



Focus Environmental, Inc.

ENGINEERING SOLUTIONS TO ENVIRONMENTAL PROBLEMS

9050 Executive Park Drive
Suite A-202
Knoxville, TN 37923

(865) 694-7517
Fax (865) 531-8854

January 12, 2001

Mr. Dana Schnobrich
3M Corporation
ET&S, Bldg. 42-2E-27
P.O. Box 33331
St. Paul, MN 55133-33331

Subject: Thermal stability of perfluorinated alkyl sulfonyl compounds

Dear Dana:

As you requested, Focus Environmental (Focus) has prepared this letter report to address the thermal stability of perfluorinated alkyl sulfonyl compounds.

INTRODUCTION

3M Corporation (3M) manufactures perfluoroalkylsulfonyl fluoride and various derivatives of this compound. In general, the fluorocarbon chains generally range from C₄ to C₈ in length. For example, the structure of perfluorooctylsulfonyl fluoride is CF₃-(CF₂)₆-CF₂-SO₂F. Many of these fluorinated compounds produced by 3M have an R_f-CF₂-SO₂-R' structure where R_f is typically a perfluorinated alkyl chain and R' is a functional group. This letter report discusses the thermal stability of these fluorinated sulfonyl compounds relative to incineration of these compounds in hazardous waste incinerators, cement kilns and municipal solid waste incinerators.

THERMAL STABILITY OF PERFLUORINATED COMPOUNDS

In general, compounds containing only carbon and fluorine atoms (perfluorinated compounds), are more thermally stable than chlorinated organics and hydrocarbons. This high thermal stability results because these compounds typically have very high C-F bond energies (1). The addition of non-fluorinated atoms or groups to perfluorinated compounds however, will typically result in lower thermal stability for the new compound. This lower thermal stability results because the non-fluorinated atoms or groups have lower bond energies that are easier to break with thermal energy than the C-F bonds.

BATTELLE REPORT

A report on the thermal decomposition of fluorochemicals was recently prepared by Battelle Memorial Institute (2). The report states that under high temperature conditions, the C-S bond between the perfluoroalkyl group and the sulfur group is always weaker than the C-C bond within the perfluoroalkyl group. Battelle estimated bond energies for three perfluoroethyl sulfonyl compounds (C₃F₇-SO₂-R') and found bond energies for the C-S bond of about 63 to 64

Kilocalories per mole (Kcal/mole) (2). Battelle also estimated the bond energy for an anion ($\text{C}_3\text{F}_7\text{-SO}_3^-$) at 78.3 Kcal/mole and a radical ($\text{C}_3\text{F}_7\text{-SO}_3^\bullet$) at 20.4 Kcal/mole (2).

UNIVERSITY OF DAYTON THERMAL STABILITY RESEARCH

The EPA's RCRA permitting program for hazardous waste incinerators required that a thermal stability ranking system be developed to estimate the relative thermal stabilities of the Appendix VIII constituents from 40 CFR 261. Initially the EPA used Heat of Combustion as a thermal stability ranking index but received significant criticism from the scientific community. Because of this criticism, the EPA had the University of Dayton Research Institute (UDRI) develop a new system based on high temperature vapor phase stability in a laboratory-scale reactor with two seconds of residence time under low oxygen conditions (3). Sixty-six chemical compounds were examined and these chemicals were ranked based on their thermal stability during the vapor phase reaction. The thermal stability ranking parameter is defined as the temperature required to obtain 99% destruction of a compound at two seconds residence time and low oxygen conditions [T99(2)]. A compound such as benzene for example, with a T99(2) of 2102°F, has a higher thermal stability than toluene which has a T99(2) of 1643°F. The T99(2) thermal stability ranking parameter is not a predictor of the temperature necessary to obtain a Destruction and Removal Efficiency (DRE) of 99% in a full-scale hazardous waste incinerator. It is only usable as a thermal stability ranking predictor. The UDRI vapor phase temperatures necessary to obtain a 99% DRE will always result in far higher DREs in a full-scale hazardous waste incinerator.

