Characterization of Emissions of Dioxins and Furans from Ethylene Dichloride (EDC), Vinyl Chloride Monomer (VCM) and Polyvinyl Chloride (PVC) Facilities in the United States. III. Oxychlorination Catalyst.

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INTRODUCTION

This is the third in a series of reports of results from the Dioxin Characterization Program of the Vinyl Institute (VI)[1,2,3] comprising analyses of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/F) in products and emissions from EDC, VCM and PVC resin manufacturing facilities in the US. This paper includes results of testing of used or "spent" EDC oxychlorination catalyst from the two types of catalyst configurations used in the manufacturing process: fixed bed and fluid bed.

EXPERIMENTAL

Samples of catalyst were obtained during normal maintenance of the oxychlorination reactors. Representative samples were drawn utilizing five- to eight-point composite sampling if possible. Some facilities drew replicate samples and results from such samples are averaged. Analyses (EPA test method 1613[4]) were validated by Data/Analysis Technologies, Inc. of Dublin, OH.

RESULTS

Nine samples of catalyst representing seven facilities from six companies were analyzed. These sites represent 53 percent of the estimated US EDC production in 1995. Based on EDC production, sites representing 63 and 52 percent of the total spent catalyst generation from the surveyed fixed and fluid bed production respectively was sampled.

Spent catalyst is discarded in three ways: RCRA hazardous waste landfill, secure landfill and off-site incineration. For sampled sites, a PCDD/F release factor is reported as g TEQ/1000 metric tons (kmt) EDC production. Disposal methods and release factors are shown in Table 1.

Two methods are used to extrapolate data from sampled sites to unsampled sites. The "Most Likely" estimate is generated by applying the *average* grams PCDD/F per ton of EDC production over *all* sampled sites utilizing a given technology (fixed bed or fluid bed) to unsampled sites using that same technology. The "Upper Bound" estimate is generated by applying *the highest observed* grams concentration PCDD/F per ton of EDC production for *any* site utilizing a given technology to unsampled sites utilizing that technology. Totals are obtained by summing individual site determinations, whether sampled or estimated. "Most Likely" and Upper Bound" estimates are generated by technology for each of the disposal methods, and are shown in Table 2.

Congener distributions for the samples are presented in Table 3. Individual congener concentrations are reported in ng/g. The total for each sample is reported on the basis of toxic equivalents (TEQ) utilizing the International Toxicity Equivalency Factors (I-TEF). In order to be conservative, for the purposes of estimating overall releases congeners that are not detected are assumed present at half the detection limit.

DISCUSSION

This project involves characterizing potential emissions from manufacture of EDC, VCM and PVC in the United States. One step in the "balanced" process for manufacture of EDC involves reaction of HCl, O_2, and ethylene over a copper catalyst. This is the "oxychlorination" step.

With respect to estimated emissions of PCDD/F from spent catalyst, it appears that discarded fluid bed catalysts have lower PCDD/F concentrations than fixed bed systems. This may be due to lower average residence times for fluid bed catalyst, which is lost from the catalyst bed by particle attrition and recovered in wastewater treatment. Higher concentrations of PCDD/F in wastewater treatment solids are found for fluid bed plants. Fixed bed catalyst remains in place from installation until the beds are regenerated. Lower concentrations of PCDD/F are found in wastewater treatment solids in these facilities, as there is no particle attrition.

One of the fixed bed sites has a significantly higher concentration of PCDD/F, and as such this single sample drives the "Upper Bound" calculation. At this time we have no good explanation for this sample, but it may involve time in service or other production related issues. Factors that influence the concentration of PCDD/F on catalyst are being studied.

Table 3 reports total potential releases to each of these repositories even though human exposure to material so discarded is highly unlikely. By convention, material deposited in RCRA landfills is not included in overall estimates of industry releases. In the absence of direct sampling data from offsite combustors, in order to be conservative VI has assumed that all the PCDD/F sent to these sites is released. Unsurveyed sites are assumed to discard catalyst to secure landfills.

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REFERENCES

[1] The Vinyl Institute is a Business Unit of The Society of the Plastics Industry, Inc.

[2] W. F. Carroll, Jr., F. E. Borrelli, P. J. Garrity, R. A. Jacobs, J. W. Lewis, R. L. McCreedy and A. F. Weston, "Characterization of Emissions of Dioxins and Furans from Ethylene Dichloride (EDC) Vinyl Chloride (VCM) and Polyvinyl Chloride (PVC) Facilities in the United States. I. Resin, Treated Wastewater and Ethylene Dichloride" *Chemosphere*, **37**, 1957-1972 (1998).

