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## Comparison of the fixed-bed and batch leaching characteristics of aromatic compounds in residually trapped crude oils and oily wastes

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### Abstract

The fixed-bed dissolution characteristics were characterized for five aromatic components in two crude oils residually trapped in glass beads and two refinery residuals containing an oily phase. Good agreement between predicted and experimental results for the fixed-bed dissolution of benzene, toluene, ethylbenzene, *p*- and *m*-xylenes, and naphthalene (BTEXN) from the two crude oils was observed over a wide range (three to four orders of magnitude) in aqueous effluent concentrations. The partition coefficients used to describe the experimental leaching curves agreed well with those independently measured from multiple-batch aqueous extractions. For the two refinery residuals, good agreement between predicted and experimental fixed-bed dissolution was also observed for a one- to two-orders of magnitude range in leachate concentrations. These results illustrate a methodology for predicting time-dependent leaching behavior for an oily residual using partition coefficients measured from batch leaching tests. In addition, it was found that when the oil content of the oily residuals was accounted for, the partition coefficients measured for BTEXN for the oily residuals were similar to those for the crude oils. In the absence of batch measurements for a given oily residual, this latter result suggests that the time-dependent leaching behavior, under local equilibrium conditions, can be estimated from measurements of only the contaminant concentrations in the waste and the oil content. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Leaching; Dissolution; Petroleum hydrocarbons; BTEX

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## 1. Introduction

To characterize the leaching of chemicals from a solid waste, typically a batch leaching test known as the toxicity characteristic leaching procedure, TCLP, is used [1,2]. In current approaches to risk assessment, it is assumed that the leachate concentration measured by the TCLP will last indefinitely. A more general approach accounts for the fact that the source concentration will decrease with time—this has been called the finite source approach [3,4].

A good method for assessing time-dependent source concentrations is to conduct a fixed-bed test. An alternative approach is to estimate the partition coefficient for a given compound from a TCLP leachate analysis and a total waste analysis, then use a dissolution model to predict fixed-bed leaching. Batch extractions conducted at varying leachate/waste ratios can also be used. This alternative batch method can be more reliable for predicting partition coefficients, especially for oily wastes for which a fraction of the contaminant may not be available for leaching.

The motivation for the research presented here was to develop a methodology for assessing and describing the leaching characteristics of media contaminated with oily material and to demonstrate this methodology with leaching behavior for BTEXN from a model oily waste (crude oil residually trapped in a porous medium) and from actual refinery oily residuals. Specific objectives are given below.

(1) Demonstrate the suitability of equilibrium dissolution models for analysis and prediction of fixed-bed leaching behavior, over a wide range of leachate concentrations, for solid wastes that contain an oily phase.

(2) Show how the leaching behavior of oily residuals can be generalized for various contaminants and wastes.

(3) Demonstrate the dominant influence of the oil content of the residual on the leaching behavior.

(4) Demonstrate a methodology for comparing batch leachate tests to fixed-bed leaching for oily wastes, and show how parameters derived from batch leachate tests can be used to both analyze and estimate fixed-bed leaching curves.

## 2. Materials

Several residuals from oil refineries have been evaluated by the Environmental Protection Agency (EPA) for potential classification as newly 'listed wastes' [5,6]. Two of the refinery residuals evaluated by the EPA, a refinery hydro-refining catalyst (HRC) and a crude oil tank bottoms sludge (TBS), were selected for this study. Samples of these two residuals were obtained from the American Petroleum Institute. The HRC residuals were microporous alumina-supported metal catalysts. The catalysts also contained a heavy gas oil which had been added to the hydro-refining reactor during decommissioning. The TBS residuals were taken from a refinery crude oil (medium-range API gravity) feed storage tank. The residuals had been dewatered by large-scale centrifugation at the refinery prior to sampling.

Samples of HRC and TBS were sent to an independent laboratory (Pace Laboratories, Houston, TX) for total constituent analysis (EPA Method 8260) and for TCLP extraction

Table 1  
Concentrations of BTEXN for two refinery residuals

	HRC			TBS		
	CL <sup>a</sup> waste <sup>b</sup> (mg/kg)	CL <sup>a</sup> leachate <sup>c</sup> (mg/l)	UH <sup>a</sup> leachate <sup>d</sup> (mg/l)	CL <sup>a</sup> waste <sup>b</sup> (mg/kg)	CL <sup>a</sup> leachate <sup>c</sup> (mg/l)	UH <sup>a</sup> leachate <sup>d</sup> (mg/l)
Benzene	< 12.5	0.140	0.280	2.5	0.070	0.088
Toluene	250	0.460	0.736	17.5	0.260	0.332
Ethylbenzene	17.5	0.130	0.184	< 6.25	< 0.050	0.031
<i>m</i> and <i>p</i> -xylenes	60	0.450	0.389	40	0.220	0.210
Naphthalene	< 33	0.026	0.105	7.5	< 0.100	0.042

<sup>a</sup>CL = contract laboratory; UH = University of Houston laboratory.

<sup>b</sup>EPA Method 8260.

<sup>c</sup>TCLP Extraction—EPA Method 1311 with zero headspace extraction and  $L/S = 20 \text{ cm}^3/\text{g}$ ; analyses by EPA Methods 5030 and 8260.

<sup>d</sup>UH batch extraction for  $L/S = 20 \text{ cm}^3/\text{g}$  interpolated from data for a series of batch extractions at various  $L/S$  ratios using Eq. (8). Analysis by purge and trap GC/PID.

(EPA Method 1311) and leachate analysis (EPA Methods 5030 and 8260) to determine the initial levels of benzene, toluene, ethylbenzene, *m*- and *p*-xylenes, and naphthalene (BTEXN) in both the waste and the leachate. Leachate analyses utilizing a multiple-batch leaching procedure were conducted in the University of Houston (UH) laboratory (described under Section 3.2). The results from these residuals and leachate analyses for BTEXN are shown in Table 1.

