DEVELOPMENT OF A METHOD UTILIZING DRUM HEADSPACE VOC
CONCENTRATION AS A WASTE CHARACTERIZATION TOOL

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ABSTRACT

Pretest waste characterization for the bin-scale tests at the Waste Isolation Pilot Plant (WIPP) required sampling for volatile organic compounds (VOCs) from within transuranic (TRU) waste drums. Although the bin-scale tests have been postponed, the development and demonstration of accurate waste characterization methods continues. The objectives of extensive sampling of waste drums 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. A method to estimate the VOC concentration between layers of confinement from a single headspace sample collected beneath the drum filter of a vented waste drum is investigated. This method of characterizing the void space within a drum could eventually lead to a significant reduction in sampling time and cost. A model based on fundamental principles of transport phenomena is developed to estimate the VOC concentration throughout a waste drum based on the knowledge of the transport properties and the measured drum headspace VOC concentration. Model and experimental results are compared.

INTRODUCTION

Pretest waste characterization for the bin-scale tests at the Waste Isolation Pilot Plant (WIPP) originally specified sampling for volatile organic compounds (VOCs) from three areas within transuranic (TRU) waste drums (drum headspace, the large polymer bag headspace, and the innermost layers of confinement headspace). The Environmental Protection Agency (EPA) expects all layers of confinement in a container will have to be sampled until the Department of Energy can demonstrate to the EPA, based on data collected, that sampling of all layers is either unnecessary or can be safely reduced. 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.

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. The regulatory requirements specify maximum acceptable concentrations for certain VOCs in all layers of confinement. The WIPP conditional no-migration determination (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.

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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. The method described in this paper does not currently address the equilibrium relationship between the gas and waste phases.

VOC TRANSPORT MODEL IN A VENTED DRUM

A VOC transport model is developed to estimate the steady-state VOC gas-phase concentration throughout a waste drum containing a VOC-laden waste. The model assumes that over a small time period, a steady state or quasi-steady state exists between all layers of confinement and that the VOC concentration within each layer of confinement does not change significantly because of the presence of a VOC-contaminated waste in the drum. In addition, a steady-state assumption implies that the process does not experience any significant variations in temperature. The model consists of a series of material balance equations describing steady-state VOC transport between each void volume.

A filter vent located on the waste drum lid to prevent the accumulation of hydrogen and other gases generated via radiolysis allows diffusion of the VOCs into the surrounding environment. Waste drums both contain a rigid polymer drum liner with a small hole punctured in its lid and a large polyethylene bag inside the liner. Smaller polymeric bags may be located inside the large bag. The waste is located within the innermost layer of bags. A general schematic of a simulated waste drum configuration used in lab-scale VOC transport experiments is shown in Fig. 1.

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The innermost layer of confinement is referred to as the first void volume. The drum headspace is the final or n^{th} void volume. The innermost layer of confinement contains the VOC-laden waste. This layer of confinement may be small polymer bags or the large polymer bag which lines the inside of the rigid drum liner. The average VOC transport rate from the innermost layer of confinement is primarily the result of VOC permeation and is defined by the equation

$$r_1 = \alpha_1 (c_1 - c_2) \quad , \quad (\text{Eq. 1})$$

where

- r_1 = VOC transport rate from innermost void volume, mol s^{-1}
- α_1 = $\phi A_{p1} P/x_{p1}$, $\text{m}^3 \text{s}^{-1}$
- ϕ = VOC permeability coefficient, $\text{m}^3 (\text{STP}) \text{m N}^{-1} \text{s}^{-1}$
- A_{p1} = surface area of innermost layer of confinement across which VOC permeates, m^2
- P = absolute pressure, N m^{-2}
- x_{p1} = boundary thickness of innermost layer of confinement, m
- c_i = VOC concentration within i^{th} void volume at standard temperature and pressure, mol m^{-3} .

