067	0.01509	0.01509	0.000007	0.000007	0.000007	0.15	0.076250	0.076250
1,2,3,4,7,8-HxCDD	0.025	0.00455	0.02500	< 0.000018	< 0.000013		0.022	0.004201	0.022000
1,2,3,6,7,8-HxCDD	0.049	0.00812	0.04900	< 0.000021	< 0.000012		0.038	0.006587	0.014033
1,2,3,7,8,9-HxCDD	0.041	0.00695	0.04100	< 0.000019	< 0.000012		0.026	0.004700	0.026000
Total HxCDD	1.5	0.30644	0.30644	N.A.	N.A.		0.86	0.201020	0.201020
1,2,3,4,7,8-HxCDF	0.024	0.00466	0.01340	< 0.00001	< 0.000007		0.045	0.007040	0.022740
1,2,3,6,7,8-HxCDF	0.025	0.00458	0.01390	< 0.00001	< 0.000006		0.042	0.006357	0.021230
1,2,3,7,8,9-HxCDF	0.014	0.00284	0.00748	< 0.000024	< 0.000013		0.016	0.002841	0.016000
2,3,4,6,7,8-HxCDF	0.037	0.00618	0.00109	0.000021	0.000011	0.000005	0.067	0.010127	0.013808
Total HxCDF	0.23	0.05144	0.05144	0.000006	0.000005	0.000005	0.46	0.093610	0.093610
OCDD	0.1	0.02453	0.02453	0.00017	0.000073	0.000080	0.19	0.038600	0.038600
OCDF	0.01	0.00289	0.00585	0.000055	0.000028	0.000011	0.022	0.005071	0.011800
1,2,3,7,8-PeCDD	0.03	0.00530	0.03000	< 0.000024	< 0.000012		0.021	0.003830	0.021000
Total PeCDD	0.85	0.28737	0.28737	N.A.	N.A.		0.55	0.154525	0.154525
1,2,3,7,8-PeCDF	0.033	0.00601	0.01321	< 0.000017	< 0.000009		0.038	0.006103	0.019240
2,3,4,7,8-PeCDF	0.064	0.01006	0.03390	< 0.000008	< 0.000005		0.085	0.012689	0.042720
Total PeCDF	0.53	0.11892	0.11892	N.A.	N.A.		0.97	0.325413	0.325413
2,3,7,8-TCDD	0.0056	0.00159	0.00560	< 0.000022	< 0.000013		0.0034	0.001290	0.003400
Total TCDD	0.44	0.11450	0.11450	0.000005	0.000005	0.000005	0.24	0.064480	0.064480
2,3,7,8-TCDF	0.038	0.00654	0.01082	< 0.00001	< 0.000007		0.029	0.004830	0.014840
Total TCDF	0.96	0.21064	0.21064	N.A.	N.A.		1.1	0.369900	0.369900

"<" =Not Detected, the Associated Value is the Detection Limit.

N.A. =Detection limits are not available for total concentrations.
"B" =The Constituent was Detected in an Associated Blank.
"J" =The Concentration is an Estimate. The Constituent Was Positively Identified at a Trace Value
or is a Nontarget Constituent for which no Calibration was Performed.
Average
Detected =The average of the samples, excluding those that were not detected.

Exhibit 3-24**Summary of Combined 1992-1993 Dioxin/Furan Sampling Results
CKD 2,3,7,8, TCDD Toxicity Equivalence (ppm)**

Plant	As Generated	As Managed	Sample Year
River-Festus, MO ^a	$2.475 \times 10^{-4} \text{ }^b$	$1.955 \times 10^{-4} \text{ }^b$	1992 and 1993
Holnam-Tijeras, NM	$3.2 \times 10^{-5} \text{ }^b$	ND	1992
Heartland-Independence, KS ^a	3.6×10^{-6}	6.8×10^{-7}	1993
LaFarge-Fredonia, KS ^a	1.5×10^{-6}	$9.0 \times 10^{-6} \text{ }^b$	1992
Giant-Harleyville, SC ^a	8.2×10^{-7}	4.3×10^{-6}	1992
Ash Grove-Inkom, ID	1.3×10^{-7}	5.3×10^{-8}	1993
Independent-Catskill, NY	4.0×10^{-8}	ND	1992
Calaveras-Tehachapi, CA	7.5×10^{-8}	4.5×10^{-8}	1993
Keystone-Bath, PA ^a	$6.7 \times 10^{-8} \text{ }^b$	3.6×10^{-7}	1993
Holnam-Artesia, MS	8.0×10^{-9}	5.0×10^{-8}	1993
Ash Grove-Chanute, KS ^a	ND	ND	1992

^a - Hazardous Waste Burner^b - Denotes average of two samples

ND denotes a non-detect

In several instances the volatile organic compound methylene chloride was detected in as generated CKD samples. In each instance, however, this compound was also detected in one or more of the corresponding quality assurance blanks, including method, trip, field, and equipment blanks. Therefore, its presence in the CKD sample is attributed to contamination of the sample. Methylene chloride is a common laboratory contaminant, the presence of which at low concentrations is not unexpected and is usually attributed to contamination of the ambient atmosphere in the laboratory.

In several instances, volatile organic compounds were detected in CKD at only one or two facilities, usually near the detection limit. The compounds acetone, carbon disulfide, chlorobenzene, chloroform, ethyl benzene, tetrachloroethene, trichloroethene, and xylene are in this category. Acetone was detected at only one facility. Carbon disulfide, chlorobenzene, chloroform, ethyl benzene, and tetrachloroethene were measured just above the detection limit at only one facility each. Trichloroethene was measured just above the detection limit at only two facilities, and xylene was also detected at only two facilities. The Agency believes that no further consideration should be given to these compounds for purposes of this report because their measured levels are near the analytical detection limit and they do not appear to be present in CKD on an industry-wide basis.

Two volatile organic compounds were detected several times, but only in the samples analyzed by one of the two laboratories that conducted the volatile organics analyses. The Agency believes that

their detection is due solely to laboratory contamination or artifacts of the process of analyzing the samples that are unique to the laboratory that reported the analytes as detected. The compounds acetonitrile and trichlorofluoromethane are in this category. Acetonitrile was detected in all of the CKD samples analyzed at one laboratory but in none of the CKD samples analyzed at the other laboratory. Trichlorofluoromethane was detected in five of the CKD samples analyzed at one laboratory but in none of the CKD samples analyzed at the other laboratory. The Agency believes that no further consideration should be given to these compounds for purposes of this Report to Congress because their presence is due solely to laboratory contamination or artifacts of the analytical procedures used.

Four other volatile organic compounds were reported as detected in several CKD samples and are believed to be present due to sample contamination during the process of collecting and analyzing the samples or from artifacts of the analytical procedures. These compounds are benzene, 2-butanone, isobutyl alcohol and toluene. Additionally, the as generated CKD sample from one facility³⁴ had considerably higher levels of these compounds than did samples from the other facilities. The Agency believes that the integrity of the sample is suspect and therefore should not be considered. The Agency believes that no further consideration should be given to these compounds for purposes of this Report to Congress because their presence is believed to be due to laboratory contamination or artifacts of the analytical procedures.

No as managed CKD samples were subjected to analysis for volatile organics because the Agency believed that any such compounds, even if present in the as generated CKD, would have separated from the CKD due to prolonged exposure of the CKD to the elements (i.e., up to six months).

Semi-Volatile Organics

As was the case with volatile organic constituents, the Agency also considered it unlikely that volatile organic compounds would be present in this material (i.e., temperature of 300° F or more, very dry matrix). To confirm this, semi-volatile organic compounds were analyzed in as generated and as managed CKD samples from six facilities. None of the semi-volatile compounds were detected in either the as generated or as managed CKD samples.

The Agency believes that the semi-volatile organic compounds should not be considered further for purposes of this Report to Congress because they do not appear to be present in CKD, and accordingly, has not included them in the analysis that follows later in this report.

Pesticides

Thirteen target pesticide compounds were analyzed in as generated and as managed CKD samples from 11 facilities. Three of the target pesticide compounds were detected at a total of two facilities. Endrin and heptachlor epoxide were both detected in as generated CKD at one facility. Endosulfan was detected in both as generated and as managed CKD at another facility.

Because only three pesticide compounds were detected in CKD samples at only one facility each, the Agency believes that the pesticides do not warrant further consideration for this Report to Congress because they do not appear to be present in CKD on an industry-wide basis. Accordingly, the pesticide compounds are not included in the analysis that follows later in this report.

³⁴ Calaveras Cement Company, Tehachapi, CA facility. The results of the split sample analysis were similar.

PCBs

Seven PCB compounds were analyzed in as generated and as managed CKD samples from 11 facilities. None of the target PCB compounds were detected in either the as generated or as managed CKD samples obtained by EPA.