For the crude oil tank bottoms sludge good agreement was observed between leachate analyses in this (UH) laboratory and the contract lab (Pace) using a zero headspace extraction (ZHE) technique. For the HRC residual, reasonable agreement was observed for leachate concentrations of all compounds except naphthalene. Agreement between a similar modified batch extraction method and the standard TCLP has been previously demonstrated for various soil types contaminated with petroleum hydrocarbon mixtures [7]. The UH batch leachate results for all of the compounds including naphthalene agreed well with the initial leachate levels from the fixed-bed experiments (see Section 5). The residuals were also extracted by solvent extraction to determine the oil content (see Section 3.3). The oil contents were measured to be 159 000 and 110 000 mg/kg for the HRC and the TBS residuals, respectively. The residual oil contents were measured,

Table 2  
Properties of crude oils for leaching studies<sup>a</sup>

	Light crude	Medium crude
API Gravity @ 60°C:	55	30
Composition: saturates (wt.%)	92	60
Aromatics (wt.%)	7	25
Polars (wt.%)	1	15

<sup>a</sup>Obtained from the American Petroleum Institute.

Table 3  
Concentrations of BTXN in oils (initial levels in the oil phase reported by the American Petroleum Institute)

	Light crude (mg/kg)	Medium crude (mg/kg)
Benzene	5380	1430
Toluene	14000	4590
<i>p</i> and <i>m</i> -xylene	10100	6030
Naphthalene	960	320

so that fixed-bed leaching characteristics and partition coefficients could be more directly compared for the two residuals with those for two crude oils. These two crude oils were also obtained from the American Petroleum Institute. Some properties of the crude oils are shown in Table 2, and concentrations of BTEXN in the crude oils are shown in Table 3.

### 3. Experimental methods

To characterize the leaching behavior of the residuals and the oils, fixed-bed experiments were conducted and the effluent concentrations were measured over a wide concentration range (e.g. 10 to 0.001 mg/l for BTEXN). The data were subsequently modeled using an equilibrium dissolution model (see Section 4). Batch extractions were also used to determine waste–leachate partition coefficients and initial leachate concentrations (extrapolated to a leachate to waste ratio of zero) and compared with partition coefficients and initial leachate concentrations obtained from the fixed-bed studies. Two batch extraction methods were used in this study: (1) the conventional single-batch extraction (leachate/waste ratio = 20 cm<sup>3</sup>/g) method and (2) a multiple-batch extraction method carried out at various leachate/waste ratios (see Section 3.2).

Concentrations of benzene, toluene, *m*- and *p*-xylenes, ethylbenzene, and naphthalene (BTEXN) were monitored in these experiments. Aqueous phase concentrations were analyzed using purge and trap/gas chromatography (GC) with a photoionization detector (PID). Details of the purge and trap/GC analytical procedure are presented elsewhere [8]. The components in the leachate were also analyzed periodically by GC/mass spectroscopy (MS) by two outside laboratories using EPA Methods 5030 and 8260 to observe possible interference from other compounds as the BTEXN leachate levels decreased.

#### 3.1. Fixed-bed experiments

A typical experimental set-up is shown in Fig. 1. The apparatus and fittings were either stainless steel or glass with the exception of two Teflon ferrules in the inlet and outlet compression fittings. All glassware including the glass beads was washed sequentially with soap, DI water, 30% nitric acid, DI water, methanol and DI water. The

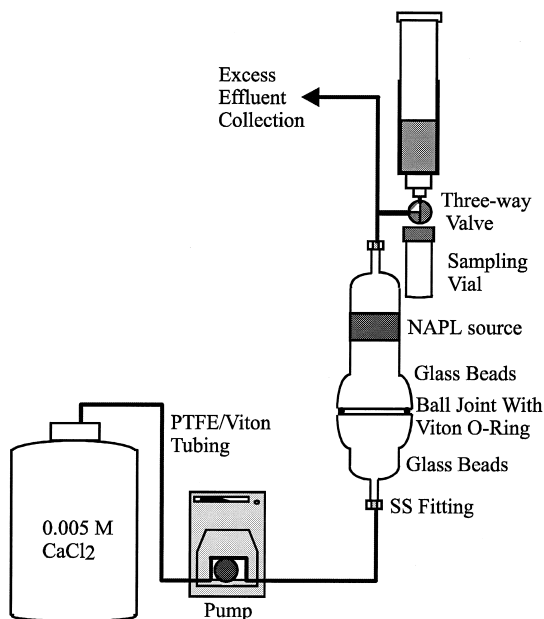


Fig. 1. Typical experimental set-up for residual leaching experiment. The zone labeled as 'NAPL source' corresponds to either refinery oily residuals or crude oils pre-mixed with glass beads.

glass beads were then dried and baked at 450°C for 4 h. All materials used (except for the residuals and oils) were autoclaved before use. The columns had an inner diameter of 4 cm and an overall length of 19 cm. The residuals and the crude oil pre-mixed with glass beads were packed to a thickness of 2.5 cm sandwiched between clean 30–50 μm glass beads (Polysciences). Apart from the clean glass beads used downstream and upstream of the zone containing crude oils or oily residuals, no filters were used in the experiments. The amounts of oil pre-mixed with glass beads were 0.57 and 0.78 g for the light and medium crude oils, respectively, which corresponded to approximately 5–7% oil saturation. The amounts of the HRC and TBS residuals used were 46 g and 41 g, respectively.

An autoclaved solution of 0.005 M CaCl<sub>2</sub> (which simulates typical groundwater ionic strength) was passed through the columns in an up-flow mode at a flow rate of 150 cm<sup>3</sup>/day. This flow rate corresponds to an interstitial velocity of 30 cm/day. From the interstitial velocity and source length, a length to interstitial velocity ratio ( $L/v$ ) of 0.08 day through the source zone was estimated for all four column experiments. These  $L/v$  ratios are at least an order of magnitude lower than those expected in the field ( $L/v > 1$  day). Based on the results of earlier experiments [9–11] no significant interparticle pore-scale mass transfer limitations were expected at this  $L/v$  ratio. The effluent was allowed to flow into 50 ml borosilicate glass syringes and the concentrations of BTEXN in the effluent were monitored with time. The system was designed in this way so that aqueous samples could be obtained with no headspace. Later in the experiment, the flow rate was reduced by a factor of 10 to check for potential mass transfer limitations.

