

INCINERABILITY RANKING OF HAZARDOUS ORGANIC COMPOUNDS

by

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INTRODUCTION

Since the regulation of hazardous waste by the USEPA, both the Agency and the regulated community have been searching for means of evaluating incinerator performance. The concept of a "trial burn," a series of tests designed to evaluate the ability of an incinerator to process waste to certain standards, was developed; and surrogates were introduced (1) for hazardous and solid waste and for Principal Organic Hazardous Constituents, or POHCs. In essence, the incinerator's ability to destroy waste was based on its performance in destroying the POHCs.

Destruction and Removal Efficiency (DRE) is used by EPA to express incinerator performance. The DRE of a POHC is calculated as follows:

$$DRE = \frac{(W_{in} - W_{out})}{W_{in}} \times 100 \quad (2)$$

Where W_{in} and W_{out} are the mass flow rates of the POHC input and output (at the stack) respectively.(2)

As regulations and policies regarding trial burns developed, it became apparent to all concerned that DRE determinations were rapidly becoming extremely expensive and time consuming. It is not unusual to see trial burn costs approaching 2% of the capital costs of the facility. Largely responsible for these costs was the requirement that several types of POHCs be evaluated, resulting in the use of multiple sampling trains. The process of obtaining representative samples could take a week, or longer. Sample processing and analysis, also expensive, would drag out the time-span between trial burn and results to over three months. The objective for regulators and regulated alike

was to search for a less expensive approach. The approach was similar to that taken for POHCs and solid waste: find a surrogate for the waste being burned and develop a cheap, quick analytical method for the analysis of the surrogate. Several compounds, e.g., Sulfur hexafluoride (SF_6) and Freons^R fluorocarbons, were put forth as candidates.(3)

Because of its high thermal and chemical stability and the fact that it is inexpensive and non-toxic, SF_6 received much attention as a surrogate. Quick, relatively inexpensive, and reliable methods were developed for its analysis, and initial evaluation began in 1984.(4) A system employing a gas chromatograph, equipped with an electron capture detector (GC/ECD), was used to obtain SF_6 concentrations in stack gas every 2 to 4 minutes, a much shorter time than the sampling time required for sampling trains. Equipment set-up, operation, and calculation of results could be done in 1-1/2 days (4), a far cry from three months.

Since that time, a great deal of effort, time and money has been spent, both in the United States and Canada (5), to exhaustively evaluate SF_6 as a POHC or waste surrogate.

During the same time period, the concept of using a standard POHC mixture (a "POHC Soup") for trial burns, by employing a group of compounds with a range of chemical and physical characteristics, was developed. A paper describing the rationale and results of that effort is being given at this conference.(6)

Both of these efforts have been researched extensively at the laboratory stage (5, 6, 7). An evaluation program at pilot scale for the USEPA Combustion

Research Facility (CRF) was proposed in 1987. The CRF has two pilot-scale (3×10^6 Btu/hr) incinerators, a liquid injection system and a rotary kiln. The SF_6 /"POHC Soup" program was performed in the liquid injection system. This paper describes the DRE results and discusses the implication of this work and of other researchers.

Interest in assuring and demonstrating compliance with RCRA permit conditions has also concerned the hazardous waste community. Trial burns are prohibitively expensive to carry out on a routine or even annual basis, with not much gained in the process. This approach still leaves "gaps in coverage," where incinerator performance may be unknown. It became apparent, after initial research at EPA, that residence time, temperature and turbulence were not the only factors to consider in the evolution of incineration criteria. The Toxic Substance Control regulations (8) for PCB incineration reflected that realization, and stipulated not only time and temperature, but also a minimum stack O_2 concentration as well as a minimum combustion efficiency of 99.9% are required.

This paper concentrates on the evaluations of SF_6 and the "POHC Soup" as trial burn surrogates.

EXPERIMENTAL BACKGROUND

The experimental program was executed at the USEPA Combustion Research Facility's Liquid Injection System (LIS). Figure 1 is a sketch of the unit, showing each of the elements that make up the incinerator and the air pollution control system.