The Agency believes that PCBs should not be considered further for purposes of this Report to Congress because they do not appear to be present in CKD, and accordingly, has not included them in the analysis that follows later in this report.

Radionuclides

Raw materials are the major source of common, natural radionuclides that may be found in cement kiln dust because such materials are part of the earth's crust. Therefore, for example, if the limestone used in the manufacture of cement was slightly enhanced with background levels of the radioisotopes of uranium or thorium, slightly enhanced levels of these radionuclides would be expected to be present in the cement kiln dust. In order to properly evaluate any potential risks associated with management of CKD, the Agency conducted radiochemical analyses on samples of CKD for a number of the natural elements. The Agency also decided to analyze the samples for man-made elements, which could be present in raw materials due to their prior release in the environment, for example, from fallout from above-ground nuclear weapons testing and from the explosion of a satellite containing plutonium in the earth's atmosphere.

The Agency conducted gross alpha, gross beta, and gamma analyses as well as isotopic analysis involving chemical separations for the following specific analytes: radium-226, plutonium-238, plutonium-239, uranium-234, uranium-235, uranium-238, thorium-227, thorium-228, thorium-230 and thorium-232.^{35,36} Gamma analyses and plutonium isotopic analyses were performed on the as generated CKD samples from all 20 facilities and also on the as managed CKD samples from six of these facilities. Gross alpha and beta analyses and isotopic analyses for the other specific analytes listed above were determined for all of the CKD samples from six of the facilities.

Several of the naturally occurring radionuclides were detected in the CKD samples collected by EPA, including isotopes of lead, radium, uranium, thorium, and potassium. With the possible exception of uranium and potassium, the radiological activities determined for the naturally occurring radionuclides are considered to be within the range of activities normally found in environmental samples of comparable composition. That is, the activity levels observed for these radionuclides measured in CKD are expected to be no different than, for example, those found in samples of soil and rock that are randomly selected and sampled.

The activity levels for the uranium isotopes may be considered to be slightly higher than average values for these isotopes found naturally in soils and rocks. However, based on the equilibrium state of

³⁵ The radionuclide analyses were performed by EPA's National Air and Radiation Environmental Laboratory. The analytical methods that were used for the samples associated with this study are presented in the EPA document entitled *Eastern Environmental Radiation Facility Radiochemistry Procedures Manual* (doc. # EPA 520/5-84-006).

³⁶ The following radionuclides can be detected by the gamma spectroscopy method used in this sampling and analysis program: Be-7, Na-22, K-40, Cr-51, Mn-54, Co-56, Co-57, Co-58, Fe-59, Co-60, Zn-65, Sr-85, Y-88, Zr-95, Nb-95, Ru-103, Ru-106, Cd-109, Ag-110, Sn-113, Sb-124, Sb-125, I-131, Ba-133, Cs-134, Cs-136, Cs-137, Ba-140, La-140, Ce-141, Ce-144, Hg-203, Bi-206, Bi-207, Tl-208, Pb-212, Bi-214, Pb-214, Ra-226, Ra-228, U-235, U-238.

the isotopes, the levels are consistent with the expected values for environmental samples containing natural uranium which has not undergone any isotopic separation, enhancement, or depletion process. This demonstrates that the observed uranium activity levels are due to unaltered natural uranium. In addition, there is great variability in the natural concentrations of the isotopes of uranium in soils and rocks. Also, the incineration process in a cement kiln could reasonably be expected to slightly increase the concentration of the isotopes of uranium due to the substantial reduction in volume of the fuels burned and materials processed in the kiln. Therefore, the activity levels of uranium isotopes and decay products, and thorium isotopes as well, are consistent with what would be expected in the residual material resulting from the processing of materials containing naturally-occurring radionuclides.

For the man-made elements, the Agency subjected the samples from the 1992 EPA sampling program to gamma scan analysis. Certain samples from four of the facilities were also subjected to gross alpha and gross beta analyses, and isotopic analysis involving chemical separations for isotopes of plutonium, uranium and thorium. Based on the results, the Agency proceeded to analyze all of the samples for the plutonium isotopes.³⁷ Also, all of the CKD samples from the six facilities sampled by EPA in 1993 were analyzed for the man-made elements. Two of the man-made elements were detected³⁸ in CKD samples as follows. Three samples of as managed CKD had detectable levels of plutonium-239. Cesium-137 was detected in CKD samples as follows: in as generated and as managed CKD at four facilities; in as generated CKD two facilities; and in the TCLP extract of the as generated CKD from one facility. This is consistent with prior findings that, due to past above-ground weapons testing, very small amounts of Pu-239 and Cs-137 are routinely detected in soils and comparable media.

For the man-made radionuclides, the radiological activities determined for the EPA samples are considered to be within the range of activities normally found in environmental samples of comparable composition.

In summary, the Agency considers that the radiological activities determined for the whole CKD samples collected by EPA to be within the range of activities found in environmental samples of comparable composition. That is, the activity levels observed for the radionuclides measured in CKD are expected to be no different than, for example, those found in samples of soil and rock that are randomly selected and sampled. Nevertheless, because the Agency's sampling and analytical program did reveal detectable amounts of certain radionuclide species in CKD samples, it has decided to include certain of them in the risk analysis on the basis of their presence at levels exceeding defined risk criteria. Chapter 6 of this report identifies the radionuclide species that were included in the risk analysis along with the basis for their inclusion.

3.3.3 Leachable Concentrations

EPA has established four sets of tests, or characteristics, that are used to determine whether a given waste stream should be managed as a hazardous waste. Of these four characteristics that define RCRA-designated hazardous wastes (ignitability, corrosivity, reactivity, and toxicity), only toxicity is relevant to CKD. This is because CKD is a solid, inorganic, non-flammable substance that is not

³⁷ This included re-analysis of the samples from the original four facilities. The Agency considers the original analytical results to be valid analytical data. The re-analyses were conducted for comparison purposes.

³⁸ The analytical detection limit for the EPA radionuclide analyses is considered to be the minimum detectable activity (MDA) value. MDA is the smallest activity that must be present in a sample in order to yield a count rate that will be detected with 97½ % probability given detection criteria that give a 2½ % probability of falsely detecting activity in a blank sample. (The confidence levels cited here are those used by EPA for its analysis of the EPA samples.)

ignitable or reactive. Although CKD is highly alkaline, it is not considered corrosive under EPA's definitions, because the characteristic does not apply to solid materials. Examining the characteristic of toxicity in CKD is important in that the test is designed specifically to evaluate the potential for toxic trace metals to leach and migrate from solid wastes.

Metals

To assess the potential of CKD to exhibit the toxicity characteristic, EPA performed TCLP and SPLP leachate analyses of subsamples of the CKD samples. EPA compared the maximum and average concentrations (i.e., mass of a particular constituent per unit volume of extract) in TCLP and SPLP leachates from as generated and as managed CKD, as collected from all available sources, with TCLP standards for arsenic, barium, cadmium, chromium, lead, mercury, selenium, and silver. The results of these comparisons are presented in Exhibits 3-25 and 3-26. These comparisons show that, in general, concentrations of trace metals are well below their corresponding TCLP standards. In fact, for some constituents, the maximum observed leachate concentration is more than an order of magnitude below the corresponding regulatory standard. Among these data, however, four samples (two TCLP, two SPLP extracts) of a total group of 244 samples of as generated dust analyzed for lead yielded concentrations greater than the TCLP standard of 5 parts per million (ppm) (see Exhibit 3-25); the maximum concentration for these four samples was 16.5 ppm. Also, two samples of a group of 129 samples of as generated dust analyzed for selenium yielded concentrations greater than the TCLP standard of 1.0 ppm; the maximum concentration of these two samples was 1.711 ppm. As shown in Exhibit 3-26, one of 88 samples of as managed dust analyzed for barium yielded a concentration higher than the TCLP standard (102.000 ppm versus 100.0 ppm), and one of 88 samples of as managed dust analyzed for cadmium yielded a concentration above the TCLP standard (2.55 ppm versus 1.0 ppm).

The reader should note that the outcome of the above analysis may change if EPA revises several existing TC levels and promulgates TC levels for new chemicals based on updated national primary drinking water standards (NPDWS). Specifically, EPA recently revised the NPDWS for barium, cadmium, chromium, lead, and selenium to 2 mg/L, 0.005 mg/L, 0.1 mg/L, 0.015 mg/L, and 0.05 mg/L, respectively. EPA also established a NPDWS for nickel at 0.1 mg/L.

Because most of the target metals analytes were detected in all of the EPA CKD samples, the Agency believes it appropriate to carry consideration of these elements through the decision rationale and risk assessment process of this report, which means that the presence of these elements in CKD will influence the Agency's decision-making on the RCRA regulatory status of CKD.