### 3.2. Batch experiments

Glass bottles of varying size (from 40 ml to 5 l) with Teflon lined tops were used as batch extractors. For the crude oil experiments, custom-made bottles with teflon-lined tops on both ends were used. The batch extractions were carried out at least in duplicate for each water/oil (crude oils) or water/solid (refinery residuals) ratio. All glassware and caps were autoclaved before use. The batch experiments were conducted with autoclaved 0.005 M  $\text{CaCl}_2$  to be consistent with the leachate used for the fixed-bed experiments and to also improve the separation characteristics of the wastes and leachate following agitation. In the case of residuals, the extractors were tumbled end-over-end for 48 h. For the crude oils, they were allowed to equilibrate for one week without any agitation to avoid dispersion of oil droplets. At the end of the equilibration time aqueous samples were drawn using a glass syringe with a long syringe needle. A few ml of the leachate was then displaced from the syringe, and the syringe needle was removed to ensure that any oil was removed from the sample. The sample was then injected into a 40 ml EPA volatile organic analyte, VOA, vial (Fisher Scientific) containing 0.005 M  $\text{CaCl}_2$  water with negligible head space, and analyzed by purge and trap GC/PID within two hours. No centrifugation or filtering of the leachate was carried out prior to analysis. For the residuals, which were agitated during batch leaching, the solids were allowed to settle by gravity for 24 h prior to sampling. Centrifugation in general was not used for the multiple-batch extractions. For one of the batch extractions, however, a duplicate was centrifuged at 2000 rpm for 30 min, for a comparison in leachate analyses before and after centrifugation. No differences in the levels of BTEXN in the leachates were observed. In addition, clear leachates were observed for all of the batch extractions.

### 3.3. Oil content measurement

Measurements of the oil content in the residuals were made with the following procedure. Fifteen grams of residual were extracted for a total of five times—once in methanol followed by four times in methylene chloride. During each extraction the residual and 30 ml of solvent were put on a shaker for 15 min and then sonicated for 30 min. The solvent was then decanted and replaced with the next 30 ml aliquot of clean solvent. The solvent was evaporated in a sand bath at 55°C for methanol and 35°C for methylene chloride until the weight of the extract was constant. The extractions were carried out in triplicate for each residual and the oil content was determined gravimetrically.

## 4. Mathematical framework for data analysis

### 4.1. Modeling of fixed-bed leaching for oily residuals

Assuming that local equilibrium applies in the zone of contamination and that the total oil content in an oily waste and the contaminant partition coefficients do not

change significantly with time, the effluent leachate concentrations can be described by the following equation:

$$C_i^{L*} = 1 - \frac{1}{2} \operatorname{erfc} \left[ \sqrt{\frac{\operatorname{Pe}}{4t^*}} (1 - t^*) \right] - \frac{1}{2} \exp(\operatorname{Pe}) \operatorname{erfc} \left[ \sqrt{\frac{\operatorname{Pe}}{4t^*}} (1 + t^*) \right] \quad (1)$$

where  $C_i^{L*} = C_i^L / C_{i0}^L$  is a non-dimensionalized effluent concentration,  $C_{i0}^L$  is the initial leachate concentration in the effluent from a fixed-bed,  $\operatorname{Pe}$  is the Peclet number which characterizes the amount of dispersion of the contaminant in the fixed-bed ( $\operatorname{Pe}$  is defined as  $vL/D$ , where  $v$  is the interstitial velocity,  $L$  is the length of the fixed-bed, and  $D$  is the dispersion coefficient),  $\operatorname{erfc}$  is the complementary error function, and  $t^*$  is a non-dimensionalized time given by:

$$t^* = \frac{\frac{v}{L}t}{1 + \frac{Q}{V^{\text{PL}}} K_i^{w-L}} = \frac{\frac{Q}{V^{\text{PL}}}t}{1 + \frac{Q}{V^{\text{PL}}} K_i^{w-L}} \quad (2)$$

where  $Q$  is the leachate flow rate (L/day),  $V^{\text{PL}}$  is the volume of pore water associated with the waste (L),  $M^w$  is the mass of the waste (kg), and  $K_i^{w-L}$  is the partition coefficient of a contaminant between the waste and the leachate (L/kg). (See Section 4.2 for a discussion on how to obtain  $C_{i0}^L$  and  $K_i^{w-L}$  from batch extractions). For contaminants which have sufficiently large values of  $K_i^{w-L}$  (nearly all compounds of interest in the majority of oily wastes, even wastes with oil contents as low as 1 wt.%, will have partition coefficients large enough, e.g. benzene, toluene, etc.), the quantity  $M^w K_i^{w-L} / V^{\text{PL}} \gg 1$ , so that  $t^*$  simplifies to:

$$t^* \cong \frac{Q}{M^w K_i^{w-L}} t \quad (3)$$

Eq. (1) is a non-dimensionalized version of an equation which was originally developed for describing the fixed-bed sorption/desorption of dilute solutes from ion exchange resins [12] and later for soils [13]. Eq. (1) will be used to compare batch and fixed-bed leaching data, assuming that local equilibrium conditions exist for the waste. For a given waste mass and leachate flow rate, the equilibrium leaching can be determined from two parameters: the partition coefficient for chemicals in the waste and the Peclet number describing the amount of dispersion in the waste zone.

It will be shown that Eq. (1) provides an adequate description of the leaching behavior of unweathered light and medium crude oils trapped in non-sorbing media and for actual residuals for a portion of the leaching curve. For actual wastes that have been weathered or aged, some of the contaminant may be readily available for leaching but another fraction of the contaminant may become rate-limited due to slow release from the solid matrix which has been exposed to contamination for long periods of time [14–16] or from the weathered oily phase itself [17]. A modification to Eq. (1) which incorporates rate limitations for a fraction of the contaminant can be used to incorporate rate-limited leaching (see Section 5).

#### 4.2. Modeling of batch experiments

The leaching history of an oily waste can be predicted by Eq. (1) if the initial level of the contaminant in the waste and a leachate concentration from at least one batch extraction at a given liquid/solid ratio are known. From this information the partition coefficient,  $K_i^{w-L}$ , and the initial leachate concentration expected for fixed-bed leaching,  $C_{io}^L$ , can be determined. Typically, the concentration of the contaminant in the waste is determined by direct analysis of an oily extract of the waste. However, for complex oily matrices it may be difficult to obtain accurate measurements of contaminant concentrations in the waste due to interference from other compounds present in the waste. An alternative approach is to perform aqueous batch extractions at various leachate/waste ratios. Using this approach the waste concentrations, leachate concentrations, and partition coefficients can be determined. Approaches for obtaining  $K_i^{w-L}$  and  $C_{io}^L$  from both (1) a single-batch extraction coupled with a waste analysis and (2) multiple-batch extractions at various leachate/waste ratios are described below.

