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April 4, 1996

Project No. 95-284

Mr. Zaki Naser
US Ecology, Inc.
Post Office Box 578
Beatty, Nevada 89003

Transmittal
Supplement to MTR Equivalency Calculations
Cell 12 Design Report, Exhibit D
US Ecology, Inc.
Beatty, Nevada

Dear Mr. Naser:

In response to your request, transmitted herein are supplementary calculations to those provided in Exhibit D of the *Cell 12 Design Report* (TRC Environmental Solutions, Inc., March 1996). That report was submitted to the Nevada Division of Environmental Protection (NDEP) on March 8, 1996 as Appendix S of the revised Part B permit renewal application for the US Ecology, Inc. (USE) hazardous waste management facility located near Beatty, Nevada.

The design for the lower component of the Cell 12 bottom (secondary) composite liner is an engineered alternative to that of the Minimum Technology Requirements (MTR) as prescribed in federal regulations at 40 CFR 264.301(c)(1)(i)(B). The MTR Equivalency Demonstration in Exhibit D of the *Cell 12 Design Report* included calculations which demonstrated the equivalency of the noted portion of the Cell 12 liner system to that of MTR. Those previous calculations compared a compacted clay liner (CCL) to a geosynthetic clay liner (GCL) in combination with a prepared subgrade material layer at the base of the landfill. In addition, a CCL was compared to a GCL on the landfill slopes. Conservative leachate heads were used in the calculations based on reasonable operating assumptions. Leachate chemistry was provided by USE for use in the calculations.

We understand that NDEP has asked that the Cell 12 MTR Equivalency Demonstration be revised to reflect updated leachate chemistry data, and that the assumed leachate head be increased to 12 inches on the cell base and to an equivalent elevation over the Leak Detection System (LDS) sumps.

The supplementary calculations provided as Attachment 1 include the requested analysis and reflect more concentrated leachate chemistry based on data provided the week of March 18, 1996 by USE. For the purpose of the calculations, we modeled the solute breakthrough time for the two organic constituents (i.e., chloroform and tetrachloroethene) and the two inorganic constituents (i.e., chromium and cadmium) with the highest individual concentrations shown in the data.

The calculations in Attachment 1 model the two leachate head scenarios requested by NDEP. The first scenario applies 12 inches of head to nonsump cell base locations, while the second scenario carries the elevation of that head over and applies it to the LDS (secondary) sumps. The latter scenario results in an applied head of 39 inches at the LDS (secondary) sumps.(1) Under these conservative long-term operating conditions, the modeling with 39 inches of head showed the necessity to increase the thickness of the compacted fine-grained material layer which underlies the GCL at the base of Cell 12 from 9 to 18 inches at sump locations in order to retain MTR equivalency with regard to solute breakthrough time.

Upon further investigation into the behavior of CCLs in arid environments, we have included an additional evaluation. A 3-foot-thick CCL with a hydraulic conductivity of no more than $1 \times 10^{-7}$ centimeters per second (cm/sec) is specified by MTR as the lower component of a bottom (secondary) composite liner. However, it has been shown that CCLs desiccate relatively quickly in desert areas. In a personal communication with David E. Daniel, Ph.D.(2) of the University of Texas at Austin, Dr. Daniel stated that there is a "good possibility to a high probability" of CCL desiccation within 10 years in an arid environment. Accordingly, for calculated CCL solute breakthrough times we have shown both the nondessicated and desiccated results. This adjustment has not similarly been applied to the compacted fine-grained material layer which underlies the GCL at the base of Cell 12, because that layer is specified as a silty sand (obtained by screening naturally occurring soils from the site) which is designed to achieve a balance of a relatively low hydraulic conductivity (e.g., on the order of $1 \times 10^{-5}$ cm/sec) but without the amount of clay that would have a high potential for substantial desiccation to occur.

The results of the supplementary calculations in Attachment 1 are summarized below, coupled with a reiteration of the results from the previous calculations (the latter are provided for comparison purposes):

| STEADY FLUX OF WATER AT CELL BASE | | | | |
|---|---|---|---|---|
| APPLICATION | COMPONENT TYPE | FLUX ($cm^3/cm^2$-sec)(3) | | |
| | | Head = 39 inches | Head = 12 inches | Head = 1.2 inches |
| Cell 12 Nonsump | 7 mm GCL plus 9 inches soil | – | $2.2 \times 10^{-8}$ | $2.7 \times 10^{-9}$ |
| Cell 12 Sump | 7 mm GCL plus 18 inches soil | $7.1 \times 10^{-8}$ | – | – |
| MTR | 3 feet CCL (without desiccation) | $2.1 \times 10^{-7}$ | $1.3 \times 10^{-7}$ | $1.0 \times 10^{-7}$ |

– = Not modeled.

(1) The total of 39 inches of head is derived from the sum of 12 inches of head above the noted liner component at a location along the perimeter of the sumps, plus the 15-inch depth of the LDS (secondary) sumps, plus the 12-inch depth of the Leachate Collection and Removal System (primary) sumps.

(2) Dr. Daniel is a renowned expert on the performance of clay and geosynthetic liner systems, and has performed numerous studies and published many papers in this field.

(3) Values have been rounded.

| SOLUTE BREAKTHROUGH TIME AT CELL BASE | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| APPLI-CATION | COMPO-NENT TYPE | SOLUTE CONSTITUENT | BREAKTHROUGH TIME (years)(4) | | | | | |
| | | | Head = 39 inches | | Head = 12 inches | | Head = 1.2 inches | |
| | | | Step Function Method A | Distribution Coefficient Method B | Step Function Method A | Distribution Coefficient Method B | Step Function Method A | Distribution Coefficient Method B |
| Cell 12 Nonsump | 7 mm GCL plus 9 inches soil | Chromium$^{+3}$ | – | – | 60 to 130 | 130,000 | – | – |
| | | Chromium$^{+6}$ | – | – | 30 to 60 | 2,100 | – | – |
| | | Cadmium | – | – | 750 to 1,700 | 400 | – | – |
| | | Zinc | – | – | (5) | (5) | 5,000 to 11,000 | 7,900 |
| | | Chloroform | – | – | NA(6) | 44,000 | NA(6) | 44,000 |
| | | Tetrachloroethene | – | – | NA(6) | 1,200,000 | – | – |
| Cell 12 Sump | 7 mm GCL plus 18 inches soil | Chromium$^{+3}$ | 40 to 80 | 79,000 | – | – | – | – |
| | | Chromium$^{+6}$ | 20 to 40 | 1,300 | – | – | – | – |
| | | Cadmium | 450 to 980 | 240 | – | – | – | – |
| | | Zinc | (5) | (5) | – | – | – | – |
| | | Chloroform | NA(6) | 28,000 | – | – | – | – |
| | | Tetrachloroethene | NA(6) | 750,000 | – | – | – | – |
| MTR | 3 feet CCL (without desiccation) | Chromium$^{+3}$ | 5 to 50 | 63,000 | 8 to 80 | 98,000 | – | – |
| | | Chromium$^{+6}$ | 2 to 20 | 1,000 | 4 to 40 | 1,600 | – | – |
| | | Cadmium | 60 to 640 | 200 | 100 to 1,000 | 300 | – | – |
| | | Zinc | (5) | (5) | (5) | (5) | 100 to 1,000 | 940 |
| | | Chloroform | NA(6) | 3,400 | NA(6) | 5,300 | NA(6) | 5,300 |
| | | Tetrachloroethene | NA(6) | 92,000 | NA(6) | 140,000 | – | – |
| | 3 feet CCL (desiccated after 10 years) | Chromium$^{+3}$ | 5 to 10(7) | 10(7) | 8 to 10(7) | 10(7) | – | – |
| | | Chromium$^{+6}$ | 2 to 10(7) | 10(7) | 4 to 10(7) | 10(7) | – | – |
| | | Cadmium | 10(7) | 10(7) | 10(7) | 10(7) | – | – |
| | | Zinc | (5) | (5) | (5) | (5) | 10(7) | 10(7) |
| | | Chloroform | NA(6) | 10(7) | NA(6) | 10(7) | NA(6) | 10(7) |
| | | Tetrachloroethene | NA(6) | 10(7) | NA(6) | 10(7) | – | – |

– = Not modeled.
NA = Not Applicable.

