Polychlorinated Dibenzo-p-dioxins in the Environment from Ceramics and Pottery Produced from Ball Clay

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Introduction

Polychlorinated dibenzo-p-dioxins (CDDs) have been found in ball clay mined from specific geological regions of the United States [1] and Europe [2]. The congener profile and isomer distribution of the dioxins in this ball clay are distinctive and 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. The source of the dioxins has yet to be established. Clay samples originating from mines in the states of Mississippi, Kentucky, and Tennessee in the United States have been analyzed and contain dioxin concentrations ranging from 0.5 to 3.5 ppb I-TEQ. Approximately 1.1 million metric tons of ball clay was 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 [3]. The use of ball clay as an anti-caking agent in various animal feeds has been discontinued after it was discovered to have been responsible for elevated dioxin levels in chickens [4,5]. Several processed ball clay samples and samples representative of the ceramic products in the various stages of the manufacturing process have been collected from a ceramic manufacturer and analyzed for the presence of dioxins and furans (CDD/CDFs). The data suggests that the dioxins could be released to the atmosphere during the manufacturing process and that the dioxins in the clay dust may represent a potential occupational exposure.

Materials and Methods

Processed ball clay, clay dust collected in a manufacturing facility, molded unfired products, and the final fired ceramic product were collected from a ceramic facility and analyzed for the presence of CDD/CDFs. The analytical procedures for specific isomer identifications, and congener profile have been described in detail elsewhere [1]. 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-^{13}C CDD/CDFs 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 analyzed on a Kratos Concept HRGC/HRMS operated in the lock mass drift correction mode using isotope dilution techniques.

Results and Discussion:

The results of the analyses are presented in Table 1. The dioxin concentrations found in the processed ball clay samples from the facility were comparable to the average values and average I-TEQ determined previously for samples collected in other locations [6]. Moreover, the isomer distribution and congener profile are remarkably similar to the ball clay samples analyzed previously exhibiting the characteristic teta-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 1/8 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 product which showed that no dioxins were present at the limit of detection (0.2 parts-per trillion for 2,3,7,8-TCDD). These results were confirmed from the analyses of another 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. 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 [7]. Vogt et al [8] have demonstrated that CDD/CDFs 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 [9]. Theoretically, in incinerators, unimolecular destruction of CDD/CDFs 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 [10]. Considering that the typical firing temperature of most ceramic and pottery are well within the range reported to cause destruction of CDD/CDFs, 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 [11] and considering the firing process for most ceramics and pottery involves a period of gradual increasing temperatures, it seems possible that the dioxins may volatilize and evaporate into the atmosphere before the temperature reaches that which 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.

If the dioxins are being released to the atmosphere instead of being destroyed, this may prove to be a significant source of dioxins to the environment considering that the average I-TEQ for the ball clay is 1.5 ppb [6]. Of the nearly 1.1 million metric tons of ball clay mined in the United States in 1998, approximately 1million metric tons are used to make various ceramics and pottery products. To our knowledge, no 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. The USEPA is presently considering these issues.

It is also interesting to note that dust samples collected in a ceramic manufacturing facility by OSHA 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. We also thank David Cleverly, Matthew Lorber, and John Schaum of the USEPA ORD and Dwain Winters of the USEPA OPPTS for their useful consultations. 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 [ppt, dw]

Matrix:	Raw Ball Clay	Clay Mixture	Clay Molded (Unfired)	Ceramic (Fired)
Congener:				
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 (0.2)
Total TEQ	**3172.5**	**413.8**	**429.9**	-

ND = Not Detected (LOD)
Duplicate samples were processed and analyzed and the % difference did not exceed 20%.
Furans were not detected at the listed detection limits.