

## An Assessment of Polychlorinated Dibenzo-*p*-Dioxins and Furans in Raw Materials for Cement Production

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### 1. Introduction

During the past few years, cement kilns have emerged as one of the major thermal technologies for elimination of chemical wastes. The potential emissions of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzo-furans (PCDFs) during the operation of kilns for waste treatment is a matter of some concern. These emissions, however, should be viewed in light of the well-recognized ubiquity of selected PCDDs/PCDFs in the environment. Through limited testing, the data has indicated that dioxins/furans (dioxins) were present in the feed slurry for cement production<sup>1</sup>. The present report deals with a comprehensive assessment of dioxin and furan concentrations in the primary raw materials (limestone and fire clay) of cement production. The studies were initiated under the auspices of the Continental Cement Company (CCC), Hannibal, Missouri. The objective of the study was to ascertain the presence of dioxin and furan congeners and determine their concentrations in cores from limestone and fire clay quarries and to decipher whether the dioxin/furan deposition occurred during limestone formation or through depositions subsequent to the rock formation.

### 2. Experimental

Studies were conducted with a carefully-conceived experimental protocol to achieve a high degree of accuracy and precision and to eliminate contamination of materials during various stages of operation such as sampling, transportation, geological examination, grinding and homogenization, and chemical determination. A flow diagram of the protocol is shown in Figure 1 and elements of the protocol are discussed in the following sections.

#### *Sampling*

The two principle raw materials, limestone and fire clay, were sampled through coring at quarries and mines which are in use currently or are planned to be used in the future by CCC. The diameter of the cores was 5 cm, the length of the cores varied with the thickness of the formation. Four active limestone quarry faces (i.e., E.Cut, Harbourn, Genovise and Sanders) and three clay pits (i.e., Scego, Hollandsworth and Skouby) were cored. The core sampling grid for limestone was designed to clarify whether the dioxins deposition occurred during sediment

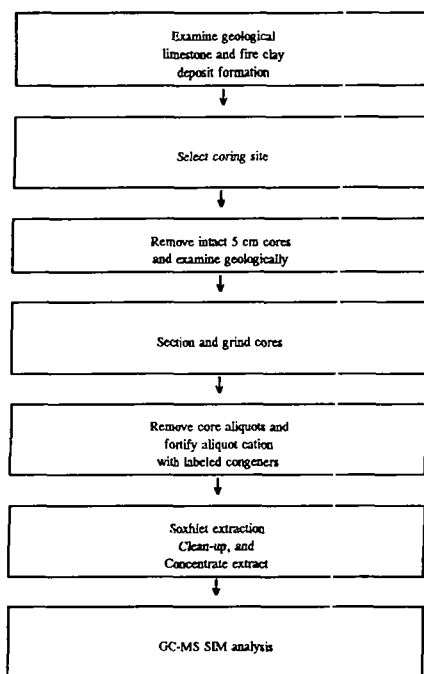


Figure 1. Flow Schematic of Experimental Protocol

accumulation or after the rock had been indurated. The sampling of the fire clay was based on the unique characteristics such as the uniform lithology and impervious nature of these materials. A total of 14 limestone and 12 fire clay cores were obtained in duplicate. The limestone sampling was carried out during the week of August 2, 1995, and the fire clay samples were collected between August 10-16, 1995. The samples were logged, packaged and shipped to the University of Missouri-Rolla for geological evaluation.

### *Geological Evaluation - Limestone Core Selection*

The intervals of the limestone cores that were chosen for analysis were based on the following postulations: (1) the dioxin was potentially a primary constituent, accumulating with the sediment; or (2) the dioxin was potentially added secondarily to the limestone after the rock had been indurated.

If the dioxin was a primary constituent it would have originated from, or been associated with, the fossil material which makes up most of the rock; therefore, intervals for sampling were chosen that were mostly fossil debris (crinoid remains) and not obviously affected by any later-supplied contaminant. The ideal material for a sample with dioxin as a primary constituent is typical Burlington Limestone, which originated from a shallow water marine deposit more than 350 million years ago.

In considering dioxin as a secondary constituent, several features were examined: (1) The dolomitized portions of the rock, would have taken place a short time after deposition (not in recent times). (2) Other segments of the limestone cores that warranted sampling were the parts that contain cavities or vugs (larger cavities) and stylolites. Their formation involved movement of pore water or groundwater which dissolved portions of the original limestone. Such a process could possibly have transported dioxin. (3) A more recent possible secondary contamination site

is the rock at the top of the quarry sections in contact with the glacial till or soil horizon. The dioxin contamination might have been carried through the unconsolidated material and concentrated on the much less porous and irregular (corroded) surface of the limestone.

#### *Geological Evaluation - Fire Clay Core Selection*

The rationale for choosing analytical sample intervals in the fire clay was based on the unique characteristics of fire clay. If dioxin did accumulate contemporaneously with the clay, almost any part of the clay core could be taken as a representative sample because the fire clay lithology is quite uniform. Therefore, if dioxin was a primary constituent with the fire clay, its distribution should also be uniform. Exceptions to this reasoning may be the clays at the top and bottom of the pits, as discussed below.