(4) Values have been rounded.
(5) Calculations for zinc were not completed since cadmium and chromium exist at higher concentrations.
(6) This analysis method is not applicable to organic constituents (see Distribution Coefficient Method B).
(7) The CCL cannot sustain a solute breakthrough time greater than 10 years because the clay desiccates and cracks. Calculated values in excess of 10 years have been adjusted to the 10-year value.

With regard to the solute breakthrough time calculations, as indicated in Exhibit D of the *Cell 12 Design Report*, note that the theory for Step Function Method A models the breakthrough time of the first constituent molecule, while the theory for Distribution Coefficient Method B models the later time when half of the original concentration breaks through the subject liner component.[8]

As modified by increasing the thickness (from 9 to 18 inches) at sump locations of the compacted fine-grained material layer which underlies the GCL, the attached supplementary calculations verify that the Cell 12 liner design will provide equivalent or superior performance to the MTR standard liner cross section. The lower component of the Cell 12 bottom (secondary) composite liner has a lesser water flux and greater solute breakthrough times than those of the MTR standard liner.

In a separate but related matter, please note that we have made a minor correction to the original Method B solute breakthrough time calculation regarding the distribution coefficient for inorganic constituents (i.e., zinc). This reflects a correction of the coefficient's logarithm base from $\log_{10}$ to $\ln_e$. Accordingly, provided as Attachment 2 are revised pages which should be substituted for their predecessors in Exhibit D of the *Cell 12 Design Report*. As can be seen, this correction does not alter the conclusions drawn from the calculation.

We believe that the leachate heads modeled in the attached supplementary calculations reflect a conservative long-term operating condition for Cell 12. Regulations and guidance for MTR equivalency do not require such an assumption. However, the regulations do mandate 12 inches as the maximum leachate depth over the <u>top</u> (primary) liner system, and as the <u>basis</u> for the minimum leachate removal rate which must be achievable by the LDS. In our opinion, the proposed Cell 12 design (including the revision in sump locations) exceeds the performance of a CCL-based liner design.

We hope this letter and attached calculations are responsive to your needs. We await your direction regarding revisions to the *Cell 12 Design Report* to reflect the modified liner configuration at sump locations. Please call if you have any questions or we may be of any further assistance.

Sincerely,

Scott M. Brown
Project Director

SMB/JB:dr
Attachments

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(8) The methodology for Step Function Method A is outlined in Exhibit D of the *Cell 12 Design Report* starting on Page D-26, and that for Distribution Coefficient Method B is outlined starting on Page D-32.

cc: Zia Qureshi, American Ecology Corporation
Dave Tolbert, US Ecology, Inc.
Miro Knezevic, TRC Environmental Solutions, Inc.
Eric Walther, TRC Environmental Solutions, Inc.
Chris Hansen, TRC Environmental Solutions, Inc.
Robert Van Hyning, TRC Environmental Solutions, Inc.

ATTACHMENT 1

SUPPLEMENT TO MTR EQUIVALENCY CALCULATIONS
CELL 12 DESIGN REPORT, EXHIBIT D
US ECOLOGY, INC.
BEATTY, NEVADA

# ENVIRONMENTAL SOLUTIONS, INC.

By [illegible] Date 25 Mar 96 Subject ADDENDUM TO COMPARISON OF GCL ± CSL AND CCL Sheet No. 1 of 17
Chkd. By EC Date 2 APRIL 96 Proj. No. 95-284

PURPOSE

Calculate, for additional inorganic and organic constituents, measures of leachate migration that test equivalence to a minimum technology requirement (MTR) compacted clay component (of the bottom composite liner) of the engineered alternative used in previous calculations contained in Appendix 1 to Exhibit D (Liner MTR Equivalency Demonstration Cell 12).

APPROACH

Apply to the additional constituents the same approach, assumptions (where possible), general methodology (mathematical derivations), Method A (step function) and Method B (distribution coefficient) used in previous calculations.

# ENVIRONMENTAL SOLUTIONS, INC.

By [illegible] Date 25 Mar 96 Subject ADDENDUM TO COMPARISON Sheet No. 2 of 17
Chkd. By EC Date 2 APRIL 96 OF GCL ± CSL AND CCL Proj. No. 95-284

ASSUMPTIONS (NEW AND MODIFIED FROM PREVIOUS CALCULATION)

- Leachate head on the bottom liner, which was 0.1 foot in the previous calculation, is increased to 1 foot at the request of the Nevada Division of Environmental Protection (NDEP). However, it should be recognized that the relatively dry waste and extremely low precipitation at the Beatty, Nevada site cannot create such a large head. Further, a leachate control pump would make it difficult to create a head at all.
- Compacted clay lower component of MTR bottom composite liner will desiccate and crack by the end of 10 years, allowing breakthrough of leachate at that time according to Dr. David Daniel of the University of Texas at Austin (see Attachment A).

# ENVIRONMENTAL SOLUTIONS, INC.

By BJW Date 22Mar96 Subject ADDENDUM TO COMPARISON Sheet No. 3 of 17
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ASSUMPTIONS (continued)

- Chromium, the inorganic constituent with the highest measured concentration in leachate at the site, is half each in its hexavalent and trivalent oxidation states, to be conservative relative to monitoring data in the literature (see Attachment A.B for data showing $C_{Cr+6} = 0.39\,C_{Cr}$).

- Inorganic constituents in leachate at highest concentrations are chromium (total) at 12 milligrams per liter ($mg\ l^{-1}$) and cadmium at 1.5 $mg\ l^{-1}$, based on information provided by US Ecology, Inc. (see Attachment A.C).
- Organic constituents in leachate at highest concentrations are tetrachloroethene (PCE) at 29 $mg\ l^{-1}$ and chloroform at 7.9 $mg\ l^{-1}$ (vs. 0.24 $mg\ l^{-1}$ in previous calculation), based on information provided by US Ecology, Inc (see Attachment A.C).

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# ENVIRONMENTAL SOLUTIONS, INC.

By [illegible] Date 23 Mar 96 Subject ADDENDUM TO COMPARISON OF GCL ± CSL AND CCL Sheet No. 4 of 17
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ASSUMPTIONS (continued)

- Chromium cation exchange, in its +3 and +6 oxidation states (tri + hexavalent) has 1 equivalent = $\frac{1}{3}$ and $\frac{1}{6}$ g mole, respectively.
- Cadmium is divalent, the same as zinc in the previous calculation, for which 1 equivalent = $\frac{1}{2}$ g mole.
- Distribution coefficients ($K_d$) for chromium +3 and +6 = $\ln^{-1} 7.7\ cm^3 g^{-1}$ (= 2208 $cm^3 g^{-1}$) and $\ln^{-1} 3.6\ cm^3 g^{-1}$ (= 36.6 $cm^3 g^{-1}$), respectively, and for cadmium $K_d = \ln^{-1} 1.9\ cm^3 g^{-1}$ (= 6.7 $cm^3 g^{-1}$), according to Dragun (1988) as shown in Attachment A.D.
- Octanol-water partition coefficient for tetrachloroethene ($K_{ow\ PCE}$) = $\log_{10}^{-1} 3.4$ (= 2512), according to Howard (1990) as shown in Attachment A.E.
- Other assumptions are the same as in previous calculation.
- GCL = geosynthetic clay layer
  CSL = compacted soil layer
  CCL = compacted clay layer

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# ENVIRONMENTAL SOLUTIONS, INC.

By [illegible] Date 23 Mar 96 Subject ADDENDUM TO COMPARISON OF GCL ± CSL AND CCL Sheet No. 5 of 17

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METHODOLOGY, GENERAL

Same as in previous calculation.

METHOD A (for inorganic migration)

Same as in previous calculation.

METHOD B (for inorganic and organic adsorptive retardation, using distribution and octanol-water partition coefficients)

Same as in previous calculation.