Exhibit 3-25

Comparison of Maximum and Average Metals Concentrations in As Generated Dust with TC Standards

As Generated CKD-TCLP Test Results (parts per million)									
Analyte	TC Standard	Number of Samples	Maximum Concentration	Ratio of Maximum Concentration to Standard	Maximum Concentration Minus Standard	Average Concentration	Ratio of Average Concentration to Standard	Average Concentration Minus Standard	Number of values > Standard
Arsenic	5.0	227	0.636	0.13	-4.364	0.02035	0.004	-4.979	0
Barium	100	227	9.190	0.09	-90.810	0.59762	0.006	-99.402	0
Cadmium	1.0	227	0.508	0.51	-0.492	0.01480	0.015	-0.985	0
Chromium	5.0	227	1.290	0.26	-3.710	0.04571	0.009	-4.954	0
Lead	5.0	227	9.718	1.94	4.718	0.21396	0.043	-4.786	2
Mercury	0.2	227	0.022	0.11	-0.178	0.00083	0.004	-0.199	0
Selenium	1.0	112	1.711	1.71	0.711	0.07302	0.073	-0.926	2
Silver	5.0	227	0.166	0.03	-4.834	0.04147	0.008	-4.958	0
As Generated CKD-SPLP Test Results (parts per million)									
Arsenic	5.0	17	0.014	0.003	-4.987	0.00606	0.001	-4.994	0
Barium	100	17	1.860	0.019	-98.140	0.50462	0.005	-99.495	0
Cadmium	1.0	17	0.004	0.004	-0.996	0.00382	0.004	-0.996	0
Chromium	5.0	17	0.128	0.026	-4.872	0.0243	0.005	-4.976	0
Lead	5.0	17	16.500	3.3	11.500	2.13729	0.427	-2.863	2
Mercury	0.2	17	0.0001	0.0005	-0.1999	0.0001	0.0005	-0.1999	0
Selenium	1.0	17	0.276	0.276	-0.724	0.04578	0.046	-0.954	0
Silver	5.0	17	0.030	0.006	-4.970	0.00697	0.001	-4.993	0

Exhibit 3-26

Comparison of Maximum and Average Metals Concentrations in As Managed Dust with TC Standards

As Managed CKD-TCLP Test Results (parts per million)									
Analyte	TC Standard	Number of Samples	Maximum Concentration	Ratio of Maximum Concentration to Standard	Maximum Concentration Minus Standard	Average Concentration	Ratio of Average Concentration to Standard	Average Concentration Minus Standard	Number of values > standard
Arsenic	5.0	74	0.867	0.173	-4.133	0.05958	0.0119	-4.940	0
Barium	100	74	102.000	1.020	2.000	2.15876	0.0216	-97.841	1
Cadmium	1.0	74	2.550	2.550	1.550	0.08654	0.0865	-0.913	1
Chromium	5.0	74	1.290	0.258	-3.710	0.13824	0.0277	-4.862	0
Lead	5.0	74	4.570	0.914	-0.430	0.33766	0.0675	-4.662	0
Mercury	0.2	70	0.100	0.500	-0.100	0.00385	0.0192	-0.196	0
Selenium	1.0	66	0.303	0.303	-0.697	0.05055	0.0506	-0.949	0
Silver	5.0	73	0.500	0.100	-4.500	0.04772	0.0095	-4.952	0
As Managed CKD-SPLP Test Results (parts per million)									
Arsenic	5.0	14	0.013	0.003	-4.987	0.00416	0.0008	-4.996	0
Barium	100	14	0.869	0.009	-99.131	0.39564	0.0040	-99.604	0
Cadmium	1.0	14	0.004	0.004	-0.996	0.00336	0.0034	-0.997	0
Chromium	5.0	14	0.373	0.075	-4.627	0.09348	0.0187	-4.907	0
Lead	5.0	14	1.790	0.358	-3.210	0.50310	0.1006	-4.497	0
Mercury	0.2	14	0	0.002	-0.200	0.00012	0.0006	-0.200	0
Selenium	1.0	14	0.086	0.086	-0.914	0.02348	0.0235	-0.977	0
Silver	5.0	14	0.026	0.005	-4.974	0.00706	0.0014	-4.993	0

Dioxins and Furans

As expected due to the extremely insoluble nature of dioxins and dibenzofurans, Exhibit 3-27 shows that no homologs, except OCDD, were detected in TCLP extracts using detection limits ranging from 0.000003 µg/L to 0.000037 µg/L. Total OCDD was detected in two TCLP extracts of as generated CKD samples obtained from non-hazardous waste fuel burning facilities; the measured levels are 0.00017 µg/L and 0.00011 µg/L.

Based on these results, the Agency does not believe that leachable dioxins and furans should be considered further for purposes of this Report to Congress, and accordingly, has not included them in the analysis that follows later in this report.

General Chemistry

EPA did not conduct TCLP analyses of any as generated or as managed CKD for the general chemistry parameters. In addition, as discussed earlier in this chapter, EPA did not expect total cyanide to be present in CKD; therefore, EPA also did not conduct TCLP analyses for cyanide (i.e., as specified in 40 CFR §261, Appendix II, "If a total analysis of the waste demonstrates that individual analytes are not present in the waste, or that they are present but at such low concentrations that the appropriate regulatory levels could not possibly be exceeded, the TCLP need not be run").

Based on the preceding discussion, the Agency believes that cyanide should not be considered further for purposes of this Report to Congress, and accordingly, has not included it in the analysis that follows later in this report.

Volatile Organics

The Agency did not conduct TCLP analyses of the CKD for any of the volatile organic compounds due to EPA's expectations that low or non-detectable total concentrations of the volatile organic constituents would be found in CKD materials (i.e., as specified in 40 CFR §261, Appendix II, "If a total analysis of the waste demonstrates that individual analytes are not present in the waste, or that they are present but at such low concentrations that the appropriate regulatory levels could not possibly be exceeded, the TCLP need not be run"). The Agency believes that the futility of performing such analyses was demonstrated by the fact that no volatile organic constituents were confirmed present in CKD.

Based on the preceding discussion, the Agency believes that the volatile organic compounds should not be considered further for purposes of this Report to Congress, and accordingly, has not included them in the analysis that follows later in this report.

Semi-Volatile Organics

The Agency did not subject CKD leachates to analysis for semi-volatile organic compounds because EPA did not expect that any semi-volatile organic constituents would be found in CKD materials (i.e., as specified in 40 CFR §261, Appendix II, "If a total analysis of the waste demonstrates that individual analytes are not present in the waste, or that they are present but at such low concentrations that the appropriate regulatory levels could not possibly be exceeded, the TCLP need not be run"). The Agency believes that the futility of performing such analyses was demonstrated by the fact that no semi-volatile organic constituents were confirmed present in CKD.

Exhibit 3-27

TCLP Concentrations of Dioxins and Dibenzofurans in As Generated CKD (µg/L)

ANALYTE	HW-1 Sample 1	HW-1 Sample 2	HW-2	HW-3	NH-1	NH-2	NH-3	MAXIMUM	AVERAGE	AVERAGE DETECTED
1,2,3,4,6,7,8-HpCDD	< 0.000019	< 0.000023	< 0.000009	J 0.000016	J 0.000021	< 0.000028	< 0.00003	0.00003	0.000021	0.000019
Total HpCDD	N.A.	N.A.	N.A.	J 0.000032	J 0.000021	J 0.000019	N.A.	0.000032	0.000018	0.000024
1,2,3,4,6,7,8-HpCDF	< 0.000017	< 0.000012	< 0.000003	< 0.000008	< 0.000017	< 0.000014	< 0.000009	<0.000017	<0.000011	
1,2,3,4,7,8,9-HpCDF	< 0.000015	< 0.000018	< 0.000005	< 0.00001	< 0.000019	< 0.000019	< 0.000014	<0.000019	<0.000014	
Total HpCDF	N.A.	N.A.	J 0.000007	N.A.	N.A.	N.A.	N.A.	0.000007	0.000007	0.000007
1,2,3,4,7,8-HxCDF	< 0.00001	< 0.00001	< 0.000004	< 0.000005	< 0.000006	< 0.00001	< 0.000007	<0.00001	<0.000007	
1,2,3,6,7,8-HxCDF	< 0.000008	< 0.00001	< 0.000003	< 0.000003	< 0.000006	< 0.000009	< 0.000006	<0.00001	<0.000006	
1,2,3,7,8,9-HxCDF	< 0.00002	< 0.000024	< 0.000006	< 0.000004	< 0.000012	< 0.00001	< 0.000012	<0.000024	<0.000013	
2,3,4,6,7,8-HxCDF	< 0.000021	< 0.000007	J 0.000006	J 0.000004	< 0.000016	< 0.000015	< 0.000008	0.000021	0.000011	0.000005
Total HxCDF	N.A.	N.A.	J 0.000006	J 0.000004	N.A.	N.A.	N.A.	0.000006	0.000005	0.000005
OCDD	< 0.000035	B 0.000037	B 0.000027	J 0.000077	0.00017	0.00011	J 0.000057	0.00017	0.000073	0.000080
OCDF	< 0.000026	< 0.000033	< 0.000009	J 0.000011	< 0.000022	< 0.000055	< 0.000041	0.000055	0.000028	0.000011
2,3,7,8-TCDD	< 0.000022	< 0.000013	< 0.000005	< 0.000008	< 0.000009	< 0.000017	< 0.000014	<0.000022	<0.000013	
Total TCDD	N.A.	N.A.	N.A.	J 0.000005	N.A.	N.A.	N.A.	0.000005	0.000005	0.000005

"<" =Not Detected, the Associated Value is the Detection Limit

N.A. =Detection limits are not available for total concentrations.