##### 4.2.1. Single-batch extraction and waste analysis

A component mass balance for a single-batch extraction, yields

$$M^w (C_{io}^w - C_i^w) = V^L C_i^L \quad (4)$$

where  $C_{io}^w$  is the initial concentration in the waste (mg/kg) prior to leaching,  $C_i^w$  is the concentration in the waste following leaching,  $V^L$  is the volume of leachate (L) for the batch extraction, and  $C_i^L$  is the leachate concentration (mg/l) after extraction.

At equilibrium, assuming linear partitioning, the concentration of component  $i$  in the oil and aqueous phases can be related by the equilibrium expression:

$$C_i^w = K_i^{w-L} C_i^L \quad (5)$$

Combining Eqs. (4) and (5) yields the following expression for  $K_i^{w-L}$  in terms of the measured leachate concentration,  $C_i^L$ , at a given leachate to waste ratio, and the measured waste concentration prior to extraction with leachate,  $C_{io}^w$ :

$$K_i^{w-L} = \frac{C_{io}^w}{C_i^L} - \frac{V^L}{M^w} \quad (6)$$

The  $C_i^L$  measured in a single-batch extraction method, e.g. TCLP, due to the dilution of the contaminant in the batch extractor will be lower than the initial leachate concentration from the fixed-bed. This difference between batch leachate and fixed-bed leachate concentrations can be significant for relatively water soluble components like benzene. The initial fixed-bed leachate concentration that would be in equilibrium with the waste concentration for an infinitely small leachate volume,  $C_{io}^L$ , can be determined from  $K_i^{w-L}$  and  $C_{io}^w$  as follows:

$$C_{io}^L = C_{io}^w / K_i^{w-L} \quad (7)$$

$C_{io}^L$  and  $K_i^{w-L}$  obtained from a single-batch extraction and waste analysis can then be used to compare batch leaching data with fixed-bed leaching data.



#### 4.2.2. Multiple-batch extractions at various leachate to waste ratios

If in Eqs. (4) and (5) there are two unknowns,  $K_i^{w-L}$  and  $C_{io}^w$ , then Eq. (6) can be rearranged to

$$\frac{1}{C_i^L} = \frac{1}{C_{io}^w} \left( \frac{V^L}{M^w} \right) + \frac{K_i^{w-L}}{C_{io}^w} \quad (8)$$

A plot of  $1/C_i^L$  vs.  $V^L/M^w$  should yield a straight line with slope,  $1/C_{io}^w$ , and intercept,  $K_i^{w-L}/C_{io}^w$ , from which the initial concentration of the component in a waste,  $C_{io}^w$ , and its partition coefficient,  $K_i^{w-L}$ , can be determined. The leachate concentrations can then be determined using Eq. (8) for any liquid/waste ratio. The leachate concentration that would be in equilibrium with the waste concentration for an infinitely small leachate volume,  $C_{io}^L$ , can also be determined from  $K_i^{w-L}$  and  $C_{io}^w$  with Eq. (7). Examples of the use of Eq. (8) for obtaining partition coefficients are described below for the two crude oils and the two refinery residuals.

## 5. Results and discussion

### 5.1. Crude oil experiments

#### 5.1.1. Batch experiments

The data from multiple-batch equilibrium experiments are plotted in Figs. 2 and 3 for the light and medium crude oils, respectively. The data are plotted as the reciprocal of the equilibrium aqueous concentration vs. volume of water per unit mass of oil as suggested by Eq. (8). The mass of oil,  $M^o$ , and the partition coefficient,  $K_i^{o-L}$ , were

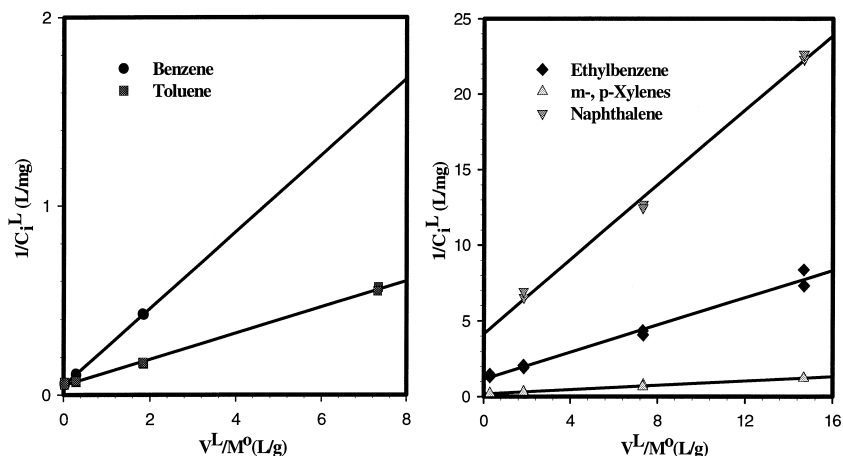


Fig. 2. Multiple-batch extractions of light crude oil at different oil/water ratios. Data are shown for benzene and toluene in (a) and for ethylbenzene, *m*- and *p*-xylenes, and naphthalene in (b). The parameters,  $K_i^{o-L}$  and  $C_{io}^L$ , were determined from these data using Eq. (8). Each data point is an average of triplicate analyses.

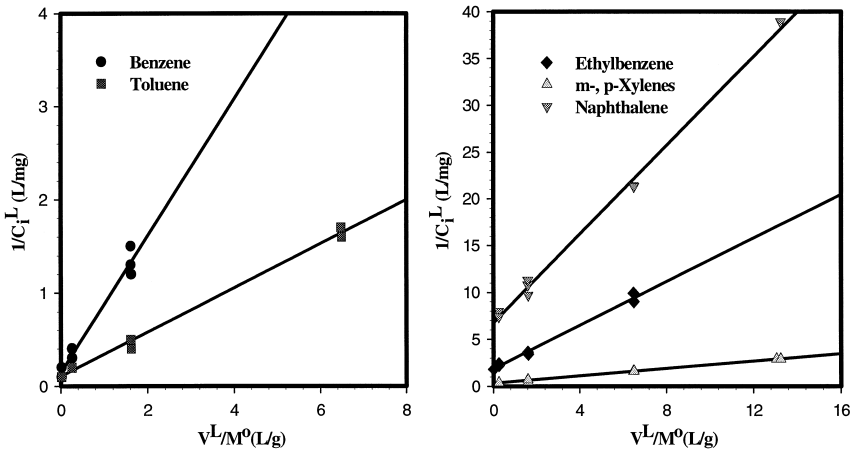


Fig. 3. Multiple-batch extractions of medium crude oil at different oil/water ratios. Data are shown for benzene and toluene in (a) and for ethylbenzene, *m*- and *p*-xylenes, and naphthalene in (b). The parameters,  $K_i^{o-L}$  and  $C_{io}^L$ , were determined from these data using Eq. (8). Each data point is an average of triplicate analyses.

