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DETERMINATION OF DRUM AGE CRITERIA AND PREDICTION FACTORS BASED ON PACKAGING CONFIGURATIONS

EXECUTIVE SUMMARY

Headspace sampling for volatile organic compounds (VOCs) is a characterization requirement for contact-handled (CH) transuranic (TRU) waste containers to be sent to the Waste Isolation Pilot Plant for disposal. Prior to performing headspace sampling, "drum age criteria" (DAC) need to be met for headspace samples to be valid. DACs are estimates of the time required for VOCs in a drum to reach 90 percent of the equilibrium steady-state concentration within the different layers of confinement. In addition, headspace sampling performed after the DAC has been met can be correlated to the VOC concentration in the innermost layer of confinement by the use of prediction factors (PFs), which are multipliers to be applied to the headspace concentration. A set of DACs and PFs for CH-TRU wastes were previously determined assuming conservative packaging configurations in terms of number of layers, presence of a rigid drum liner, and filter diffusivity. A major fraction of the CH-TRU waste is not packaged pursuant to these conservative configurations and would benefit from the application of packaging-specific DACs and PFs.

This report presents the results of a study to determine packaging-specific DACs and PFs, based upon current packaging practices and plans for future packaging configurations. DACs can be reduced up to an order of magnitude by the use of specific packaging options. For waste in a 55-gallon drum, the most dramatic improvement in DACs would result from the elimination of the rigid drum liner, from the removal of the rigid drum liner lid, or from an increase in the size of the hole in the rigid drum liner. For all payload containers, reducing the number of bag layers and improving the filter diffusivity result in lower DACs. The results from this study can be used to reduce the DAC requirement for existing, as well as, future waste forms and packaging configurations, thereby reducing the need for holding times and additional storage capacity at the sites.

The concept of DACs can also be applied to standard waste boxes (SWBs) to determine the "holding time" after waste packaging for headspace sampling. Because rigid drum liners are not used within SWBs, the DACs for the SWB packaging configurations currently in use at the U.S. Department of Energy sites are lower than those for drums.

1.0 INTRODUCTION

Drum age criteria (DAC) are estimates of the time required for volatile organic compounds (VOCs) in a container of contact-handled transuranic (CH-TRU) waste to reach 90 percent of the equilibrium steady-state concentration within the different layers of confinement. The DAC is the time period that must elapse after waste packaging in order for a headspace gas sample for VOCs to be valid. Once the DAC is satisfied and the headspace sampled for VOCs, prediction factors (PFs) can be used to correlate the headspace concentration with the VOC concentration in the innermost layer of confinement. DACs and PFs have been determined based on conservative packaging configurations as reported in Connolly et al. (1998). The current DAC and PF requirements are too restrictive for wastes that are not packaged as in the "bounding case." Waste packaging at several sites includes fewer bag layers; better filters in both bags, drums and other waste containers; more efficient filter sizes and materials; and the absence of the 90-mil rigid drum liner. The current DACs also impose a storage requirement on planned treatment facilities, as the requirement for headspace sampling of VOCs cannot be met until the DAC is satisfied.

2.0 PURPOSE AND SCOPE

The purpose of this study was to develop packaging-specific DACs and PFs that can be used at the U.S. Department of Energy (DOE) sites without the need to use bounding values for the entire CH-TRU waste inventory. A matrix of DACs and PFs has been developed that can be used to define packaging-specific parameters for the entire CH-TRU waste inventory. This report also clarifies the DAC and PF requirements for waste containers with different packaging and venting histories.

The scope of this report includes different packaging configurations used to package 55-gallon drums at the DOE sites. In addition, this report extends the concept of DACs to standard waste boxes (SWBs) and presents the "holding times" needed before headspace sampling of SWBs for VOCs.

3.0 SUMMARY OF PREVIOUS ANALYSIS FOR BASELINE DACS

The current limits for DACs (Connolly et al., 1998) are categorized based on the waste form and packaging as follows:
Waste Types I and IV, Solidified Inorganics and Solidified Organics. These wastes are assumed to be packaged in two drum liner bags, in a rigid drum liner with a 0.375-inch diameter hole, in a 55-gallon drum fitted with a filter with a hydrogen diffusivity of 4.2E-06 moles/second/mole fraction.

Waste Types II and III, Solid Inorganics and Solid Organics. These wastes are assumed to be packaged in three inner bags and two drum liner bags, in a rigid drum liner with a 0.375-inch diameter hole, in a 55-gallon drum fitted with a filter with a hydrogen diffusivity of 4.2E-06 moles/second/mole fraction.

These values were obtained from testing performed at the Idaho National Engineering and Environmental Laboratory (Connolly et al., 1998). The current DACs are also a function of the waste container packaging and venting history as follows:

Category 1 **Containers that have been packaged for a period of at least one year and are newly vented.** For this configuration, the DACs are 22 days for Waste Types I and IV and 18 days for Waste Types II and III. The DACs apply from the date of venting.

Category 2 **Containers that are unvented and are sampled at the time of venting.** For this configuration, the DACs are 127 days for Waste Types I and IV and 48 days for Waste Types II and III. The DACs apply from the time of waste packaging. In addition, if the sampling in this case is taken inside the rigid liner, the PF is 1 because the VOCs achieve equilibrium throughout the waste packaging within the rigid liner.

Category 3 **Containers that are newly generated in a vented condition.** For this configuration, the DACs are 225 days for Waste Types I and IV and 142 days for Waste Types II and III. The DACs apply from the times of waste packaging and venting, which are the same. This is the most restrictive case that is being applied to the entire CH-TRU inventory at this time.