"B" =The Constituent was Detected in an Associated Blank.

"J" =The Concentration is an Estimate. The Constituent Was Positively Identified at a Trace Value or is a Nontarget Constituent for which no Calibration was Performed.

Average

Detected =The average of the samples, excluding those that were not detected.

HW-1 -- Keystone Cement Co., Bath, PA

HW-2 -- River Cement Co., Festus, MO

HW-3 -- Heartland Cement Co., Independence, KS

NH-1 -- Ash Grove West, Inc., Inkom, ID

NH-2 -- Calaveras Cement Co., Tehachapi, CA

NH-3 -- Holnam, Inc., Artesia, MS

The Agency believes that the semi-volatile organic compounds should not be considered further for purposes of this Report to Congress because they do not appear to be present in CKD, and accordingly, has not included them in the analysis that follows later in this report.

Pesticides

EPA conducted TCLP leachate analyses for pesticides using as generated CKD from six facilities. There were no pesticide compounds detected in the TCLP leachates.

The Agency believes that the pesticides do not warrant further consideration for this Report to Congress because they do not appear to be present in CKD on an industry-wide basis. Accordingly, the pesticide compounds are not included in the analysis that follows later in this report.

PCBs

The Agency conducted TCLP leachate analyses for PCBs on samples of the as generated CKD collected from six facilities. EPA did not detect any PCB compounds in the TCLP leachates.

Because there were no PCB compounds detected in any of the CKD samples obtained by EPA, the Agency believes that they do not warrant further consideration for the purpose of this Report to Congress. Accordingly, the PCB compounds are not included in the analysis that follows later in this report.

Radionuclides

The Agency conducted gross alpha, gross beta, and gamma analyses as well as isotopic analysis involving chemical separations for the following specific analytes on TCLP leachates of CKD: radium-226, plutonium-238, plutonium-239, uranium-234, uranium-235, uranium-238, thorium-227, thorium-228, thorium-230 and thorium-232. Gamma analyses and plutonium isotopic analyses were performed on TCLP leachates of as generated CKD from six of the facilities. Gross alpha and beta analyses and isotopic analyses involving chemical separations for the other specific analytes listed above were determined for all of the CKD samples from six of the facilities.

Several of the TCLP leachates of the as-managed CKD samples had elevated levels of potassium-40 compared to the other aqueous samples. Potassium-40 is a naturally occurring radionuclide of relatively high natural abundance. It is reasonable to expect that the leaching process would concentrate the potassium-40, thereby producing the elevated activity levels. Since potassium-40 is a beta emitter, this would also explain the somewhat elevated gross beta activities of the TCLP leachate samples. In addition, Cesium-137 was detected in the TCLP extract of one sample of the as generated CKD sample.

For the man-made radionuclides, the radiological activities determined for the EPA samples are considered to be within the range of activities normally found in environmental samples of comparable composition.

As discussed earlier in this chapter, the Agency considers that the radiological activities determined for the whole CKD samples collected by EPA to be within the range of activities found in environmental samples of comparable composition. That is, the activity levels observed for the radionuclides measured in CKD are expected to be no different than, for example, those found in samples of soil and rock that are randomly selected and sampled. Nonetheless, because EPA detected several radionuclide species in CKD samples, it has decided to include certain of them in the risk analysis on the

basis of their presence at levels exceeding defined risk criteria. Chapter 6 of this report identifies the radionuclide species that were included in the risk analysis along with the basis for their inclusion.

3.4 STATISTICAL ANALYSES OF CKD CHARACTERIZATION RESULTS

As discussed in the previous sections of this chapter, the Agency detected potentially significant concentrations of certain trace metals and dioxins and furans in both the as generated and as managed forms of CKD. In an attempt to better understand the significance of these findings, EPA conducted a number of additional analyses.

The Agency notes at the outset that a number of caveats apply to this analysis and the results obtained thereby. These caveats limit the extent to which the results can reasonably be used to draw inferences or conclusions concerning the influence of cement kiln design and operating factors on CKD constituent concentrations. First, most of the CKD composition data in EPA's possession were obtained from one-time "grab" sampling at operating cement plants. The Agency believes that this was the general method employed to generate the PCA Survey and PCA Report data, as well as EPA's 1992 and 1993 field sampling data. Consequently, the data ascribed to a particular facility were collected at a particular point in time, and may or may not accurately reflect the typical composition of CKD or clinker over an extended period of time. In this regard, EPA notes that examination of some of the time series (process control) data submitted by some facility operators in response to the Agency's RCRA §3007 request indicate significant variation, on a day-to-day basis, in the concentrations of major CKD constituents; it seems reasonable that trace constituents may also vary in this manner. Second, the Agency's understanding of the CKD data provided by respondents to the PCA Survey is quite limited; information on collection methods and conditions is largely absent. Thus, for example, CKD constituent concentrations that are attributed to the burning of hazardous waste may actually have been collected when the cement kiln in question was not burning hazardous waste at all or under normal operating conditions.

3.4.1 Metals

As indicated above, for potentially important trace metal constituents, data were available from the following sources and were used for these analyses:

- 1992 EPA Sampling Data
- Individual 1991 Portland Cement Association (PCA) Surveys
- PCA CKD Metals Analysis Report (Draft and Final - January, 1992)
- Bureau of Mines (BOM) Information Circular 8885 (1982)

The Agency conducted the additional analyses of the metals data in three primary steps:

- Step 1 - Examine the concentration data from each source to determine if the measurements are random samples from a normal distribution. If appropriate, calculate a random concentration, the value of which lies between zero and the detection limit for the analytical measurement method, for constituent concentrations that were reported by the laboratory as "undetected."
- Step 2 - Compare the metal constituent concentrations from each of the data sources to determine if there are significant differences between the mean concentrations.³⁹ If

³⁹ The Agency used mean values in the parametric statistical tests described in this section after establishing that the data are

significant differences are not found, then the data from these sources may be assumed to be drawn from the same population and can be combined for subsequent analysis.

- Step 3 - Examine the data for correlations or trends that may suggest how metals concentrations may be influenced by the design and operating characteristics of individual cement kilns.

A detailed description of these analyses and the results obtained thereby are presented in a Technical Background Document for this Report to Congress which is available in the RCRA docket.

For Step 1, EPA observed substantial improvement in the test for normality (the Shapiro-Wilk statistic) in most cases by including the calculated concentrations for the "undetected" constituents. Moreover, substituting these randomly calculated non-zero concentrations for the "undetected" constituent concentrations results in concentrations that are in all cases normally distributed; that is, the hypothesis that the data are normally distributed could not be rejected at the 95 percent confidence level for any material type, analysis type, or constituent. As mentioned above, because standard statistical analyses presuppose normally distributed data, all of the Agency's subsequent analyses are based upon the inclusion of these calculated data.

In Step 2, EPA compared the calculated means from each of the other data sources to the EPA sampling data means using the student t-test. The EPA data served as the basis of comparison because the Agency has the highest level of confidence in its own data set. These comparisons of the means resulted in the following observations:

- Most of the means from the various sources are not significantly different from the EPA sampling data means (at the 95 and 99 percent confidence level).
- For those means that are significantly different from the EPA sampling data at the 95 percent confidence level, most are **higher** than the EPA sampling data means. By combining these data, the effect would be to **increase** the calculated mean constituent concentrations from the original EPA measurements. All subsequent analyses would be **more conservative** as a result.
- For those means that are significantly **lower** than the EPA sampling data, all but three have substantial overlap between the minimum and maximum concentrations reported for each data source. This suggests that the difference may be an artifact of the sampling technique (i.e., the sampling was not random) and that therefore one cannot reject the hypothesis that the samples are from the same population. Further, differences in means did not involve "critical" constituents (i.e., those flagged as hazardous constituents) except for antimony (discussed below).
- Only three mean concentrations were found to be significantly lower than the corresponding EPA sampling data value and to not have overlap in the range of observed concentrations. All three of these are mean concentrations for antimony and were calculated from PCA Report 2 and Bureau of Mines sources for "as generated" dust using "TCLP" and "Total" analytical methods. The reason for this anomaly is not known. It is interesting to note, however, that the mean antimony values reported in PCA Report 2 were two to three orders of magnitude lower than those in PCA Report 1, for reasons that

normally distributed. Parametric statistics require use of the mean rather than some other measure of central tendency, such as the median.

are not fully explained in PCA Report 2 (the final report). Because of this significant, unexplained swing in reported values, the Agency is inclined to discount these data. In addition, the mean antimony concentrations in the EPA and Bureau of Mines data sets differ by only a factor of about two.

