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METHOD OF CHARACTERIZING VOID VOLUME HEADSPACE IN VENTED TRANSURANIC WASTE SLUDGE DRUMS USING LIMITED SAMPLING DATA

Kevin J. Liekhus and Michael J. Connolly
EG&G Idaho, Inc.
P.O. Box 1625
Idaho Falls, ID 83415-3625
(208)526-2974

Pat M. Arnold and Gerald A. O'Leary
EG&G Rocky Flats, Inc.
P.O. Box 464
Golden, CO 80402
(303)966-2056

ABSTRACT

The Department of Energy must demonstrate to the Environmental Protection Agency that a drum headspace sample is representative of the volatile organic compounds (VOCs) within the entire void space of the waste container in order to demonstrate compliance in the future when drums could be directly emplaced in the Waste Isolation Pilot Plant in New Mexico. A test program is underway at the Idaho National Engineering Laboratory to determine if the drum headspace VOC concentration is representative of the concentration in the entire drum void space and demonstrate that the VOC concentration in the void space of each layer of confinement can be estimated using a model incorporating diffusive and permeative transport principles and limited waste drum sampling data. A comparison of model predictions of VOC concentration in the innermost layer of confinement with actual measurement from transuranic waste sludge drums demonstrate that the model may be useful in characterizing VOC concentration throughout entire drum void volume.

I. INTRODUCTION

Currently, characterization of transuranic (TRU) waste destined for the Waste Isolation Pilot Plant (WIPP) requires detailed characterization of the volatile organic compound (VOC) concentration in the void volume headspaces (drum headspace, the large polymer bag headspace, and the innermost layers of confinement headspace) of the waste drums. The objectives of the extensive sampling are to obtain a representative sample from each layer of confinement to identify volatile and gaseous constituents, verify process knowledge of the drum contents, and demonstrate compliance with regulatory requirements. The Department of Energy (DOE) must demonstrate to the Environmental Protection Agency (EPA) that a drum headspace sample is representative of the VOCs within the entire void space of the waste container in order to demonstrate compliance in the future when drums could be directly emplaced in the WIPP. The WIPP conditional no-migration determination (NMD) specifies that the EPA expects that all layers of confinement in a container will have to be sampled until DOE can demonstrate, based on data collected, that sampling of all layers is either unnecessary or can be safely reduced.

The regulatory requirements specify maximum acceptable concentrations for certain VOCs in all layers of confinement. The WIPP conditional NMD requirements specify the maximum average concentration of three hazardous constituents (carbon tetrachloride, methylene chloride, and trichloroethylene). The NMD also states that it must be demonstrated that no layer of confinement contains a mixture of gases and VOCs that could become flammable when mixed with air. An important issue is whether gas samples must be collected from all layers of confinement to obtain representative headspace samples from a waste drum to meet these requirements. A systematic means of describing the VOC concentrations within the innermost layer of confinement, based on the drum headspace concentration, would suggest that the drum headspace sample is representative.

A test program is underway at the Idaho National Engineering Laboratory to determine if the drum headspace VOC concentration is representative of the concentration in the entire drum void space and demonstrate that the VOC concentration in the void space of each layer of confinement can be estimated using a model incorporating theoretical diffusive and permeative transport principles and limited waste drum sampling data. The test program consists of three stages. In the first two stages, a model was developed to demonstrate that VOC transport from vented lab-scale waste drums could be calculated based on measured or estimated transport parameters and prior knowledge of the initial VOC concentration inside the drum. The final stage investigates the applicability to characterize VOC concentration in actual vented waste drums. This paper presents the application of a transport model to estimate the VOC concentration within the innermost layer of confinement of vented waste sludge drums based on process knowledge and the measured VOC concentration in the drum headspace.

II. VOC TRANSPORT MODEL

A transport model was developed to estimate the VOC concentration in void volumes within a vented drum containing a waste that is a source of VOC emissions. Model parameters are defined from knowledge of drum headspace VOC concentration and waste drum configuration. A waste sludge drum consists of a vented drum with a rigid drum liner that contains the waste sludge wrapped inside two layers of polyethylene. A small opening in the drum liner lid allows gas and vapor transport between the drum liner and drum headspaces. The waste drum configuration includes the type of filter vent in the drum lid, the dimensions of the opening the drum liner lid, and the thickness of large polymer bags surrounding the waste. The model consists of a series of material balance equations describing steady-state VOC transport from each distinct void volume in the drum.