Using a combination of vapor phase testing and thermochemical reaction kinetic theory, UDRI estimated the relative thermal stabilities of all 280 Appendix VIII constituents. Numerical listings of the T99(2) rankings were published in the EPA's Technical Implementation Document for the Boiler and Industrial Furnace Regulations in March 1992 (4). The University of Dayton Research Institute (UDRI) found that hydrocarbon compounds containing the C-S bond have very low thermal stability (4,5). I would also expect perfluorinated alkyl sulfonyl compounds to have relatively low thermal stabilities because the C-S bond is still the weak link in the structure.

This thermal stability ranking was important because the RCRA permitting process allowed hazardous waste incinerators to only incinerate compounds on the Appendix VIII list below the highest ranking compound that was successfully destroyed at a 99.99% Destruction and Removal Efficiency. Consequently most RCRA trial burn tests were conducted using the highest ranked compounds on the EPA's thermal stability ranking index. None of these high ranking compounds contain a C-S bond. Focus does have confidential data however, for a test burn at a liquid and fume incinerator where methyl mercaptan (CH_3SH) was incinerated with a DRE of >99.995%. No methyl mercaptan was found in the stack gas above the detection limit. The fume incinerator was operating at an average temperature of 1591°F. About 98.5% of the methyl mercaptan was present in the vent gas being fed to the incinerator and about 1.5% of the methyl mercaptan was in a liquid waste. Because of the limited amount of full-scale DRE data on compounds with a C-S bond, I have prepared Table 1. Table 1 summarizes bond energies for the weakest bond in the compound, experimental and calculated T99(2) thermal stability values and actual full-scale DRE data from hazardous waste incinerators for various compounds some

of which contain C-S bonds. The purpose of this table is to show that compounds with low bond energies, such as the perfluorinated alkyl sulfonyl compounds, will be destroyed at high DREs in incineration systems. As can be seen from Table 1, perfluorinated alkyl sulfonyl compounds probably have C-S bond energies ranging from <20 to <78 Kcal/mole (2). The C-S bond for example, for the C₃ perfluorinated alkyl sulfonyl fluoride (C₃F₇SO₂F) is estimated to be 63.9 Kcal/mole (2). I would expect the C-S bond energies for the C₄ to C₈ perfluorinated alkyl sulfonyl compounds, the actual 3M products, to be similar for the C₃ compounds given in the Battelle report.

As can be seen in Table 1, the C-S bond energies in the perfluorinated alkyl sulfonyl compounds probably range from <20 to <78 Kcal/mole. By inference from the data in Table 1, the T99(2) for the perfluorinated alkyl sulfonyl compounds is probably in the 1200 to 1500°F range and the full-scale DREs at 1800°F are likely to be >99.9999% (>6-9s). In fact, chloroform with a C-Cl bond energy of 77.6 Kcal/mole has been destroyed at the 7-9s level at 1640°F (7).

Sulfur hexafluoride (SF₆), a more thermally stable compound than the perfluorinated alkyl sulfonyl compounds, with a SF₅-F bond energy of 93 Kcal/mole (12), has been tested in a full-scale rotary kiln incinerator. During this trial burn, an SF₆ DRE of 99.9998% was obtained at rotary kiln/secondary combustion temperatures of 1730/1920°F (10). At rotary kiln/secondary combustion temperatures of 1510/1700°F, the SF₆ DRE was found to be 99.994% (10).

Figure 1 is a plot of T99(2) versus the weakest bond energy for compounds in Table 1. A linear regression of the Table 1 data indicates a possible correlation between T99(2) and the bond energy. Based on the regression equation shown in Figure 1, the estimated T99(2) for the perfluorinated propylsulfonyl fluoride (C₃F₇SO₂F), with a C-S bond energy of 63.9 Kcal/mole, is estimated to be 1015°F. This is consistent with the other T99(2) data in Table 1 for compounds containing C-S bonds and indicates a very low thermal stability for the perfluorinated propylsulfonyl fluoride.

INCINERATION

Based on the data shown in Table 1, I would expect perfluorinated alkyl sulfonyl compounds to be destroyed at DREs >6-9s in any incinerator operated at a combustion gas temperature of 1800°F with a combustion gas residence time at temperature of at least 2 seconds. The degree of destruction of the perfluorinated alkyl sulfonyl compounds will depend on the type of incinerator, the temperature and residence time in the incinerator and how the perfluorinated alkyl sulfonyl compounds are fed to the incinerator.

