

## 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 (USDA), the U.S. Food and Drug Administration (FDA), and EPA 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 that soybean meal added to chicken feed was the source of dioxin contamination (Ferrario et al., 2000). Further investigation showed that the CDD contamination came from the ball clay added to the soybean meal 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 samples showed elevated levels of CDDs with a congener profile similar to the CDD profiles found in the soybean meal, 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 that 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 to 45 million years ago. The Mississippi Embayment ball clays are secondary clays composed 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. The 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).

1 The plasticity of ball clay makes it an important natural resource for the ceramic industry.  
2 The breakdown of the ceramic uses of ball clay is 33% for floor and wall tile, 24% for sanitary  
3 ware, 11% for pottery, and 32% for other industrial and commercial uses (Virta, 2000). A minor  
4 use of ball clay was as an anticaking agent in animal feeds, but this use has been banned by FDA  
5 (Headrick et al., 1999). Total mining of ball clay in 1999 was 1.14 million metric tons (Virta,  
6 2000).

### 8 **13.3. LEVELS OF DIOXIN-LIKE COMPOUNDS IN BALL CLAY**

9 The joint EPA/FDA and USDA investigation of ball clay as a source of dioxin  
10 contamination in animal feeds resulted in sampling the clay at an operational mine in western  
11 Mississippi. Eight samples of raw (unprocessed) ball clay were collected from an open mining  
12 pit at a depth of about 10 to 15 m. Samples were prepared and analyzed by EPA using EPA  
13 Method 1613 (Ferrario et al., 2000). The concentrations of the CDDs/CDFs present in the raw  
14 ball clay samples from the one mine are shown in Table 13-1. The limits of detection:limits of  
15 quantification for the CDDs/CDFs in the clay samples were 0.5:1 pg/g (ppt, dry weight) for the  
16 tetras; 1:2 pg/g for the pentas, hexas, and heptas; and 5:10 pg/g for the octas. The mean  
17 concentrations of all of the CDDs exceeded 100 ppt (dry weight).

18 OCDD was found at the highest concentration in all of the samples, followed by either  
19 1,2,3,4,6,7,8-HpCDD or 1,2,3,7,8,9-HxCDD. The maximum OCDD concentration in the eight  
20 samples was approximately 59,000 pg/g. The most toxic tetra- and penta-congeners were present  
21 at unusually high concentrations in all of the samples, with average concentrations of 711 pg/g  
22 and 508 pg/g for 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD, respectively. Although the ball clays  
23 showed elevated levels of 2,3,7,8-substituted CDDs, they showed very low levels of 2,3,7,8-  
24 substituted CDFs. In addition, there was a consistent ratio within the HxCDD congener  
25 distribution across all samples (i.e., 1,2,3,7,8,9-HxCDD was present at higher concentrations  
26 than the other 2,3,7,8-substituted HxCDD congeners). The average percent distribution among  
27 the three individual 2,3,7,8-hexa congeners was 5:17:78. This congener pattern was observed in  
28 all the raw ball clay samples analyzed.

29 The mean total TEQ<sub>DF</sub>-WHO<sub>98</sub> for the raw ball clay was determined to be 1,513 pg/g dry  
30 weight; 2,3,7,8-TCDD accounted for 47% of the TEQ<sub>DF</sub>-WHO<sub>98</sub>, followed by 1,2,3,7,8-PeCDD  
31 at 34%. As expected, even though present at the highest concentration, OCDD contributed less

1 than 1% percent of the total  $TEQ_{DF-WHO_{98}}$  due to its relatively small WHO-TEF. In  
2 comparison, the typical range of background  $TEQ_{DF-WHO_{98}}$  concentrations in North American  
3 urban and rural surface soils samples are 2 to 21 pg/g and 0.1 to 6 pg/g, respectively (U.S. EPA,  
4 2000b). In soil samples, all 2,3,7,8-CDD/CDF congeners are detected, and 2,3,7,8-TCDD  
5 represents less than 1% of total CDD/CDF present. The most prevalent congeners in soils are  
6 OCDD followed by OCDF. Table 13-2 compares the mean CDD/CDF congener group  
7 concentrations in ball clay with the mean congener group concentrations in rural and urban  
8 background soils. This comparison indicates there are few similarities between the ball clay and  
9 soils in the congener group distributions.