Based upon this analysis, EPA concluded that the majority of the calculated mean concentrations for the EPA sampling data are not significantly different than the means from the other sources. The few concentration means that are significantly different do not adversely affect the overall analysis, for the reasons discussed above. Consequently, the Agency believed that it was reasonable to combine, or pool, the data from all of the available sources prior to conducting subsequent (Step 3) analyses.

Nonetheless, because in the next phase of the analysis the constituent data were examined in light of plant-specific design and operating factors, the available data set does not include observations from all active portland cement plants; it does, however, contain data from a substantial percentage of them (47 of the 115 active facilities). That is, because the analysis presented here focuses on cement kiln design and operating factors, only those composition data that can be attributed to specific plants or design and operating factors can be used. Accordingly, the data from the two PCA reports and the 1982 Bureau of Mines cement kiln dust study have not been used in this analysis, because these documents present no information on the design and operating factors of interest, nor do they identify the specific facilities that gave rise to the data presented therein.

EPA's next step was to attempt to determine whether CKD trace metal constituent concentrations might be affected by cement kiln design and operating factors. Given the disparities noted earlier in net CKD generation rates between kiln types and especially across fuel types, EPA focused its examination on these two variables. Accordingly, the Agency conducted t-test comparisons of the mean concentrations of trace metals in CKD found within these respective groups. Results of these analyses are presented below.

T-test to Examine Hazardous Waste Burning Effects. For this analysis, EPA pooled the data from both available sources, i.e., those containing material composition data and an indication of whether the corresponding facility does or does not burn hazardous wastes as fuel. The Agency calculated the mean of the metal concentration data for each Sample Type and Analysis Type subgroup. EPA then compared the mean concentration for each metal within each sub-group for those facilities burning hazardous wastes with those that do not. EPA used the t-test to determine whether the null hypothesis can be rejected for two means representing the same population at a given confidence level.

The majority of the means were not significantly different at the 95 percent confidence level for these two sub-groups; that is, there is no statistically significant difference in the mean concentration of most metals in most material and sample types in CKD generated by kilns burning hazardous waste versus those not burning hazardous waste. Exhibit 3-28 lists those means that may be considered different at a 95 percent confidence level.

Exhibit 3-28

T-test Comparison of Fuel Burning Effects on Metals Concentrations
(includes only EPA^a and PCA Survey Data)

Constituent	Sample Type	Analysis Type	Mean Concentration (ppm)		
			Kilns Burning HW	Kilns Not Burning HW	Ratio (HW + non-HW)
Cadmium	As Generated	Total	1.4×10^{-1}	5.2×10^0	2.7
Chromium	As Generated	Total	3.9×10^{-1}	1.6×10^{-1}	2.4
Lead	As Generated	Total	5.3×10^{-2}	2.0×10^{-2}	2.6
Thallium ^b	As Generated	Total	1.8×10^0	2.8×10^{-1}	.066
Arsenic	As Generated	TCLP	7.2×10^{-3}	1.2×10^{-2}	0.58
Barium	As Generated	TCLP	9.8×10^{-1}	3.9×10^{-1}	2.5
Cadmium	As Generated	TCLP	4.1×10^{-3}	1.7×10^{-2}	0.25
Nickel ^b	As Generated	TCLP	1.4×10^{-2}	5.3×10^{-2}	0.26
Selenium	As Generated	TCLP	3.4×10^{-2}	9.3×10^{-2}	0.37
Thallium ^b	As Generated	TCLP	2.0×10^{-2}	5.4×10^{-1}	.037
Mercury ^b	As Generated	SPLP	1.0×10^{-4}	9.8×10^{-5}	1.06
Nickel	As Generated	SPLP	1.4×10^{-2}	1.3×10^{-2}	1.07
Thallium ^b	As Generated	SPLP	2.3×10^{-2}	2.0×10^{-1}	0.12
Aluminum ^b	As Managed	Total	7.3×10^{-3}	1.5×10^{-4}	0.48
Arsenic	As Managed	Total	1.8×10^{-1}	9.9×10^0	1.8
Barium ^b	As Managed	Total	2.3×10^{-2}	1.4×10^{-2}	1.6
Cadmium ^b	As Managed	Total	2.7×10^{-1}	6.0×10^0	4.5
Chromium ^b	As Managed	Total	4.5×10^{-1}	2.1×10^{-1}	2.1
Mercury ^b	As Managed	Total	9.7×10^{-1}	3.4×10^{-1}	2.8
Lead ^b	As Managed	Total	1.1×10^{-3}	1.2×10^{-2}	8.8
Selenium ^b	As Managed	Total	1.4×10^{-1}	7.5×10^0	1.9
Silver ^b	As Managed	TCLP	3.0×10^{-2}	6.2×10^{-2}	0.48
Cadmium	As Managed	TCLP	1.8×10^{-1}	3.3×10^{-2}	5.5
Mercury	As Managed	TCLP	6.0×10^{-3}	1.2×10^{-3}	5.2
Selenium ^b	As Managed	TCLP	8.2×10^{-2}	3.4×10^{-2}	2.4
Chromium	As Managed	SPLP	1.8×10^{-1}	2.7×10^{-2}	6.8
Silver ^b	As Managed	EP	3.3×10^{-3}	5.0×10^{-2}	.065
Cadmium ^b	As Managed	EP	2.2×10^{-3}	1.4×10^{-1}	.016
Lead	As Managed	EP	2.9×10^{-2}	1.4×10^0	.020
Aluminum ^b	As Managed	RAI	2.3×10^{-4}	1.6×10^{-4}	1.4

^a 1993 sampling and analysis data not included.

^b Confidence level of 99 percent.

Cadmium, chromium, and lead are found at mean concentrations in as generated CKD that are from 2.4 to 2.7 times higher in dust from facilities burning hazardous wastes than in CKD from facilities not burning hazardous waste fuels. On the other hand, thallium concentrations are decidedly lower in the dust generated by the hazardous waste-burning kilns (and at the 99 percent confidence level); this pattern holds not only for total concentrations but also for results of both leaching procedures (TCLP and SPLP). A number of other constituents are found at significantly lower concentrations in TCLP leachate in CKD from hazardous waste-burning kilns relative to non-hazardous waste burning kilns, including arsenic, cadmium, nickel, and selenium. However, barium is found at higher concentrations in the leachates from hazardous waste-burning kilns.

For as managed CKD, a number of heavy metals are found at significantly higher concentrations in dust from kilns burning hazardous wastes; these include arsenic, barium, cadmium, chromium, mercury, lead, and selenium. Only aluminum is found at a lower mean concentration. Leach test results are somewhat inconsistent, with some constituents (e.g., cadmium) exhibiting higher concentrations in dust from hazardous waste-burning kilns using one leach test (TCLP), and the opposite result using a different though similar leach test (EP).

Overall, certain metals appear to be present at a consistently higher mean concentration in CKD generated by kilns burning hazardous waste than in CKD generated by kilns not using this type of alternative fuel. Lead, cadmium, and chromium are the most prominent examples.

T-test to Examine Influence of Kiln Type (Dry vs. Wet). For this analysis, EPA pooled the data from both available sources, i.e., those containing material composition data and an indication of whether the corresponding facility has dry or wet kilns (only four plants nationwide have both). The Agency calculated the mean of the metal concentration data for each Sample Type and Analysis Type subgroup. EPA then compared the mean concentration for each metal within each sub-group for those facilities with wet kilns to those that have dry kilns. This was performed with the t-test to determine whether the null hypothesis can be rejected, i.e., the two means represent the same population at a given confidence level.

The majority of the means were not significantly different at the 95 percent confidence level for these two sub-groups; those means that are significantly different at this confidence level are presented in Exhibit 3-29.

No statistically significant differences between the wet and dry process are apparent in the total metals concentrations of as generated CKD. For four metals, however, TCLP test results are higher for dust generated by the dry process kilns; mean concentrations of aluminum, cadmium, nickel, and selenium in TCLP leachate from dry kiln as generated dust ranged from 2.4 to 4.4 times those from wet kiln as generated dust. Antimony levels as determined by the SPLP test appear to be almost twice as high for dust from the wet process as from the dry process.