If dioxin is of secondary origin, there are several other targets to be considered, each related to the postulated origin of the fire clay deposits. The first postulation of origin is that the development and uniformity is due to warm waters migrating up through initially complex clays and other minerals to "homogenize" them to a uniform character. If any dioxin was present in the water, it would probably have been confined to the base of the clay deposit due to the impervious nature of the clayey sediments (the sandstone and sandy clay). Hence, the lower portions of the cores were chosen for sampling and analysis.

The second postulation of origin is that surface waters traveled down to the clay through overlying sediment, soil or till, and dioxin may have become concentrated in the upper portion of the clay deposits, again since migration through the impervious clay would have been unlikely. Thus, the upper portion of the clay unit was also sampled and analyzed.

Finally, the irregular, reddish-maroon colored areas in the fire clay deposits could have evolved from: (1) areas of oxidation of iron in place, or (2) the colored areas may have evolved from the transportation of iron oxide into the clay from oxygenated water moving through parts of the clay. If this water was dioxin-bearing, then dioxin should be associated with the reddish/maroon parts of the deposit which were accordingly selected for sampling and analysis.

#### *Chemical Analysis*

Selected sections of cores were first manually broken in 5-10mm pebbles with clean carbon steel hammers. The fire clay samples were then reduced to powder form in a blender. The crushed samples were sieved to remove particles larger than 200 microns. A strict procedure for cleaning all sample reduction devices was followed to avoid any systematic or accidental contamination of the samples. Furthermore, process blanks consisting of solvent washed silica gel were included as the quality assurance/quality control (QA/QC) samples such as the trip blanks, matrix blanks and reagent blanks.

The determination of PCDD/PCDF concentrations in the processed materials was carried out with a methodology similar to the US EPA methodology for soils and sediments (method 8270). The methodology involved homogenization of sample and removal of an aliquot. The aliquots were fortified with suitable  $^{13}\text{C}$  and  $^{37}\text{Cl}$  labeled internal standards and surrogates. The fortified samples were extracted in Soxhlet apparatus with dichloromethane. The extracts were cleaned over an alumina and silica gel column and further fractionated with a glass fiber-carbon column. The extracts were concentrated under nitrogen. The concentrated extract was injected into a 30m x 0.25mm (i.d.) fused silica capillary column with bonded polysiloxane stationary phase.

The dioxin and furan separations were achieved by programming the column oven temperatures from 120°-300°C/5°C per minute. The separated components were analyzed with a quadrupole mass spectrometer. The selected chromatographic and mass spectrometric parameters permitted separation and quantitation of congener classes. The quadrupole mass spectrometer was operated in the selected ion monitoring (SIM) mode. In addition,

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approximately 30% of the sample extracts were also reanalyzed with a high resolution gas chromatography (HRGC) and a high resolution mass spectrometer (HRMS) system.

### 3. Results and Discussion

The quantitation of dioxins and furans was limited to the sum of the tetra through octa congeners. A summary of the results is presented in Table 1a and 1b.

#### *Limestone*

The octachlorodibenzo-*p*-dioxin (OCDD) was the only PCDD congener detected above the 0.5 parts per trillion (ppt) level. OCDD was found in 27 of the 28 samples with concentration levels ranging from 2.5 ppt to 88 ppt. The highest concentration level (88 ppt) occurred at 21.5 feet deep in the Harbourn-02 sample, which is a chert nodule. The other levels were found in samples obtained below 53 feet deep near the base of the Eurlington formation.

No samples had detectable levels of OCDF (above 0.5 ppt). Only two samples had a detectable level of any furan; E Cut-01 indicated 2 ppt of HpCDF and Genovise-01 indicated 0.8 ppt of TCDF.

#### *Fire Clay*

Seventeen of the 23 samples had detectable OCDD levels. The concentration levels ranged from 3 ppt to 25 ppt. The high concentrations were found in samples obtained at depths greater than 48 feet. The highest reading (25 ppt) occurred at 50 feet deep in Hollandsworth-02 which is typical claystone. The other high values occurred near the base of the clay deposit. The concentrations in samples from close proximity to the surface were below the detectable limit of 0.5 ppt.

Only one sample, Hollandsworth-01D, had any detectable level of furans with results of 3 ppt of OCDF.

#### *Comparisons*

Sampling was performed in May, 1995 on the fire clay and limestone used in the slurry. The results of that sampling and analysis showed a pattern similar to the one obtained in the present study: all fire clay and limestone samples had detectable levels of OCDD, only three limestone samples had any furan detectable levels, and only one fire clay sample had a detectable level of a furan.

All slurry samples, in the previous study results reported by Schreiber<sup>1</sup>, were found to contain detectable levels of OCDD and only two samples had detectable levels of furans. Since the slurry is a mix of fire clay, limestone, and water, the detected OCDD and furans must have been present in at least one of the slurry components.

