

13. BALL CLAY

13.1 INTRODUCTION

The purpose of this chapter is to evaluate the potential for environmental releases of dioxin-like compounds during the mining of ball clay and its subsequent uses. The presence of dioxin-like compounds in ball clay was discovered in 1996 as a result of an investigation to determine the sources of relatively high levels of dioxin found in two chicken fat samples during a national survey of poultry. The survey was conducted jointly by the U.S. Department of Agriculture and U.S. Environmental Protection Agency to assess the national prevalence and concentrations of CDDs, CDFs, and coplanar PCBs in poultry (Ferrario et al., 1997). The results of the investigation indicated soybean meal added to chicken feed was the source of dioxin contamination (Ferrario, Byrne and Cleverly, 2000). Further investigation showed that the CDD contamination came from the ball clay added to the soymeal as an anticaking agent. The ball clay was added at approximately 0.3% to 0.5% of the soybean meal. Samples of raw ball clay were subsequently taken at the mine of origin in Mississippi. Analysis of the ball clay obtained from the active mine showed elevated levels of CDDs having a congener profile similar to the CDD profiles found in the soymeal, chicken feed and immature chickens.

13.2 CHARACTERISTICS OF MISSISSIPPI EMBAYMENT BALL CLAYS

The ball clays from the mine discussed above are part of a larger ball clay resource which spans portions of western Kentucky, Tennessee, and Mississippi. These clays were deposited along the shores of the Mississippi Embayment during the early to middle Eocene Epoch which occurred approximately 40-45 million years ago. The Mississippi Embayment ball clays are secondary clays comprised mainly of poorly defined crystalline kaolinite. Other minerals present include illite, smectite, and chlorite. Quartz sand is the major nonclay mineral. These deposits of ball clay occur in lenses surrounded by layers of sand, silt, and lignite. These clays can have a gray appearance caused by the presence of finely divided carbonaceous particles. It is not uncommon to find black carbonized imprints of fossil leaves and other plant debris in the clay (Patterson and Murray, 1984).

The plasticity of ball clay makes this an important natural resource for the ceramic industry. The breakdown of the ceramic uses of ball clay include: 33% floor and wall tile;

24% sanitary ware; 11% pottery; and 32% other industrial and commercial uses (Virta, 2000). A minor use of ball clay was as an anticaking agent in animal feeds, which has subsequently been discontinued by the U.S. Food and Drug Administration (Headrick et al., 1999). Total mining of ball clay in 1999 was 1.14 million metric tons (Virta, 2000).

13.3 LEVELS OF DIOXIN-LIKE COMPOUNDS IN BALL CLAY

The joint EPA/FDA and USDA investigation of ball clay as a source of dioxin contamination in animal feeds resulted in sampling the clay at an operational mine in western Mississippi. Eight samples of raw (unprocessed) ball clay were collected from an open mining pit at a depth of about 10 to 15 m. Samples were prepared and analyzed by EPA using high resolution gas chromatography coupled with high resolution mass spectrometry (HRGC/HRMS) using EPA Method 1613 (Ferrario et al., 2000). The concentrations of the CDD/CDFs present in the raw ball clay samples from the one mine are shown in Table 13-1. The Limits of Detection (LOD):Limits of Quantification (LOQ) for the CDD/CDFs in the clay samples were 0.5:1 pg/g (ppt) d.w for the tetras, 1.0:2.0 pg/g for the pentas, hexas, and heptas, and 5.0/10.0 pg/g for the octas. The mean concentrations of all of the CDDs exceeded 100 ppt (d.w.). OCDD is found at the highest concentration in all of the samples followed by either 1,2,3,4,6,7,8-HpCDD or 1,2,3,7,8,9-HxCDD. The maximum OCDD concentration in the eight samples was approximately 59,000 pg/g. The most toxic tetra- and penta-congeners were present at unusually high concentrations in all of the samples with average concentrations of 711 pg/g and 508 pg/g for 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD, respectively. Although the ball clays show elevated levels of 2,3,7,8-substituted CDDs, they show very low levels of 2,3,7,8-substituted CDFs. In addition, there was a consistent ratio within the HxCDD congener distribution across all samples (i.e., 1,2,3,7,8,9-HxCDD was present at higher concentrations than the other 2,3,7,8-substituted HxCDD congeners). The average percent distribution among the three individual 2,3,7,8-hexa congeners was 5:17:78. This congener pattern was observed in all the raw ball clay samples analyzed. The mean total TEQ_{DF-WHO₉₈} for the raw ball clay was determined to be 1,513 pg/g, d.w. 2,3,7,8-TCDD accounted for 47% of the TEQ_{DF-WHO₉₈}, followed by 1,2,3,7,8-PeCDD at 34%. As expected, even though present at the highest concentration, OCDD contributed less than 1% percent of the total TEQ_{DF-WHO₉₈} due to its relatively small WHO-TEF. In

