A Study of Hydrating Dioxin by Extract of Effective Microorganisms

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1. Purpose

Dioxin is created at fast speed in incinerating process to burn industrial waste and other hazardous wastes due to various chloride and vinyl chloride. In Europe and in the States, the dioxin problem has been already resolved because of strict government guidelines established several years ago. However, in Japan, it was only December 1, 1997 when the law to enforce local governments to measure the level of dioxin emitted from waste incinerators run by the local governments became effective. The authors applied extracts of effective microorganisms and ceramics powder to a waste incinerator run by a local government to test their effectiveness to hydrate dioxin.

2. Experiment

A local government incinerator which processes 5,000 tons of waste per year was used for the experiment. One kilogram of ash from one day of incinerator operation was taken for two separate days of regular operation to serve as control sample. Experimental sample of 1 kg ash was taken from the ash of one experimental operation in which, prior to incinerating waste, 1kg of ceramics powder including extracts of effective microorganisms was spread per ton of waste, then extract of effective microorganisms was sprayed 30 minutes later. Thirty-five grams each of sample was taken from control and experimental samples, placed in homogenizer to homogenize with 10 lt. of acetone, filtered by Milex-HV_{13}, and dried under low pressure. The dried substance was resolved in MeOH and analyzed by a spectroscope in accordance with dioxin/antibody-enzyme reaction test prescribed by United Sates Environmental Agency. In this experiment, 2,3,7,8 dioxin were used as standard. PCB or benzyl chloride, after being immersed in ceramics powder and extract of effective microorganisms, was placed under electrolysis to confirm that Cl^- moved toward + by using EPMA and that Cl^- was fixed in a stable form to cement which was newly developed to trap Cl^-.

3. Results

Standard dioxin 0.1ppm liquid showed 2.832 for OD, and 0.01ppm liquid showed 1.857. The control sample showed 3.756, while the experimental sample showed 1.511. Additional testing is underway by MS and EPMA to confirm that over 90% of dioxin was successfully hydrated by applying ceramics powder and extract of effective microorganisms.

Hydrating Dioxin by Extract from Effective Microorganisms (EMZ)

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PURPOSE

High density of dioxin is generated in the process of incinerating industrial and other hazardous wastes which includes various chloride including vinyl chloride. Toxicity of dioxin is very strong, specially, that of 2,3,7,8-T_4CDD are considered the strongest on earth. In addition, serious effects of environmental estrogens (exogenous chemicals that disrupt the functions of hormones when they enter human and animal bodies) on ecological system are often reported to confirm that various chemical substances are the cause for polluting earth environment and damaging human health.

One of the major countermeasures to suppress dioxin is to maintain temperature above 900C in incinerators to facilitate complete burning. EMZ and EMZ ceramics which are usually applied to save energy can bring complete burning in ordinary incinerators; thereby, suppressing dioxin being generated.

This experiment was conducted in a municipal incinerator to determine the effect of EMZ and EMZ ceramics powder to suppress dioxin being generated and to analyze the mechanism of suppression.

EXPERIMENT-1

Experimental Method

A municipal government incinerator which processes 5000 tons of waste per year was used for the experiment. One kilogram of ashes from one day of incinerator operation was collected for two separate days of regular operation to serve as control sample. In the experiment, waste was first sprayed with 1kg of EMZ ceramics (baked at 1300C) powder per ton of waste, then, 30 minutes later with 1lt. of EMZ per ton of waste prior to burning. After burning, 1kg of ashes was collected as the experimental sample. A test sample of 35 grams was taken from the control samples and the experimental sample respectively, and placed in a homogenizer to homogenize with 10ml of acetone, then filtered by Milex-HV_{13} to be dried under low pressure. The dried substance was resolved again in methanal and analyzed by spectroscope in accordance with dioxin/antibody-enzyme reaction test prescribed by United States Environmental Agency. In this measurement, higher the dioxin density, lighter the yellow color appears. The color density was determined by spectroscope to identify dioxin. Pure 2,3,7,8-T_4CDD of 0.01ppm and 0.1ppm were used as the standard in this experiment.