# ENVIRONMENTAL SOLUTIONS, INC.

By BMW Date 23Mar96 Subject ADDENDUM TO COMPARISON Sheet No. 6 of 17
Chkd. By EC Date 2 APRIL 96 OF GCL & CSL AND CCL Proj. No. 95-284

CALCULATIONS

Use Equation 5A from previous calculation to calculate fluxes, written as follows:

$$F_v = K\left(1 + \frac{h}{T}\right)$$

For the bottom liner (subscript BL):

$$F_{v\,GCL/BL} = 5 \times 10^{-10}\,\frac{cm}{s}\left(1 + \frac{1\,ft \cdot 304.8\,\frac{mm}{ft}}{7\,mm}\right)$$

$$F_{v\,GCL/BL} = 2.23 \times 10^{-8}\ cm^3\ cm^{-2}\ sec^{-1}$$

Although $K_{GCL} \ll K_{CSL}$, the flux through the
$(5 \times 10^{-10}\,\frac{cm}{s})$ $(10^{-5}\,\frac{cm}{s})$
CSL is limited to the flux that can penetrate the overlying GCL, hence $F_{v\,CSL} = F_{v\,GCL}$

$$F_{v\,CSL/BL} = 2.23 \times 10^{-8}\ cm^3\ cm^{-2}\ sec^{-1}$$

For the CCL bottom liner,

$$F_{v\,CCL/BL} = 10^{-7}\,\frac{cm}{s}\left(1 + \frac{1\,ft}{3\,ft}\right)$$

$$F_{v\,CCL/BL} = 1.33 \times 10^{-7}\ cm^3\ cm^{-2}\ sec^{-1}.$$

# ENVIRONMENTAL SOLUTIONS, INC.

By [illegible] Date 23 Mar 96 Subject ADDENDUM TO COMPARISON OF GCL ± CSL AND CCL Sheet No. 7 of 17

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CALCULATIONS (continued)

Method A calculations of breakthrough time for inorganic constituents, using Equation 14 from previous calculation, written as follows:

$$t_i = \frac{T \rho_c \, CEC \, a_i \, m_i \, f_s \, \phi}{F_v \, C_{im}} \qquad (23)$$

For the bottom liner (superscript A for Method A)

$$t^A_{Cr^{+6}/GCL/BL} = \frac{7\,mm \frac{1\,cm}{10\,mm} \; 67 \frac{lb}{ft^3} \; 453.59 \frac{g}{lb} \; \frac{1\,ft^3}{30.48^3\,cm^3}}{2.23\times10^{-8}\,cm^2\,cm^{-2}\,s^{-1} \; 6\times10^{-3} \frac{g\,Cr^{+6}}{l} \frac{l}{10^3\,cm^3}}$$

$$= \frac{60\times10^{-3}\,equiv.\,Cr^{+6}}{100\,g.\,clay} \; \frac{1\,g\,mole\,Cr^{+6}}{6\,equiv.\,Cr^{+6}} \; 51.996 \frac{g\,Cr^{+6}}{g\,mole\,Cr^{+6}} \cdot 0.01 \times 0.3$$

# ENVIRONMENTAL SOLUTIONS, INC.

By [illegible] Date 23 Mar 96 Subject ADDENDUM TO COMPARISON OF GCL ± CSL AND CCL Sheet No. 8 of 17

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CALCULATIONS (continued)

$$t^A_{Cr^{+6}/GCL/BL} = 8.78 \times 10^7 \text{ sec} = 2.8 \text{ yr. to } 6.9 \text{ yr for CEC of } 150 \tfrac{meq}{100g}.$$

$$t^A_{Cr^{+3}/GCL/BL} = \frac{a_{Cr^{+3}}}{a_{Cr^{+6}}} t^A_{Cr^{+6}/GCL/BL} = \frac{\frac{1 \text{ g mole } Cr^{+3}}{3 \text{ equiv. } Cr^{+3}}}{\frac{1 \text{ g mole } Cr^{+6}}{6 \text{ equiv. } Cr^{+6}}} t^A_{Cr^{+6}/GCL/BL} = 5.6 \text{ to } 14 \text{ yrs.}$$

$$t^A_{Cr^{+6}/CSL/BL} = \frac{9 \text{ in } \frac{2.54 \text{ cm}}{\text{in}} \; 108 \frac{lb}{ft^3} \; 453.59 \frac{g}{lb} \; \frac{1 \text{ ft}^3}{30.48^3 \text{ cm}^3}}{2.23 \times 10^{-8} \text{ cm}^3 \text{ cm}^{-2} \text{ s}^{-1} \times 6 \times 10^{-3} \frac{g \; Cr^{+6}}{l} \cdot \frac{1 \; l}{10^3 \text{ cm}^3}}$$

$$\cdot \frac{16 \times 10^{-3} \text{ equiv. } Cr^{+6}}{100 \text{ g. CS}} \frac{1 \text{ g mole } Cr^{+6}}{6 \text{ equiv. } Cr^{+6}} \cdot 52 \frac{g \; Cr^{+6}}{g \text{ mole } Cr^{+6}} 0.01 \times 0.2$$

$$t^A_{Cr^{+6}/CSL/BL} = 8.20 \times 10^8 \text{ sec} = 26 \text{ yr to } 56 \text{ yr for CEC of } 35 \tfrac{meq}{100g}$$

$t^A_{Cr^{+3}/CSL/BL}$ = 52 to 112 yrs, using same equation as for GCL.

$$t^A_{Cr^{+6}/CCL/BL} = \frac{3 \text{ ft } 30.48 \frac{cm}{ft} \; 127 \frac{lb}{ft^3} \; 453.59 \frac{g}{lb} \; \frac{1 \text{ ft}^3}{30.48^3 \text{ cm}^3}}{1.33 \times 10^{-7} \text{ cm}^3 \text{ cm}^{-2} \text{ s}^{-1} \times 6 \times 10^{-3} \frac{g \; Cr^{+6}}{l} \frac{1 \; l}{10^3 \text{ cm}^3}}$$

$$\cdot \frac{3 \times 10^{-3} \text{ equiv. } Cr^{+6}}{100 \text{ g. CC}} \frac{1 \text{ g mole } Cr^{+6}}{6 \text{ equiv. } Cr^{+6}} 52 \frac{g \; Cr^{+6}}{g \text{ mole } Cr^{+6}} \times 0.01 \times 0.2$$

$$t^A_{Cr^{+6}/CCL/BL} = 12.1 \times 10^7 \text{ sec} = 3.8 \text{ yr to } 38 \text{ yr for max. CEC of } 30 \tfrac{meq}{100g}.$$

$t^A_{Cr^{+3}/CCL/BL}$ = 7.6 to 76 yrs, using same equation as for GCL.

# ENVIRONMENTAL SOLUTIONS, INC.

By EJW Date 23 Mar 96 Subject ADDENDUM TO COMPARISON OF GCL ± CSL AND CCL Sheet No. 9 of 17

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CALCULATIONS (continued)

For cadmium breakthrough of bottom liners, apply Equation 14 twice to note that:

$$t_{Cd} = t_{Cr^{+6}} \frac{a_{Cd}}{a_{Cr^{+6}}} \frac{\mathcal{M}_{Cd}}{\mathcal{M}_{Cr^{+6}}} \frac{C_{Cr^{+6}m}}{C_{Cd\,m}} \qquad (24)$$

$$t^{A}_{Cd/GCL/BL} = 2.8\ yr \underbrace{\frac{\frac{1\ g\ mole\ Cd}{2\ equiv.\ Cd}}{\frac{1\ g\ mole\ Cr^{+6}}{6\ equiv.\ Cr^{+6}}} \frac{112.40\ \frac{g\ Cd}{g\ mole\ Cd}}{52\ \frac{g\ Cr^{+6}}{g\ mole\ Cr^{+6}}} \frac{6\times10^{-3}\ \frac{g\ Cr^{+6}}{l}}{1.5\times10^{-3}\ \frac{g\ Cd}{l}}}_{25.95}$$