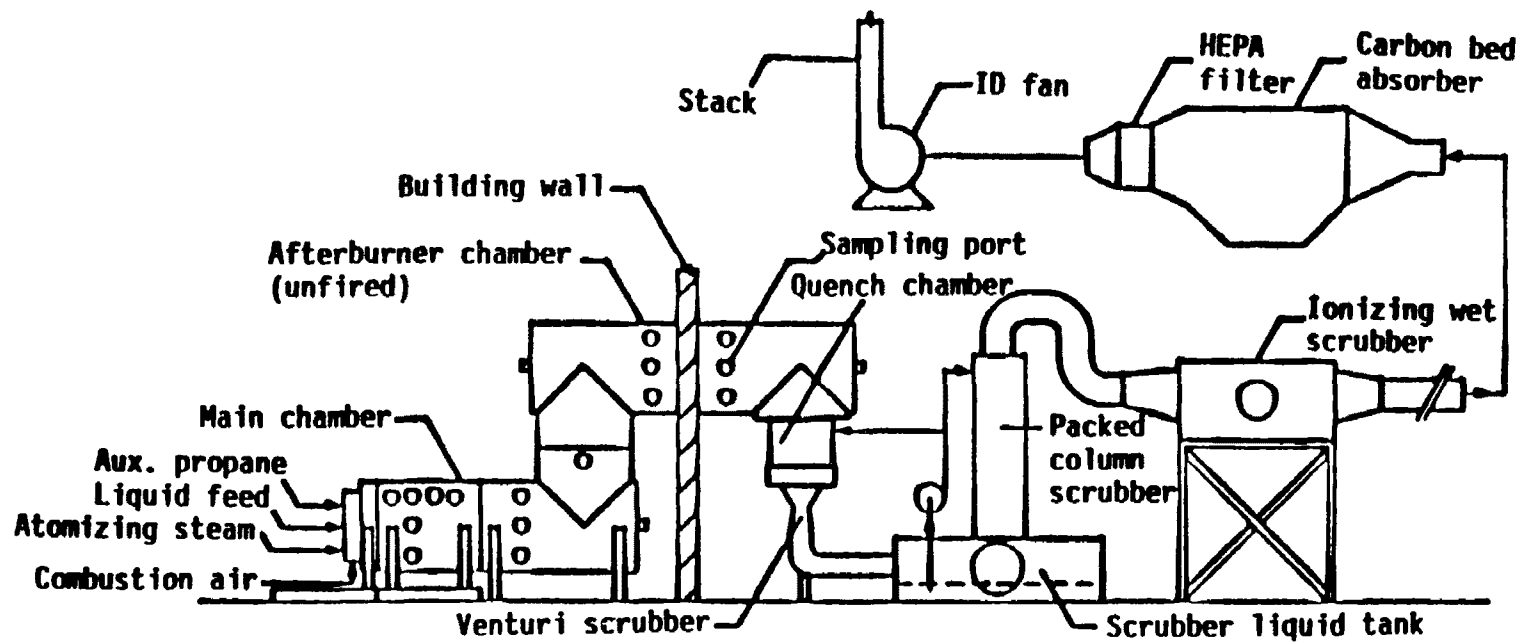


Figure 1. CRF liquid injection system.

The LIS is fired with liquid waste, and propane is used to maintain temperature control. Combustion air is supplied by forced-draft fan. The waste mixture containing the "POHC Soup" was stored in a stainless steel vessel and pumped continuously to the LIS.(9) SF_6 was injected into the liquid feed stream as a gas, where it dissolved into the liquid phase just prior to incineration.

Sampling of the stack gas for both SF_6 and the POHCs was done at the exit of the air pollution control systems, just after the ionizing wet scrubber (IWS). Even though the gas passes through additional gas cleanup, sampling further downstream was not conducted. The final gas cleanup is unique to this facility and is not standard for commercial and private incinerators. Table 1 shows the experimental conditions and the DRE results for the SF_6 and the POHC components.

Oxygen and incinerator temperature were varied as part of a designed experiment. All other variables, such as waste composition and flow rates, were kept constant.