#### 11 **13.4. EVIDENCE FOR BALL CLAY AS A NATURAL SOURCE**

12 Several lines of evidence suggest that dioxin-like compounds in ball clay are of natural  
13 origin. The clay samples were obtained from undisturbed deposits. It is unknown how human  
14 activity could have contaminated these deposits without disturbing them. The EPA laboratory in  
15 Athens, Georgia, analyzed the Mississippi mine clays using a broad screen for anthropogenic  
16 contaminants and no compounds were found outside of the normal range. All known  
17 anthropogenic sources of dioxin have associated with them a wide variety of other contaminants.  
18 The absence of elevated levels of other compounds is strong evidence that the dioxins found in  
19 the clay are not the result of waste disposal.

20 The congener profiles of ball clay do not match those of known anthropogenic sources.  
21 Cleverly et al. (1997) reported on the congener profiles that are typical of known anthropogenic  
22 sources of dioxin-like compounds in the United States. These analyses were used as a basis for  
23 comparison to the profile of the raw ball clay.

24 The congener pattern characteristic of waste combustion sources differs significantly  
25 from the ball clay profile in several aspects. In combustion source emissions, all 2,3,7,8-  
26 substituted CDD and CDF congeners are measured, and 2,3,7,8-TCDD is usually 0.1 to 1% of  
27 total CDD/CDF mass emitted. In ball clay, 2,3,7,8-TCDD is approximately 5% of total mass of  
28 dioxins present. As with the ball clay, the most prevalent 2,3,7,8-Cl-substituted CDD congeners  
29 in most incinerator emissions are OCDD and 1,2,3,4,6,7,8-HpCDD; however, combustion  
30 emissions contain appreciable amounts of CDFs, of which the 1,2,3,4,6,7,8-HpCDF, OCDF,  
31 1,2,3,4,7,8-HxCDF, 2,3,7,8-TCDF and 2,3,4,6,7,8-HxCDF congeners dominate.

1           The combustion of wood generates a congener profile not unlike that of waste incinerator  
2 (i.e., the ratio of CDD:CDF is <1), and all laterally substituted congeners can be detected in  
3 emissions. The combustion of tree bark produces a congener profile in which the CDD:CDF  
4 ratio is >1, showing only minimal and barely detectable levels of CDFs in the smoke, the  
5 exception being that 2,3,7,8-TCDF is present at approximately 2% of total mass. The dominant  
6 congener in tree bark combustion emissions is OCDD (>30% total CDD/CDF mass), followed by  
7 1,2,3,4,6,7,8-HpCDD and 1,2,3,7,8,9-HxCDD.

8           The congener profile of 2,4-D salts and esters seems to mimic a combustion source  
9 profile in the number of congeners represented and in the minimal amount of 2,3,7,8-TCDD  
10 relative to all 2,3,7,8-Cl substituted congeners. Nevertheless, unlike the combustion source  
11 profile, the 1,2,3,7,8-PeCDD and the 1,2,3,4,6,7,8-HpCDF constitute major fractions of total  
12 CDD/CDF contamination present in 2,4-D. The congener profile of technical-grade PCP is  
13 clearly dominated by OCDD and 1,2,3,4,6,7,8-HpCDD; however, only trace amounts of 2,3,7,8-  
14 TCDD are detected in PCP, and 1,2,3,4,6,7,8-HpCDF and OCDF constitute roughly 15% of  
15 typical formulations.

16           Metal smelting and refining processes, such as secondary aluminum, copper, and lead  
17 smelting, also have all the 2,3,7,8-Cl-substituted CDD/CDF congeners in stack emissions. In  
18 secondary aluminum smelting, 2,3,7,8-TCDD is less than 0.1% of total CDDs/CDFs, whereas  
19 PeCDF is nearly 25% of total emissions of dioxin-like compounds, and the CDD/CDF ratio is  
20 <1. Secondary copper operations show a similar pattern of CDD/CDF emissions, but with five  
21 compounds dominating emissions: 1,2,3,4,7,8-HxCDF; 1,2,3,6,7,8-HxCDF; 1,2,3,4,6,7,8-  
22 HpCDF; OCDF; OCDD; and 1,2,3,4,6,7,8-HpCDD. In iron ore sintering, the dominant congener  
23 in emissions of 2,3,7,8-Cl-substituted compounds is 2,3,7,8-TCDF.