substituted for  $M^w$  and  $K_i^{w-L}$ , respectively. The partition coefficients and the initial concentrations of the different components in the oil,  $C_{io}^o$ , obtained from these plots are shown in Table 4. The initial concentrations in the oil,  $C_{io}^o$ , determined from multiple-batch extractions compare well with those independently measured by direct analysis of the crude oils (Table 3). The partition coefficients for the light crude oil are consistent with values (not shown) recently reported for BTXN partitioning from tridecane [8]. The partition coefficients for the medium crude are lower than those for the light crude. This is consistent with a comparison of partition coefficients observed for various oils [18]. The lower partition coefficients for BTEXN for the medium crude oil are most likely due to higher molecular weights of the medium crude relative to the light crude. Decreases in partition coefficients (expressed in units of L/kg) with an increase in the average molecular weight of the hydrocarbon phase are predicted from theory and has

Table 4

Comparison of oil/water partition coefficients for two crude oils calculated from batch extractions and from fixed-bed leaching curves

	Light Crude			Medium Crude		
	$C_{io}^o$ multiple batch (mg/kg)	$K_i^{o-L}$ multiple batch (L/kg)	$K_i^{o-L}$ fixed-bed (L/kg)	$C_{io}^o$ multiple batch (mg/kg)	$K_i^{o-L}$ multiple batch (L/kg)	$K_i^{o-L}$ fixed-bed (L/kg)
Benzene	4900	250	400	1400	190	180
Toluene	14500	740	900	4200	440	450
Ethylbenzene	2200	2600	2500	860	1600	1450
<i>m</i> and <i>p</i> -xylenes	14000	2800	2700	5100	1800	1600
Naphthalene	810	3350	3200	420	2800	2500

also been confirmed experimentally for various hydrocarbon mixtures [8,19–22]. Molecular weights were not determined in this study for the light and medium crude oils, but it is expected that molecular weights would be higher for the medium crude.

### 5.1.2. Fixed-bed experiments

The experimental and calculated curves for dissolution of BTEXN from the light and medium crude oils are shown in Figs. 4 and 5, respectively. The aqueous concentrations are plotted vs. time. For a flow rate of  $150 \text{ cm}^3/\text{day}$  (corresponds to a source length to velocity ratio,  $L/v$ , of 0.08 day) the effluent concentrations follow equilibrium dissolution for a three- to four-orders of magnitude reduction in concentration. The flow rate was decreased from  $150 \text{ cm}^3/\text{day}$  to  $15 \text{ cm}^3/\text{day}$  after 18 days. The data following this decrease in flow rate do not indicate any increase in concentrations which would be expected if there were significant mass transfer resistances. The data from the fixed-bed columns were modeled using Eqs. (1) and (3). Since the solid phase in this case was glass beads, and no sorption to the glass beads was expected, the mass of the oil,  $M^o$ , and the partition coefficients between oil and water,  $K_i^{o-L}$ , were substituted for  $M^w$  and  $K_i^{w-L}$  in Eq. (3). The partition coefficients for the fixed-bed experiments were determined by fitting Eq. (1) to the experimental fixed-bed leaching data. A Peclet number of 30 was used in the calculations to characterize the dispersion in the residually trapped hydrocarbon zone for both columns and all five components. As shown in Table 4, the fitted oil/water partition coefficients for these compounds from the fixed-bed experiments compare well with those determined independently from the multiple-batch extractions. The initial leachate concentrations,  $C_{i0}^L$ , used for the fixed-bed calculations were those of the initial leachate from the column rather those calculated from the multiple-batch extractions for  $V^L/M^o = 0$ . The initial leachate concentrations for

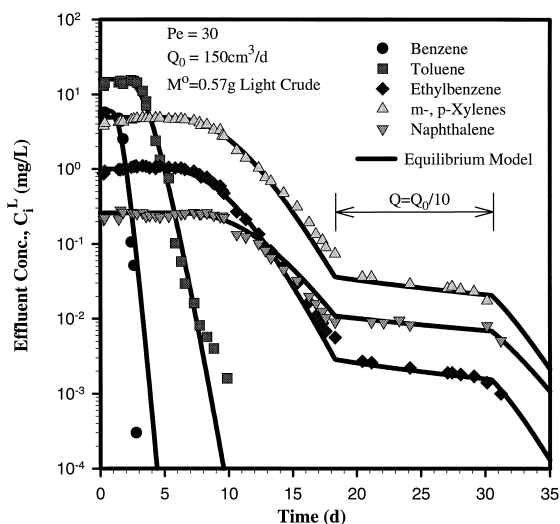


Fig. 4. Dissolution of BTEXN from light crude oil trapped in glass beads. Note that a decrease in flow rate did not result in increases in concentrations indicating that the dissolution process was equilibrium controlled at the experimental conditions (leachate to interstitial velocity ratio,  $L/v = 0.08$  day).