$t^{A}_{Cd/GCL/BL} = 73\ yr$

to 182 yr for max. $CEC_{GCL} = 150\ \frac{meq.}{100\ g.}$

$t^{A}_{Cd/CSL/BL} = 26\ yr \times 25.95$

$= 674\ yr$

to 1475 yr for max. $CEC_{CSL} = 35\ \frac{meq}{100\ g.}$

$t^{A}_{Cd/CCL/BL} = 3.84\ yr \times 25.95$

$= 100\ yr.$

to 1000 yr. for max $CEC_{CCL} = 30\ \frac{meq.}{100\ g.}$

CALCULATIONS (continued)

Method B calculations of breakthrough time for inorganic constituents use Eq. 22 from previous calculation written as follows:

$$t_i = \frac{T}{F_v}(\phi + \rho_c K_{di}) \qquad (25)$$

$$\text{or } t_i = \frac{T}{F_v}\rho_c K_{di} \quad \text{if } \phi << \rho_c K_{di} \qquad (26)$$

For bottom liners:

$$t^B_{Cr^{+6}/GCL/BL} = \frac{7\,mm \cdot \frac{1\,cm}{10\,mm}\left(0.3 + \frac{67\,\frac{lb}{ft^3}\;453.59\,\frac{g}{lb}}{30.48^3\,\frac{cm^3}{ft^3}}\;36.6\,\frac{cm^3}{g}\right)}{2.23\times10^{-8}\,cm^3\,cm^{-2}\,s^{-1}}$$

$t^B_{Cr^{+6}/GCL/BL} = 1.24\times10^9$ sec $= 39$ yr and $\phi\,(=0.3) << \rho_c K_{di}$.

Hence, applying Eq. 26 twice, $\frac{t_i}{t_j} = \frac{K_{di}}{K_{dj}}$ (28)

$$t^B_{Cr^{+3}/GCL/BL} = \frac{2208}{36.6}\,\frac{cm^3/g}{cm^3/g}\,t^B_{Cr^{+6}/GCL/BL} = 2377\text{ yr.}$$

# ENVIRONMENTAL SOLUTIONS, INC.

By EJW Date 23Mar96 Subject ADDENDUM TO COMPARISON Sheet No. 11 of 17
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CALCULATIONS (continued)

$$t^B_{Cr^{+6}/CSL/BL} = \frac{9\,in\,\frac{2.54\,cm}{in}\left(0.2 + \frac{108\,\frac{lb}{ft^3}\,453.59\,\frac{g}{lb}}{30.48^3\,\frac{cm^3}{ft^3}}\,36.6\,\frac{cm^3}{g}\right)}{2.23\times10^{-8}\,cm^3\,cm^{-2}\,s^{-1}}$$

$t^B_{Cr^{+6}/CSL/BL} = 6.51\times10^{10}$ sec = 2065 yr and $t^B_{Cr^{+3}/CSL/BL} = 124{,}559$ yr

$$t^B_{Cr^{+6}/CCL/BL} = \frac{3\,ft\,30.48\,\frac{cm}{ft}\left(0.2 + \frac{127\,\frac{lb}{ft^3}\,453.59\,\frac{g}{lb}}{30.48^3\,\frac{cm^3}{ft^3}}\,36.6\,\frac{cm^3}{g}\right)}{1.33\times10^{-7}\,cm^3\,cm^{-2}\,s^{-1}}$$

$t^B_{Cr^{+6}/CCL/BL} = 5.13\times10^{10}$ sec = 1628 yr and $t^B_{Cr^{+3}/CCL/BL}$ = 98,214 yrs.

For cadmium breakthrough times, apply Eq. 25 twice as follows:

$$t_{Cd} = t_{Cr^{+6}}\,\frac{\phi + \rho_c K_{dCd}}{\phi + \rho_c K_{dCr^{+6}}} \qquad (29)$$

Because $\phi << K_{di}$, Eq. 29 can be simplified to

$$t_{Cd} = t_{Cr^{+6}}\,\frac{K_{dCd}}{K_{dCr^{+6}}} \qquad (28)$$

again

Using Eq. 28, we get:

$$t^B_{Cd/GCL/BL} = 39\ yr\ \underbrace{\frac{6.7\ cm^3/g}{36.6\ cm^3/g}}_{0.183}$$

$= 7$ yr.

CALCULATIONS: (continued)

$t^B_{Cd/CSL/BL} = 2065\ yr \times 0.183 = 378\ yr.$

$t^B_{Cd/CCL/BL} = 1628\ yr \times 0.183 = 298\ yr.$

Method B calculation of the time for an organic constituent to break through a liner uses Eq. 21 from the previous calculation written as follows:

$$t_i = \frac{T}{F_v}\left(\phi + \frac{\rho_c}{\rho_w} K_{owi}\right) \qquad (30)$$

Because $\phi << \frac{\rho_c}{\rho_w} K_{owi}$, Eq. 30 can be simplified to the following expression:

$$t_i = \frac{T}{F_v}\frac{\rho_c}{\rho_w} K_{owi} \qquad (31)$$

Breakthrough times for chloroform were provided in the previous calculation. Breakthrough times for PCE can be related to those of chloroform by applying Eq. 31 twice to get the following expression:

$$t_{PCE} = t_{CHCl_3}\frac{K_{ow_{PCE}}}{K_{ow_{CHCl_3}}} \qquad (32)$$

# ENVIRONMENTAL SOLUTIONS, INC.

By BJW Date 24 Mar 96 Subject ADDENDUM TO COMPARISON OF GCL ± CSL AND CCL Sheet No. 13 of 17

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CALCULATIONS (continued)

$$t^{B}_{PCE/GCL/BL} = 830\,yr \frac{2512}{93}$$

$$= 22{,}419\,yr$$

$$t^{B}_{PCE/CSL/BL} = 43{,}600\,yr \frac{2512}{93}$$

$$= 1.18 \times 10^{6}\,yr$$

$$t^{B}_{PCE/CCL/BL} = 5300\,yr \frac{2512}{93}$$

$$= 143{,}157\,yr.$$

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# ENVIRONMENTAL SOLUTIONS, INC.

By EGW Date 24Mar96 Subject ADDENDUM TO COMPARISON Sheet No. 14 of 17
Chkd. By EC Date 2 APRIL 96 OF GCL + CSL AND CCL Proj. No. 95-284

FINDINGS

The flux of water through the MTR and engineered alternative lower component of the bottom composite liner under the driving force of the newly increased heads is found to be as follows:

| POSITION | LINER | WATER FLUX ($cm^3 cm^{-2} s^{-1}$) |
|---|---|---|
| BOTTOM | GCL+CSL | $2.23 \times 10^{-8}$ |
| | CCL (nondesiccated) | $1.33 \times 10^{-7}$ |

The time for each constituent to break through each alternative is found for each calculation method (A and B) to be as follows (Note: some values are rounded. Also, Method A gives the breakthrough time of the first constituent molecules, while Method B gives the latter time when the half the original concentration breaks through.)

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# ENVIRONMENTAL SOLUTIONS, INC.

By RJW Date 24 Mar 96 Subject ADDENDUM TO COMPARISON OF GCL + CSL AND CCL Sheet No. 15 of 17
Chkd. By EC Date 2 APRIL 96 Proj. No. 95-284

FINDINGS (continued)

| POSITION | LINER | CONSTITUENT | BREAKTHROUGH TIME (yrs) STEP FUNCTION METHOD A | DISTRIBUTION COEFFICIENT METHOD B |
|---|---|---|---|---|
| BOTTOM | GCL + CSL | Chromium$^{+3}$ | 58 to 126 | 127,000 |
| | | Chromium$^{+6}$ | 29 to 63 | 2100 |
| | | Cadmium | 750 to 1660 | 400 |
| | | Chloroform (1) | NA | 44,000 |
| | | PCE | NA | 1,200,000 |
| | CCL (desiccated) | Chromium$^{+3}$ | 8 to 10 (2) | 10 (2) |
| | | Chromium$^{+6}$ | 4 to 10 (2) | 10 (2) |
| | | Cadmium | 10 (2) | 10 (2) |
| | | Chloroform (1) | NA | 10 (2) |
| | | PCE | NA | 10 (2) |
| | CCL (non-desiccated) | Chromium$^{+3}$ | 8 to 80 | 100,000 |
| | | Chromium$^{+6}$ | 4 to 40 | 1600 |
| | | Cadmium | 100 to 1000 | 300 |
| | | Chloroform | NA | 5,300 |
| | | PCE | NA | 140,000 |

NA = Not Applicable
(1) Chloroform breakthrough time taken from previous calculation.
(2) CCL cannot sustain a breakthrough time longer than 10 years because it desiccates and cracks as noted in Attachment A.A and Assumptions.