comparison, the typical range of background TEQ_{DF-WHO98} concentrations in North American urban and rural surface soils samples are 2 to 21 pg/g and 0.1 to 6 pg/g, respectively (see Volume 3: Properties, Environmental Levels, and Background Exposures, EPA/600/P-00/001Bc). In soil samples, all 2,3,7,8-CDD/CDF congeners are detected, and 2,3,7,8-TCDD represents less than one percent of total CDD/CDF present. The most prevalent congeners in soils are OCDD followed by OCDF. Table 13-2 compares the mean CDD/CDF congener group concentrations in ball clay to the mean congener group concentrations in rural and urban background soils. This comparison indicates there are no similarities in the congener group distributions between the ball clay and soils.

13.4 EVIDENCE FOR BALL CLAY AS A NATURAL SOURCE

Several lines of evidence suggest that dioxin-like compounds in ball clay are of natural origin:

- The clay samples were obtained from undisturbed deposits. It is unknown how human activity could have contaminated these deposits without disturbing them.
- EPA's Laboratory in Athens, Georgia, analyzed the Mississippi mine clays using a broad screen for anthropogenic contaminants and no compounds were found outside of the normal range. All known anthropogenic sources of dioxin have associated with them a wide variety of other contaminants. The absence of elevated levels of other compounds is strong evidence that the dioxins found in the clay are not the result of waste disposal.
- The congener profiles of ball clay do not match known anthropogenic sources (these profiles are presented in Chapters 2 - 8 of this Volume). Cleverly et al. (1997) reported on the congener profiles that are typical of known anthropogenic sources of dioxin-like compounds in the United States. These analyses were used as a basis for comparison to the profile of the raw ball clay.
 - The congener pattern characteristic of waste combustion sources differs significantly from the ball clay profile in several aspects. In combustion source emissions, all 2,3,7,8-substituted CDD and CDF congeners are measured and 2,3,7,8-TCDD is usually 0.1 to 1.0 percent of total CDD/CDF mass emitted. In ball clay, 2,3,7,8-TCDD is approximately 5% of total mass of dioxins present. As with the ball clay, the most prevalent 2,3,7,8-Cl substituted CDD congeners in most incinerator emissions are OCDD and 1,2,3,4,6,7,8-HpCDD. However, combustion emissions contain appreciable amounts of CDFs of which the 1,2,3,4,6,7,8-HpCDF, OCDF, 1,2,3,4,7,8-HxCDF, 2,3,7,8-TCDF and 2,3,4,6,7,8-HxCDF congeners dominate.
 - The combustion of wood generates a congener profile not unlike that of waste incinerator, (i.e., the ratio of CDD/CDF < 1), and all laterally substituted

congeners can be detected in emissions. The combustion of tree bark produces a congener profile in which the CDD/CDF ratio is > 1 , showing only minimal and barely detectable levels of CDFs in the smoke, the exception being that 2,3,7,8-TCDF is present at approximately 2% of total mass. The dominant congener in tree bark combustion emissions is OCDD ($> 30\%$ total CDD/CDF mass), followed by 1,2,3,4,6,7,8-HpCDD and 1,2,3,7,8,9-HxCDD.

