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# Dibenzo-p-dioxins in the Environment from Ceramics and Pottery Produced from Ball Clay Mined in the United States

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#### **Abstract**

Processed ball clay samples used in the production of ceramics and samples of the ceramic products were collected and analyzed for the presence and concentration of the 2,3,7,8-Cl substituted dibenzo-p-dioxins and -furans (PCDDs/PCDFs). The processed ball clay had average PCDD concentrations of 3.2 ng/g TEQ, a congener profile, and isomer distribution consistent with those found previously in raw ball clay. The PCDF concentrations were below the average limit of detection (LOD) of 0.5 ppg/g. The final fired ceramic products were found to be free of PCDDs/PCDFs at the limit of detection. A consideration of the conditions involved in the firing process suggests that the PCDDs, if not destroyed, may be released to the atmosphere and could represent an as yet unidentified source of dioxins to the environment. In addition, the PCDDs in clay dust generated during manufacturing operations may represent a potential occupational exposure.

**Keywords:** polychlorinated dibenzo-p-dioxins, processed ball clay, ceramics, sources

### 1. Introduction

found in ball clay from specific geological regions of the United States (Ferrario et al., 1999) and other regions in Europe (Jobst and Aldag, 2000; Rappe and Andersson, 2000). Ball clay had been discovered as the source of 2,3,7,8-Cl substituted PCDDs contamination in fryer chickens (Ferrario et al, 1998; Ferrario and Byrne, 2000), catfish (Cooper et al., 1996), and other animal products (Hayward et al., 1999) grown in the United States. All of the affected animals had been fed a diet of animal feed containing ball clay used as an anti-caking additive. The congener profile and isomer distribution of these dioxins in ball clay have characteristic features apparently unique to this particular type of clay. These characteristic features do not match those from other known dioxin sources and it has been suggested that the dioxins may be of natural origin (Rappe et al., 1998; Ferrario and Byrne, 2000). The process by which these dioxins originated has yet to be determined and is under investigation.

Raw clay samples originating from mines in the states of Mississippi, Kentucky, and Tennessee in the United States contain PCDD concentrations ranging from 0.5 to 3.5 ng/g World Health Organization - Toxic Equivalents (WHO-TEQ), calculated for dioxins only. Approximately 1.1 million metric tons of ball clay were mined in the United States in 1998. The primary markets for this clay include floor and wall tiles, sanitary ware, sculptural pottery, and various ceramic products, including electrical porcelain, fiberglass, fine china, dinnerware, and glazes. Lesser amounts are used as fillers, extenders, and binders, in asphalt emulsions, pesticides, and rubber. It is also used to make firebrick blocks, common bricks, high-alumina bricks, waterproofing seals, and drilling mud (US Department of the Interior, 1998).

Raw ball clay is selectively mined and transported as "balls" or lumps and undergoes a series of processes which make it ready for use. The first stage of processing is to shred the moist lumps of ball clay using flatbed shredders to form a homogeneous mixture of pieces approximately 3.8 cm in size. The mixture is fed to impact mills, each mill having a furnace, cyclone, and baghouse. As the clay pieces are fed into the mill, hot air (121°C; 340 cmm) from the furnace impinges on the clay lumps and they are dried and simultaneously pulverized to form the product which is referred to as "airfloated ball clay". This clay with a moisture of <3 % is blown into a cyclone for particulate separation and packaging (Personal communications, Old Hickory Clay Company).

Several processed ball clay samples and samples representative of the

ceramic products in the various stages of the manufacturing process were collected from a ceramic manufacturer and analyzed for the presence of 2,3,7,8-Cl substituted PCDDs and PCDFs to determine if they were present in the final products.

# 2. Experimental

*Materials*: Processed ball clay, clay dust collected in a manufacturing facility, molded unfired product, and the final fired ceramic product were collected from a ceramic facility and analyzed for the presence of 2,3,7,8-Cl substituted PCDD/PCDFs.