The compounds used in the test mixture were toluene (70%), chlorobenzene (10%), pentachlorobenzene (10%) and tetrachloroethylene (10%). This combination of compounds resulted in a mixture which contained both volatile components and semivolatiles. Stack sampling of these components was accomplished with the VOST (USEPA Method 0030) and Modified Method 5 (USEPA Method 0010). The SF_6 sampling method was proportional gas sampling, with the sample being fed directly to GC/ECD.

Table 1. Data Table - Temperature, Oxygen and DREs (number of nines)

Experiment	Afterburner		DRE				
	Exit Temperature, °C	Exit Oxygen %	SF ₆ *	Tetra-chloro-ethylene*	Toluene*	Chloro-benzene*	Pentachloro-benzene*
1	1030	2.3	4.35	5.40	6.19	6.11	7.80
2	1114	3.3	3.59	5.52	6.21	6.04	7.52
3	943	5.6	3.33	6.14	7.10	6.38	7.34
4	1274	1.3	7.00	5.51	6.11	6.40	7.30
5	1091	5.1	5.31	5.74	5.85	4.14	6.98
6	945	8.2	4.17	6.66	6.68	6.66	7.41
7	1310	4.5	5.33	5.34	5.59	5.80	7.49
8	1077	9.2	3.44	5.85	5.74	6.28	7.35
9	1175	8.0	5.70	6.70	7.55	6.54	7.43
10	1105	4.7	3.96	5.16	6.39	5.68	7.44

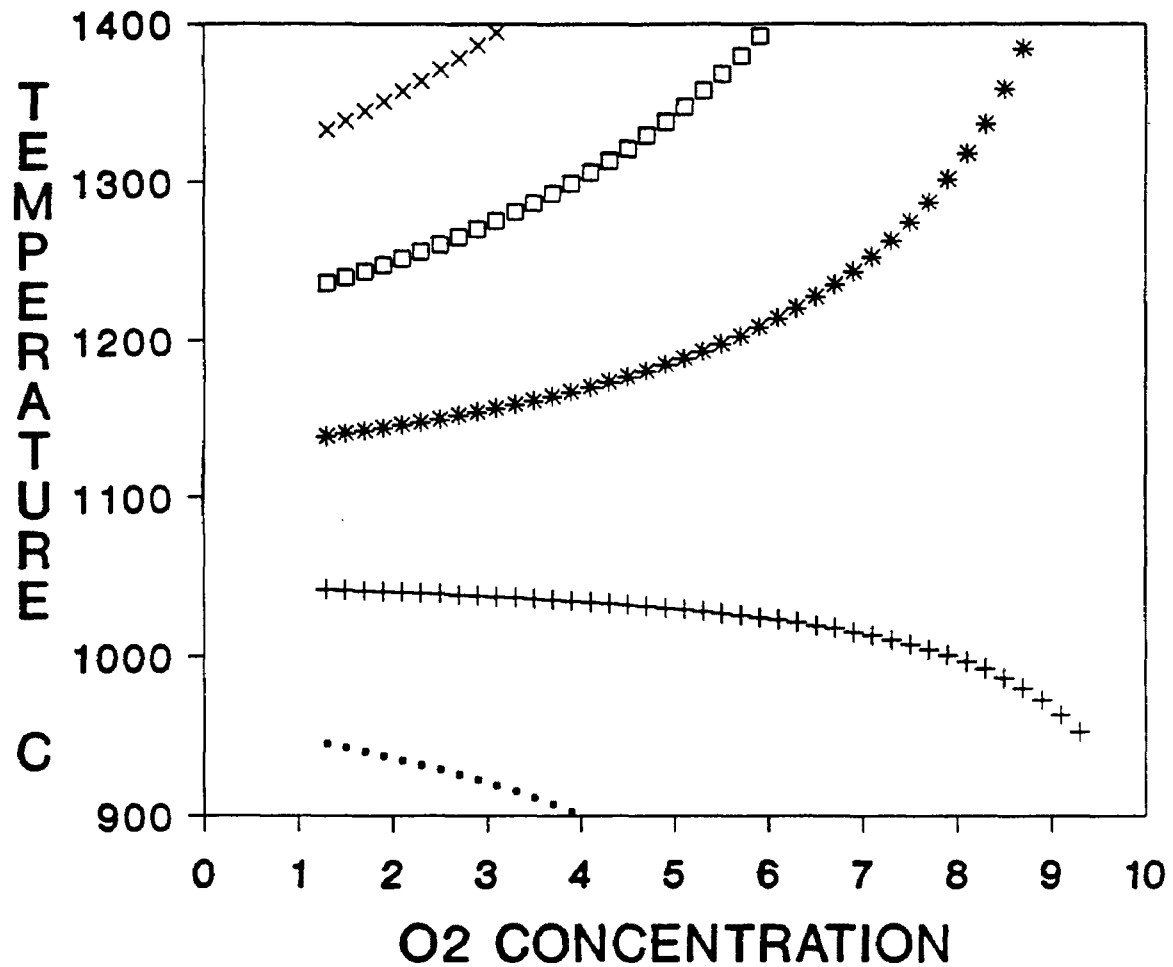
*Calculated DRE by the formula $DRE = -\log \left(\frac{1-DRE}{100} \right)$