4.0 METHODOLOGY FOR DETERMINING PACKAGING-SPECIFIC DACS

This report addresses the derivation of DACs to expand available options for Category 3 based on specific packaging configurations. Compliance with the DACs under Category 1 is not an issue because most of the retrievably stored drums in the system have been in storage well over a one-year period prior to venting. Category 2 DACs also apply to retrievably stored wastes and are easily met.
Category 3 applies to newly generated wastes, including wastes to be generated from planned treatment facilities. The biggest impact of the current DACs is on waste containers belonging to this category. Because CH-TRU waste at the different DOE sites is packaged in a variety of ways, a matrix of representative packaging configurations (instead of a single bounding case) was developed for each of the two physical waste forms (solidified and solid) to adequately represent the DOE CH-TRU waste inventory belonging to Category 3. The selection of representative packaging configurations for the DAC analysis was based on the following criteria:

- A review of the TRUPACT-II Content Codes (TRUCON) document (DOE, 1999), which is a compilation of site-specific waste form information, including the different methods used to package the waste at each of the DOE sites. Based on the review of the TRUCON document, all TRUCON code packaging configurations have been summarized as 38 common configurations as listed in Attachment A. These 38 configurations were then divided into two groups: packaging configurations included in Waste Type I and Waste Type IV

TRUCON codes (14 configurations), and packaging configurations included in Waste Type II and Waste Type III TRUCON codes (38 configurations).

- An informal survey of some of the DOE sites expected to generate and package CH-TRU waste in the future.

- A preliminary sensitivity analysis performed to determine which factors most influence the DACs. The details of this sensitivity analysis are presented in Attachment B.

The 38 configurations listed in Attachment A and future packaging options to be used by the sites were consolidated for the DAC analysis based on the frequency of use for the packaging configuration and the sensitivity analysis. Packaging configurations for which the DACs were not expected to differ significantly were represented by a single configuration. Packaging configurations currently not allowed by the TRUPACT-II Safety Analysis Report (SAR) (DOE, 1999) (e.g., filtered bag configurations for Waste Types I and IV) or not used by the sites on a regular basis (e.g., the use of inner bags for Waste Types I and IV) were eliminated from further consideration. The final matrix of selected packaging configurations is shown in Table 1 for Waste Types I and IV and in Table 2 for Waste Types II and III. These selected packaging configurations address DAC dependence on the following parameters:

- Type and number of bag layers
- Presence of rigid drum liner
- Size of hole in the rigid drum liner
- Diffusivity of drum filter.

Table 1
Packaging Configurations for Waste Type I and IV Drums

Case	Packaging Configuration	Rigid Liner	Drum Filter Diffusivity
1	no plastic bags	0.3" diameter hole	3.7×10^{-6} m/s/mf
2	no plastic bags	1" diameter hole	3.7×10^{-5} m/s/mf
3	no plastic bags	no lid	3.7×10^{-6} m/s/mf
4	1 liner bag	0.3" diameter hole	3.7×10^{-6} m/s/mf
5	1 liner bag	1" diameter hole	3.7×10^{-5} m/s/mf
6	2 liner bags	no rigid liner	3.7×10^{-6} m/s/mf
7	2 liner bags	1" diameter hole	3.7×10^{-6} m/s/mf
8	2 liner bags	1" diameter hole	3.7×10^{-5} m/s/mf
9	2 liner bags	no lid	3.7×10^{-6} m/s/mf
10	2 liner bags	no lid	3.7×10^{-5} m/s/mf

Table 2
Packaging Configurations for Waste Type II and III Drums

Case	Packaging Configuration	Rigid Liner	Drum Filter Diffusivity
1	no plastic bags	0.3" diameter hole	3.7×10^{-6} m/s/mf
2	2 inner bags, 1 liner bag	0.3" diameter hole	3.7×10^{-5} m/s/mf
3	2 inner bags, 1 liner bag	1" diameter hole	3.7×10^{-6} m/s/mf
4	2 inner bags, 1 liner bag	1" diameter hole	3.7×10^{-5} m/s/mf
5	3 inner bags, 2 liner bags	no rigid liner	3.7×10^{-6} m/s/mf
6	3 inner bags, 2 liner bags	0.3" diameter hole	3.7×10^{-5} m/s/mf
7	3 filtered inner bags, 2 filtered liner bags	0.3" diameter hole	3.7×10^{-6} m/s/mf
8	5 inner bags, 1 liner bag	1" diameter hole	3.7×10^{-5} m/s/mf
9	5 inner bags, 1 liner bag	no lid	3.7×10^{-6} m/s/mf
10	2 inner bags, 1 liner bag	no lid	3.7×10^{-6} m/s/mf
11	2 inner bags, 1 liner bag	no liner	3.7×10^{-6} m/s/mf

m/s/mf = moles per second per mole fraction.

These are the key variables that impact the DACs and that are of interest to the sites in packaging CH-TRU wastes. The configurations listed in Tables 1 and 2 address Category 3 wastes (newly generated, vented containers) for which DACs are limiting. Some retrievably-stored wastes, which may have been packaged to meet the worst-case limits in the TRUPACT-II SAR (DOE, 1999), fall under Categories 1 or 2 for which the conservative DACs from Connolly et al. (1998) would easily be satisfied.

Application of DACs to SWBs

Attachment A also presents the packaging configurations used at the DOE sites for wastes loaded directly into SWBs. These packaging configurations range from no bag layers to five inner layers in one SWB liner bag. Because no rigid liners are used in SWBs, it was expected that the DACs for this spectrum of SWB packaging configurations would fall within a narrow range and could be encompassed by the following configurations:

- SWBs with one SWB liner bag
- SWBs with five inner bags and one SWB liner bag.

The inner bags are the same as those used in drums. The SWB liner bags are large bags lining the SWBs with a thickness of 14 mil and a surface area of 8.85E+04 sq. cm (DOE, 1999). Conservative estimates indicate that the void volume inside the bag layers and in the SWB headspace is 10 percent of the total SWB volume (IT Corporation, 1999).

For the configurations presented in Tables 1 and 2, and the SWB configurations, the methodology for determining DACs was identical to that used in Connolly et al. (1998). The DACs are presented in Section 6.0.

5.0 METHODOLOGY FOR DETERMINING PACKAGING-SPECIFIC PFS

This section describes the methodology used for the determination of PFs for the configurations shown in Tables 1 and 2 and the SWB configurations. This methodology is based on the analysis presented in Connolly et al. (1998). The PF is a variable with a unique value for each VOC and packaging configuration that, when multiplied by the measured VOC concentration in the container headspace, predicts the concentration of the VOC in the innermost confinement layer.