Results from the total metals concentrations tests (acid digestion and RAI⁴⁰) on as managed CKD are striking. Significantly higher concentrations of aluminum, arsenic, barium, cadmium, chromium, copper, mercury, lead, titanium, and zinc are found in the CKD from the wet process kilns; mean concentration differences range from a factor of about two to almost ten, and most of the differences in mean concentration are significant at the 99 percent confidence level. TCLP results for aluminum and chromium are similar. Additional test results from use of the EP method show higher

⁴⁰ The Agency used x-ray diffraction data for metal oxides reported in the PCA surveys to estimate total constituent concentrations of specific metals. These estimated total constituent concentrations have been designated "RAI" in the Report.

Exhibit 3-29

**T-test Comparison of Kiln Type on Metals Concentrations
(includes only EPA^a and PCA Survey Data)**

Constituent	Sample Type	Analysis Type	Mean Concentration (ppm)		
			Dry Kilns	Wet Kilns	Ratio (Dry + Wet)
Aluminum	As Generated	TCLP	1.1×10^{-1}	4.3×10^{-2}	2.4
Cadmium	As Generated	TCLP	1.8×10^{-2}	4.0×10^{-3}	4.4
Nickel ^b	As Generated	TCLP	5.6×10^{-2}	1.4×10^{-2}	4.0
Selenium ^b	As Generated	TCLP	1.1×10^{-1}	3.2×10^{-2}	3.5
Antimony	As Generated	SPLP	2.7×10^{-2}	4.6×10^{-2}	0.58
Arsenic	As Managed	Total	1.1×10^1	1.9×10^1	0.57
Barium ^b	As Managed	Total	8.9×10^1	2.9×10^2	0.30
Cadmium ^b	As Managed	Total	1.3×10^1	2.8×10^1	0.46
Chromium ^b	As Managed	Total	2.4×10^1	4.9×10^1	0.50
Mercury ^b	As Managed	Total	2.8×10^{-1}	1.2×10^0	0.24
Lead ^b	As Managed	Total	1.5×10^2	1.3×10^3	0.11
Aluminum	As Managed	TCLP	6.1×10^{-2}	2.1×10^{-1}	0.29
Chromium	As Managed	TCLP	9.6×10^{-2}	2.0×10^{-1}	0.48
Arsenic ^b	As Managed	EP	5.2×10^{-2}	1.4×10^{-2}	3.8
Selenium ^b	As Managed	EP	3.6×10^{-2}	3.7×10^{-1}	0.10
Aluminum ^b	As Managed	RAI	1.7×10^4	2.0×10^4	0.82
Copper	As Managed	RAI	1.2×10^2	3.0×10^2	0.40
Titanium ^b	As Managed	RAI	1.0×10^3	2.2×10^3	0.45
Zinc ^b	As Managed	RAI	3.6×10^2	2.2×10^3	0.17

^a 1993 sampling and analysis data not included.

^b Confidence level of 99 percent.

concentrations of selenium in as managed CKD from the wet process, though for most constituents, any differences in mean concentration are not statistically significant.

EPA can discern few overall trends from these results. Lead concentrations seem to be lower in CKD when using the dry process rather than the wet process, and total metals concentrations seem to be generally higher in as managed dust from the wet process. Otherwise, there do not appear to be consistent trends in metals content of these materials with respect to kiln technology type.

To better understand the determinants of trace metal concentrations in CKD, EPA wanted to determine whether there might be design and/or operating factors that influence contaminant

concentrations in a direct manner. Therefore, as a next step, EPA examined the correlation between chemical concentration and four individual variables (kiln age, kiln length, recycling rate, and percentage of fuel consumption supplied by coal), to examine the validity of the hypothesis that each in isolation is directly and linearly related to the concentration of individual metallic constituents.

Linear correlation analysis is a quantitative technique that is used to estimate the degree to which two variables are related. Strong positive linear correlation means that as the value of one variable increases, the value of the other increases in direct proportion. Conversely, negative linear correlation means that as the value of one variable increases, the other decreases in direct proportion. Correlation analysis can therefore be used to identify variables that may be useful in explaining or even predicting the value of a variable or phenomenon of interest, and is particularly useful as a preliminary step leading to application of more sophisticated quantitative techniques, such as multiple regression analysis.

The Pearson Correlation Coefficient measures the strength of the linear relationship between two variables; the coefficient value ranges from -1 to +1. When two variables are highly and positively correlated, the coefficient approaches +1. Alternatively, if the variables are negatively correlated (value between -1 and 0), the variables are related inversely. A correlation of zero means that each variable has no linear predictive value with respect to the other. For purposes of its analysis, EPA assumed that Pearson Correlation Coefficient values *greater* than +.75 or *less* than -.75 indicate that a given variable has a possibly significant effect on constituent concentration. EPA has made this assumption because in all likelihood, constituent concentrations in CKD and other materials are a function of several variables, rather than a simple linear function of just one. The Agency's purpose was to identify potentially significant variables for possible further analysis, and to ensure that it did not overlook any clear or dominant explanatory variables. EPA's threshold value of +/- .75 is an arbitrary level to identify those variables that appear to signify or be used to "predict" trace constituent levels.

EPA tested four factors for correlation with constituent concentration values:

- Kiln age;
- Kiln length;
- CKD recycling rate; and
- Percent of energy consumption supplied by coal.

EPA chose these factors because it appears that they may have some impact on the distribution of metallic and non-metallic constituents in the kiln system and CKD.

The Agency examined kiln age because the predominant kiln type being used has changed over time; in recent years many older wet process kilns have been replaced with more energy efficient dry process kilns. Dry and wet process kilns have different material residence times, temperature profiles, and other operating characteristics that may influence constituent concentrations. Moreover, the physical age and condition of a unit may affect its operating performance and, thereby, the characteristics of both product (clinker and cement) and waste (CKD). The kiln length influences the amount of time that dust and raw materials remain in the kiln, possibly altering their chemical composition. Because metallic (and other inorganic) constituents are not destroyed in the kiln system, their build up in and removal from the kiln system can be key factors in influencing the composition of CKD. CKD recycling rates may be a good indicator of the importance of these phenomena. Finally, EPA analyzed the possibility that the percentage of the energy consumed in making cement clinker that is supplied by coal may correlate with the concentrations of certain constituents in the CKD and other materials. A significant negative correlation may suggest that the use of alternative fuels (e.g., hazardous wastes) exerts an important influence on, for example, the composition of CKD (e.g., with respect to heavy metal concentrations).

In the majority of the cases in which EPA observed extreme (very high or low) Pearson correlation coefficient values there are a small number of observations (eight or less). Significant coefficient values (as defined within this context) are few for the analyses that involved larger data sets. Thus, it is difficult to draw any broad conclusions regarding the possible importance of the operating factors that EPA has examined here with respect to constituent concentrations. Nonetheless, there are some interesting findings from this analysis, which are discussed below.

Correlation Analysis of Kiln Age. No significant correlations (i.e., $> .75$ or $< -.75$) are apparent in the as generated CKD data for kiln age. For as managed dust, EP test results suggest both positive (antimony, molybdenum, selenium, and silver) and negative (arsenic, mercury, and zinc) correlations with kiln age. There are no instances of extreme coefficients for any constituent for more than one analysis type using the combined data. For cement, chromium and nickel concentrations are highly and positively correlated with kiln age, as reflected in both total and TCLP test results, while selenium is negatively correlated using these two analysis types. The impact of this finding is limited by the small number of data points (four to seven). TCLP leachate for mercury is positively correlated while total mercury concentration is somewhat negatively correlated.

EPA found no constituents with extreme correlation coefficients using the EPA sampling data. The results using only the PCA data parallel those using the combined data set for cement and as managed CKD because the PCA data set comprises almost all of the data points for cement and as managed CKD.

Correlation Analysis of Kiln Length. In the combined data set, there are no extreme correlation coefficient values from analysis of the as generated CKD data. For the EPA data for as managed dust, the analysis suggests both positive (antimony, molybdenum, and selenium) and negative (arsenic, mercury, and zinc) correlations with kiln length. It is noteworthy that this pattern with the same metals also appeared in the kiln age analysis presented above. Again, sample sizes for this analysis were quite limited (two to eight). A different analysis type ("RAI") indicates a strong positive correlation between kiln length and zinc concentration in as generated CKD. No instances of extreme coefficients resulted for any constituent for more than one analysis type for kiln length.

There are no constituents with extreme correlation coefficients using the EPA sampling data, and no constituents have extreme coefficients for more than one analysis type using PCA Survey Data. The EP and RAI results are, of course, identical to those from the combined data set, because these analysis types are not represented in the EPA data. In the very limited data (three observations from two facilities) for as generated CKD provided in the PCA Survey responses, total concentrations of arsenic, beryllium, cadmium, nickel, vanadium, and zinc have a strong negative correlation with kiln length, while total chromium and lead positively correlate with kiln length.