Analysis: The analytical procedures for specific isomer identifications, and congener profile have been described in detail elsewhere (Ferrario et al., 1999). Briefly, the analytical procedure is as follows: final ceramic products were cracked and pulverized into a fine powder with a mortar and pestle; processed ball clay and the clay mix actually used to make the ceramic were free-flowing and did not need grinding. Approximately two to five grams of the powder was mixed with an equal amount of anhydrous sodium sulfate and loaded into a glass fiber extraction thimble. The samples were fortified with a mixture containing 100 picograms each of the seventeen 2,3,7,8-13C PCDD/PCDFs and extracted with benzene in a Soxhlet extraction apparatus. The extracts were solvent exchanged into hexane and "cleaned-up" with sequential acidified/basic silica gel, alumina, and PX-21 graphitized carbon column chromatography. Samples were then fortified with 13C internal standards and analyzed on a Kratos Concept HRGC/HRMS operated in the lock mass drift correction mode at 10,000 resolution using isotope dilution techniques.

# 3. Results and discussion

The results of the analyses are presented in Table 1. The 2,3,7,8-Cl substituted PCDDs concentrations found in the processed ball clay samples from the ceramic facility (average TEQ = 3.2 ng/g) were comparable to the average values and average TEQ determined previously (1.5 ng/g) for samples collected in other locations. Moreover, the isomer distribution and congener profile are remarkably similar to the ball clay samples analyzed previously exhibiting the characteristic tetra-isomer profile, predominance of the 1,2,3,7,8,9-HxCDD among the toxic hexa-isomers and the absence of furans at comparable

concentrations. This demonstrates the stable and reproducible nature of these isomer patterns in the ball clay. As expected, the concentration determined for the clay mix actually used to make the ceramic and the pressed unfired product are nearly identical. As is evident from Table 1, the concentrations and TEQ are approximately 12.5 % of the levels determined for the processed ball clay. These results are consistent and proportional to the amount of ball clay actually used in the final mix according to the manufacturer.

The most interesting results were obtained from the analyses of the final fired ceramic products which showed that no dioxins were present at the limit of detection (0.2 pg/g for 2,3,7,8-TCDD). These results were confirmed from the analyses of a second fired ceramic product from another batch but known to have been made using the ball clay. The absence of dioxins in the fired ceramic would be expected considering the extreme thermal conditions in a kiln during the firing of ceramics and pottery.

Prior to firing, ceramics and pottery ware are dried at various temperatures and for various periods of time depending on the weight of the ware, the density of the setting, the water content of the clay, the air flow in the kiln and its ability to remove the evaporated vapor. This drying time can vary from several hours for light industrial ware to weeks or even months for large hand made sculptured pieces weighting hundreds of pounds. During the actual firing process the temperature is then slowly increased so that the quartz mineral and clay crystal particles can interact with the flux and other additives during the vitrification process to form the familiar hard brittle ceramic. The temperatures and heating time vary depending on the desired characteristics but temperatures typically exceed 1000°C. The ceramics in this study were fired at approximately 1200°C. During a typical initial firing for pottery and some ceramics called bisque or "single fire', temperatures reach 1400°C over an 8 hour period (Hansen, 1996).

Vogt et al. (1987) have demonstrated that PCDD/PCDFs formation is promoted downstream from the combustion zone of a furnace where the temperatures of the combustion off-gases have cooled to temperatures between 200-450°C. At temperatures of approximately 800°C, decomposition is enhanced to a rate of 99.95% depending on the time of exposure (Stehl and Lamparski, 1977). Theoretically, in incinerators, unimolecular destruction of PCDD/PCDFs at 99.99% can occur at 977°C with a retention time of 1 second to as little as 5 microseconds, if the temperature is increased to 1725°C (Shaub and Tsang, 1983). Considering that the typical firing temperature of most ceramic and pottery are well within the range reported to cause destruction of PCDD/PCDFs, it is highly

unlikely that the finished fired ceramic products would contain detectable concentrations of dioxins.

However, another important issue to consider is whether or not the dioxins have been destroyed or just volatilized during the period of time allowed for the increase in temperature within the kiln. Since dioxins can volatilize at temperatures ranging from 421°C to 510°C (Mackay et al., 1992) and considering the firing process for most ceramics and pottery involves a period of gradually increasing temperatures, it seems possible that the dioxins may volatilize and evaporate into the atmosphere before a temperature can be reached that is sufficient for their destruction. It is not known whether the volatilized dioxins would be destroyed by the higher temperatures reached at later stages within the kiln and/or stack.