At steady-state conditions, there is no accumulation of VOCs within any layer of confinement, the concentrations of VOCs are constant within each layer of confinement, and the VOC transport rate across each layer of confinement is equal to a constant rate. The primary mechanisms for gas transport across a confinement layer are permeation across a polymeric layer, diffusion through air across an opening in the layer, and diffusion through a filter vent in the case of a drum filter or filtered bag. One or all of these mechanisms of transport may be operating depending on the characteristics of the confinement layer.

Model Assumptions

The following assumptions were made in developing the PF methodology:

1. All gases exhibit ideal behavior.

2. Temperature and pressure are constant.

3. An equilibrium exists between the VOC-contaminated waste and the vapor phase in the innermost layer of confinement. Thus, the VOC concentration within the innermost confinement layer is constant.

4. A sufficient period of time has elapsed (i.e., the DAC has been satisfied) such that the VOC transport rates across all layers of confinement are equal and at steady-state. Thus, the VOC concentration within a void volume is constant and there is no accumulation of gas within any confinement layer.

5. The VOC concentration within a void volume is uniform at all times. Thus, there are no concentration variations within a single void volume.

6. Multiple layers of inner bags and liner bags are treated as a single inner bag or liner bag with a total thickness equal to the product of the number of such layers and the thickness of the individual layer.

7. The concentration of the VOC outside the container is zero. Thus, there is rapid transport by diffusion and convection of the VOC outside the container to maintain a zero concentration outside the drum.

8. All VOC properties and confinement layer properties are constant and uniform.

For each of the various layers of confinement that may be present in a container, the rate of VOC transport across each confinement layer, r, is defined as follows:

Inner Bag (Twist and Tape)

Equation 1

$$r = \frac{\phi\, c\, \rho\, A_{ib} P}{n_{ib}\, x_{ib}} \Delta y_{ib} = \frac{K_{ib}}{n_{ib}} \Delta y_{ib}$$

where,

ϕ	=	76 T / (273.15 P) (dimensionless)
c	=	gas concentration at standard temperature (273.15 °K) and pressure (1 atmosphere) from ideal gas law, P/RT (4.46 x 10^{-5} mol cm^{-3})
T	=	gas temperature (°K)
ρ	=	VOC permeability [cm^3 (STP) cm^{-1} sec^{-1} $(cm\ Hg)^{-1}$ = 10^{10} Ba]
A_{ib}	=	surface area of inner bag (cm^2)
P	=	gas pressure (cm Hg)
n_{ib}	=	number of inner bags in packaging configuration
x_{ib}	=	thickness of inner bag (cm)
Δy_{ib}	=	VOC mole fraction difference across inner bag (dimensionless)
K_{ib}	=	inner bag VOC transport characteristic (mol sec^{-1})
R	=	gas constant (6236.6 cm Hg cm^3 mol^{-1} $°K^{-1}$)

Liner Bag (Twist and Tape)

Equation 2

$$r = \frac{\phi\, c\, \rho\, A_{lb} P}{n_{lb}\, x_{lb}} \Delta y_{lb} = \frac{K_{lb}}{n_{lb}} \Delta y_{lb}$$

where,

A_{lb}	=	surface area of liner bag (cm^2)
n_{lb}	=	number of liner bags in packaging configuration

x_{lb} = thickness of liner bag (cm)

Δy_{lb} = VOC mole fraction difference across liner bag (dimensionless)

K_{lb} = liner bag VOC transport characteristic (mol sec^{-1}).

Inner Bag (Filtered)

Equation 3

$$r = (\frac{\phi\ c\ \rho\ A_{ib} P}{n_{ib}\ x_{ib}} + \frac{D^{*}_{VOC-bf}}{n_{ib}})\ \Delta y_{ib} = \frac{K_{ib}}{n_{ib}}\ \Delta y_{ib}$$

where,

D^{*}_{VOC-bf} = VOC-bag filter diffusion characteristic (mol s^{-1}), which is calculated by the following equation:

Equation 4

$$D^{*}_{VOC-bf} = \frac{D_{VOC-air}}{D_{H_2-air}}\ D^{*}_{H_2-bf}$$

where,

$D_{VOC-air}$ = VOC diffusivity in air (cm^2 sec^{-1})

D_{H_2-air} = hydrogen diffusivity in air (cm^2 sec^{-1})

$D^{*}_{H_2-bf}$ = hydrogen-bag filter diffusion characteristic (mol sec^{-1}).

Liner Bag (Filtered)

Equation 5

$$r = (\frac{\phi\ c\ \rho\ A_{lb} P}{n_{lb}\ x_{lb}} + \frac{D^{*}_{VOC-bf}}{n_{lb}})\ \Delta y_{lb} = \frac{K_{lb}}{n_{lb}}\ \Delta y_{lb}$$

where all variables have been previously defined.

Rigid Drum Liner

Equation 6

$$r = \frac{P\, D_{VOC-air}\, A_{rl}}{R\, T\, x_{rl}}\, \Delta y_{rl} = K_{rl}\, \Delta y_{rl}$$

where,

A_{rl}	=	cross-sectional area of the hole in the rigid drum liner lid (cm^2)
x_{rl}	=	diffusional path length across hole in the rigid drum liner lid (cm)
Δy_{rl}	=	VOC mole fraction difference across the rigid liner (dimensionless)
K_{rl}	=	rigid liner transport characteristic (mol sec^{-1})

The VOC-diffusivity in air, $D_{VOC\text{-}air}$, can be estimated at low pressures using an equation developed from a combination of kinetic theory and corresponding-states arguments shown below (Liekhus, 1995):

Equation 7

$$D_{VOC-air} = 2.745 \times 10^{-4}\, \frac{T^{1.823}}{P}\, [p_{c-VOC}\, p_{c-air}]^{1/3}\, [T_{c-VOC}\, T_{c-air}]^{-1/2}\, [\frac{1}{M_{VOC}} + \frac{1}{M_{air}}]^{1/2}$$

where,

M_{VOC}	=	molecular weight of VOC (g/mol)
M_{air}	=	molecular weight of air (29 g/mol)
$p_{c\text{-}VOC}$	=	critical pressure of VOC (atm)
$p_{c\text{-}air}$	=	critical pressure of air (36.4 atm)
$T_{c\text{-}VOC}$	=	critical temperature of VOC (°K)
$T_{c\text{-}air}$	=	critical temperature of air (132°K).