Burner Combustion - I would expect the highest DREs to be obtained when the perfluorinated alkyl sulfonyl compounds are fed to a liquid burner and incinerated in a flame. Incineration of high Btu liquids in a burner typically results in burner flame temperatures from 2500 to over 3500°F. The actual temperature is a function of the type burner, the excess air being mixed with the fuel or waste and the heat content of the waste or fuel. Flame temperatures of over 3000°F are not unusual in a burner. Residence times in a burner are only tenths of a second, but because of the high flame temperatures, most of the destruction of the liquid occurs in the burner flame.

Blending perfluorinated alkyl sulfonyl compounds into high Btu liquids and burning the blended waste in an incinerator or cement kiln burner will result in the highest DREs. I would expect that incineration of perfluorinated alkyl sulfonyl compounds in a burner flame would result in Destruction and Removal Efficiencies of well over 99.9999% (>6-9s) for these compounds. As evidence of this, SF₆ which is a much more thermally stable compound than perfluorinated alkyl sulfonyl compounds, was fed to a cement kiln burner with DREs measured at greater than 6-9s (9).

Rotary Kiln Incinerators and Cement Kilns - If the perfluorinated alkyl sulfonyl compounds are fed as solid materials to incinerators, I would expect somewhat lower DREs because the compounds would not be exposed to flame temperatures in a burner. As long as the perfluorinated alkyl sulfonyl compounds are exposed in the gas phase to about 1800⁰F for at least two seconds, I would expect DREs of over 6-9s. DREs for perfluorinated alkyl sulfonyl compounds fed as solid materials would be highest for rotary kiln incinerators with secondary combustion chambers and cement kilns with mid-kiln solid feed systems because these units have longer residence times at high temperature. The University of Dayton Research Institute has shown in vapor phase studies, that residence time is a very strong factor affecting the high temperature destruction of polychlorinated biphenyls and other organic compounds. Increasing residence time from 0.95 to 3.84 seconds at 1300⁰F increased destruction of various thermally stable organics from 2 to 17 times (13). Rotary kiln incinerators typically have total high temperature residence times from 5 to 10 seconds and cement kilns typically have total high temperature residence times of 10 seconds.

Municipal Waste Incinerators - In 1998, 8% of the nation's household waste was incinerated in municipal solid waste incinerators (14). It is therefore reasonable to assume that about 8% of 3M's perfluorinated alkyl sulfonyl compound products may eventually be incinerated in municipal solid waste incinerators.

Municipal solid waste incinerators typically do not have liquid waste burners and so perfluorinated alkyl sulfonyl compound products that are fed to a municipal solid waste incinerator will be fed as solids. Large municipal solid waste incinerators are typically designed for about 250 tons per day of municipal refuse, generally have a grate type design for incineration of the refuse, do not have secondary combustion chambers and usually have waste heat recovery boilers. Historically, these large municipal solid waste incinerators have had a reputation for operating at lower temperatures and residence times and at poorer combustion conditions than hazardous waste incinerators and cement kilns. There are also numerous, smaller municipal solid waste incinerators which are designed for about 50 tons per day of municipal refuse, use a controlled air (pyrolytic) primary chamber, have secondary combustion chambers and also recovery energy from the hot combustion gases.

Because of the recently promulgated municipal waste combustor New Source Performance Standards and Emission Guidelines (40 CFR 62 Subpart FFF), large municipal waste incinerators now have emission standards for carbon monoxide and dioxin emissions. In order to meet these emission standards, many municipal waste incinerators have been operating for a