- The congener profile of 2,4-D salts and esters seems to mimic a combustion source profile in the number of congeners represented, and in the minimal amount of 2,3,7,8-TCDD relative to all 2,3,7,8-Cl substituted congeners. Nevertheless, unlike the combustion source profile, the 1,2,3,7,8-PeCDD and the 1,2,3,4,6,7,8-HpCDF constitute major fractions of total CDD/CDF contamination present in 2,4-D.
- The congener profile of technical grade pentachlorophenol (PCP) is clearly dominated by OCDD and 1,2,3,4,6,7,8-HpCDD. However, only trace amounts of 2,3,7,8-TCDD are detected in PCP, and 1,2,3,4,6,7,8-HpCDF and OCDF constitute roughly 15% of typical formulations.
- Metal smelting and refining processes, such as secondary aluminum, copper and lead smelting, also have all the 2,3,7,8-Cl substituted CDD/CDF congeners in stack emissions. In secondary aluminum smelting, 2,3,7,8-TCDD is less than 0.1% of total CDD/CDFs whereas PeCDF is nearly 25% of total emissions of dioxin-like compounds, and the CDD/CDF ratio is < 1 . Secondary copper operations show a similar pattern of CDD/CDF emissions, but with five compounds dominating emissions: 1,2,3,4,7,8-HxCDF, 1,2,3,6,7,8-HxCDF, 1,2,3,4,6,7,8-HpCDF, OCDF, OCDD, and 1,2,3,4,6,7,8-HpCDD. In iron ore sintering, the dominant congener in emissions of 2,3,7,8-Cl substituted compounds is 2,3,7,8-TCDF.
- A number of studies have shown that natural processes can produce chlorinated aromatic compounds including dioxin-like compounds. Gribble (1994) reviewed the biological production of a wide variety of halogenated organic compounds in nature. For example, the Mississippi salt march grass "needlerush" (*Juncus roemerianus*) contains the aromatic compound 1,2,3,4-tetrachlorobenzene and the blue-green alga, *Anacystis marina* naturally contains chlorophenol (Gribble, 1994). The soil fungus, *Penicillium sp.*, produces 2,4-dichlorophenol, and the common grasshopper is known to secrete 2,5-dichlorophenol (Gribble, 1994). Urhahn and Ballschmiter (1998) also provide a good review of the chemistry of the biosynthesis of chlorinated organic compounds under natural conditions. It has been hypothesized that CDDs, CDFs, and other chlorinated aromatic compounds can be naturally formed from halogenated humic substances and halomethanes through chloroperoxidase-mediated reactions in undisturbed peat bogs (Silk et al., 1997). A similar chloroperoxidase-mediated biochemical formation of CDD/CDFs from chlorophenols was achieved under laboratory conditions by Oberg and Rappe (1992). It has been observed that chlorophenols can be biosynthesized (Gribble, 1994; Silk et al., 1997), and that chlorophenols are readily adsorbed into peat-bentonite mixtures (Virarghavan and Slough, 1999). Hoekstra et al. (1999) offered

the hypothesis that 2,3,7,8-TCDD, 1,2,3,7,8-PeCDD, and 1,2,3,7,8,9-HxCDD can be naturally formed in soils of coniferous forests from chlorinated phenol. These same congeners are also the predominant congeners in the ball clay from the Mississippi Embayment. Although none of these natural processes can be directly attributed to the presence of dioxin in ball clay, the existence of such mechanisms lends plausibility to a hypothesis that they are of natural origin.