### 4. Conclusions

Recent studies have shown that a number of chlorinated dioxin and furan congeners, most noticeably OCDD, result from natural processes and are quite ubiquitous in the environment. This conclusion is strengthened by the results of the present study. OCDD/OCDF were found in deep rock formations and lead to the conclusion that these congeners were formed and deposited at the time of rock formation rather than subsequently transported. Furthermore, the levels of dioxins and furans in raw material varied considerably which agrees with the previous studies' results.

### 5. References

<sup>1</sup>Schreiber, R. (1995): Dioxin Emissions and Cement Kiln Operations. Presented at Dioxin '95, Edmonton, Alberta, Canada.

Table 1a. Geological Features and Concentrations of OCDD/OCDF in Limestone

Location (Property) & Sample Number	Sample Interval (ft)	Geological Features	OCDD (ppt)	OCDD Dupl. (ppt)	OCDF (ppt)	OCDF Dupl. (ppt)
Limestone Quarries						
E Cut-01	7.85-08.15	Weathered, cherty portion near top of core; possible surficial contamination.	8.5	3.5	2-HpCDF	<0.5
E Cut-02	37.9-38.6	Dolomitic portion of core; possible presence due to dolomitization or recent surface water.	2.5	3.5	<0.5	<0.5
E Cut-03	45.0-45.7	Near base of Burlington Formation; possible migration along base of formation above impervious Hannibal Shales.	15	12.5	<0.5	<0.5
Genovise-01	3.8-4.5	Weathered, cherty portion near top of core; possible surficial contamination.	6.5	9	0.8-TCDF	<0.5
Genovise-02	28.1-28.7	Dolomitic layer, quite ferruginous (limonitic).	9	6.5	<0.5	<0.5
Genovise-03	47.7-46.5	Dolomitic layer ferruginous (limonitic); vuggy and porous.	9.5	7.5	<0.5	<0.5
Genovise-04	51.5-52.3	Fairly typical Burlington Limestone; possible presence as primary constituent of the fossil material; near base of Burlington Formation; possible migration along base of formation above Impervious Hannibal Shales.	4.5	74	<0.5	<0.5
Harbour-01	13.3-13.95	Vuggy nature; good porosity; possible surficial contamination.	5	3.5	<0.5	<0.5
Harbour-02	21.3-21.65	Contains chert nodule; possible presence due to trapping in chert.	88	54	<0.5	<0.5
Harbour-03	35.9-36.5	Typical Burlington crinoidal limestone; probably not altered secondarily except for cementation.	5.5	<0.5	<0.5	<0.5
Harbour-04	54.1-54.75	Vuggy, slightly dolomitic limestone; good porosity.	9	14.5	<0.5	<0.5
Sanders-01	47.2-47.8	Typical Burlington limestone; possible presence from an internal (fossil) source.	3.5	5	<0.5	<0.5
Sanders-02	53.8-54.45	Typical Burlington limestone; stylolite seams indicating solution of primary rock	10	25	<0.5	<0.5
Sanders-03	57.4-58.0	Vuggy lens interval at the base of the Burlington Formation.	17	35	<0.5	<0.5

**Table 1b. Geological Features and Concentrations of OCDD/OCDF in Fire Clays**

Location (Property) & Sample Number	Sample Interval (ft)	Geological Features	OCDD (ppt)	OCDD Dupl. (ppt)	OCDF (ppt)	OCDF Dupl. (ppt)
Fire Clay Pits						
Seego-01	2.8-5.0	Possible surface contamination.	<0.5	<0.5	<0.5	<0.5
Seego-02	20.8-21.75	Mottled maroon clay; reason for mottling uncertain	5	10	<0.5	<0.5
Seego-03	23.0-24.0	Black, carbonaceous (organic?) clay.	14.5	N/A	<0.5	<0.5
Seego-04	49.1-49.5	Typical flint clay; no carbonaceous matter.	5	<0.5	<0.5	<0.5
Seego-05	61.7-62.35	Sandstone underlying clay; potential aquifer for contaminants in the clay pit.	6.5	<0.5	<0.5	<0.5
Hollandsworth-01	40.1-40.5	Sandy and slightly carbonaceous clay.	5	3	<0.5	3-OCDF
Hollandsworth-02	50.0-50.4	Typical claystone.	25	13.5	<0.5	<0.5
Hollandsworth-03	63.25-64.75	Slightly sandy interval near the base of the clay.	3.5	20	<0.5	<0.5
Skouby-01	11.8-12.2	Carbonaceous material (plant stems).	4.5	<0.5	<0.5	<0.5
Skouby-02	29.8-30.65	Carbonaceous material (plant stems).	7	<0.5	<0.5	<0.5
Skouby-03	34.3-35.1	Different appearance than adjacent; more typical claystone; more plastic and wet.	5	9	<0.5	<0.5
Skouby-04	55.85-56.45	Lower part of clay deposit.	13	8	<0.5	<0.5

N/A Not Analyzed