In the case of M small bags containing all waste inside a drum, the model only calculates an average rate of VOC transport of r_1 from each bag. The total rate of VOC transport from all

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small bags is Mr_1 . The VOC transport rate from the surrounding large polymer bag into the drum liner headspace is defined, in general, as

$$r_{n-2} = \alpha_{n-2} (c_{n-2} - c_{n-1}) , \quad (\text{Eq. 2})$$

which will be equivalent to Eqn (1) if the large bag is the innermost layer of confinement. The presence of multiple layers of small or large polymer bags is probable. For the purpose of model calculations, the multiple layers are assumed to be equivalent to a single polymer layer with a thickness equal to the sum of all the individual layers.

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

$$r_{n-1} = \beta_{n-1} (c_{n-1} - c_n) , \quad (\text{Eq. 3})$$

where

$$\begin{aligned} \beta_{n-1} &= D A_{d,n-1} / x_{d,n-1} \\ D &= \text{VOC-air diffusivity, m}^2 \text{ s}^{-1} \\ A_{d,n-1} &= \text{cross-sectional area of hole in drum liner lid, m}^2 \\ x_{d,n-1} &= \text{diffusional length across hole in drum liner lid, m.} \end{aligned}$$

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

$$r_n = \frac{D'RT}{P} (c_n - c_{n+1}) , \quad (\text{Eq. 4})$$

where

$$\begin{aligned} D' &= \text{VOC filter diffusion characteristic, mol s}^{-1} \\ R &= \text{gas constant, N m mol}^{-1} \text{ K}^{-1} \\ T &= \text{temperature, K} \\ P &= \text{pressure, N m}^{-2} \\ c_{n+1} &= \text{VOC concentration outside drum, mol m}^{-3}. \end{aligned}$$

Thus, in the case where the waste is contained in M small polymer bags, the VOC transport rates from all void volumes are assumed to be equal or nearly equal,

$$Mr_1 = r_2 = r_3 = r_4 \quad (\text{Eq. 5})$$

The VOC concentration outside the vented waste drum is assumed to equal zero. The values of α and β can be calculated based on process knowledge. Rearranging eqns (1-5), the VOC concentration in each layer of confinement can be estimated based on the knowledge of the measured drum headspace VOC concentration, c_4 ;

$$c_3 = c_4 + \frac{r_4}{\beta_3} , \quad (\text{Eq. 6})$$

$$c_2 = c_3 + \frac{r_4}{\alpha_2} , \quad (\text{Eq. 7})$$

$$c_1 = c_2 + \frac{r_4}{\alpha_1} . \quad (\text{Eq. 8})$$

The model assumptions are summarized below.

1. The primary mechanism for VOC transport across the polymer bags is permeation and across the drum liner headspace and drum headspace is diffusion.
2. The VOC concentration throughout each void volume is uniform and is zero outside the waste drum.
3. All VOC properties and drum configuration remain constant.
4. It is assumed that an equilibrium exists between the vapor phase and any VOC-containing source in the innermost layer of confinement. The equilibrium relationship between the VOC-containing waste and the vapor phase may slowly change over time but is assumed to be relatively constant over a short sampling period.

LAB-SCALE VOC TRANSPORT EXPERIMENTS

Lab-scale VOC transport experiments were developed to measure the VOC concentration throughout a vented waste drum that contained simulated VOC-laden waste sludge. Two experimental trials were performed to demonstrate the influence of the type of VOC and the number of layers of confinement. Each simulated sludge had a mass composition of approximately 85% liquid base and 15% calcium silicate. The liquid base was approximately 40% Texaco Regal oil and 60% VOCs. In the first trial, 100 g of simulated waste sludge containing methylene chloride, 1,1,1-trichloroethane (TCA), 1,1,2-trichloro-1,2,2-trifluoroethane (Freon-113), carbon tetrachloride, and trichloroethylene (TCE) were placed inside the large polyethylene bag inside a waste drum. In the second trial, 100 g of simulated waste sludge containing methanol, cyclohexane, TCA, toluene, and p-xylene were placed inside each of two small polyethylene bags within a waste drum. Each sludge sample was placed in a small unsealed glass jar to prevent direct contact with the polyethylene bag.