A. Model Equations

The polyethylene bags are the innermost layer of confinement and the headspace immediately surrounding the waste is referred to as the first void volume. The second and third void volumes are the drum liner and drum headspaces, respectively. The VOC transport rate from the innermost layer of confinement is defined by the equation

$$r_1 = \alpha\,(c_1 - c_2)\ . \qquad (1)$$

The rate of VOC transport from the drum liner is defined as

$$r_2 = \beta\,(c_2 - c_3)\ . \qquad (2)$$

The rate of VOC transport from the drum headspace across the filter vent is defined as

$$r_3 = \frac{D^*}{c_g}\,(c_3 - c_\infty)\ . \qquad (3)$$

The total gas concentration can be estimated using the ideal gas law

$$c_g = \frac{RT}{P}\ . \qquad (4)$$

The values of α and β are calculated based on process knowledge. The VOC concentration in the drum headspace, c_3, is determined from analysis of gas samples collected below the filter vent. The VOC concentrations in the other void volumes are estimated using Equations (1) through (4).

$$c_2 = c_3 + \frac{r_3}{\beta}\ , \qquad (5)$$

and

$$c_1 = c_2 + \frac{r_3}{\alpha}\ . \qquad (6)$$

B. Model Assumptions

The following assumptions were made in order to estimate the relationship between the VOC concentration measured in the drum headspace and the VOC concentrations in the other void volumes:

DISCLAIMER

1. An equilibrium exists between the vapor phase and the VOC source in the innermost layer of confinement.

2. All VOC transport rates from all void volumes are equal and at steady state.

3. The primary mechanisms for VOC transport are permeation across the polymer bags and diffusion across the drum liner and drum headspaces.

4. The boundary thickness across the innermost layer of confinement is equal to twice the thickness of one polyethylene bag.

5. The VOC concentration throughout each void volume is uniform and is zero outside the waste drum.

6. All VOC properties and other model parameters remain constant.

III. VOC TRANSPORT EXPERIMENTS

The drum headspace and the gas headspace inside the innermost layer of confinement were sampled in 14 drums containing waste sludges. The waste consisted of inorganic or organic sludges. In order to assure that the assumption of steady-state VOC transport across all layers of confinement was applicable, all drums were vented for a period of at least 8 weeks.

Drum headspace gas samples were collected by inserting a needle through the carbon composite filter vent. The drum and drum liner lids were then removed and a gas sample collected from the gas headspace with the innermost polyethylene bags. The data quality objectives outlined in the Quality Assurance Program for the WIPP Experimental-Waste Characterization Program were maintained.[1]

IV. MODEL CALCULATIONS

Model parameters were measured or estimated from available process knowledge. The bag surface area was estimated to be 2,565 cm^2. This corresponds to the maximum cross-sectional area of the drum liner. From process knowledge, each polyethylene bag was assumed to be 10 mils (0.025 cm) thick. The cross-sectional area of the opening in the drum liner lid is 5.07 cm^2. The average thickness of the liner lid was approximately 0.5 cm; however, the diffusion length was estimated to be 1.4 cm. The VOC permeability coefficients were measured across polyethylene using a mixed-component chromatographic detection method. The diffusivities of most VOCs in air at a given temperature and pressure were identified in the literature.[2] In the case where diffusivity data could not be identified, the VOC diffusivity in air was estimated using the equation[3]

$$D_{AB} = 2.745 \times 10^{-4} \frac{T^{1.823}}{\Pi} \left[p_{cA}\, p_{cB}\right]^{1/3} \left[T_{cA}\, T_{cB}\right]^{-1/2} \left[\frac{1}{M_A} + \frac{1}{M_B}\right]^{1/2} . \quad (7)$$

The VOC diffusion characteristic across the filter vent were measured in experiments performed at EG&G Idaho. The measured VOC diffusion characteristics ranged from 9×10^{-7} to 2×10^{-6} mol s^{-1}. The waste drums were maintained at ambient room temperature and pressure. When necessary, a temperature of 25°C and a pressure of 61.0 cm Hg were used in model calculations.

V. EXPERIMENTAL AND MODEL RESULTS

From process knowledge of model parameters and the measured VOC concentration in the drum headspace below the filter vent, model estimates of VOC concentration inside the innermost layer of confinement were calculated. A comparison of the predicted concentration to the measured concentration inside the innermost polyethylene bag for carbon tetrachloride, 1,1,1-trichloroethane (TCA), 1,1,2-trichloro-1,2,2-trifluoroethane (Freon-113), methylene chloride, toluene, meta- and para-xylene, trichloroethylene (TCE), and methanol are shown in Figures 1 and 2.

VI. DISCUSSION

In each figure, the solid diagonal corresponds to predicted value being exactly equal to measured

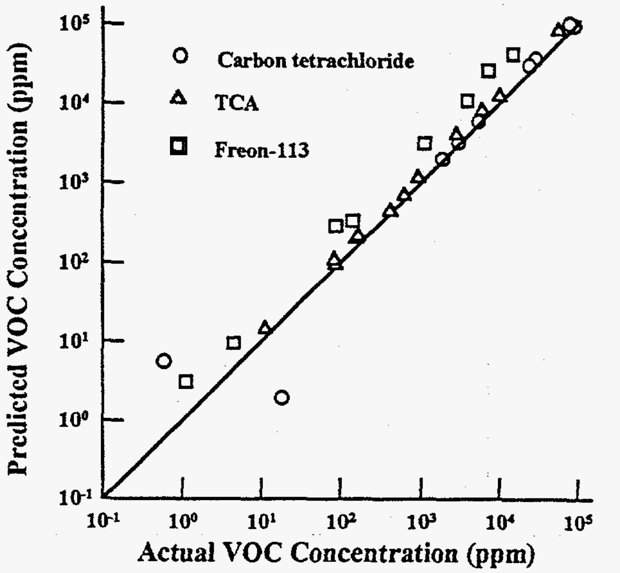

Figure 1. Comparison of estimated and actual inner bag headspace concentrations of VOCs found in organic waste sludge drums.