ANALYSIS OF RESULTS - SF₆

To gain as much information about the behavior of the POHC/SF₆ DREs with respect to the two variables, a regression analysis was performed for each data set, one for each compound. Table 2 lists the results of the regression analysis, the model used and the correlation coefficient.

Figure 2 is a contour plot with independent variables, temperature and afterburner exit oxygen concentration, on the Y and X axis respectively. The SF₆ DRE (expressed in the number of nines) is displayed as contours of the regression surface. This figure demonstrates why it is so hard to make solid judgments about the relationship between DRE and a single variable. As the figure clearly illustrates, whether DRE goes up or down with increasing O₂

SF₆ DRE VS T, O₂



DRE		
• 3-9's	+ 4-9's	* 5-9's
□ 6-9's	× 7-9's	

Figure 2. SF₆ DRE vs. T, O₂.

depends on the operating temperature. At 950°C, DRE increases from about 3-nines to nearly 4-nines as oxygen increases. At 1350°C, the same change results in the opposite effect, dropping the DRE from greater than 7-nines to less than 5-nines DRE as oxygen increases.

Table 2. Data Table

Compound	Model	Correlation Coefficient
SF ₆	1st Order	0.77
Toluene	1st Order	0.45
Tetrachloroethylene	1st Order	0.75
Chlorobenzene	2nd Order	0.76
Pentachlorobenzene	2nd Order	0.68

At this point, it is stressed that the regression analysis and the resulting figures developed from it should only be used in general, not predicting absolute DRE figures for specific compounds. Until additional data and developed, these relationships should only be applied to the CRF incinerator and can only be used to describe the relationship between dependent (DRE) and independent (Temp. and O₂) variables within the range of the experiment. Extrapolation of the results outside the range is risky.

In the laboratory work done on the thermal decomposition of SF₆ at the University of Dayton Research Institute (UDRI) (7), it was determined that SF₆ destruction was independent of oxygen concentration, indicating the mechanism to be unimolecular decomposition. Although Figure 2 shows an effect of O₂ on SF₆ DRE, it may not mean that O₂ specifically causes the changes. What is not depicted is that as the O₂ concentration increases, air to fuel ratios and incinerator residence times change concurrently. The variation in SF₆ DRE may

be related to those effects and is not necessarily inconsistent with the UDRI results.

Figure 3 is a plot of the SF_6 DREs versus temperature with 3 data sets illustrated. The data shown as diamonds were the SF_6 DRE-temperature relationship calculated from the data supplied in References 5 and 7. This was calculated for a 2-second residence time and represented the DRE temperature relationship for SF_6 exclusive of any other physical or chemical effects.

The data plotted as Xs were data from the work conducted at the Alberta Environmental Centre (5) in which the effect of the presence of refractory on SF_6 DRE was evaluated. As one can see, the presence of refractory in the reactor had a marked effect on the DRE-temperature relationship, reducing the required temperature by some 200°C.

The third data set plotted in Figure 3 was the CRF data, and shows the regression line for those data points. Here, as with the Canadian data, there is a marked difference in SF_6 DRE-temperature behavior. While some of the difference could be attributed to the presence of refractory and residence time changes in the incinerator, the authors feel that there is more to it than that. Since the laboratory data (UDRI) were taken with non-flame systems, in which the substances underwent an extremely narrow temperature distribution, SF_6 DRE should not be expected to be similar, since in flame conditions, SF_6 would "see" or experience a wide range of temperatures in the incinerator environment. At any rate, the behavior is not the same, and more investigation is warranted.