The automated VOC transport experimental configuration used in these experiments is shown in Fig. 2. Each of the four lab-scale waste drums in the experimental configuration was a scaled-down version of a Department of Transportation (DOT) 17C drum. Each waste drum contained a modified, high-density, rigid polyethylene drum liner. The nominal wall thickness of the liner of 2.3×10^{-4} m. The liner lid thickness varied across the lid. A hole was drilled in the drum lid and a NFT-020 (Nuclear Filter Technology Corp.) carbon-composite filter was screwed securely in the hole. A hole with a diameter of 9.5×10^{-4} m was drilled in the liner lid directly below the carbon composite filter in the drum lid. Inside the drum liner was a large polyethylene bag supported by a wire cage that may have contained simulated waste sludge or smaller polyethylene bags that contained the simulated waste sludge. All bags had a nominal bag thickness of 1×10^{-5} m.

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Measurements of the VOC concentrations were made from headspace of each small bag, the large bag, and the underneath the drum lid. Ambient laboratory temperature and barometric pressure were made on each sampling day. Samples were collected from each drum generally

twice a week. The total trial period lasted approximately 90 days. A 3-point initial standard calibration was established prior to each test period. Sample blanks were analyzed at the beginning and end of the sample sequence to determine if there were any interference or residual VOCs in the sampling system. One sample duplicate was randomly selected and analyzed on each sampling day.

Headspace samples were collected by evacuating the manifold system to a vacuum then back-filling the gas sampling loops. The gas sample flowed into the selected sampling loop until the pressure equilibrated to ambient pressure. Between samples, the automated gas sampling system evacuated the sampling manifold and gas sampling loops. Samples were transferred from the gas sampling loop to the gas chromatograph injector and analyzed by a flame ionization detector.

EXPERIMENTAL AND MODEL RESULTS

Model parameters were measured or estimated from available process information. Model input included specifying the total surface area, diffusional area, void volume, bag thickness, and diffusional pathway length for small and large bags. The maximum surface area of the small polymer bag was 0.26 m². The maximum surface area of the large bag was estimated to be 1.28 m². The actual bag surface area available for permeation is less than the total bag surface area. Small bags in intimate contact with each other, contact between small bags and the large bag as well as the large bag resting on the drum liner floor all decrease the total available surface area. The actual surface area of each bag in each drum could not be measured. For the lab-scale waste drums, the total permeable bag surface area was estimated to be 75% of the total bag surface area. The diffusional length between drum liner and drum headspace void volumes was estimated to equal the sum of the hole diameter and liner lid thickness. This length was 0.014 m.

The VOC permeability coefficients across the polyethylene bag were measured at 25°C and used in model calculations. The diffusivity of most VOCs in air at a given temperature and pressure were identified in the literature.¹ In the case where diffusivity data could not be identified, the VOC diffusivity in air was estimated using Slattery-Bird equation,²

$$D_{AB} = 2.745 \times 10^{-4} \frac{T^{1.823}}{P} [p_{cA} p_{cB}]^{1/3} [T_{cA} T_{cB}]^{-1/2} \left[\frac{1}{M_A} + \frac{1}{M_B} \right]^{1/2} \quad (\text{Eq. 9})$$

The diffusivity equation was also used to correct for any difference in temperature and pressure observed in the experiments. The VOC diffusion characteristic across a NFT-020 carbon composite filter was measured at 25°C. The temperature in the drum headspace of a lab-scale waste drum maintained at ambient room temperature varied between 24°C and 25.5°C during all trials. A constant temperature of 24.7°C was used in model calculations for the waste drums maintained at room temperature. The ambient pressure varied between 8.51 x 10⁴ N m⁻² and 8.69 x 10⁴ N m⁻² during the experiments. A constant pressure of 8.60 x 10⁴ N m⁻² was used in all model calculations.