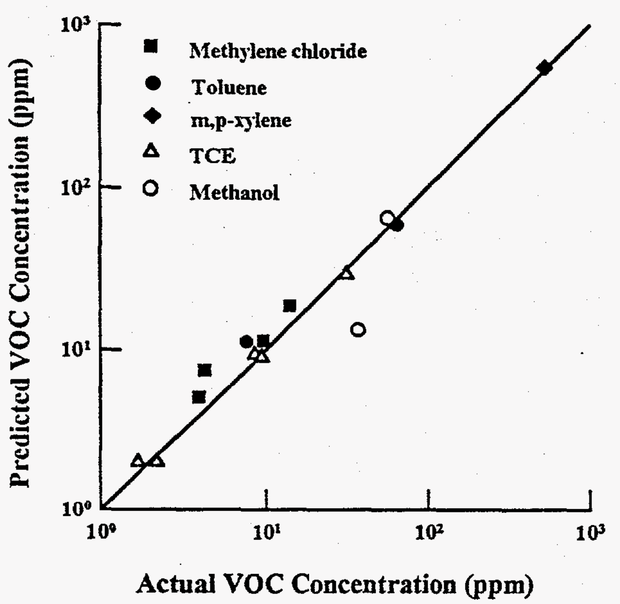

Figure 2. Comparison of estimated and actual inner bag headspace VOC concentrations.

values. The model was accurate in estimating the concentration in the innermost bag for most VOCs. In the case of Freon-113, the model results were significantly higher than actual results. This may be an advantageous feature where conservative estimates of VOC concentration are predicted. However, the model will be more useful if model estimates are closer to actual measured values. The significant deviation is indicative that the Freon-113 permeability used in model calculations may be lower than that in actual waste drums. In a series of experiments designed to determine the permeability of different VOCs across polyethylene, single component and VOC gas mixtures were used. Experimental results indicated that the permeability of some VOCs in the presence of other VOCs is greater than when only one VOC is passed over the polymer film. In these permeability experiments, the maximum concentration of any one VOC was approximately 1,000 ppm. In the gas samples taken from the sludge drums, the carbon tetrachloride concentration was as high as 100,000 ppm. The effect of VOC interactions on the permeability across a polymer film is currently under investigation.

The assumption of uniform VOC concentration in each void volume is made to simplify model calculations. The specification of a diffusion length across the drum liner that is greater than the actual drum thickness is a simple means of accounting for the concentration gradient that exists near the drum liner opening. The effective diffusion length assumed across the drum liner lid only effects the predicted concentration difference across the drum liner. The relative difference decreases as the total VOC concentration in the drum headspace increases. At high VOC concentrations, variability in the permeability coefficient has a greater effect on the estimated concentration than does the effective diffusion length across the drum liner lid. As conditions arise that make the assumptions of uniform VOC concentration more valid, the effective diffusion length will approach the minimum distance separating the two void volumes. The effective diffusion length used in these model calculations was selected because the value resulted in the ratio of predicted VOC concentration in the drum headspace to drum liner headspace of approximately 0.9. A means to better estimate the effective diffusion length is being investigated.

Another potential advantage of characterizing the VOC content throughout a waste drum is the possibility, with the appropriate thermodynamic data, to estimate the VOC content in the waste matrix. This could result in eliminating the need to sample the waste matrix itself.

ACKNOWLEDGMENTS

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NOMENCLATURE

A_d cross-sectional area of opening in drum liner lid, cm^2
α $\psi \rho A_{p1} P/x_{p1}$, $cm^3 s^{-1}$
A_{p1} permeable surface area of innermost layer of confinement, cm^2
β $D A_d/x_d$
c_g total gas concentration in waste drum, mol cm^{-3}
c_i VOC concentration within i^{th} void volume, mol cm^{-3}
c_∞ VOC concentration outside drum, mol cm^{-3}
D VOC-air diffusivity, $cm^2 s^{-1}$
D^* VOC filter diffusion characteristic, mol s^{-1}
D_{AB} mass diffusivity for VOC(A)-air(B) system, $cm^2 s^{-1}$
M_i molecular weight of species i
P pressure, cm Hg
p_{ci} critical pressure of species i, atm
Π pressure, atm
P_s standard pressure = 76.0 cm Hg
ψ TP_s/PT_s
R gas constant = 6236 cm^3 (cm Hg) $mol^{-1} K^{-1}$
r_1 VOC transport rate from innermost void volume, mol s^{-1}
ρ VOC permeability coefficient, cm^3 (STP) $cm^{-1} s^{-1}$ $(cm Hg)^{-1}$
T temperature, K
T_{ci} critical temperature of species i, K
T_s standard temperature = 273.15 K
x_d diffusional length across opening in drum liner lid, cm
x_{p1} boundary thickness of innermost layer of confinement, cm

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