number of years now at higher temperatures and better combustion conditions as evidenced by lower carbon monoxide stack concentrations (15). For perfluorinated alkyl sulfonyl compounds being fed as solids to a municipal solid waste incinerator, I would expect DREs of about 4-9s to >6-9s depending on the type of incinerator and the combustion gas temperature and residence time in the unit. For a refractory municipal solid waste incinerator with a combustion gas temperature of 1800°F and a residence time of two seconds or more, I would expect perfluorinated alkyl sulfonyl compound DREs to be about 6-9s or greater. For refractory municipal solid waste incinerators operating at a combustion gas temperature of 1600°F with residence times of one second, I would expect lower perfluorinated alkyl sulfonyl compound DREs, in the range of 4-9 to 5-9s. A municipal solid waste incinerator with water-wall energy recovery might also have lower perfluorinated alkyl sulfonyl compound DREs than refractory units operating at 1800°F because the energy recovery surfaces are much cooler than a refractory surface is. These relatively cool energy recovery surfaces might result in a lower time-temperature history for a small amount of the combustion gas thereby possibly resulting in slightly lower overall DREs for the perfluorinated alkyl sulfonyl compounds.

A significant degree of thermal decomposition of the perfluorinated alkyl sulfonyl compounds should occur in the municipal incinerator from localized pyrolysis of the solid wastes on the grates. Localized pyrolysis can happen in a municipal incinerator burning solid wastes when oxygen can not get to the combustion site fast enough because of oxygen diffusion limitations. The oxygen diffusion limitations occur because of the difficulty in obtaining even distribution of underfire air through the bed of burning waste. When the solid waste is burning on the grates, the perfluorinated alkyl sulfonyl compounds will be exposed to either oxidative or pyrolytic flame combustion, thus enhancing the over-all DREs due to exposure of these compounds to high flame temperatures.

SUMMARY

In my opinion, the thermal stability of compounds containing a C-S bond such as the perfluorinated alkyl sulfonyl compounds, is very low. This conclusion is based on the Battelle estimates for C-S bond energy for perfluorinated alkyl sulfonyl compounds (2) and the bond energy, T99(2) and full-scale DRE data presented in Table 1. The low estimated bond energies of the perfluorinated alkyl sulfonyl compounds and the data in Table 1 indicate to me that incineration of these compounds in rotary kiln incinerators and cement kilns at $\geq 1800^{\circ}\text{F}$ and a residence time of at least two seconds, should result in DREs for the perfluorinated alkyl sulfonyl compounds of greater than 6-9s. Incineration of the perfluorinated alkyl sulfonyl compounds in municipal solid waste incinerators should result in DREs of about 4-9s to >6-9s depending on the type of municipal incinerator being used and the combustion gas temperature and residence time.

Sincerely,



Jim Cudahy, P.E.
President

REFERENCES

1. Tsang, W., D.R. Burgess Jr. and V. Babushok, "On the Incinerability of Highly Fluorinated Organic Compounds", *Combustion Science and Technology*, Vol. 139, 1998, pp 385-402.
2. Dixon, D., "Fluorochemical Decomposition Processes Quantification and Assessment", Battelle Memorial Institute, Pacific Northwest Division, October 22, 2000
3. Taylor, P.H., B. Dellinger and C.C. Lee, "Development of a Thermal Stability Based Ranking of Hazardous Organic Compound Incinerability", *Environmental Science & Technology*, March 1990, pp 316-328.
4. USEPA, Technical Implementation Document for EPA's Boiler and Industrial Furnace Regulations, EPA-530-R-92-011, Appendix H, March 1992.
5. Letter from Dr. Philip H. Taylor to W. R. Schofield on the estimated thermal stability of five sulfur containing organic compounds, December 28, 1995.
6. Moran, T., et al, "Evaluating the Combustion Operational Parameters that Impact the Destruction and Removal Efficiency of Hydrogen Cyanide", 1999 Incineration Conference, University of California, Orlando, FL, May 10-14, 1999, pp 481-486.
7. Permit Writers Guide to Test Burn Data Hazardous Waste Incineration, EPA, Cincinnati, OH, EPA/625/6-86/012, September 1986.
8. Jackson, K., M. Dunham and R. Westbrook, "Overview of Transportable Incinerator Operations at the Sikes Disposal Pits Superfund Site", 1993 Incineration Conference, University of California, Knoxville, TN, May 3-7, 1993, pp 499-509.
9. England, W. G. et al, "Measurement of Hazardous Waste Incineration Destruction and Removal Efficiencies Using Sulfur Hexafluoride as a Chemical Surrogate", paper presented at the 79th Annual Meeting Air Pollution Control Association, Minneapolis, MN, June 22-27, 1986
10. Trenholm, A., C. Lee and H. Jermyn, "Full-Scale POHC Incinerability Ranking and Surrogate Testing", 17th Annual RREL Hazardous Waste Research Symposium, EPA Office of Research and Development, Washington, D.C., EPA/600/9-91/002, April 1991, pp 79-88.
11. Tirey, D., B. Dellinger, P. Taylor and C. Lee, "Pyrolytic Thermal Degradation of a Hazardous Waste Incinerability Surrogate Mixture", 15th Annual RREL Hazardous Waste Research Symposium, EPA Risk Reduction Engineering Laboratory, Cincinnati, OH, EPA/600/9-90/006, February 1990, pp 21-31.
12. Tsang, W. and W. Shaub, "Surrogates as Substitutes for Principal Organic Hazardous Constituent Validation of Incinerator operation", Second Conference on Municipal, Hazardous and Coal Waste Management, Miami Beach, FL, December 1983.
13. USEPA, Laboratory Evaluation of High-Temperature Destruction of Polychlorinated Biphenyls and Related Compounds, EPA-600/2-77-228, December 1977.
14. Repa, E. W., "Solid Waste Disposal Trends", *Waste Age*, April 2000, pp 262-265
15. Hasselriis, F. and M. Gaskin, "Modification of Existing refractory Municipal Waste Incinerator with Electrostatic Precipitator to Achieve a 99% Reduction in Dioxin Emissions", 88th Annual Meeting Air & Waste Management Association, San Antonio, TX, June 18-23, 1995.