SF₆ THERMAL DECOMPOSITION PILOT/LAB COMPARISON

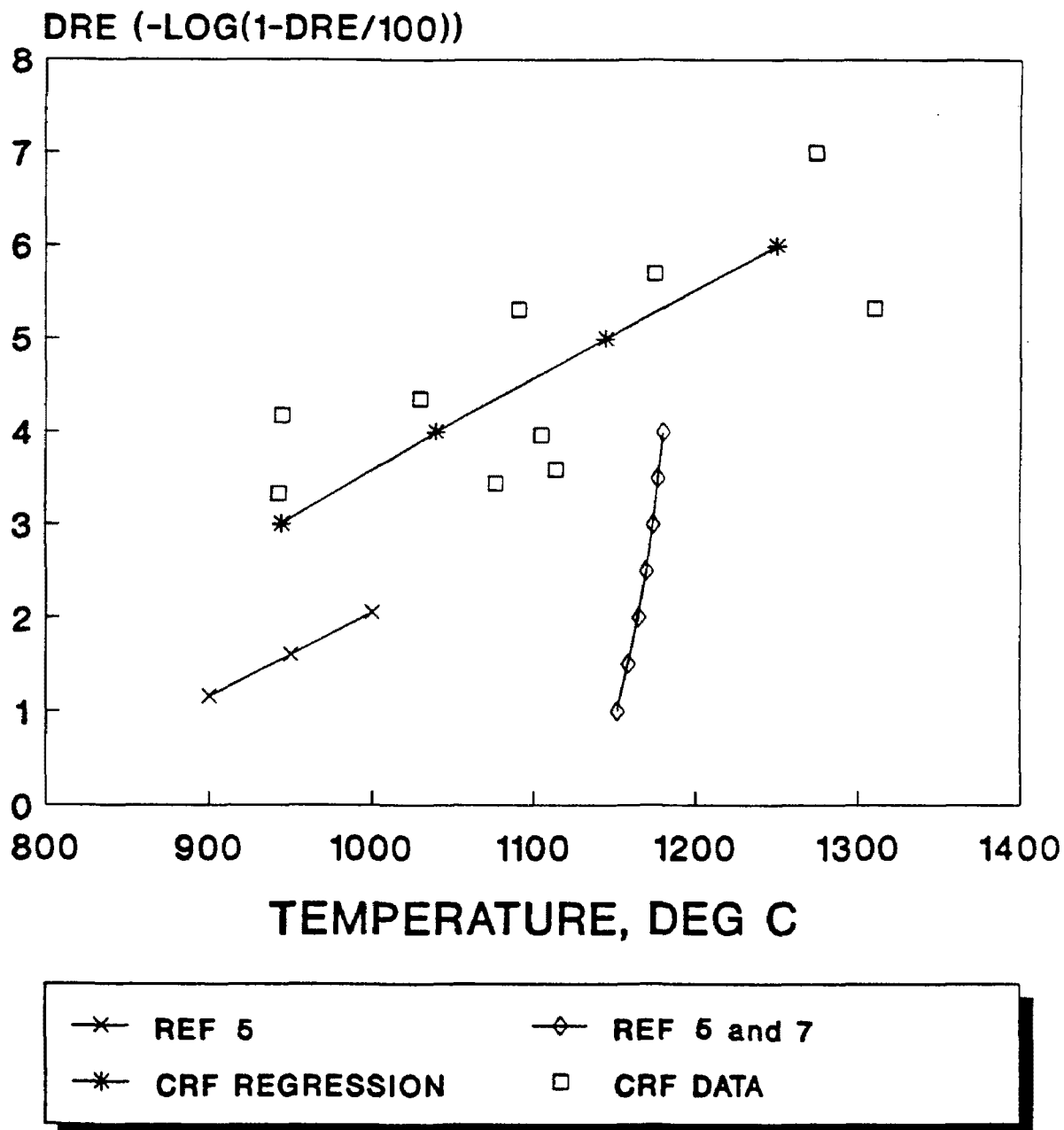


Figure 3. SF₆ Thermal decomposition pilot/lab comparison.