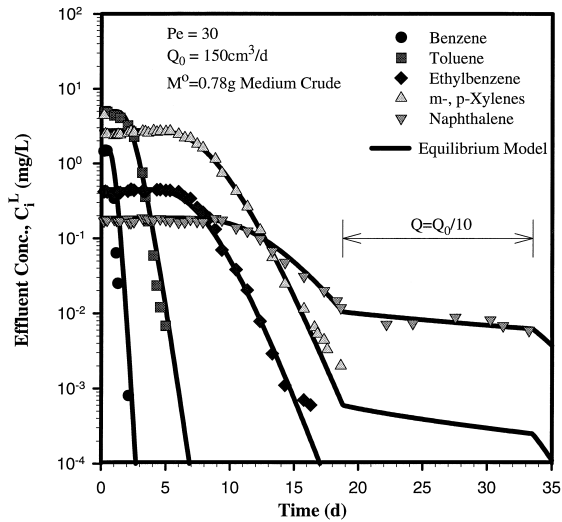


Fig. 5. Dissolution of BTEXN from medium crude oil trapped in glass beads. Note that a decrease in flow rate did not result in increases in concentrations indicating that the dissolution process was equilibrium controlled at the experimental conditions (leachate to interstitial velocity ratio,  $L/v = 0.08$  day).

benzene and toluene were lower than those predicted from batch extractions (approximately 70% lower for benzene and 30% lower for toluene), while the concentrations for ethylbenzene, *m*- and *p*-xylenes, and naphthalene agreed well with the batch extractions. This indicated that volatile losses were the likely cause for the lower benzene and toluene concentrations which could have occurred while pre-mixing the glass beads and oil during packing of the fixed-beds.

In Fig. 6 relative concentrations of BTEXN from both oils are plotted against the dimensionless time parameter,  $t^* = Qt/M^0 K_i^{o-L}$ . The concentrations were normalized with respect to the early effluent concentrations and the fitted oil/water partition coefficients. The non-dimensionalized data were modeled using Eq. (1). The normalized data for the two oils and the five components (BTEXN) coincide indicating that the dissolution process can be generalized for different crude oils and contaminants. This suggests that dissolution data obtained for one component for a given oil can be used to predict dissolution histories of other components if their partition coefficients are known and provided equilibrium leaching conditions are observed. One should be cautious when extrapolating these results to highly viscous and weathered hydrocarbon mixtures for which mass transfer limitations from the hydrocarbon phase may be important [17].

## 5.2. Oily residuals experiments

### 5.2.1. Batch experiments

The data from multiple-batch equilibrium experiments are plotted in Figs. 7 and 8 for HRC and TBS, respectively. The data are plotted as the reciprocal of the equilibrium

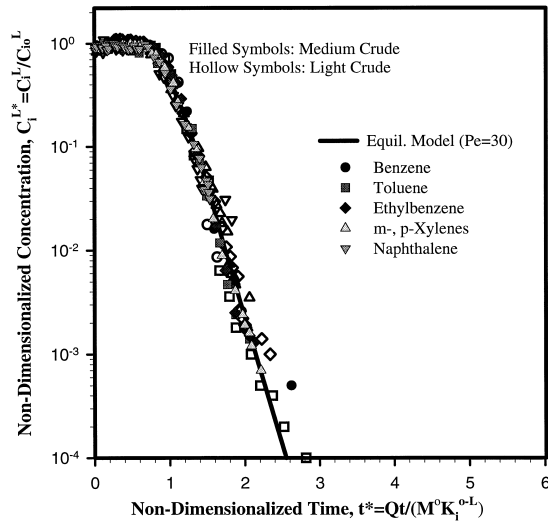


Fig. 6. Non-dimensionalized plots for the dissolution of BTEXN from light and medium crude oils trapped in glass beads. When differences in partitioning are accounted for, the curves for all five components and the two oils coincide.

aqueous concentration vs. volume of water per unit mass of waste as suggested by Eq. (8). The partition coefficients,  $K_i^{w-L}$ , obtained from these plots are shown in Table 5. For comparison,  $K_i^{w-L}$  values calculated for a single-batch extraction using Eq. (6) and the data obtained from the outside analyses of the residuals (Table 1) are also shown.

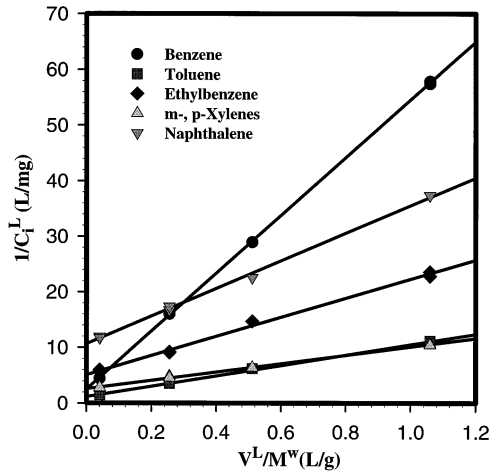


Fig. 7. Multiple-batch extractions of a hydro-refining catalyst (HRC) at different solid/water ratios. The parameters,  $K_i^{w-L}$  and  $C_{i0}^L$ , were determined from these data using Eq. (8). Each data point is an average of duplicate analyses.

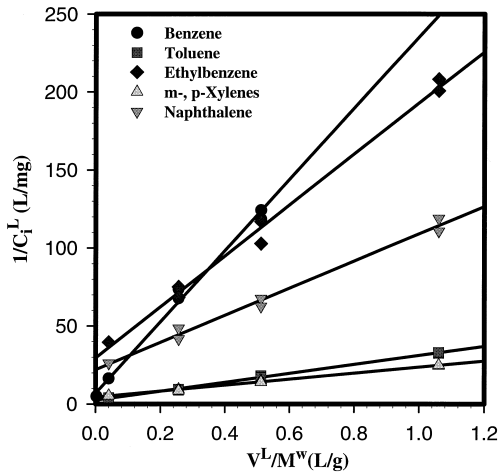


Fig. 8. Multiple-batch extractions of a crude oil tank bottoms sludge (TBS) at different solid/water ratios. The parameters,  $K_i^{w-L}$  and  $C_{i0}^L$ , were determined from these data using Eq. (8). Each data point is an average of duplicate analyses.

Two important points can be made from the data of Table 5. The first point is that when the partition coefficients are based on the oil content of the residuals ( $K_i^{o-L} = K_i^{w-L}/w^o$ , where  $w^o$  is the weight fraction of oil), the values are within the range of those observed for the two crude oils. For these residuals, it is therefore likely that the contaminants reside in the oily phase within the matrix, and also that these batch extractions reflect equilibrium conditions. If the partition coefficients were significantly higher than those

Table 5  
Summary of results from multiple- and single-batch extractions of HRC and TBS

	HRC			TBS		
	$K_i^{w-L}$ multiple batch <sup>a</sup> (L/kg-w)	$K_i^{o-L}$ multiple batch <sup>b</sup> (L/kg-o)	$K_i^{o-L}$ single batch <sup>c</sup> (L/kg-o)	$K_i^{w-L}$ multiple batch <sup>a</sup> (L/kg-w)	$K_i^{o-L}$ multiple batch <sup>b</sup> (L/kg-o)	$K_i^{o-L}$ single batch <sup>c</sup> (L/kg-o)
Benzene	49	310	–	30	270	140
Toluene	125	800	3300	85	780	430
Ethylbenzene	300	1900	720	180	1650	–
m- and p-xylenes	350	2200	710	230	2100	1500
Naphthalene	430	2700	–	250	2300	–

Notes:<sup>a</sup>Partition coefficient based on total waste mass. Partition coefficients were determined from multiple-batch extractions using Eq. (8).