Experimental Results

The value of OD (measured by spectroscope) of the standard dioxin solution of 0.01ppm showed 1.857 and 2.832 for the solution of 0.1ppm. The control sample (before the treatment) measured 3.756, while the experimental sample (after the treatment) measured 1.511, which indicated 58.7% reduction.

The fact that the ashes of the burnt waste which was sprayed with EMZ measured lower level of dioxin indicates that EMZ has power to suppress dioxin being generated.

EXPERIMENT-2

Based on the results of the experiment-1, a follow-up experiment was conducted to increase the effect of EMZ to suppress dioxin being generated.

Experimental Method

Another municipal incinerator (which processes 80 tons per day) was used as the experimental site. One kilogram of ashes from regular operation was collected as the control sample. One liter of EMZ and 1kg of EMZ ceramics powder per ton of waste were sprayed to waste before burning. A total 80 lt. of EMZ and 80kg of EMZ ceramics powder were applied. The EMZ treated waste was burnt in the incinerator (the highest temperature was 900C), and 1kg of ashes was collected as the experimental sample.

Analysis

Fifty grams of test sample were taken from the control and the experimental samples respectively by a wooden spoon and were isolated, extracted, and refined in the following manner.

After adding 100ml of normal hexane and isolating the substance from oil, Milex-HV_{13} filter was used to degrease and to obtain normal hexane extract. One hundred milliliters of such reagent as dichloromethane chloroform were added then exposed to ultrasonic wave for 30 minutes to enhance extraction efficiency. After applying two kinds of filters to further refine the substance, a rotary evaporator was used to remove all liquid to obtain almost transparent dried substance. Chloroform extract and 50ml of acetone were added to the dried substance. After exposing to ultrasonic wave for 30 minutes (to facilitate resolution), the mixture was placed in centrifugal separator. The supernatant liquor was then placed in rotary evaporator to dry under low pressure to obtain acetone extract, to which twenty milliliters of methanal were added again to be dried to be reduced to 1/3 of the original volume .

After completing the above process, the control and the experimental test samples were analyzed by gas chromatography mass spectrum (GC-MS).

Experimental Results

Measurements (ng/g, ng=1g/1billion) of dioxin by GC-MS (conducted at the department of Science and Engineering of Nihon University) are shown in Table-1 for both the control and the experimental samples.

A sum of PCDD and PCDF was used as a measurement unit.

The control sample showed a sum of PCDD and PCDF at 227ng/g, while the experimental sample showed 21.35ng/g, i.e., 94% of dioxin was suppressed.

The experimental sample was also analyzed at a research institute in Canada which reported a sum of PCDD and PCDF at 39.28ng/g which is considered within an error range, compared to 21.35ng/g.

The emission controls over dioxin in Japan subjects only gas; however, more than 80% of dioxin stay in ashes. This experiment measured dioxin content in ashes; therefore, dioxin content in gas in this experiment should be reduced well over 90%.

Theoretical Mechanism of Dioxin Suppression by EMZ

About EMZ

Effective microorganisms (EM) is a collection of photosynthetic bacteria, lactic acid bacteria, yeast, actinomycetes, Aspergillus in liquid. The mixture of EM, various plants of Okinawa, and highly nutritious rice bran is fermented and exposed to ozone to dissolve oxidant to obtain liquid with low molecular antioxidant. Various plants of Okinawa used in EMZ production bring in a large variety of minerals (metal) in EMZ.

EMZ contains various bio-active substances (amino acid, peptide, enzyme) and vitamins. (Ref. "Measurement of Extract from Effective Microorganism" by Sato, Hoshimura, Higa 29a, NQ2 Applied Physics Conference, 1997. "Isolation and

Identification of Bio-active Substances Extracted from Effective Microorganisms" by Sato, Hoshimura, Higa A-6 Japanese Society of Microbial Ecology, 1998.) EMZ also contains compounds which have antioxidant power.