The TCA drum headspace concentration as a function of time during both trials is shown in Figs. 3 and 4. The curves in Fig. 3 show the concentration increasing rapidly, reaching a maximum value, then steadily decreasing during the course of the experiment. This suggests that

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the amount of sludge in the waste drums in Trial 1 was insufficient to maintain the VOC concentration. This trend was observed for the other VOCs also. The TCA concentration did not decrease as rapidly during the second trial where more simulated waste sludge was present. However, when the ratio of drum headspace VOC concentration-to-innermost layer of confinement VOC concentration were plotted as a function of time, the ratio approached an asymptotic value regardless of the time-dependent nature of the VOC concentration for most compounds. A comparison of experimental results and model predictions of the average VOC drum headspace-to-large bag headspace concentration ratio in Trial 1 are shown in Figs. 5 and 6. Experimental results from Trial 2 showing the drum headspace-to-small bag headspace concentration ratio are summarized in Figs. 7 and 8. The predicted ratio for TCA is shown in Fig. 7. Model predictions were not calculated for the other VOCs because their permeability across the polyethylene bags had not yet been determined.

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DISCUSSION

The time required for the concentration ratios of TCE, toluene, and p-xylene to reach a constant value was considerably greater than for the other VOCs. In fact, the ratios for toluene and p-xylene continue to increase during the entire test period. A direct correlation between the time required to reach a near-steady value for the concentration ratio and the VOC vapor pressure is shown in Tables I and II. This relationship suggests that newly packaged waste drums cannot be characterized immediately after packaging and the necessary waiting period is dependent, in part, on the types of VOCs expected in the waste matrix as well as the total VOC content in the waste matrix.

The comparison of the model predictions to the experimental concentration for those VOCs that reached near-constant values suggests that the VOC steady-state transport model may be useful in characterizing VOC concentrations throughout actual waste drums. Experimental results presented in Figs. 5 through 8 show that near-constant concentration ratios result after a finite period of time after drum enclosure even as the VOC concentration decreases due to source depletion. This fact increases the potential application of the model to vented waste drums that are not at steady state. However, the applicability of the model in cases where the VOC concentration changes due to temperature variations has not been demonstrated. The model can estimate the VOC concentration throughout a waste drum at a particular time based on the drum headspace sample collected at that time. In the future, the VOC concentration within actual waste drums will be measured and compared to model predictions.

CONCLUSIONS

A VOC steady-state transport model has been developed to estimate VOC concentration within a vented waste drum based on the measured VOC concentration in the drum headspace below the filter vent. The model was successful in predicting the VOC concentration within the innermost layer of confinement in lab-scale waste drums containing simulated VOC-laden sludges.

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Table 1. Comparison of VOC vapor pressure and approximate average time, t_{ss} , when near-constant drum headspace-to-large bag VOC concentration ratio was reached during Trial 1.

VOC	P_{vap} (mm Hg)	t_{ss} (days)
methylene chloride	430.5	14
Freon-113	334.4	18
1,1,1-TCA	133.5	52
carbon tetrachloride	115.2	55
TCE	69.1	62

Table 2. Comparison of VOC vapor pressure and approximate average time, t_{ss} , when near-constant drum headspace-to-small bag VOC concentration ratio was reached during Trial 2.

VOC	P_{vap} (mm Hg)	t_{ss} (days)
1,1,1-TCA	133.5	14
methanol	126.4	14
cyclohexane	97.6	24
toluene	28.4	>75
p-xylene	8.8	>75

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Figure 1. Schematic of lab-scale vented waste drum.

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Figure 2. Automated VOC transport experimental configuration.

Figure 3. TCA concentration in drum headspace of lab-scale waste drums during Trial 1.

Figure 4. TCA concentration in drum headspace of lab-scale waste drums during Trial 2.

Figure 5. Comparison of average experimental and predicted drum headspace-to-large bag concentration ratio for Freon-113, TCA, and TCE during Trial 1.

Figure 6. Comparison of average experimental and predicted drum headspace-to-large bag concentration ratio for methylene chloride and carbon tetrachloride during Trial 1.

Figure 7. Average experimental drum headspace-to-small bag concentration ratio for methanol and TCA and predicted TCA concentration ratio during Trial 2.

Figure 8. Average experimental drum headspace-to-small bag concentration ratio for toluene, p-xylene, and cyclohexane during Trial 2.