[3] W. F. Carroll, Jr., T. C. Berger, F. E. Borrelli, R. A. Jacobs, J. W. Lewis, R. L. McCreedy, D. R. Tuhovak and A. F. Weston, "Characterization of Emissions of Dioxins and Furans from Ethylene Dichloride (EDC), Vinyl Chloride Monomer (VCM) and Polyvinylchloride (PVC) Facilities in the United States. II. Wastewater Treatment Solids and Aqueous Hydrochloric Acid," *Organohalogen Compounds* **32,** 447 (1997)

[4] Method 1613; "Tetra- through Octa- Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS. Revision B; US EPA 1994.

Table 1. Disposal method and results for catalyst by site.

Site Number	Catalyst Disposal Method			Result (ng TEQ/g) ND= DL/2	PCDD/F (mg TEQ/kmt EDC) ND=DL/2
	RCRA Landfill	Secure Landfill	Incineration		
105	X		X	1.5	0.055
107		X			
128	X				
132	X			15	0.34
135					
138		X			
156	X				
159		X		14.5	0.41
171		X			
175		X			
180	X				
182		X		150	8.1
201	X	X		0.22	0.018
204	X		X	0.59	0.069
206		X		22	0.49
By Mass	**24%**	**48%**	**28%**		

Table 2. Summary of catalyst testing and extrapolation by technology

Site Type	Dis-posal Mode	Sampled Capacity, U.S. (kmt/y)	Sampled Release, (g I-TEQ/y)	U.S. EDC Capacity, (kmt/y)	Most Likely (g I-TEQ/y)	Upper Bound (g I-TEQ/y)
Fixed Bed, Surveyed	**RCRA**	1,300	0.36	1,600	0.90	2.8
	Secure	1,800	0.79	3,500	3.8	15
	Inc.	300	0.016	300	0.016	0.016
Subtotal: [a]		3,400	1.2	5,400	4.7	18
Fluid Bed, Surveyed	**RCRA**	650	0.015	2,300	0.089	0.13
	Secure	600	0.010	1,200	0.037	0.051
	Inc.	1,200	0.080	1,200	0.080	0.080
Subtotal: [a]		2,450	0.11	4,700	0.21	0.26
Unsurveyed Sites [b]				1,000	1.8	8.1
Industry Total		5,850	1.31	11,100	6.7	26

[a] Subtotal is obtained by adding the three disposal categories.

[b] Includes non-VI production and unknown/unsurveyed technologies. Assume secure landfill disposed and emission factor for fixed bed sites.

Table 3. PCDD/F concentrations in catalyst samples, ng/g, by site. [a]

	105	132	159-1	159-2	182A	182B	201	204	206-1,2
Congener									
2,3,7,8-TCDD	0.015	0.018	ND 0.0012	ND 0.00048	0.39	0.38	ND 0.0037	ND 0.00089	0.51
1,2,3,7,8-PeCDD	0.032	0.13	0.013	0.018	2.1	2	ND 0.003	ND 0.0024	1.3
1,2,3,4,7,8-HxCDD	0.075	0.4	0.094	0.098	4.9	4.8	0.0063	ND 0.006	0.89
1,2,3,6,7,8-HxCDD	0.13	0.89	0.41	0.43	7.7	7.8	0.039	ND 0.0055	2.5
1,2,3,7,8,9-HxCDD	0.18	0.62	0.27	0.27	6.4	6.2	0.023	ND 0.0048	3
1,2,3,4,6,7,8-HpCDD	1	9	17	15	100	90	0.18	0.28	7.1
OCDD	0.94	85	140	130	340	270	0.89	3.9	22
2,3,7,8-TDCF	0.02	0.098	0.013	0.018	6.5	6.4	0.0019	ND 0.0029	2.8
1,2,3,7,8-PeCDF	0.75	1.7	0.4	0.53	62	66	0.0045	0.13	22
2,3,4,7,8-PeCDF	0.32	1.5	1.2	1.1	37	37	0.0048	0.028	5.6
1,2,3,4,7,8-HxCDF	3.7	23	22	23	340	320	0.03	1.7	45
1,2,3,6,7,8-HxCDF	5.6	19	15	15	310	320	0.012	0.37	77
1,2,3,7,8,9-HxCDF	0.66	9.2	9.1	7.7	110	99	0.005	0.086	14
2,3,4,6,7,8-HxCDF	0.18	19	26	24	130	140	ND 0.00082	0.14	8.2
1,2,3,4,6,7,8-HpCDF	24	500	450	430	2800	2700	0.37	8.2	180
1,2,3,4,7,8,9-HpCDF	0.21	24	59	53	540	450	0.028	2.1	7.9
OCDF	1.2	1400	1400	1300	3400	2700	200	230	110
I-TEQ	1.5	15	15	14	150	150	0.22	0.59	22

[a]Individual congeners reported as actual. Totals only are expressed as TEQ.
[b]Duplicate samples are treated as an average.