24           A number of studies have shown that natural processes can produce chlorinated aromatic  
25 compounds, including dioxin-like compounds. Gribble (1994) reviewed the biological  
26 production of a wide variety of halogenated organic compounds in nature. The Mississippi salt  
27 march grass “needlerush” (*Juncus roemerianus*) contains the aromatic compound 1,2,3,4-  
28 tetrachlorobenzene, and the blue-green alga *Anacystis marina* naturally contains chlorophenol.  
29 The soil fungus *Penicillium sp.* produces 2,4-dichlorophenol, and the common grasshopper is  
30 known to secrete 2,5-dichlorophenol.

1           Urhahn and Ballschmiter (1998) also provide a good review of the chemistry of the  
2 biosynthesis of chlorinated organic compounds under natural conditions. It has been  
3 hypothesized that CDDs, CDFs, and other chlorinated aromatic compounds can be naturally  
4 formed from halogenated humic substances and halomethanes can be formed through  
5 chloroperoxidase-mediated reactions in undisturbed peat bogs (Silk et al., 1997). A similar  
6 chloroperoxidase-mediated biochemical formation of CDDs/CDFs from chlorophenols was  
7 achieved under laboratory conditions by Oberg and Rappe (1992).

8           It has been observed that chlorophenols can be biosynthesized (Gribble, 1994; Silk et al.,  
9 1997), and that chlorophenols are readily adsorbed into peat-bentonite mixtures (Virarghavan and  
10 Slough, 1999). Hoekstra et al. (1999) offered the hypothesis that 2,3,7,8-TCDD, 1,2,3,7,8-  
11 PeCDD, and 1,2,3,7,8,9-HxCDD can be naturally formed in soils of coniferous forests from  
12 chlorinated phenol. These same congeners are also the predominant congeners in the ball clay  
13 from the Mississippi Embayment. Although none of these natural processes can be directly  
14 connected with the presence of dioxin in ball clay, the existence of such mechanisms lends  
15 plausibility to a hypothesis that they are of natural origin.

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

26           In summary, no anthropogenic sources have been identified that explain the levels and  
27 profiles of CDDs/CDFs present in the clay. On the other hand, no definitive scientific evidence  
28 has been brought forward that identifies the principal chemical and physical mechanism involved  
29 in the selective chemical synthesis of CDDs under the conditions inherent in the formation of  
30 ball clays some 40 million years ago.

1 **13.5. ENVIRONMENTAL RELEASES OF DIOXIN-LIKE COMPOUNDS FROM THE**  
2 **MINING AND PROCESSING OF BALL CLAY**

3 In 1995, approximately 993 million kg of ball clay was mined in the United States (Virta,  
4 2000). Multiplication of the mean  $TEQ_{DF-WHO_{98}}$  concentration in mined ball clay by the total  
5 amount of ball clay mined in 1995 gives an estimate of 1,502 g  $TEQ_{DF-WHO_{98}}$  contained in all  
6 the ball clay mined in 1995. It is unknown whether any of these CDDs are released to the  
7 environment during the mining, initial refining, and product handling. As discussed above, most  
8 ball clay is used to produce ceramics through a process of high-temperature vitrification. The  
9 temperatures found in ceramic kilns are well above the levels needed for both volatilization and  
10 destruction of CDDs. Despite these high temperatures, it is unclear whether some release occurs,  
11 and no stack measurements have yet been made. Therefore, insufficient evidence is available to  
12 make even a preliminary estimate of releases, and this activity is classified as a Category “E”  
13 source.

**Table 13-1. Concentrations of CDDs determined in eight ball clay samples in the United States**

Congener	Concentration (pg/g, dry weight)				
	Mean	Median	Minimum	Maximum	TEQ <sub>DF</sub> -WHO <sub>98</sub>
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 with 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); Ferrario et al. (2000).