POHC RANKING

Figure 4 is a contour plot of the relationship between conditions necessary to achieve 6-nines SF_6 DRE and that of the individual POHCs. It also illustrates why looking at one variable at a time can be confusing. At low O_2 concentrations, tetrachloroethylene requires only 900°C for 6-nines while at 4.5% O_2 , 1250°C is required, surpassing that for chlorobenzene, which was more stable at the lower O_2 concentrations. Pentachlorobenzene DREs were never below 6-nines and therefore are not plotted.

Ranking the POHCs is shown in Figure 4. This figure illustrates that rankings can change, depending on combustion conditions. This is also true depending on the nature of the experimental device.

Table 3 is a list of rankings of POHCs derived from Figure 4 and from data supplied by UDRI in Reference 9. Although not definitive, the research into POHCs and POHC rankings have produced results which seem to make surrogate use even more questionable than when it was first suggested.

Table 3. POHC Ranking With O_2 Present^a

	UDRI	LIS Incineration	
		Low O_2 (1.5%)	High O_2 (5%)
SF_6	1	1	2
Tetrachloroethylene	2	4	3
Toluene	5	2	1
Pentachlorobenzene	3	5	5
Chlorobenzene	4	3	4

^a1 being most stable; 5 being least stable.

POHC RANKING

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	UDRI	LIS Incineration	
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Tetrachloroethylene	2	4	3
Toluene	5	2	1
Pentachlorobenzene	3	5	5
Chlorobenzene	4	3	4

^a1 being most stable; 5 being least stable.

RELATIVE POHC STABILITY

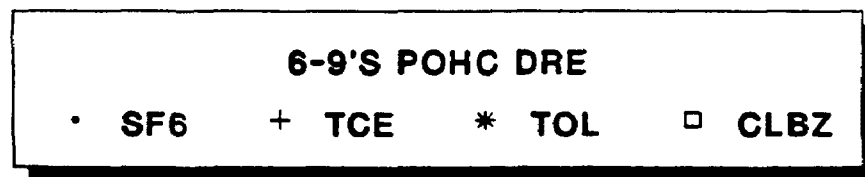
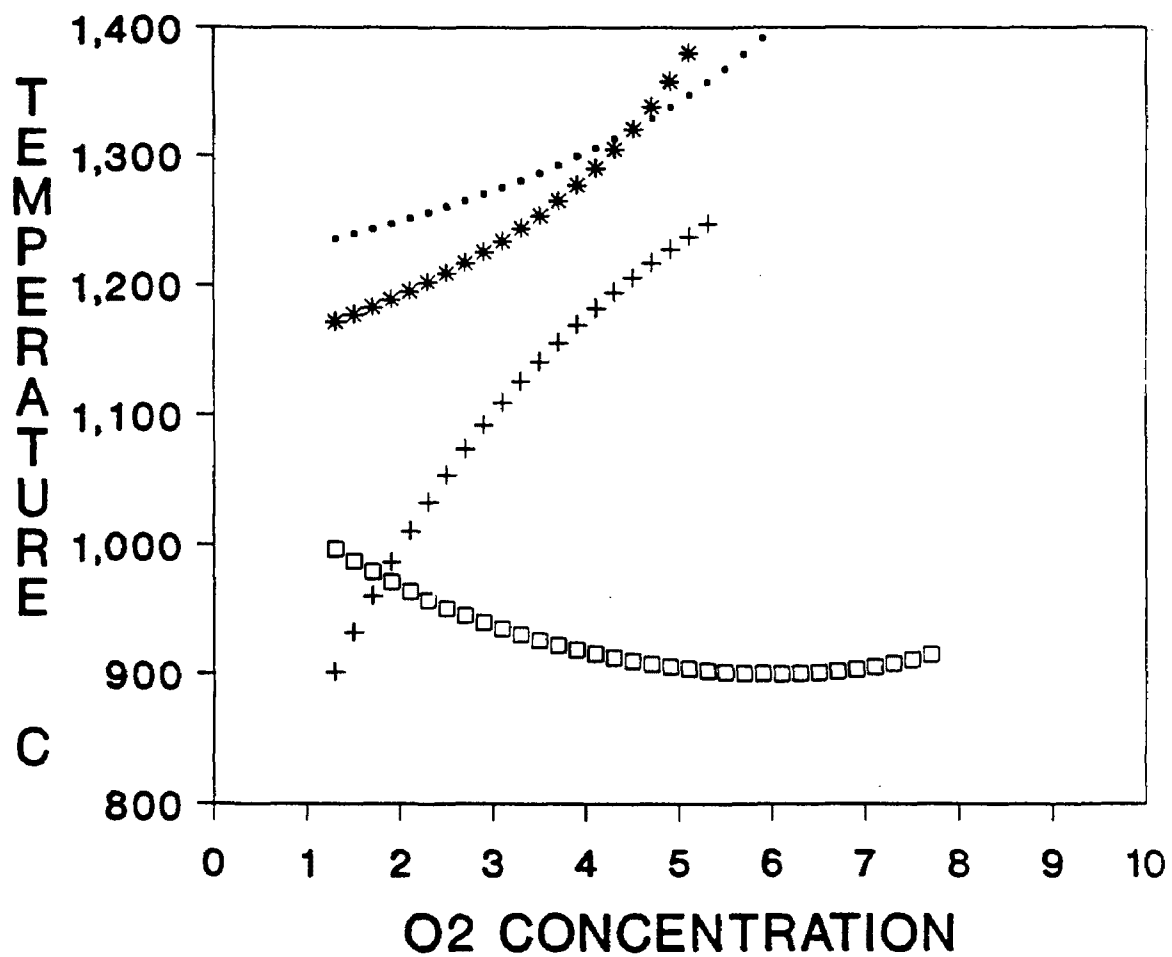