Container Filter

Equation 8

$$r = n_{cf}\ D^{*}_{VOC-cf}\ \Delta y_{cf} = n_{cf}\ D^{*}_{VOC-cf}\ y_{hs}$$

where,

Δy_{cf}	=	VOC mole fraction difference across the container filter (dimensionless)
y_{hs}	=	VOC mole fraction measured in container headspace (dimensionless)
n_{cf}	=	number of container filters in packaging configuration
D^{*}_{VOC-cf}	=	VOC-container filter diffusion characteristic (mol sec^{-1}), which is calculated through the following equation:

Equation 9

$$D^{*}_{VOC-cf} = \frac{D_{VOC-air}}{D_{H_2-air}} D^{*}_{H_2-cf}$$

where,

D^{*}_{H2-cf} = Hydrogen-container filter diffusion characteristic (mol sec^{-1}).

Sequential substitution and rearrangement of terms yields the following relationship for the innermost confinement layer VOC concentration as a function of the measured container headspace VOC concentration:

Equation 10

$$y_{icl} = y_{hs}\ [1 + n_{cf} D_{voc-cf} (\sum_{i=1}^{nl} \frac{n_i}{K_i})]$$

where,

y_{icl}	=	innermost confinement layer VOC mole fraction (dimensionless)
n_i	=	number of type "i" confinement layers in packaging configuration
K_i	=	transport characteristic of type "i" confinement layer (mol sec^{-1})
nl	=	number of different confinement layer types.

Multiplying both sides of Equation 10 by a conversion factor (10^6 ppm/mole fraction) yields the following final equation for the prediction factor:

Equation 11

$$Y_{icl} = Y_{hs} \, [1 + n_{cf} D_{voc-cf} (\sum_{i=1}^{nl} \frac{n_i}{K_i})]$$

where,

Y_{icl} = innermost confinement layer VOC concentration (ppm)

Y_{hs} = measured VOC concentration in container headspace (ppm).

Thus, the prediction factor, PF, is:

Equation 12

$$PF = [1 + n_{cf} D_{voc-cf} (\sum_{i=1}^{nl} \frac{n_i}{K_i})]$$

Using this equation, the PFs for the representative configurations listed in Tables 1 and 2 and the two SWB configurations can be established.

6.0 RESULTS AND CONCLUSIONS

Tables 3 and 4 present a summary of the DACs and PFs for the packaging configurations listed in Tables 1 and 2. Table 5 lists the DACs and PFs for the two SWB configurations. Depending on the packaging configurations, the DACs can range from a few months to a few days. As shown in the tables, the use of packaging-specific information can reduce the DACs and PFs considerably. The following conclusions can be drawn from the results presented in Tables 3 and 4:

- The most significant reduction in DACs for drums is for packaging configurations that do not use a rigid drum liner or that do not use the lid on the drum liner. The rate-limiting step for the VOCs to reach equilibrium is the solubility and permeation through the liner. Absence of the liner or the liner lid eliminates this rate-limiting step. In addition, the larger the size of the hole in the liner lid, the smaller the DAC.

- Fewer bag layers result in smaller DACs and PFs, but the impact is less than removing the rigid liner or liner lid.

-

- Better filters in the drum result in smaller DACs. The use of filters in bags is less important, because the permeation of VOCs from the bags is significant compared to the diffusion through the filter.

- All SWB packaging configurations currently in use at the sites can be bound by the DACs shown in Table 5, with the maximum DAC being 56 days for SWBs. The SWB DACs are considerably lower than those for drums due to the absence of a rigid liner.

The matrices presented in Tables 3, 4 and 5 can be used with future TRUPACT-II SAR and Waste Isolation Pilot Plant Resource Conservation and Recovery Act Part B Permit amendments to specify lower DACs and PFs for different waste packaging configurations in drums and SWBs. The Revision 19 initiative of the TRUPACT-II SAR, expected to be submitted to the U.S. Nuclear Regulatory Commission in the near future, can use this study to classify the CH-TRU waste inventory for newly generated wastes pursuant to the matrices in Tables 3, 4 and 5. In addition, the DACs in Tables 3, 4 and 5 can be incorporated into the Automated TRUPACT-II Authorized Methods for Payload Control (e-TRAMPAC) and linked to the packaging description of the waste. Lower DACs can also be specified for retrievably stored wastes (Categories 1 and 2), for wastes with no confinement layers, and for treated waste forms for which the absence of VOCs can be established and documented.