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CONCLUSIONS

As concluded in the previous calculation that used more realistic leachate heads on the bottom alternative components, the water flux through the engineered alternative would be less than the water flux through the regulatory specified MTR compacted clay component (undesiccated), and much less than that through desiccated clay.

Also as concluded in the previous calculation, the times for representative constituents cadmium, chloroform and tetrachloroethene (PCE) to break through the engineered alternative lower component are much longer than a site-specific period of performance such as 40 years. Only with hexavalent chromium do the first molecules (step function Method A) appear to break through the engineered alternative before 40 years, assuming the lowest cation exchange capacity and the unrealistically high head.

The break through times for the engineered alternative

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# ENVIRONMENTAL SOLUTIONS, INC.

By [illegible] Date 25 Mar 96 Subject ADDENDUM FOR COMPARISON OF GCL±CSL AND CCL Sheet No. 17 of 17
Chkd By EC Date 2 APRIL 96 Proj. No. 95-284

CONCLUSIONS (continued)

are longer than those for the MTR compacted clay, hence equivalency is demonstrated for this measure of leachate migration. The compacted clay cannot sustain a breakthrough time longer than 10 years before it will desiccate and crack, as noted in Attachment A.A.

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ATTACHMENT A,A

# ENVIRONMENTAL SOLUTIONS, INC.

## MEMORANDUM

TO: File

FROM: Chris Hansen

December 27, 1995

Project No. 95-284

Record of Telephone Conference with
David Daniel, Ph.D. regarding GCLs
American Ecology Corporation
Beatty Facility, Nevada Cell 12 Design

This memorandum summarizes the discussions from a telephone conference held on December 19, 1995 at 9:00 a.m. Pacific Standard Time (PST) with Dr. David Daniel of the University of Texas at Austin. The purpose of the call was to discuss various issues related to geosynthetic clay liners (GCLs), including their equivalency to compacted clay liners (CCLs) in landfill liner systems.

The call was prompted by ongoing negotiations with the Nevada Division of Environmental Protection (NDEP) regarding the use of a GCL in lieu of a CCL as the lower component of the bottom composite liner for the design of Cell 12 at the American Ecology Corporation's (AEC) facility located near Beatty, Nevada.

Participants in the telephone conference were:

- David Daniel, Ph.D. - University of Texas at Austin
- Jo Gayle Simmons - American Ecology Corporation
- Dick Ellison, Ph.D. - Environmental Solutions, Inc.
- Eric Walther, Ph.D. - Environmental Solutions, Inc.
- Scott Brown - Environmental Solutions, Inc.
- Chris Hansen - Environmental Solutions, Inc.

Key issues discussed during the telephone conference are described as follows:

- Dr. Daniel summarized the activities and results of recent large-scale test plots (test plots were ±30 m long with 90 cm of cover soil) conducted in Cincinnati, Ohio:
  - The purpose of the test was to evaluate the internal shear strength of hydrated GCLs with a 1.5 factor of safety by evaluating their performance on 3H:1V and 2H:1V slopes. Five tests were run at 3H:1V and ten were run at 2H:1V. The GCLs were placed dry on a wet subgrade and were allowed to hydrate. The GCLs and overlying layers were cut and then observed for movement.
  - All five test plots at 3H:1V did not fail, and eight of the ten test plots at 2H:1V did not fail. Two of the 2H:1V test plots did fail, which occurred at the GCL/geomembrane interface: a Bentomat and a Claymax GCL.
  - One 2H:1V test plot produced somewhat erratic behavior. It was a Gundseal test plot, which partially hydrated in an irregular patchwork pattern.
  - Results show that internal friction angles of GCLs decline with increases in normal stresses. For example, at low normal stresses GCL has an internal friction angle of approximately 20 degrees, while at normal stresses approximating a loaded landfill cell (100 feet of overburden) GCL has an internal friction angle of approximately 8 degrees.
  - The test plot results are considered to confirm findings in literature. A workshop was held in August 1995 to discuss the test plot results and a written report will be released by the United States Environmental Protection Agency (EPA) likely in February 1996.

- Dr. Daniel provided comments on a verbal description of draft calculations prepared by Dr. Walther regarding GCL and CCL chemical adsorption capacity:
  - Need to address diffusion (in addition to advection), which may be a significant component of chemical transport in thin GCLs.
  - The assumed total porosity numbers of 0.75 and 0.437 should be reduced to effective porosities in the range of 0.1 to 0.3.
  - The assumed permeability of the GCL with a 10,000 psf overburden pressure should be about an order of magnitude less than it is when the cell is not loaded (e.g., use $3x10^{-10}$ centimeters per second (cm/sec) loaded versus $3x10^{-9}$ cm/sec unloaded).
  - Prefers an approach based on cation exchange capacity for the purpose of comparing GCL and CCL chemical adsorption capacity, rather than one based on the time for chemical transport through the two media.
  - Is aware of landfill designs with an adsorptive layer placed above the GCL for the purpose of providing additional chemical adsorption capacity.
  - Need to tie the significance of liner chemical adsorption capacity to site-specific conditions, such as the nature of the vadose zone, ground water and potential contaminant receptors. For landfills in arid environments, contaminant fate and transport should be evaluated before looking at a liner's adsorption capacity.
- Dr. Daniel stated that a GCL is a "more sensible" choice (than a CCL) in an arid environment. A GCL is more "survivable" than a CCL. There is a "good possibility to a high probability" of desiccation of a CCL in an arid environment within 10 years. Soil suction in an arid environment may be on the order of tens to 100s of atmospheres (bars).
- Dr. Daniel had one of his Ph.D. students conduct a test in which a 4- by 8-foot sheet of GCL was hydrated in a tank, next drained and desiccated for 30 days with hot air blowers, and then flooded with water again. The results showed that the desiccated GCL's cracks healed within about three hours, and the rehydrated GCL returned to its original permeability.
- Dr. Daniel mentioned that Richard Anderson of the Texas Natural Resource Conservation Commission looks favorably on GCLs, and would likely be receptive to a telephone conversation on the issue.
- In a discussion of various media which may be used to prepare slope subgrades to mitigate the potential to puncture an overlying GCL, Dr. Daniel mentioned that asphalts are "creepy" (i.e., have a tendency to creep) materials which may lubricate the interface.
- On the issue of GCL puncture resistance, Dr. Daniel stated that owners should do all that is possible to mitigate the issue through design and Construction Quality Assurance (CQA), but there is still some risk such as through operator error. Owners may wish to consider adding a low-permeability soil layer below the GCL (to provide a thicker barrier against puncture).
- On the issue of the need for GCL field tests, Dr. Daniel stated that this was not brought up in recent conversations he has had with Cathe Pool (of NDEP). He said it would be hard to imagine a GCL field test with a useful objective.

Although not discussed in the telephone conference, attached to this memorandum is a copy of a SAGEOS Geosynthetics Analysis Service report on the Cincinnati workshop regarding the GCL test plots (see above).

CH/LP:pm
Attachment

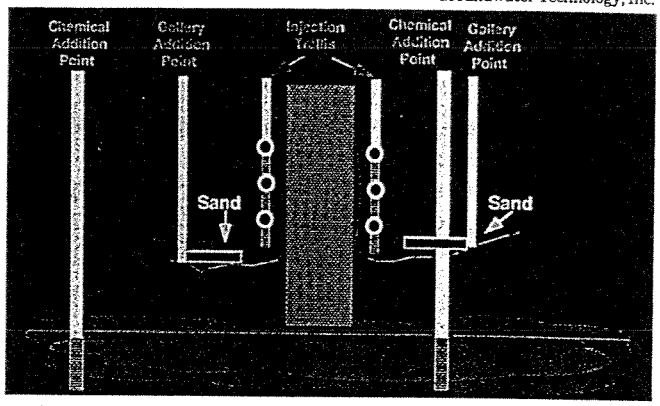
cc: Dick Ellison
Miro Knezevic
Scott Brown
Eric Walther

ATTACHMENT A.B

PROCESS PROFILE

# IN SITU PROCESS CONVERTS TOXIC $Cr^{+6}$ TO NON-TOXIC $Cr^{+3}$

Groundwater Technology, Inc.