- CDD/CDFs have been found in other clays quite distant from Mississippi Embayment ball clay deposits. No evidence of anthropogenic sources have been discovered in these areas either. Recently the presence of the CDDs have been discovered in kaolinitic clay mined in Germany (Jobst and Aldag, 2000). Because no anthropogenic source could be determined to explain the presence and levels of CDDs in the ball clay, Jobst and Aldag (2000) speculated that the CDDs were the result of an unknown geologic process. In addition, the German clay also has a congener profile similar to that observed in the Mississippi ball clay with an absence of CDFs at comparable concentrations and the predominance of the 1,2,3,7,8,9-HxCDD among the toxic hexa-CDDs. The similarity in the congener profiles in ball clay mined in the United States and Germany suggests a common origin to the CDDs present in these clays (Ferrario, Byrne, and Cleverly, 2000).

In summary, no anthropogenic sources have been identified that explain the levels and profiles of CDD/CDFs present in the clay. On the other hand, no definitive scientific evidence has been brought forward that identifies the principal chemical and physical mechanism involved to cause the selective chemical synthesis of CDDs under the conditions inherent to the formation of ball clays some 40 million years ago. In order to further understand the origin of CDDs in these clays, EPA is currently planning systematic evaluation of the distribution of CDDs in these clay deposits and the surrounding area.

13.5 ENVIRONMENTAL RELEASES OF DIOXIN-LIKE COMPOUNDS FROM THE MINING AND PROCESSING OF BALL CLAY

In 1995, approximately 993 million kg ball clay was mined in the United States (Virta, 2000). Multiplication of the mean $TEQ_{DF-WHO_{98}}$ concentration in mined ball clay by the total amount of ball clay mined in 1995 gives an estimate of 1,502 grams $TEQ_{DF-WHO_{98}}$ contained in all the ball clay mined in 1995. It is unknown if any of these CDDs are released to the environment during the mining, initial refining and product handling. As discussed above, most ball clay is used to produce ceramics through a process of high temperature vitrification. The temperatures found in ceramic kilns are well above the levels needed for both volatilization and destruction of CDDs. Even though these high

temperatures exist, it is unclear whether some release occurs and no stack measurements have yet been made. Therefore, insufficient evidence is available to make even a preliminary estimate of releases and this activity is classified as a category "E" source.

Table 13-1. Concentrations of CDDs Determined in Eight (8) Ball Clay Samples in the U.S.

Congener	Concentrations (pg/g, dry weight)				
	Mean	Median	Minimum	Maximum	TEQ _{DF} -WHO ₉₈
2,3,7,8-TCDD	711	617	253	1,259	711
1,2,3,7,8-PeCDD	508	492	254	924	508
1,2,3,4,7,8-HxCDD	131	134	62	193	13
1,2,3,6,7,8-HxCDD	456	421	254	752	46
1,2,3,7,8,9-HxCDD	2,093	1,880	1,252	3,683	209
1,2,3,4,6,7,8-HpCDD	2,383	2,073	1,493	3,346	24
OCDD	20,640	4,099	8,076	58,766	2
Total TEQ					1,513

Source: Ferrario et al. (2000).

Table 13-2. Comparison of the Mean CDD/CDF Congener Group Distribution in Ball Clay to the Mean Congener Group Distributions in Urban and Rural Soils in North America

Congener Group	Mean Concentration (pg/g, dry weight)		
	Raw Ball Clay	Urban Background Soil	Rural Background Soil
TCDD	3,729	36.1	2.3
TCDF	6	23.5	6.8
PeCDD	4,798	18.1	4.1
PeCDF	2	40.8	12.7
HxCDD	6,609	31.7	22.7
HxCDF	6	23.5	21.9
HpCDD	6,194	194.4	114.7
HpCDF	9	46.4	37.3
OCDD	11,222	2,596	565.1
OCDF	11	40.2	33.5
Total CDD/CDF	32,586	3,067.1	821.3

Sources: Adapted from U.S. EPA (2000a) and Ferrario, Byrne and Cleverly (2000).