Table 3
DACs and PFs for Waste Type I and IV Packaging Configurations for Drums

DAC/PF by VOC	Packaging Configuration*									
	Case 1	Case 2	**Case 3**	**Case 4**	**Case 5**	**Case 6**	Case 7	**Case 8**	Case 9	Case 10
DAC (Days)	**111**	19	**4**	**188**	**71**	**31**	**151**	**110**	106	**84**
Flammable VOCs					**PF**					
Acetone	1.3	1.3	1.0	1.4	2.1	1.2	1.2	2.8	1.2	2.5
Benzene	1.3	1.3	1.0	1.4	1.7	1.1	1.1	2.1	1.1	1.8
1-Butanol	1.3	1.3	1.0	1.3	1.7	1.1	1.1	2.0	1.1	1.7
Chlorobenzene	1.3	1.3	1.0	1.3	1.5	1.0	1.1	1.6	1.0	1.3
Cyclohexane	1.3	1.3	1.0	2.0	7.9	2.3	2.4	14.5	2.3	14.2
1,1-Dichloroethane	1.3	1.3	1.0	1.4	1.9	1.1	1.1	2.4	1.1	2.1
1,2-Dichloroethane	1.3	1.3	1.0	1.3	1.6	1.0	1.1	1.8	1.0	1.5
1,1-Dichloroethene	1.3	1.3	1.0	1.4	2.3	1.2	1.2	3.3	1.2	3.0
cis-1,2-Dichloroethene	1.3	1.3	1.0	1.4	1.7	1.1	1.1	2.1	1.1	1.8
Ethyl benzene	1.3	1.3	1.0	1.3	1.7	1.1	1.1	2.0	1.1	1.7
Ethyl ether	1.3	1.3	1.0	1.6	3.9	1.5	1.5	6.5	1.5	6.2
Methanol	1.3	1.3	1.0	1.4	2.5	1.2	1.3	3.6	1.2	3.3
Methyl ethyl ketone	1.3	1.3	1.0	1.4	2.0	1.1	1.2	2.6	1.1	2.3
Methyl isobutyl ketone	1.3	1.3	1.0	1.4	2.0	1.1	1.2	2.7	1.1	2.4
Toluene	1.3	1.3	1.0	1.3	1.5	1.0	1.1	1.6	1.0	1.3
1,2,4-Trimethylbenzene	1.3	1.3	1.0	1.3	1.6	1.1	1.1	1.8	1.1	1.5
1,3,5-Trimethylbenzene	1.3	1.3	1.0	1.3	1.6	1.1	1.1	2.0	1.1	1.6
o-Xylene	1.3	1.3	1.0	1.3	1.6	1.0	1.1	1.8	1.0	1.5
m-Xylene	1.3	1.3	1.0	1.3	1.7	1.1	1.1	2.0	1.1	1.7
p-Xylene	1.3	1.3	1.0	1.3	1.4	1.0	1.1	1.5	1.0	1.2
Nonflammable VOCs					**PF**					
Bromoform (Tribromomethane)	1.3	1.3	1.0	1.3	1.3	1.0	1.0	1.4	1.0	1.1
Carbon tetrachloride	1.3	1.3	1.0	1.4	1.8	1.1	1.1	2.3	1.1	2.0
Chloroform	1.3	1.3	1.0	1.4	1.7	1.1	1.1	2.1	1.1	1.8
Methylene chloride (dichloromethane)	1.3	1.3	1.0	1.4	1.8	1.1	1.1	2.2	1.1	1.9
1,1,2,2-Tetrachloroethane	1.3	1.3	1.0	1.3	1.4	1.0	1.0	1.4	1.0	1.1
Tetrachloroethene	1.3	1.3	1.0	1.3	1.5	1.0	1.1	1.6	1.0	1.3
1,1,1-Trichloroethane	1.3	1.3	1.0	1.4	2.0	1.1	1.2	2.7	1.1	2.4
Trichloroethene	1.3	1.3	1.0	1.3	1.5	1.0	1.1	1.7	1.0	1.4
1,1,2-Trichloro-1,2,2-trifluoroethane	1.3	1.3	1.0	1.5	3.6	1.5	1.5	5.9	1.5	5.6

*Packaging configurations for each case are defined in Table 1.

Table 4
DACs and PFs for Waste Type II and III Packaging Configurations for Drums

DAC/PF by VOC	Packaging Configuration*										
	Case 1	**Case 2**	Case 3	**Case 4**	**Case 5**	**Case 6**	**Case 7**	Case 8	Case 9	Case 10	Case 11
DAC (Days)	**113**	**51**	**52**	**42**	**14**	**67**	**134**	56	40	25	9
Flammable VOCs	PF										
Acetone	1.3	4.5	1.1	1.6	1.1	4.7	1.4	1.9	1.1	1.0	1.0
Benzene	1.3	4.3	1.0	1.5	1.0	4.4	1.3	1.6	1.0	1.0	1.0
1-Butanol	1.3	4.3	1.0	1.5	1.0	4.4	1.3	1.6	1.0	1.0	1.0
Chlorobenzene	1.3	4.2	1.0	1.4	1.0	4.3	1.3	1.4	1.0	1.0	1.0
Cyclohexane	1.3	6.9	1.3	4.1	1.5	8.9	1.7	6.0	1.5	1.3	1.3
1,1-Dichloroethane	1.3	4.4	1.1	1.6	1.0	4.5	1.4	1.7	1.0	1.0	1.0
1,2-Dichloroethane	1.3	4.2	1.0	1.4	1.0	4.3	1.3	1.5	1.0	1.0	1.0
1,1-Dichloroethene	1.3	4.5	1.1	1.7	1.1	4.9	1.4	2.0	1.1	1.0	1.0
cis-1,2-Dichloroethene	1.3	4.3	1.0	1.5	1.0	4.4	1.3	1.6	1.0	1.0	1.0
Ethyl benzene	1.3	4.3	1.0	1.5	1.0	4.4	1.3	1.6	1.0	1.0	1.0
Ethyl ether	1.3	5.2	1.1	2.4	1.2	6.0	1.5	3.2	1.2	1.1	1.1
Methanol	1.3	4.6	1.1	1.8	1.1	5.0	1.4	2.1	1.1	1.0	1.0
Methyl ethyl ketone	1.3	4.4	1.1	1.6	1.0	4.6	1.4	1.8	1.0	1.0	1.0
Methyl isobutyl ketone	1.3	4.4	1.1	1.6	1.1	4.6	1.4	1.8	1.1	1.0	1.0
Toluene	1.3	4.2	1.0	1.4	1.0	4.2	1.3	1.4	1.0	1.0	1.0
1,2,4-Trimethylbenzene	1.3	4.2	1.0	1.4	1.0	4.3	1.3	1.5	1.0	1.0	1.0
1,3,5-Trimethylbenzene	1.3	4.3	1.0	1.5	1.0	4.4	1.3	1.5	1.0	1.0	1.0
o-Xylene	1.3	4.2	1.0	1.4	1.0	4.3	1.3	1.5	1.0	1.0	1.0
m-Xylene	1.3	4.3	1.0	1.5	1.0	4.4	1.3	1.6	1.0	1.0	1.0
p-Xylene	1.3	4.2	1.0	1.4	1.0	4.2	1.3	1.4	1.0	1.0	1.0
Nonflammable VOCs	PF										
Bromoform (Tribromomethane)	1.3	4.1	1.0	1.3	1.0	4.2	1.3	1.3	1.0	1.0	1.0
Carbon tetrachloride	1.3	4.4	1.1	1.5	1.0	4.5	1.4	1.7	1.0	1.0	1.0
Chloroform	1.3	4.3	1.0	1.5	1.0	4.4	1.3	1.6	1.0	1.0	1.0
Methylene chloride (dichloromethane)	1.3	4.3	1.1	1.5	1.0	4.5	1.3	1.7	1.0	1.0	1.0
1,1,2,2-Tetrachloroethane	1.3	4.2	1.0	1.3	1.0	4.2	1.3	1.4	1.0	1.0	1.0
Tetrachloroethene	1.3	4.2	1.0	1.4	1.0	4.3	1.3	1.4	1.0	1.0	1.0
1,1,1-Trichloroethane	1.3	4.4	1.1	1.6	1.1	4.6	1.4	1.8	1.1	1.0	1.0
Trichloroethene	1.3	4.2	1.0	1.4	1.0	4.3	1.3	1.5	1.0	1.0	1.0
1,1,2-Trichloro-1,2,2-trifluoroethane	1.3	5.1	1.1	2.3	1.2	5.8	1.5	3.0	1.2	1.1	1.1