Figure 4. Relative POHC stability.

CONCLUSIONS

- o SF_6 is a limited surrogate. Data showing reactivity with refractory and difficulty with using it may have reduced its apparent value
- o POHC ranking is not absolute and depends on combustion conditions
- o Toluene is the most stable of the organics at elevated temperature and O_2 levels, while SF_6 is most stable at intermediate and lower levels.

RECOMMENDATIONS

- o Modify the use of surrogates for trial burns, and specify minimum combustion conditions
- o Choose a minimum number of POHCs for trial burns
- o Use the most stable POHCs at low oxygen values, since that condition is present in most incinerator failures
- o Develop method for continuous monitoring of toluene and benzene, for performance monitoring.

REFERENCES

1. Oppelt, E.T. Incineration of Hazardous Waste - A Critical Review. JAPCA. 37: 558, 1987.
2. 40 CFR Part 264.343.
3. Tsang, W.M. and Shaub, W.M. Surrogates as Substitutes for Principal Organic Hazardous Constituent Validation of Incinerator Operation. In: Proceedings of the Second Conference on Municipal, Hazardous and Coal Wastes, Miami, FL 1983. p. 241.
4. England, W.G., Rappolt, T.J., Teuscher, L.H., Kerrin, S.L. and Mournighan, R.E. Measurement of Hazardous Waste Incineration Destruction and Removal Efficiencies Using Sulfur Hexafluoride as a Chemical Surrogate. In: Proceedings of the 79th Annual APCA Meeting, 1986. 106:162097W.
5. Pandompam, B., Liem, A.J., Frenette, R. and Wilson, M.A. Effect of Refractory on the Thermal Stability of SF₆. JAPCA. 39: 310, 1989.
6. Dellinger, B. Testing and Evaluation of a POHC/PIC Incinerability Mixture. U.S. EPA 15th Annual Research Symposium, Cincinnati, Ohio, April April 10-12, 1989.
7. Taylor, P.H. and Chadbourne, J. Sulfur Hexafluoride as a Surrogate. JAPCA. 37: 729 1987.
8. 40 CFR 761.70a.
9. Waterland, L.E. and Staley, L.J. Pilot Scale Listing of SF₆ As A Hazardous Waste Incinerator Surrogate. To be Presented at the 82nd National Meeting of the Air and Waste Management Association, Dallas, TX, 1989. Paper 89-238.4.