Correlation Analysis of Recycling Rate. For as generated CKD, only total zinc concentrations display a significant (negative) correlation with recycling rate, and this finding is based on only three observations. For as managed CKD, only a few constituents and analysis types show a strong linear relationship to recycling rates, and in most of these cases, the correlation results are based on only a few data points. Total concentrations of manganese and zinc, and EP concentrations of molybdenum and zinc are negatively correlated, while EP concentrations of antimony and TCLP concentrations of zinc are positively correlated. With the exception of the TCLP zinc concentrations, all of these correlations are influenced by very small sample sizes (two to four observations).

There are no instances of extreme coefficients for a constituent for more than one analysis type for the recycling rate variable.

Within the EPA data set, only silver and thallium concentrations in as managed dust (positive) show any significant correlation with recycling rate. In the PCA Survey data, results for the cement material type are identical to those in the combined data set. For as generated CKD, there are only three observations. These indicate significant negative correlations for total arsenic, beryllium, cadmium, nickel, vanadium, and zinc as well as significant positive correlations for chromium and lead. In as managed CKD, negative correlations are apparent for total manganese and zinc, and for EP concentrations of molybdenum and zinc; positive correlations are observed in EP results for antimony and TCLP results for vanadium and zinc. All but the last of these cases are drawn from very small data sets (two to four data points per analysis).

Correlation Analysis of Percent of Energy Consumption Supplied by Coal. For the as generated CKD data, only total zinc concentrations are strongly (negatively) correlated to coal use; this finding is based upon only three data points. For the as managed CKD data, total concentrations of manganese and zinc, EP concentrations of antimony, and zinc concentrations measured using the "RAI" method are negatively correlated with coal use. In contrast, EP concentrations of cadmium, molybdenum, silver, and zinc are positively correlated with the percentage of energy value derived from coal. Numbers of observations available in these cases range from two to twelve, and there are no instances of extreme coefficients for a constituent for more than one analysis type.

For the EPA data set, no extreme correlation coefficients appear in any material or analysis type, with the exception of total concentrations of lead, which are negatively correlated with the extent of coal use in both as generated and as managed CKD. In as generated CKD, total arsenic, beryllium, cadmium, nickel, vanadium, and zinc are negatively correlated, and total chromium and lead are positively correlated, with the extent of coal use. In as managed CKD, results are identical to those obtained using the combined data set, with the exception that TCLP concentrations of vanadium are positively correlated with the percentage of energy value derived from coal, in addition to the EP results described above.

For the PCA data, as before, cement analysis results are the same as in the combined data set.

3.4.2 Dioxins and Furans

In parallel with its examination of trace metal constituents, EPA evaluated the dioxins and dibenzofurans data for significant relationships and trends. First, the Agency attempted to determine whether or not the data obtained from Phase I and Phase II sampling are comparable and can be pooled for further analysis. This analysis was necessary because the laboratory methods used during Phase II analysis were selected specifically because they offered far greater sensitivity than those employed for Phase I analysis. T-test comparisons of individual analytes by sample type yielded the following results. No statistically significant differences at the 99 percent confidence level were observed in as generated or as managed CKD, though there were a few instances in which differences were apparent at the 95 percent level (1,2,3,4,7,8,9-heptachlorodibenzofuran in both as generated and as managed dust, and total tetrachlorodibenzodioxin in as managed dust). The means for all analytes in CKD are, as expected, considerably higher in the Phase I data than in the Phase II data, due to the more sensitive laboratory methods employed to generate the Phase II data. Phase II mean values are generally about ten to 30 percent of Phase I means in as generated CKD, while in as managed CKD, these ratios range between 15 and 50 percent.

Based upon these results, EPA concluded that, despite the absence of statistically significant differences between Phase I and Phase II results for CKD, it was probably not reasonable to combine the data for further analysis. To do so would imply that the data are all derived from the same population, an assumption that is known to be false, due to the very different ways in which the two data sets were generated.

Consequently, as a next step, the Agency ran some t-test comparisons of the dioxin and dibenzofuran constituents in the Phase II data set, i.e., the data with more detected values, to determine whether any statistically significant differences exist in CKD generated by cement kilns falling into various groups. Because of the limited number of available data points, EPA was able to conduct only two simple pair-wise comparisons:

- (1)Wet process kilns and dry process kilns; and
- (2)RCRA hazardous waste-burning kilns and non-hazardous waste burning kilns.

The results of these t-test comparisons yield, with only two exceptions, no statistically significant differences between the respective groups for any group, material type, analysis type, or analyte.

Comparisons of wet and dry process kilns produce an interesting result. As generated and as managed CKD organic constituent concentrations are generally more than one order of magnitude higher in CKD generated by dry process kilns than in CKD generated by wet process kilns.

Mean concentrations in as managed dust generated by kilns burning hazardous waste fuels (as indicated by both total and TCLP analyses) appear to be higher, often by more than one order of magnitude, than in CKD generated by kilns not burning hazardous wastes. The same pattern is observed in the totals analyses of as generated CKD, though in TCLP results, concentrations are marginally higher in the samples collected from kilns not burning hazardous waste fuels. In this latter case, however, nearly all observations are estimated values, because the corresponding measured TCLP concentrations were below detection limits. Nonetheless, these observations are constrained by the relatively small sample population (six facilities -- three RCRA hazardous waste burners and three non-hazardous waste burners) and thus the difficulty in establishing statistically significant differences between these groups. Additionally, the Agency recognizes that other types of fuel (e.g., coal) that may be either burned exclusively or else co-fired with RCRA hazardous wastes in the kilns could be significant contributors of organics and other constituents that are measured in the CKD.

3.5 CLINKER CHARACTERISTICS

During most of the facility sampling visits conducted by EPA for this study, samples of newly generated clinker were obtained and subjected to chemical analyses similar to those for cement kiln dust. There are two main reasons why EPA collected clinker samples during this study. First, the Agency wanted to be able to compare the actual and relative amounts of certain analytes in clinker with those in CKD as part of the RTC development effort. Second, the analytical data derived from analysis of the clinker samples will be used by EPA in another study. This study is entitled *Use of Hazardous Waste in Cement Production*. EPA's goal in this study is to examine how federal regulations and policies can and do affect the use of hazardous waste in cement production, and, should it be necessary, to determine the level of control necessary to protect human health and the environment.⁴¹

⁴¹ For more information, see the report titled *RCRA Implementation Study (RIS) Update: The Definition of Solid Waste* (EPA 530-R-92-021, July, 1992).

The samples of clinker that were obtained during this study are from a total of 18 facilities.⁴² Eleven of the 18 were using hazardous waste for some portion of their fuel during the EPA sampling. The other seven facilities were not using hazardous waste for fuel during the EPA sampling.

All clinker samples were analyzed for metals, radionuclides, and major ions.⁴³ Nine of those samples were also analyzed for dioxins, furans, semi-volatile organics, pesticides, and PCB's. Four of these nine samples were also analyzed for volatile organic compounds. Several sets of leachates were also prepared from the whole samples of clinker obtained during the EPA sampling visits. These TCLP and SPLP leachates were analyzed as follows: 18 sets of leachates for metals, and four sets of leachates for dioxins, furans, pesticides, PCB's, radionuclides, and major ions. Volatile organics and semi-volatile organics were not analyzed in clinker leachates because it is believed that these compounds, if present in the original whole samples, would have been driven from the samples during the leachate preparation process and thus could not be quantitated. Exhibit 3-30 presents the results of the clinker characterization for inorganics by fuel type (i.e., non-hazardous and hazardous waste fuels).

Dioxins and furans were not detected in either the whole clinker samples or in the TCLP and SPLP leachates. Thus, it was not feasible to compare dioxin and furan levels in clinker with general fuel type or other operating factors. Accordingly, dioxin and furan levels in clinker do not appear to correlate with levels found in CKD produced at the same facility, i.e., although dioxins were detected in CKD at several facilities, they were not detected in clinker produced at the same facilities.

No pesticides or PCB's were detected in either whole clinker or TCLP and SPLP leachates prepared from the whole clinker samples.

Only one volatile organic compound was detected in whole clinker. This compound is toluene. It was detected only once and its quantitated level is close to the detection limit. For reasons stated earlier, no TCLP or SPLP leachates were subjected to analysis for volatile organic compounds.

There were no semi-volatile organic compounds detected in whole clinker. There were two instances of quantitation estimates for di-n-butyl-phthalate at levels near 200 ppb. This is, however, below the established analytical method detection limit. For reasons stated earlier, no TCLP or SPLP leachates were subjected to analysis for semi-volatile organic compounds.

Several of the naturally occurring radionuclides were detected in the clinker samples collected by EPA, including isotopes of lead, radium, uranium, thorium and potassium. For the man-made elements, plutonium-238 was detected in clinker from one facility, and plutonium-239 was detected in clinker from another facility.