*Packaging configurations for each case are defined in Table 2.

Table 5
DACs and PFs for SWB Packaging Configurations

DAC/PF by VOC	Packaging Configuration	
	SWB Case 1 – One SWB Liner Bag	SWB Case 2 – Five Inner Bags & One SWB Liner Bag
DAC (Days)	**15**	56
Flammable VOCs	**PF**	
Acetone	1.0	1.1
Benzene	1.0	1.0
1-Butanol	1.0	1.0
Chlorobenzene	1.0	1.0
Cyclohexane	1.1	1.7
1,1-Dichloroethane	1.0	1.1
1,2-Dichloroethane	1.0	1.0
1,1-Dichloroethene	1.0	1.1
cis-1,2-Dichloroethene	1.0	1.0
Ethyl benzene	1.0	1.0
Ethyl ether	1.0	1.3
Methanol	1.0	1.1
Methyl ethyl ketone	1.0	1.1
Methyl isobutyl ketone	1.0	1.1
Toluene	1.0	1.0
1,2,4-Trimethylbenzene	1.0	1.0
1,3,5-Trimethylbenzene	1.0	1.0
o-Xylene	1.0	1.0
m-Xylene	1.0	1.0
p-Xylene	1.0	1.0
Nonflammable VOCs	**PF**	
Bromoform (Tribromomethane)	1.0	1.0
Carbon tetrachloride	1.0	1.1
Chloroform	1.0	1.0
Methylene chloride (dichloromethane)	1.0	1.0
1,1,2,2-Tetrachloroethane	1.0	1.0
Tetrachloroethene	1.0	1.0
1,1,1-Trichloroethane	1.0	1.1
Trichloroethene	1.0	1.0
1,1,2-Trichloro-1,2,2-trifluoroethane	1.0	1.2

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Attachment A

Packaging Configurations in TRUCON Document

Packaging Configurations in the TRUCON Document

Configuration*	Number in TRUCON	Waste Type(s)	Payload Container(s)					
			Drum	SWB OP	SWB	Bin	TDOP	Pipe
No layers	31	I, II, III, IV	X	X	X		X	
No layers, filtered inner lid	1	III	X	X				
Metal Can (II.2)	24	II	X	X	X		X	X
1 inner	9	II, III, IV	X	X	X		X	
1 inner, filtered inner lid	1	III	X	X				
1 filtered inner	8	II, III	X	X	X		X	
1 liner	26	I, II, III	X	X	X		X	
1 liner, filtered inner lid	1	III	X	X				
1 filtered liner	15	II, III	X	X	X		X	
1 inner, 1 liner	14	I, II, III	X	X	X		X	
1 filtered inner, 1 filtered liner	2	II, III	X		X			
1 inner, 1 liner, 1 filtered can	3	III	X	X				
1 filtered inner, 1 filtered liner, 1 filtered can	4	III	X	X	X			
2 inner	18	II, III, IV	X	X	X		X	X
2 inner, 1 filtered can	3	III	X	X				X
2 filtered inner	21	I, II, III, IV	X	X				X
2 filtered inner, 1 filtered can	16	I, II, III, IV						X
2 liner	29	I, II, III, IV	X	X	X	X	X	
2 filtered liner	9	II, III	X					
1 inner, 2 liner	3	II, III			X		X	
2 inner, 1 liner	29	I, II, III, IV	X	X	X		X	
2 filtered inner, 1 filtered liner	4	I, III	X	X	X			
2 inner, 1 liner, 1 filtered can	2	III	X	X				
2 filtered inner, 1 filtered liner, 1 filtered can	10	II, III, IV	X	X	X			
2 filtered inner, 1 filtered liner, 2 filtered cans	3	I, III	X	X				
2 inner, 2 liner	28	I, II, III	X	X	X			
2 filtered inner, 2 filtered liner	2	III	X	X				
2 filtered inner, 2 filtered liner, 1 filtered can	1	II	X	X				
3 inner, filtered inner lid	1	III	X	X				
3 inner, 1 liner	6	II, III	X	X	X		X	
3 inner, 1 liner, 1 filtered can	2	III	X	X				
3 filtered inner, 1 filtered liner, 1 filtered can	5	I, III	X	X				
4 inner	1	II			X			
4 inner, 1 liner	6	II, III	X	X	X		X	
4 filtered inner, 1 filtered liner, 1 filtered can	4	III	X					
3 inner, 2 liner	11	II, III	X	X	X			
4 inner, 2 liner	1	II	X	X	X			
5 inner, 1 liner	3	II, III	X	X	X		X	

*"Inner" and "liner" refer to plastic bag layers.