**To treat chromium-impacted groundwater without traditional pump-and-treat procedures, GWT uses a two-pronged approach to convert $Cr^{+6}$ (a highly reactive and mobile species) to $Cr^{+3}$ (which is generally insoluble). To expedite groundwater treatment, GWT excavates roughly 1,700 $yd^3$ of overlying soil (for treatment elsewhere). Then, a series of injection wells and trellises are used to introduce acidic ferrous sulfate solution to the aquifer**

Hexavalent chromium ($Cr^{+6}$) is a known human carcinogen, and often exists as a soluble and highly reactive metal species. As a result, groundwater contaminated with $Cr^{+6}$ often requires reclamation.

By comparison, trivalent chromium ($Cr^{+3}$) is an essential nutrient, which is insoluble in most forms. By reacting $Cr^{+6}$ with ferrous iron ($Fe^{+2}$, usually as a ferrous sulfate solution), it is reduced to $Cr^{+3}$. Insoluble ferric iron ($Fe^{+3}$) ions are also produced. Adjusting the pH to 6 or 7 after reduction causes both ions to precipitate as insoluble hydroxides ($Fe(OH)_3$ and $Cr(OH)_3$) This approach forms the basis of many commercial water-treatment systems.

To treat tainted groundwater, however, the use of iron-based precipitation requires an extensive pump-and-treat regimen, to flush the impacted aquifer. This approach is not only time- and capital-intensive, but produces byproduct sludge, which has additional transportation and disposal ramifications.

Recently, Groundwater Technology, Inc. (GWT; Trenton, N.J.) has successfully applied the traditional iron reduction and precipitation process in situ, to treat a "perched" aquifer (i.e., an aquifer whose geology isolates it from deeper aquifers or surface waters). That aquifer, and the overlying fill, at a former industrial site in Pennsylvania, had significant levels of $Cr^{+6}$ contamination.

Analysis of soil and other granular debris at the site indicated pH of 13, total chromium concentrations of 22 g/kg, with an average $Cr^{+6}$ concentration of 6.5 g/kg. An estimated 1,500-1,700 $yd^3$ of this tainted material was delineated over an area 110 by 50 ft, and extended to rougly 6-10 ft below grade.

$\frac{Cr^{+6}}{Cr} = \frac{6.5}{22} = 0.30$ (30%)

A shallow, perched aquifer, located roughly 10-12 ft below grade, discharges into a spillway that drains to the Delaware River. Analysis indicated that roughly 75,000 to 100,000 gal of water had been impacted by $Cr^{+6}$ that had leached from the overlying fill.

To remove the source of chromium leachate and gain better access to the shallow, perched aquifer, GWT excavated 1,700 $yd^3$ of tainted soil (to an average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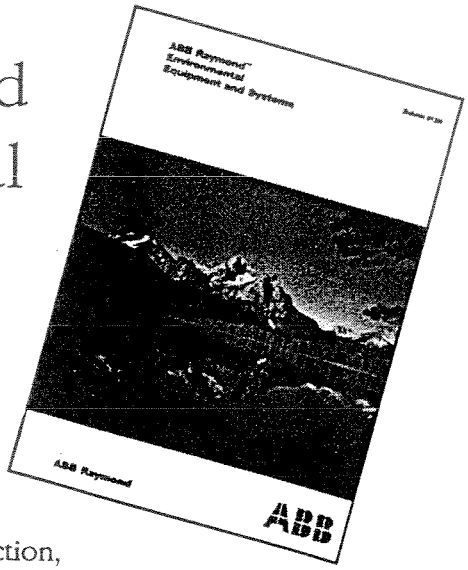


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depth of 8 ft), and sent it to a secure disposal facility for decontamination.

GWT estimated the total load of $Cr^{+6}$ in each of the three areas (granular fill, residual soils and groundwater contained in the aquifer) to be 26 lb, 9 lb and 20 lb, respectively. On a stoichiometric basis (using 3- to 4-fold excess to ensure completeness in the time desired), treatment was estimated to require 566 lb of $Fe^{+2}$, 867 lb HCl, and 1,628 lb of NaOH. The ferrous iron source chosen for the site was a solution of acidified ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$).

After two weeks of treatment and four months of monitoring, $Cr^{+6}$ concentration in the aquifer fell from to 85 ppm to below 50 ppb across most of the site. These reduced levels of $Cr^{+6}$ have been maintained for more than a year, and are verified with regular monitoring.

Unlike the use of traditional pump-and-treat methods, this approach produces no tainted sludge. At this Pennsylvania site, says GWT, this not only reduced the time and cost required to remediate the site, but simplified the permitting requirements, too. ■

*Groundwater Technology, Inc., Trenton, N.J.* **203**

PROCESS PROFILE

# CONVERT LEACHABLE METALS TO MINERALS

The patented Maectite process from Sevenson Environmental Services, Inc. (Niagara Falls, N.Y.) uses proprietary additives to fix lead, cadmium and other bivalent metal ions into a series of hardened, geochemically stable minerals. A patented companion technology, dubbed Chromtite, is available for multivalent metals, such as chromium, arsenic and others. To date, pilot- and full-scale operations have proven the technology for waste streams as varied as soil, peat and humic material, foundry sands and smelter slag, ore-processing residuals, filter cake and sludge.

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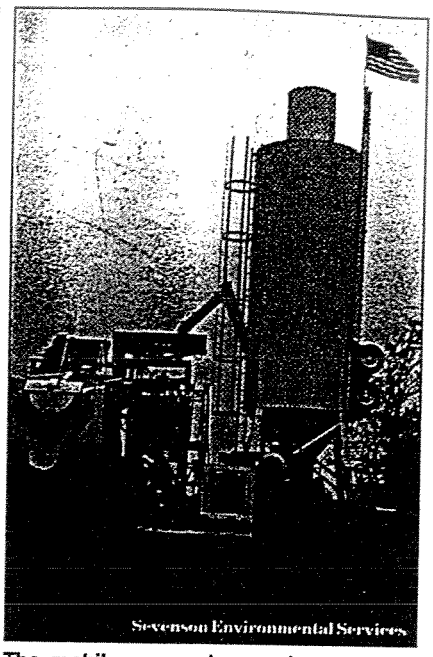


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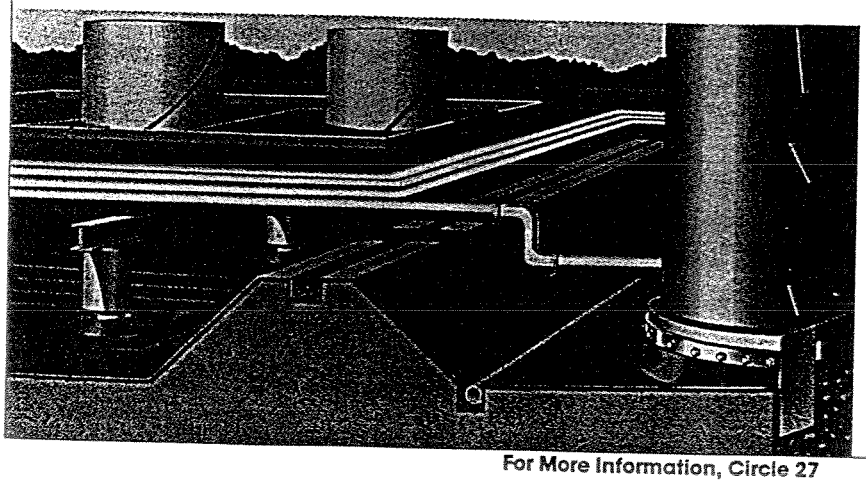

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**CHEMICAL TREATMENT OF VARIOUS IONS BY THE MAECTITE PROCESS, mg/L IN TCLP EXTRACT**

| Metal type | Application (level) | Untreated concentration range | Treated concentration range | Regulatory limit |
|---|---|---|---|---|
| Lead | Commercial (full-scale) | [illegible] | [illegible] | 5 |
| Cadmium | Commercial (full-scale) | [illegible] | [illegible] | 1 |
| Chromium | Commercial (full-scale) | [illegible] | [illegible] | 5 |
| Selenium | Commercial (pilot-scale) | [illegible] | [illegible] | 1 |
| Arsenic | Commercial (pilot-scale) | [illegible] | [illegible] | 5 |
| Mercury | Laboratory (bench-scale) | [illegible] | [illegible] | 0.2 |
| Barium | Laboratory (bench-scale) | [illegible] | [illegible] | 100 |

**Representative test results show that after treatment with the chemical additive used in the Maectite process, soils and sludges pass all leachability tests**

mass is not incorporated into the treated waste matrix. In fact, an overall volume reduction of 5–20% can be expected, thanks to the elimination of much of the interstitial space, and the conversion of a portion of the waste into denser, highly-ordered mineral crystals (with crystal morphology in the hexagonal and orthorhombic systems).