Of the nearly 1.1 million metric tons of ball clay mined in the United States in 1998, approximately 1 million metric tons are used to make various ceramics and pottery products. Assuming the average TEQ present in the ball clay mined during that year was 1.5 ng/g TEQ and all of the dioxins present in the ball clay volatilized into the environment, then the resulting total TEQ quantity of dioxins released in 1998 from ceramic/pottery production in the United States would equal 1500 g WHO-TEQ. According to the EPA Inventory of Sources of Dioxins in the United States (USEPA, 1998), the total amount of dioxins released to all environmental media (except products) were 3000 g TEQ in 1995. Since this value does not include the contribution from the dioxins in the ceramics and if these assumptions prove correct, the dioxins from the ball clay would represent an additional 50% source that has been unaccounted for. This represents a potential significant source approximately equal to the amount emitted into the atmosphere from all known U.S. incineration sources. Since the range of TEQ concentrations for the raw ball clay was from 0.5 ng/g to 3.5 ng/g TEQ, the quantity potentially released could vary considerably from the estimated value of 1500 g. It is not known if any ceramic kilns operating in the U.S. have been tested for dioxin emissions. In lieu of a systematic study designed to determine the distribution of dioxins in the various ball clay mines and to measure the amount of dioxins emitted during the firing process (volatilized and not destroyed), the relative significance of this source of dioxins to the atmosphere is unknown.

Baker and Hites (2000) calculated global mass balance estimates for PCDDs/PCDFs and discovered that there are two significant imbalances between

source and deposition rates (kg/yr) of the PCDD/PCDF homologues - 1,2,3,4,6,7,8-HpCDD and OCDD. They suggest that one possible previously unidentified source for this imbalance in OCDD is the photochemical generation of PCDD/PCDF from the fungicide, pentachlorophenol (PCP). From the data of this paper, another possible source for this imbalance in both the HpCDD and OCDD could be the volatilization of PCDDs/PCDFs from ceramic manufacturing.

Moreover, dioxins have been found in other mined products in the United States (Holcomb et al., 1999) and Europe (Rappe and Andersson, 2000) and their natural formation (Ferrario and Byrne, 2000) and omissions from source inventories have been discussed previously (Rappe and Andersson, 2000). The natural formation of dioxins in forest fires (Bumb et al., 1980), peat bogs (Silk et al., 1997), sewage sludge (Oberg et al., 1992), fir forests (Hoekstra et al., 1999) and, as yet, undiscovered sources that are unaccounted for in source inventories may help to explain the imbalances.

It is also interesting to note that dust samples collected in a ceramic manufacturing facility by OSHA personnel also contained dioxins at the same concentration as that listed in Table 1 for the non-fired mix. Depending on the bioavailability of the dioxins in the ball clay, this may represent an occupational risk to the workers in these facilities who are exposed to the dust from air inhalation and dermal contact. In the ceramic facility that supplied the samples, the owner has voluntarily discontinued the use of this type of ball clay.

# Acknowledgements

We thank the following people for their assistance in various stages of this project: Aubry Dupuy for his guidance, Stanley Mecomber and Tripp Boone for their preparation of the samples. We thank Wayne Potter and Michael Bland of OSHA for the collection of samples and informative discussions. This paper has not been subject to the USEPA publication review process and, therefore, does not necessarily reflect the views of the Agency and no official endorsement should be inferred. The mention of trade names, or commercial products constitute neither endorsement nor recommendation of use.

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TABLE 1.
Analysis of Clay Samples from a Ceramic Manufacturer [pg/g, dw]

Matrix:	Processed	Clay Mixture	Molded	Ceramic
Congener:	Ball Clay	Mixture	(Unfired)	(Fired)
2,3,7,8-TCDD	1479	191	212	ND (0.2)
1,2,3,7,8-PeCDD	1215	155	157	ND (0.6)
1,2,3,4,7,8-HxCDD	271	32	30	ND(0.6)
1,2,3,6,7,8-HxCDD	777	103	93	ND (0.6)
1,2,3,7,8,9-HxCDD	2891	395	363	ND(0.6)
1,2,3,4,6,7,8-HpCDD	7495	1129	1082	ND(0.6)
OCDD	97850	29690	23030	ND (2.0)
Σ ΤΕΟ	3173	413	427	< 1

ND = Not Detected (LOD)

Duplicate samples were processed and analyzed and the % difference did not exceed 20%. Furans were not detected at the listed dioxin detection limits.