<sup>b</sup>Partition coefficient based on oil content of waste. Partition coefficients were determined from multiple-batch extractions using Eq. (8), but based on oil rather than total waste mass ( $K_i^{o-L} = K_i^{w-L}/w^o$ ).

<sup>c</sup>Partition coefficient based on oil content of waste. Partition coefficients were determined from a single-batch extraction (EPA Method 1311) leachate (EPA Methods 5030 and 8260) and waste (EPA Method 8260) analyses (conducted by the outside lab) using Eq. (6).

measured for the crude oils, that would be an indication that non-equilibrium conditions exist. A second point that can be made is that the multiple-batch extraction method appears to be more accurate for determining partition coefficients than the single-batch extraction method which relies on less sensitive measurements of the contaminant concentration in the waste. The multiple-batch extraction method uses only aqueous leachate measurements, which are less likely to be affected by interference from other compounds during analysis.

The leachate concentrations that would be in equilibrium with the waste concentrations for an infinitely small leachate volume,  $C_{i0}^L$ , were also determined from Figs. 7 and 8 and use of Eq. (8). Good agreement between these values and those for fixed-bed leaching was observed as discussed below.

### 5.2.2. Fixed-bed experiments

The effluent curves for BTEXN from the two residuals, HRC and TBS, are shown in Figs. 9 and 10. An equilibrium model (Eq. (1)) with only one fitted parameter, the dispersion in the column, was used to describe the data. Peclet numbers of 4 and 15 were used for the HRC and the TBS residuals, respectively. The partition coefficients,  $K_i^{w-L}$ , and the initial leachate concentrations,  $C_{i0}^L$ , determined independently from batch experiments and application of Eq. (8) were used. Excellent agreement between the fixed-bed leaching data and the equilibrium dissolution model (Eq. (1)) was observed for the initial portion of the leaching curves for both residuals. In contrast to the leaching behavior observed for the crude oils trapped in glass beads, tailing in the leachate curves was observed after a one to two orders of magnitude reduction in leachate concentrations. The tailing was observed for only benzene and toluene. (These concentrations

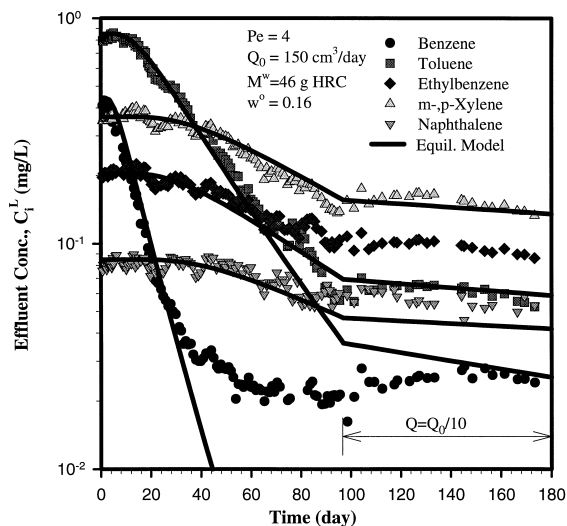


Fig. 9. Curves for leaching of BTEXN from a hydro-refining catalyst (HRC). The equilibrium curves (Eqs. (1) and (3)) are based on the partition coefficients,  $K_i^{w-L}$ , and the initial leachate concentrations,  $C_{i0}^L$ , determined independently from batch experiments.

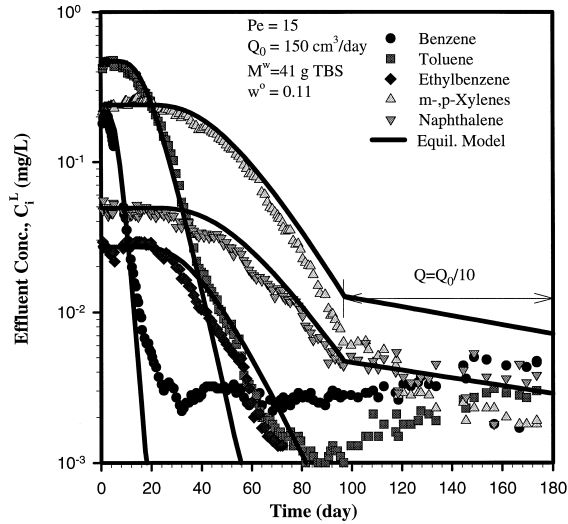


Fig. 10. Curves for leaching of BTXN from a crude oil tank bottoms sludge (TBS). The equilibrium curves (Eqs. (1) and (3)) are based on the partition coefficients,  $K_i^{w-L}$ , and the initial leachate concentrations,  $C_{i0}^L$ , determined independently from batch experiments.

were confirmed by GC/MS of samples taken at Day 118 and at the end of the experiment.) The other components more closely followed equilibrium dissolution throughout the entire 180 days of the experiment. When the flow was reduced to  $15 \text{ cm}^3/\text{day}$  after 96 days, with the exception of toluene for the TBS residual, little effect was observed on the effluent concentrations. Even for toluene leaching from TBS, only an increase in concentration of a factor of two to three was observed for a ten-fold change in flow rate. This suggests that the asymptotic leaching that was observed for benzene and toluene is not mass transfer rate-limited—a common explanation for tailing observed in fixed-bed leaching experiments [23]. A possible explanation for the tailing could be non-linear equilibrium partitioning in this low concentration range. Note that the benzene concentrations for which the tailing occurred was below the maximum contaminant level, MCL, of  $0.005 \text{ mg/l}$  for the crude oil tank bottoms sludge, but above the MCL for the hydro-refining catalyst. Therefore, for the crude oil sludge, equilibrium dissolution is valid for the entire leaching range of interest. This is not true for the HRC residual unless the desired target level were to be set at some multiple of the MCL. It is essential to know the level at which asymptotic leaching occurs and how this level compares with a desired target level. Fixed-bed leaching tests like those described here are one way to determine these levels.