Traditional solidification or encapsulation methods, such as treatment with pozzolanic cement or silicious binders, produce a monolith, which may be susceptible to degradation or leaching over time. In contrast, waste treated with Maectite additives retains the loose granular texture of soil or dehydrated matrices, so treated sites can easily be redeveloped.

The process is suitable for both in situ and ex situ treatment. Process rates are flexible, and commercial-scale operations carried out to date have ranged from 48 55-gallon drums in one day, to more than 2,000 tons in a 12-h work shift. The chemical reactions are essentially completed in the first 3–5 hours.

For in situ treatment, subsurface infiltration galleries and intercept trenches and deeper, subsurface injection wells can be installed to deliver the reagents. Groundwater and saturated soils can be treated concurrently, says the firm.

For ex situ treatment, a weigh-belt feeder, integrated with a computer-controlled, chemical-dosing system, provides precise control over the delivery rate of the liquid or powder reagents. ■

*Sevenson Environmental Services, Inc., Niagara Falls, N.Y.* **204**

*Suzanne Shelley*


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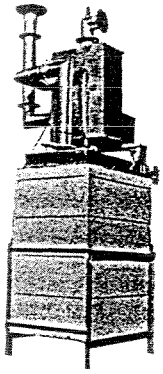

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ATTACHMENT A, B (Continued)

# The Geochemistry of Chromium Migration and Remediation in the Subsurface

by Andy Davis[a] and Roger L. Olsen[b]


## Abstract

**From a human health perspective, knowledge of Cr speciation in soils is important in assessing risk related to ingestion of Cr-contaminated soils, and in selecting appropriate remedial alternatives that are protective of ground-water quality. In this study, good agreement was found between Cr(VI) soil concentrations and the mass of Cr(VI) leached from columns over a range of Cr(III):Cr(VI) soil ratios (0.2-28) and ΣCr concentrations (27-290 mg/kg). In batch tests, adsorption of Cr(VI) to sandy soils was rapid and linear, with a $Kd_{Cr(VI)}$ of 0.2 liters/kg, suggesting Cr(VI)-contaminated vadose- and saturated-zone materials may be remediated by soil flushing or pump-and-treat methods. In column tests, soil flushing removed 85% of the soil-Cr(VI), while pump-and-treat leached only 17% of Cr attributable to aquifer contamination. Use of oxidizing agents increased Cr released from Cr(III)-contaminated soils, but only from 1.3% to 2.3% of ΣCr mass. Based on Cr speciation in soils, Cr(VI) was mobile, while Cr(III)was retained in the soil column, indicating that reduction of Cr(VI) to Cr(III), and the proportion of Cr(III) in the soil, will constrain remedial efficiency. Reduction of Cr(VI) to Cr(III), and subsequent precipitation of $Cr_xFe_{1-x}(OH)_3$, occurred in a Cr(VI)-contaminated soil augmented with $Fe^{+2}$, resulting in < 0.01 mg/l Cr in the supernatant, suggesting that in situ Cr fixation may mitigate Cr-contaminated ground water.**


## Introduction

Chromium is used in a number of commercial processes, including electroplating, leather tanning, pulp production, ore refining, and wood preservation. In lumber treatment, Cr(VI) is the predominant form, typically diluted in water to a ratio of 0.62:0.37:0.55% chromated copper arsenate solution (Radian, 1990). Environmental Cr geochemistry is well understood (Schmidt, 1984; Rai et al., 1988; Eary and Rai, 1991, Richard and Bourg, 1991), as are the precipitation, oxidation, and reduction reactions of Cr in soils, and the effect of organic complexing on Cr mobility (Bartlett and Kimble, 1976a, b; Bartlett and James, 1979; Ross et al., 1981; James and Bartlett, 1983a, b, c). This study builds on the known theoretical aspects of Cr geochemistry to explore potential application to remediation of Cr-contaminated soil and ground water.

The more toxic and mobile Cr(VI) predominates in oxidizing environments, while the less toxic and immobile Cr(III) is restricted to reducing environments (U.S. EPA, 1975; Mertz et al., 1974). Cr(VI) is generally anionic and mobile under neutral pH (Leckie et al., 1980), with mobility decreased only slightly by sorption to amorphous ferric hydroxide, and even less by sorption to clay (Rai et al., 1988). Cr(VI) solubility is controlled primarily by $PbCrO_4$ ($pK_{sp} = 13.7$; Schmidt, 1984), although $BaCrO_4$ ($pK_{sp} = 8.9$) has been shown to form rapidly under environmental conditions (Rai et al., 1988). Soluble Cr salts, e.g., $CaCrO_4$ ($pK_{sp} = 3.15$), have been suggested to precipitate in soils containing 10,400 mg/kg Cr (James, 1994).

Chromium occurs naturally in western U.S. soils, ranging from 3 to 2,000 mg/kg (geometric mean = 41 mg/kg; Shacklette and Boerngen, 1984), primarily as chromite ($FeCr_2O_4$; $K_{sp} = -28.4$), an insoluble accessory soil mineral (Schmidt, 1984). In a reducing environment, and in the absence of Fe, Cr(III) precipitates readily to form $Cr(OH)_3$ ($pK_{sp} = 6.8$; Rai et al., 1987). However, due to their similar ionic radii (Cr = 1.25 Å, Fe = 1.24 Å), Cr can easily substitute for Fe in, or form solid solutions with, amorphous ferric hydroxide (Faust and Aly, 1981), in which case, the typical stoichiometry is $Cr_{0.25}Fe_{0.75}(OH)_3$ (Eary and Rai, 1988); i.e.,

$$Cr(OH)_2^+ + 3Fe^{+3} + 10H_2O \rightleftharpoons 4\{Cr_{0.25}Fe_{0.75}(OH)_3\} + 10H^+ \quad (1)$$

This reaction has been demonstrated to decrease the solubility of Cr(VI) from various anthropogenic waste streams, while Rai et al. (1986) found that precipitation of Cr(III) hydroxide and Cr(III)-Fe hydroxide minerals maintained Cr(III) concentrations in ground water at levels below the drinking-water standard (0.1 mg/l) over a pH range of 5 to 10. However, while the geochemical behavior of Cr is well understood, the practical application of these concepts to

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the cleanup of Cr in soil and ground water has received less attention.

Previous research suggests that chemically enhanced reduction of Cr(VI) to Cr(III), and precipitation of a mixed Cr-Fe hydroxide, may represent a viable remedial technique to retard the migration of Cr in the subsurface. Conversely, aquifer flushing or soil washing to remove Cr may be enhanced by oxidation of Cr(III). These hypotheses were tested using soil and aquifer materials obtained from a former wood-treating site where copper chromate arsenate had been used, and where it was necessary to evaluate remedial alternatives. Of particular significance is the assessment of the analytical protocols used to distinguish between Cr redox forms in a soil matrix, which has been a point of contention since publication of the analytical method (U.S. EPA, 1982). Determination of Cr species in soil is important to assess risk related to ingestion of Cr-contaminated soils, in determining remediation goals that are protective of ground-water quality and human health, and in selecting appropriate remedial alternatives protective of ground-water quality. Therefore, further method evaluation using soils contaminated with a range of Cr concentrations and Cr(III)/Cr(VI) ratios was warranted.