The Agency has drawn no conclusions at this time regarding the significance of any of the clinker data. The analytical results from clinker characterization for this study are available in the EPA docket for this Report to Congress. The Agency invites comments on all aspects of this clinker characterization data, including the above findings from the Agency's preliminary analysis of the clinker data.

⁴² One of the 18 facilities was re-visited and sampled a second time for analysis verification purposes. The re-visit is not counted in the statistics or facility counts presented in this section.

⁴³ At three of the 18 facilities, more than one clinker sample was obtained for sampling and analytical quality assurance purposes.

Exhibit 3-30**Analytical Results of Clinker Analyses for Inorganics By Fuel Type
(includes only EPA^a Data)**

Constituents	HW Fuel:	No	Yes	No	Yes
	Analysis:	Total	Total	TCLP	TCLP
	Units:	mg/kg	mg/kg	mg/L	mg/L
Antimony	Number of samples	7	9	7	9
	Number of detects	5	9	6	7
	Minimum detected value	9.5	5.3	0.05	0.05
	Maximum detected value	16.5	27.9	0.09	0.08
	Average of detected values	12.2	13.4	0.06	0.06
Arsenic	Number of samples	7	9	7	9
	Number of detects	7	9	7	9
	Minimum detected value	3.8	1.4	0.002	0.002
	Maximum detected value	25.4	14.7	0.006	0.004
	Average of detected values	9.4	7.3	0.003	0.003
Beryllium	Number of samples	7	9	7	9
	Number of detects	5	9	0	0
	Minimum detected value	0.75	0.86	ND	ND
	Maximum detected value	2.4	2.7	--	--
	Average of detected values	1.5	1.4	--	--
Cadmium	Number of samples	7	9	7	9
	Number of detects	0	0	0	0
	Minimum detected value	ND	ND	ND	ND
	Maximum detected value	--	--	--	--
	Average of detected values	--	--	--	--
Chromium	Number of samples	7	9	7	9
	Number of detects	7	9	7	6
	Minimum detected value	26.1	44.3	0.02	0.02
	Maximum detected value	138	150	0.33	0.95
	Average of detected values	60.9	83.5	0.15	0.4
Lead	Number of samples	7	9	7	9
	Number of detects	7	9	6	8

Exhibit 3-30 (continued)**Analytical Results of Clinker Analyses for Inorganics By Fuel Type
(includes only EPA^a Data)**

Constituents	HW Fuel:	No	Yes	No	Yes
	Analysis:	Total	Total	TCLP	TCLP
	Units:	mg/kg	mg/kg	mg/L	mg/L
	Minimum detected value	0.77	0.68	0.002	0.002
	Maximum detected value	21	33.1	0.016	1.9
	Average of detected values	4.7	9.3	0.007	0.25

Exhibit 3-30 (continued)**Analytical Results of Clinker Analyses for Inorganics By Fuel Type
(includes only EPA^a Data)**

Mercury	Number of samples	7	9	7	9
	Number of detects	0	1	1	0
	Minimum detected value	ND	0.07	0.0002	ND
	Maximum detected value	--	0.07	0.0002	--
	Average of detected values	--	0.07	0.0002	--
Nickel	Number of samples	7	9	7	9
	Number of detects	7	9	0	1
	Minimum detected value	13.1	20.1	ND	0.03
	Maximum detected value	82	91.1	--	0.03
	Average of detected values	33.9	36.5	--	0.03
Selenium	Number of samples	7	9	7	9
	Number of detects	1	2	0	3
	Minimum detected value	0.52	0.92	ND	0.001
	Maximum detected value	0.52	1.6	--	0.014
	Average of detected values	0.52	1.3	--	0.009
Silver	Number of samples	7	9	7	9
	Number of detects	6	5	3	3
	Minimum detected value	1.5	1.1	0.01	0.01
	Maximum detected value	8.2	9.9	0.06	0.06
	Average of detected values	3.5	3	0.02	0.03
Thallium	Number of samples	7	9	7	9
	Number of detects	1	2	1	0
	Minimum detected value	0.19	0.18	0.001	ND
	Maximum detected value	0.19	0.54	0.001	--
	Average of detected values	0.19	0.36	0.001	--

^a 1993 sampling and analysis data not included.

CHAPTER THREE

CKD GENERATION AND CHARACTERISTICS

3.0	INTRODUCTION.....	1
3.1	CKD GENERATION	1
3.1.1	Dust Collection Devices	2
3.1.3	Quantities and Fate of CKD Generated	16
	Differences in CKD Generation Rates Across Process Types	16
	Differences in CKD Generation Rates Across Process Types and Fuel Usage	18
	Differences in Gross CKD Generation Rates	18
	Differences in Net CKD Generation Rates	19
	CKD Recycling	19
	Recycling Differences	21
	Differences in Fate of CKD Across Process Types	21
	Differences in Fate of CKD Across Process Types and Fuel Usage	22
3.2	CKD GROSS CHARACTERISTICS	25
3.2.1	Physical Characteristics	25
3.2.2	Bulk Chemical Characteristics	29
3.3	CKD TRACE CHARACTERISTICS	30
3.3.1	EPA Sampling Program	30
3.3.2	Total Concentrations	32
	Metals 33	
	Dioxins and Furans	37
	General Chemistry	41
	Volatile Organics	41
	Semi-Volatile Organics	44
	Pesticides 44	
	PCBs 45	
	Radionuclides 45	
3.3.3	Leachable Concentrations	47
	Metals 47	
	Dioxins and Furans	50
	General Chemistry	50
	Volatile Organics	50
	Semi-Volatile Organics	50
	Pesticides 52	
	PCBs 52	
	Radionuclides 52	
3.4	STATISTICAL ANALYSES OF CKD CHARACTERIZATION RESULTS	53
3.4.1	Metals	53
3.4.2	Dioxins and Furans	61
3.5	CLINKER CHARACTERISTICS	62

LIST OF EXHIBITS

Exhibit 3-1	Flow Chart of Gross CKD Management Pathways.....	2
Exhibit 3-2	Air Pollution Control Devices Used at Cement Kilns.....	4
Exhibit 3-3	Schematic Diagrams of Common Types of Air Pollution Control Devices.....	5
Exhibit 3-4	1990 Gross CKD Collection by Different Types of Air Pollution Control Devices.....	7
Exhibit 3-5	Relationship Between Net and Gross CKD Generated in 1990.....	8
Exhibit 3-6	Gross and Net CKD Generated (1990)	10
Exhibit 3-7	Share of Net CKD Generated and Clinker Production Capacity (1990).....	11
Exhibit 3-8	Facilities With High Net CKD Generation Relative to Clinker Capacity	12
Exhibit 3-9	Percentages of Gross CKD Recycled, Sold, and Wasted (1990)	13
Exhibit 3-10	Recycling Rates Among Facilities That Operate Dry Kilns	14
Exhibit 3-11	Recycling Rates Among Facilities That Operate Wet Kilns	15
Exhibit 3-12	Average CKD Generation Rates Per Ton of Product (1990)	17
Exhibit 3-13	Fate of CKD as a Percent of Gross CKD (1990)	23
Exhibit 3-14	Particle Size Distribution of CKD by Process Type.....	26
Exhibit 3-15	Particle Size Distribution of CKD Midwest Portland Cement Company, Zanesville, Ohio.....	27
Exhibit 3-16	Hydraulic Conductivity of Freshly Generated and Managed CKD.....	29
Exhibit 3-17	Typical CKD Bulk Constituents	31
Exhibit 3-18	Trace Metal Concentrations in As Generated CKD	34
Exhibit 3-19	Trace Metal Concentrations in As Managed CKD	36
Exhibit 3-20	Trace Elements Commonly Found in Native Soils.....	37
Exhibit 3-21	Total Concentrations of Dioxins and Dibenzofurans in As Generated CKD.....	39
Exhibit 3-22	Total Concentrations of Dioxins and Dibenzofurans in As Managed CKD	40

Exhibit 3-23	Summary of Dioxin and Dibenzofuran Concentrations in CKD.....	42
Exhibit 3-24	Summary of Combined 1992-1993 Dioxin/Furan Sampling Results CKD 2,3,7,8, TCDD Toxicity Equivalence	43
Exhibit 3-25	Comparison of Maximum and Average Metals Concentrations in As Generated Dust with TC Standards	48
Exhibit 3-26	Comparison of Maximum and Average Metals Concentrations in As Managed Dust with TC Standards	49
Exhibit 3-27	TCLP Concentrations of Dioxins and Dibenzofurans in As Generated CKD.....	51
Exhibit 3-28	T-test Comparison of Fuel Burning Effects on Metals Concentrations	56
Exhibit 3-29	T-test Comparison of Kiln Type on Metals Concentrations	58
Exhibit 3-30	Analytical Results of Clinker Analyses for Inorganics By Fuel Type	64