Attachment B

Preliminary Sensitivity Analysis on Packaging Variables Impacting Drum Age Criteria

Preliminary Sensitivity Analysis on Packaging Variables Impacting Drum Age Criteria

Background

A computer code incorporating model equations describing unsteady-state or transient gas transport in a waste drum has been developed and used to estimate the time required for the concentration of a volatile organic compound (VOC) to reach near steady-state or equilibrium concentrations in the drum.[1] The time required to reach these concentrations is defined as a drum age criterion (DAC) and is a function of the VOC and waste drum configuration.

The DAC was calculated for 30 VOCs in two different waste drum configurations under three different sampling scenarios.[2] Common features to these drum configurations was the presence of a rigid polyethylene drum liner and polymers bags, in which the waste was packaged, inside a 55-gallon waste drum. Variables in the packaging configuration include the number of polymer bags, bag thickness, and available permeable surface area surrounding the waste. One configuration is typical for solidified waste (Waste Type I and IV). Another packaging configuration is typically used for solid waste (Waste Types II and III). In addition, three different sampling scenarios were considered:

1) Newly vented existing waste drums that had achieved equilibrium conditions before venting.

2) Newly packaged vented waste drum

3) Newly packaged unvented waste drum

In the first two scenarios, the DAC represent the time required to approach steady-state conditions. In the case of the unvented waste drum, the DAC is the time required to approach equilibrium conditions.

The DAC is also a function of the chemical and physical properties of the VOC. The VOCs were screened to identify indicator VOCs that are most significant with regards to flammability issues and human health risks. The highest DAC value among the indicator VOCs in the different drum configurations and scenarios is currently used to define the minimum storage or vent time required before sampling the drum headspace. These values are summarized in Table I.

Table I
Current DACs (in days) for Different Packaging Configurations (by Waste Type) and Sampling Scenarios

	Waste Type I/IV	Waste Type II/III
Newly vented, existing	22	18
Newly packaged, vented	225	142
Newly packaged, unvented	127	48

The DACs associated with newly packaged waste drums have been identified as potentially impacting waste drum packaging and characterization processes because of the significant holding period required. As part of a study to identify ways to decrease the total holding time or DAC, a series of model calculations were performed to identify how changes in waste packaging configuration may result in smaller DACs.

Model Parameters

The following parameters were evaluated:

- Number of layers of polymer bags
- VOC permeability across polymer bags (reflecting influence of bag material)
- Presence or absence of rigid polyethylene drum liner
- Cross-sectional area of opening in drum liner lid
- Bag filter and drum filter vent diffusion characteristics.

In order to demonstrate the relative effect of changing these variables. DAC values are calculated for a baseline case as well as other cases in which one baseline parameter is changed.

Baseline Case

The packaging configuration associated with solid waste (Waste Types II/III) serves as the baseline case to demonstrate the effect of changing parameter values. The model parameters for this case are listed in Table II. Waste is packaging inside three consecutive small bags (bag thickness = 0.0125 cm). All small bags are contained within two large bags (bag thickness = 0.028 cm). All waste and polymer bags are contained inside a rigid 90-mil polyethylene liner with a 0.375-diameter opening in the liner lid. The drum vent has a hydrogen diffusion characteristic of 42 x 10^{-7} mol/s. The DAC for this waste packaging configuration is based on the DAC for toluene and is 142 days.

Layers of Polymer Bags

Three waste packaging configurations with different numbers of layers of polymer bags were considered:

1) Four small bags, two large bags

2) One large bag only
3) No polymer bags.

The computer code is written assuming the presence of at least one bag in the system. In order to simulate the case of no bags, a large bag with a larger surface area and almost no thickness (0.0001 cm) is assumed to approximate the final case. The results are summarized in Table III.

VOC Permeability and Polymer Bag Material

Different bag materials have been used or are proposed for use. Polyethylene and polyvinyl chloride bags have been used in waste packaging. Limited data showed that VOC permeability across these bags are similar.[3] Nylon bags are being considered for packaging but permeability of all indicator VOCs in this polymer is not well characterized. In order to demonstrate the effect of different polymer bag material on the DAC, the VOC permeability is varied. Low VOC permeability will increase the DAC and higher permeability will decrease. Parameter variability and results are listed in Table II.

Drum Liner and Opening in Drum Liner Lid

When a drum liner is present, an opening in the drum liner lid is required to allow gas transport from the inner polymer bags to the drum headspace below the vented drum lid. The effect of varying the cross-sectional area of the opening in the drum liner lid is listed in Table III. The DAC for a waste drum with no drum liner present is calculated and listed in Table III. It is estimated in the computer model by assuming a drum liner is present but has minimal thickness (0.0001 cm) and no lid.

Table II
Drum Age Criterion as a Function of Polymer Bag Layers and VOC Permeability

Case	Input File[a]	Indicator VOC	Waste Type II/III DAC (days)	Waste Type I/IV DAC (days)
Baseline (3 small bags, 2 large bags)	vbase	toluene	142	---
Baseline (2 large bags)	rfbase0	toluene	---	225
4 small bags, 2 large bags	vbase2a	toluene	149	---
0 small bags, 1 large bags	vbase2b rfbase1	toluene	103 ---	--- 162
0 small bags, 0 large bags (estimate)	vbase2d rfbase1b	toluene	84 ---	--- 90
Baseline ($\wp_{voc}$ = 670.e-10)[b]	See above	toluene	142	225
$\wp_{voc}$ = 67.e-10	vbase3a rfbase2a	NA	517 ---	--- 1051
$\wp_{voc}$ = 6700.e-10	vbase3c rfbase2b	NA	77 ---	--- 87

a. Output file name is "inputfile.out"
b. Units of cm^3(STP) cm cm^{-2} (cm Hg)$^{-1}$ s^{-1}

Bag Filters and Drum Filter Vents Properties

The addition of a bag filter to polymer bags is intended to facilitate the diffusion of hydrogen between layers of confinement. The presence of a bag filter inherently increases the ability of VOCs to move between layers of confinement. While bag filters can be designed to significantly reduce resistance to gas diffusion, VOC diffusivity is generally an order of magnitude less than that of hydrogen.