The data for the leaching from the refinery residuals were also non-dimensionalized in a way similar to normalization of the crude oil data. As shown in Figs. 11 and 12 the data for all of the components coincide for the equilibrium portion of the curves indicating that the leaching behavior can be generalized, for a limited but significant range of leachate concentrations, when the partition coefficients are known. This suggests that the leaching behavior of other contaminants present in a particular waste



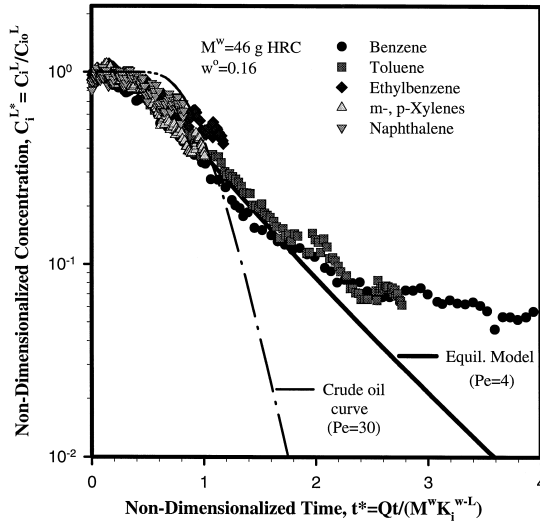


Fig. 11. Non-dimensionalized leaching curves for BTXN from a hydro-refining catalyst (HRC).

could be estimated for a similar range of normalized leachate concentrations if the waste concentrations and the partition coefficients are known. Partition coefficients can be measured directly from batch leaching tests of the waste or estimated from (1) the oil content of the waste and (2) reasonable estimates of the oil–water partition coefficients. This method would be very useful for prediction of the leachate concentrations for low solubility compounds (e.g. benzo(a)pyrene) which have health-based drinking water standards below practical detection levels in groundwater.

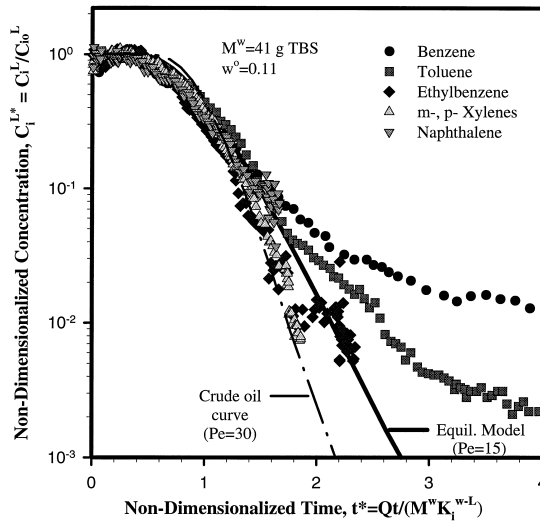


Fig. 12. Non-dimensionalized leaching curves for BTXN from a crude oil tank bottoms sludge (TBS).

### 5.2.3. Extrapolation of fixed-bed leaching curves to additional contaminants in a waste

Local equilibrium conditions may apply for many wastes contaminated with oily phases for a range of leachate concentrations of practical interest, as demonstrated for the refinery residuals in this research. A reasonable approach for estimating the leaching behavior of low solubility contaminants would be to conduct batch and fixed-bed leaching tests on a given waste for at least one contaminant that is present and which can also be measured over a reasonable concentration range in water. If equilibrium leaching is observed, then the leaching of other compounds could be predicted from the waste concentrations. These calculated leaching concentrations would provide an upper-bound estimate of the leaching concentrations that could be expected. If equilibrium leaching conditions were not observed in leaching tests for a particular waste, then more specific rate of release tests [14,24] for the contaminant of interest could then be performed.

## 6. Summary

An approach has been presented that shows how batch aqueous extraction data can be used to predict fixed-bed leaching, and the application and limitations of this approach have been illustrated with examples of two crude oils residually trapped in glass beads and two refinery residuals containing an oily phase.

It has been demonstrated that the fixed-bed leaching characteristics of benzene, toluene, ethylbenzene, *m*- and *p*-xylenes, and naphthalene (BTEXN) dissolving from a light and a medium crude oil can be described with a local equilibrium dissolution model assuming linear partitioning. The partition coefficients used to describe the experimental leaching curves agreed well with those independently measured from multiple-batch aqueous extractions. For BTEXN leaching from these crude oils, it was found that equilibrium dissolution was valid over a range of leachate concentrations spanning three to four orders of magnitude. The only unknown parameter required to fit the fixed-bed leaching data for all five components was a single value of the Peclet number, a measure of dispersion in the residually trapped hydrocarbon zone.

It was also shown that the leaching behavior of BTEXN could be generalized based on the partition coefficients of the aromatic hydrocarbons. This generalization suggested that dissolution data obtained for one component of a given oil could be used to predict dissolution of other components under equilibrium conditions.

For the two refinery oily wastes it was found that the same equilibrium dissolution model, using partition coefficients independently measured from multiple-batch experiments, described the leaching behavior for a one- to two-orders of magnitude range in leachate concentrations during the initial period of dissolution. For longer times, the leachate concentrations departed from the model calculations and approached asymptotic concentrations, thereby indicating the limitations of extending equilibrium models based on linear partitioning to lower levels of contaminant in the waste. The importance of further characterization of the asymptotic leaching for a particular waste will be dependent upon how the asymptotic levels compare to a particular compound's target leachate level (e.g. an MCL or some multiple of the MCL).

It was also found that when the oil contents of the oily residuals were accounted for, good agreement was obtained between the partition coefficients measured for BTEXN for the crude oils and those for the oily residuals. This indicated that a significant fraction of each of the contaminants in the two waste matrices was associated with the oil present in the wastes and highlights the effect that the oil content in a waste can have on the partitioning of aromatic hydrocarbons. This latter result also suggests that the time-dependent leaching behavior for an oily waste, under local equilibrium conditions, can be estimated from measurements of only the contaminant concentrations in the waste and the oil content.

## Acknowledgements

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