Minerals (metals) contained in EMZ liquid are shown in Tables 2 and 3.

Each of these minerals (metals) has a net positive charge (cation) and easily couples with Cl^- (negatively charged chloride) to form salt.

Due to free Cl^- generated during incineration, dioxin is formed. The minerals (metals) contained in EMZ trap free Cl^- and turn into stable forms of salt.

About EMZ ceramics

EMZ is mixed into clay and baked at 1300C to make EMZ ceramics which contain a large amount of calcium aluminate. Clay itself has the characteristics similar to EMZ and facilitates complete burning under relatively low temperature.

X-ray diffractometer and X-ray fluorescent emission spectrometer were used to analyze EMZ ceramics and to identify minerals (metals) contained in the clay. (Comprehensive Study of Effective Microorganisms (ceramics, EMX, EM1) by EM Research Organization, Agriculture Department of Ryukyu University, 1998.)

EMZ ceramics are hard like glass and white in color due to calcium oxide and aluminum oxide which are so-called calcium aluminate and contained abundantly in clay.

The unique power of calcium aluminate compound to fix salt together with various minerals (metals) included in EMZ, turn negatively charged chloride into salt before negatively charged chloride gets chance to become dioxin and fix such salt to ceramics.

Role of Minerals (Metals) in EMZ and EMZ Ceramics as Catalyzer

EMZ contains a large variety of minerals (metals) as explained in the previous section. Negatively charged chloride generated in incinerators in the temperature range of 500C-700C is the first step toward dioxin formation. If EMZ is sprayed at this point, chemical reaction is facilitated, and negatively charged chloride turns into simple salt such as $CaCl_2$, $MgCl_2$, $MnCl_2$, $ZnCl_2$.

Calcium aluminate compound ($CaO \cdot Al_2O_3$) which is the major content of EMZ ceramics, is powerful in stabilizing salt. On the surface of the ceramics, various chemical reactions occur at molecular level, i.e., calcium aluminate reacts to the minerals (metals) contained in EMZ, and hydrate process takes place. Gypsum contained in EMZ ceramics reacts to calcium aluminate compound ($CaSO_4 \cdot 2H_2O$)

and to water of EMZ to form hydrate ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$). During hydrate process, negatively charged chloride, if exists, is trapped in such reaction as shown below and fixed.

$3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O + 2Cl \rightarrow 3CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot 10H_2O + SO_4 + 2H_2O$

At the same time, complicated reactions occur on the surface of ceramics to fix salt in the form of mono sulfate and finally in the form of Friedel salt which is extremely stable and will never dissociate.

Chloride Suppression by EMZ and EMZ Ceramics

Testing Method

EMZ ceramics which contain more than 50% calcium aluminate compound and EMZ to which barium sulfate was added as a marker, were mixed well. The mixture was, then, placed in salt water (3% solution of manganous chloride and sodium chloride). The mixing ratio of the testing samples are shown below in Table-4.

Table-4

Sample	Calcium Aluminate Compound	Gypsum	EMZ
B0	10	3	0
B2	10	3	0.6
B4	10	3	1.2
B8	10	3	2.5

(It is assumed that 10g of EMZ ceramics contains 3g of gypsum.)

Test Results

Effectiveness of ceramics to fix salt, after being placed in salt water, was examined by scanning electron microscope (SEM). The Picture-1 was taken after being placed in salt water for four weeks.

In B0 sample, as shown in the Table-4, no EMZ is added, but calcium aluminate compound is coupled with negatively charged chloride to form plate like crystal, which confirms that compound of calcium aluminate and calcium chloride are fixed as Friedel salt by ceramics.

The SEM pictures show that the thickness of B8 sample is three times thicker than that of B0 sample, which means B8 fixes more salt than B0.

The following charts show the results of computer treated pictures of negatively charged chloride being fixed on the surface of ceramics by identifying the unique waves of negatively charged chloride through X-ray photoelectron micro analyzer.