In the same manner, the drum filter vent can be designed to have a higher hydrogen diffusion characteristic but the VOC diffusion characteristic will always be an order of magnitude lower. The results of using different filters and vents on the DAC are listed in Table IV.

Table III
Drum Age Criterion as a Function of Drum Liner and Opening in Liner Lid

Case	Input File[a]	Indicator VOC	Waste Type II/III DAC (days)	Waste Type I/IV DAC (days)
Baseline (A_{DL}=0.71 cm^2, x_d=1.2 cm)[b]	vbase	toluene	142	---
	rfbase0		---	225
1-in diameter opening in liner lid A_{DL}=5.07 cm^2, x_d=1.4 cm[c]	vbase5b	toluene	73	---
	rfbase3a		---	151
2-in diameter opening in liner lid A_{DL}=20.27 cm^2, x_d=1.4 cm	vbase5c	toluene	55	---
	rfbase3b		---	133
No lid on top of liner A_{DL}=150 cm^2,[d] x_d=1.4 cm	vbase5e	toluene	41	---
	rfbase3c		---	126
No liner (estimate)[d] A_{DL}=150 cm^2, x_d=1.4 cm, x_p= 0.0001 cm $V_{DL} = V_{DH}$ = 20,000 cm^3	vbase5i	toluene	2	---
		1,1-DCE[e]	9	---
		methanol	< 9[f]	---
		MIBK[e]	8	---
		MEK[e]	6	---
		CCl_4[e]	6	---
		CH_2Cl_2[e]	4	---
		$CHCl_3$[e]	4	---
		butanol	4	---
		TCE[e]	2	---
		chlorobenzene	2	---
		1,1,2,2-CH_2Cl_4[e]	1	---
No liner (estimate)[d] A_{DL}=150 cm^2, x_d=1.4 cm, x_p= 0.0001 cm $V_{DL} = V_{DH}$ = 20,000 cm^3	rfbase3f	toluene	---	4
		1,1-DCE[e]	---	18
		methanol	---	< 18[f]
		MIBK[e]	---	16
		MEK[e]	---	13
		CCl_4[e]	---	12
		CH_2Cl_2[e]	---	9
		$CHCl_3$[e]	---	9
		butanol	---	8
		TCE[e]	---	5
		chlorobenzene	---	4
		1,1,2,2-CH_2Cl_4[e]	---	2

a. Output file name is "inputfile.out".

b. A_{DL} = cross-sectional area of opening in drum liner lid; x_d = diffusional path length across opening.

c. Increased diffusion path length used for larger openings

d. Lid area ≈ 2,700 cm^2, but model results converge for areas equal to or greater than 150 cm^2. The case of no liner is approximated by letting liner thickness (x_p) approach zero. Total void volume assumed to be approximately 20% of drum volume (40 L) and equally divided between liner headspace and drum headspace.

e. DCE: dichloroethene; MIBK: methyl isobutyl ketone; MEK: methyl ethyl ketone; CCl_4: carbon tetrachloride; CH_2Cl_2: dichloromethane; $CHCl_3$: chloroform; TCE: trichloroethylene; CH_2Cl_4: tetrachloride

f. Methanol diffusivity is greater than that of 1,1-DCE and therefore will have a smaller DAC in this case.

Table IV
Drum Age Criterion as a Function of Polymer Bag Filters and Drum Filter Vents

Case	Input File[a]	Indicator VOC	Waste Type II/III DAC (days)	Waste Type I/IV DAC (days)
Baseline (D^{*}_{H2} = 42.e-7 mol/s)[b]	vbase rfbase0	toluene	142 ---	--- 225
D^{*}_{H2} = 420.e-7 mol/s	vbase7b rfbase7a	toluene	68 ---	--- 122
Baseline (no bag filters)	vbase rfbase0	toluene	142 ---	--- 225
Bag filters (D^{*}_{H2} = 1000.e-7 mol/s) $D^{*}_{VOC} = 0.1\ D^{*}_{H2}$	vbase6b rfbase6b	toluene	137 ---	--- 164
Bag filters (D^{*}_{H2} = 10000.e-7 mol/s) $D^{*}_{VOC} = 0.1\ D^{*}_{H2}$	vbase6a rfbase6a	toluene	110 ---	--- 88

a. Output file name is "inputfile.out"
b. D^{*} = gas diffusion characteristic of filter or filter vent

Model Parameters for Smaller DAC

The following parameters resulted in a smaller DAC compared to a baseline case:

- Decreased layers of polymer bags or thinner polymer bags
- Increased VOC permeability across polymer bags
- Larger opening in drum liner lid
- Elimination of the drum liner
- Use of bag filters
- Drum filter vents with greater hydrogen diffusion characteristic

The greatest benefit in achieving a smaller DAC value came from the elimination of the drum liner or at least the removal of the liner lid. The reduction of the available mass of drum liner for absorbing VOC vapors decreases the time to achieve near steady-state conditions.

The effect of increased bag surface area was not specifically examined. As the permeable surface area of polymer bags increases, the DAC decreases. However, since the surface area in model calculations is based on an assumption of the amount of waste in the drum and not easily manipulated in an actual waste drum, model calculations using different values for surface area were not performed.

The VOC permeability in a given polymer cannot be readily varied. Great benefit was demonstrated for highly porous drum filter vents but it is not clear that such vents are currently available. Bag filters were shown to be more beneficial for the drum containing waste sludge where the permeable area of the bags was assumed to be small. Possible fouling of the bag filter on the innermost bag may prevent credit being taken for the presence of a bag filter. Just as much benefit can be achieved by eliminating a bag layer all together.

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