Table 1. Comparison of Bond Energies, Vapor Phase Destruction and DREs from Hazardous Waste Incinerators

Compound Name	Compound Structure	Bond Energy (Kcal/mole)	T99(2) F (a)	T99(2) (Exp/Calcd)	Trial Burn DRE Data	Reference
Hydrogen cyanide	H-CN	123.8	>2732	Exp	>7-9s at 1700 F	6
Benzene	C ₆ H ₆ -H	110.9	2102	Exp	>7-9s at 1830 F	7
Chlorobenzene	C ₆ H ₅ -Cl	95.7	1814	Exp	>7-9s at 1741 F	8
Sulfur hexafluoride	SF ₆ -F	93	1688	Exp	>6-9s in CK	9
Sulfur hexafluoride	SF ₆ -F	93	1688	Exp	99.9998% at EKodak (1730/1920 F)	10,11
Sulfur hexafluoride	SF ₆ -F	93	1688	Exp	99.994% at EKodak (1510/1700 F)	10
Hydrogen sulfide	HS-H	91.2	1832	Calcd		5
Toluene	C ₆ H ₅ CH ₃ -H	88	1643	Exp	>5-9s at 1800 F	7
Trifluorochloromethane	CF ₃ -Cl	86.2	1850	Exp		11
Methyl chloride	CH ₃ -Cl	84.6	1742	Exp	>4-9s at 2040 F	7
Methylene chloride	CCl ₂ H-Cl	80.1	1499	Exp	6-9s at 1864 F	7
Perfluoroalkyl-sulfonyl	Rf-CF ₂ -SO ₂ -R'	<20 to <78				2
Chloroform	CHCl ₂ -Cl	77.6	1157	Exp	7-9s at 1640 F	7
Methyl mercaptan	CH ₃ -SH	74.7	1202	Calcd	>99.995 at 1591 F (a)	5
Carbon tetrachloride	CCl ₄ -Cl	73.1	1193	Exp	>6-9s at 1800 F	7
Ethyl mercaptan	C ₂ H ₅ -SH	66	1184	Calcd		5
Dimethyl sulfide	CH ₃ -S-CH ₃		932	Calcd		5
Dimethyl disulfide	CH ₃ SS-CH ₃		842	Calcd		5
Ethylmethane sulfonate	C ₂ H ₅ CH ₃ -SO ₃ H		734	Calcd		4
Thiourea	NH ₂ C-SNH ₂		464	Calcd		4

(a) - Confidential test data for a fume incinerator

Figure 1. T99(2) as a function of bond energy