Chart-1 shows negatively charged chloride being fixed when EMZ was 0%. The actual color picture shows red and white mixture; red representing chloride and white representing fixed salt. The picture indicates that the ceramics fix salt.

Chart-2-c) shows that negatively charged chloride changes color from red to yellow which means that chloride was turned to Friedel salt which will not change into other substance.

Changes on the Surface of EMZ Ceramics

EMZ ceramics particles in the size of 2 μ m (2/1000mm) and 10 μ m (10/1000mm) were examined under SEM (Picture-2). The picture taken after one day placement in salt water shows chloride salt growing on the ceramics surface in the form of plate like crystal. After one week placement, the picture shows that the crystal has grown larger than the ceramics particle.

Conclusion

The results described above provide sufficient evidence to prove the experimental assumption that EMZ and EMZ ceramics can successfully suppress dioxin currently emitted from incinerators.

Table-1 Dioxin Analysis

Analysis of Dioxin (in Ashes)		Before Treatment	After Treatment
	2,3,7,8-T_4CDD	5.76 g	0.26 g
	T_4CDDs	18.52	3.07
D	1,2,3,7,8-P_5CDD	2.28	0.118
I	P_5CDDs	9.89	1.89
O	1,2,3,4,7,8-H_6CDD	2.07	0.136
X	1,2,3,6,7,8-H_6CDD	3.57	0.168
I	1,2,3,7,8,9-H_6CDD	2.01	ND
N	H_6CDDs	9.82	1.75
(PCDD)	1,2,3,4,6,7,8-H_7CDD	5.68	1.01
	H_7CDD_5	10.3	ND
	O_8CDD	6.75	0.264
	Total PCDDs	76.64	8.66
	2,3,7,8-T_4CDF	4.59	1.32
	T_4CDFs	37.5	5.78
D	1,2,3,7,8-P_5CDF	5.88	ND
I	2,3,4,7,8-P_5CDF	3.38	ND
O	P_5CDFs	19.1	1.15
X	1,2,3,4,7,8-H_6CDF	8.88	ND
I	1,2,3,6,7,8-H_6CDF	7.63	0.470
N	1,2,3,7,8,9-H_6CDF	ND	ND
(PCDF)	2,3,4,6,7,8-H_6CDF	4.26	0.556
	H_6CDFs	15.3	1.03
	1,2,3,4,6,7,8-H_7CDF	19.3	0.225
	1,2,3,4,7,8,9-H_7CDF	6.55	0.287
	H_7CDD_5	10.9	0.559
	O_8CDF	7.38	1.31
	Total OCDFs	150.65	12.69
	Total (PCDDs + PCDFs)	227.29= 227ng/g	21.35ng/g

Table-2 ICP Analysis of EMX

Li	B	Na	Mg	Al	Si	P	K	Ca	Ti
≧2.5	≧1000	≧250	≧2000	≧10	≧10	≧7000	5000	≧2000	≧1

V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge
≧5	≧5	≧200	≧50	≧5	≧5	≧100	≧5	<30	<30

Se	Sr	Zr	Nb	Mo	Ag	Cd	In	Sn	Sb
≧25	≧10	≧10	<3	≧5	<7.5	≧1	<40	≧15	≧10

Te	Ba	La	Ce	Ta	W	Pt	Au	Pb	Bi
<25	≧5	<7.5	<30	<30	<250	≧10	<7.5	≧10	≧20

Table-3 Identification of Na, Mg, P, K, Ca

Na(μ g/ml)			Mg(μ g/ml)		
1st time	2nd time	Average	1st time	2nd time	Average
106	106	106	84.5	84.8	85
P(μ g/ml)			K(μ g/ml)		
1st time	2nd time	Average	1st time	2nd time	Average
168	173	170	301	310	306
Ca(μ g/ml)					
1st time	2nd time	Average			
10.9	11.0	11			