Initially, Cr(VI) adsorption data were generated using batch tests, and adsorption hysteresis evaluated using column tests. These data were used to assess potential Cr leachability and the viability of soil flushing. A representative soil was flushed with hydrogen peroxide-spiked ground water to determine if an oxidizing agent would enhance leaching of Cr from contaminated soil, and a contaminated aquifer-zone material was flushed with ground water from upgradient of the site to assess the efficacy of a pump-and-treat alternative. Finally, the feasibility of immobilizing Cr in an amorphous hydroxide was evaluated by amending Cr-bearing soils with ferrous chloride ($FeCl_2 \cdot 4H_2O$), to test subsequent leaching of Cr from the soil. The experimental design is summarized in Table 1.

## Methods

### *Materials*

Six soil samples were collected at depths ranging from 0.3 m to 7.5 m below ground surface using a rotary drill rig with a split spoon corer, and stored at 4°C until analysis. Porosity (Vomocil, 1983), moisture content (ASTM, 1986) and bulk density (Blake, 1983) were determined for each soil, total Cr (ΣCr) soil concentrations by Method 3050/7190 (U.S. EPA, 1986), and Cr(VI) soil concentrations by Method 3060/7196 (U.S. EPA, 1982), with Cr(III) concentrations determined by difference between Cr(VI) and ΣCr. Conversion of Cr(III) to Cr(VI) during transit was unlikely because Cr(III) oxidation kinetics in slightly acidic to basic environments are very slow (Eary and Rai, 1987).

Each soil sample was blended and split, with one fraction digested using $HNO_3/H_2O_2$ to extract ΣCr and the other aliquot extracted following Method 3060 with hot 3% $Na_2CO_3$/2% NaOH to dissolve all Cr(VI), while preventing reduction of Cr(VI) to Cr(III). Subsequently, ΣCr was determined by atomic absorption spectrophotometry (Method 7196), and Cr(VI) colorimetrically (Method 7190) at 540 nm by reaction with diphenylcarbazide in acid (pH 2) solution (Bartlett and James, 1979).

The 3060 digestion has been subjected to intense scrutiny (U.S. EPA, 1987a) due to the possible reduction of Cr(VI) to Cr(III) by reduced forms of Fe and Mn, or by organic carbon, which was thought to cause an apparent underestimation of the risk from ingestion of Cr-contaminated soils, in the event that Cr(VI) was mistakenly reported as Cr(III). However, recent studies (James et al., 1993) have indicated that method-induced reduction of Cr(VI) is not responsible for low recoveries, suggesting that Method 3060 is a viable procedure to determine Cr(VI) concentrations in soils. Method 3060 was used in this study due to the low concentrations of organic carbon (average = 550 mg/kg, maximum = 1200 mg/kg) and redox reactive species (e.g., Fe and Mn) in site soils (Table 2).

**Table 1. Experimental Design**

| *Experiment type* | *Soil* | *Test* | *Objective* |
|---|---|---|---|
| Batch I | A/B | Spike 1:1 soil:water solution with Cr(VI) in air. | Measure adsorption isotherms and determine $Kd_{Cr(VI)}$. |
| Batch II | F | Add $FeCl_2 \cdot 4H_2O$ to Cr(VI)-contaminated soil. | Fixation of Cr(VI) by precipitation of $Cr_xFe_{1-x}(OH)_3$. |
| Column A | A | Leach uncontaminated soil (ΣCr = 14 mg/kg) with clean ground water. | Baseline control column to determine ambient leaching. |
| Column B | B | Add Cr-contaminated ground water and Br to clean soil. | Evaluate column flow dynamics using Br tracer, and determine column-based $Kd_{Cr(VI)}$. |
| Column C | C | Leach 141 mg/kg Cr(III)-contaminated soil with clean ground water. | Control for Column D and to compare efficacy of Cr(III) vs. Cr(VI) leachability from columns F and G. |
| Column D | C | Leach 141 mg/kg Cr(III)-contaminated soil with clean ground water and 30 mg/l $H_2O_2$. | Assess potential for enhanced leaching by oxidation of Cr(III) to Cr(VI). |
| Column E | E | Leach 20 mg/kg Cr(III)-contaminated aquifer material with clean ground water. | Simulate pump-and-treat remedial alternative [Column A control based on similar ΣCr and Cr(III) concentrations]. |
| Column F | F | Leach 157 mg/kg Cr(VI)-contaminated soil with clean ground water. | Compare leachability of Cr redox species at similar concentrations (with Column C). |
| Column G | G | Leach 45 mg/kg Cr(III)-contaminated soil with clean ground water. | Evaluate leachability of lower Cr(III) concentrations (compare with Column C). |

Table 2. Bulk Soil Chemistry (mg/kg)

| *Soil:* | *A* Sand | *B* Sand | *C* Fine sand | *E* Silty sand | *F* Silty sand/clay | *G* Silty sand |
|---|---|---|---|---|---|---|
| *Column:* | *A* | *B* | *C/D* | *E* | *F* | *G* |
| *Type:* | *Backgrd.* | *Backgrd.* | *Contamin.* | *Contamin.* | *Contamin.* | *Contamin.* |
| *Zone:* | *Vadose* | *Vadose* | *Vadose* | *Saturated* | *Vadose* | *Vadose* |
| *Location:* | *Upgrad.* | *Upgrad.* | *On-site* | *Downgrad.* | *On-site* | *On-site* |
| *Depth (m):* | *0.3* | *0.3* | *0.6* | *7.5* | *0.6* | *0.6-2* |
| ***Parameter*** | | | | | | |
| Al | 63,600 | 66,000 | 63,400 | 61,100 | 67,600 | 61,500 |
| As | 2.30 | 2.25 | 23.90 | 2.00 | 39.50 | 3.10 |
| Ba | 664 | 637 | 615 | 792 | 636 | 655 |
| Br | <0.3 | <0.3 | <0.3 | <0.3 | <0.3 | <0.3 |
| Ca | 18,000 | 23,800 | 19,500 | 15,800 | 29,500 | 17,900 |
| Cd | <1 | <1 | <1 | <1 | <1 | <1 |
| Cr | 14 | 14 | 146 | 20 | 188 | 49 |
| Cr(VI) | 0.4 | 0.8 | 5 | 0.6 | 158 | 4 |
| Cr(III) | 13.6 | 13.2 | 141 | 19.4 | 30 | 45 |
| Cu | 8 | 9 | 65 | 9 | 38 | 10 |
| F | 0.30 | 1.61 | 1.59 | 1.30 | 3.40 | 1.07 |
| Fe | 18,300 | 17,600 | 18,500 | 17,200 | 20,700 | 18,300 |
| K | 26,200 | 26,100 | 24,600 | 25,900 | 25,600 | 25,500 |
| Mg | 3,370 | 5,040 | 3,760 | 3,700 | 7,560 | 3,260 |
| Mn | 300 | 350 | 320 | 340 | 430 | 300 |
| Mo | 2 | 2 | 3 | 3 | 3 | 3 |
| Na | 24,100 | 25,900 | 25,600 | 20,900 | 26,800 | 23,900 |
| Ni | 5 | 5 | 5 | 9 | 7 | 5 |
| P | 258 | 389 | 309 | 260 | 619 | 257 |
| Pb | 32 | 33 | 35 | 32 | 35 | 35 |
| Se | 0.10 | 0.05 | <0.05 | <0.05 | 0.10 | 0.10 |
| Sr | 293 | 318 | 301 | 264 | 339 | 285 |
| Ti | 1,930 | 2,200 | 2,170 | 2,320 | 2,680 | 2,050 |
| TOC | 500 | 1,200 | 1,000 | 100 | <100 | 700 |
| V | 51 | 50 | 51 | 49 | 60 | 51 |
| Zn | 28 | 33 | 32 | 30 | 43 | 27 |

$\Sigma = 169.8$
$\Sigma = 262.2$
$\Sigma = 431$
$\frac{Cr^{+6}}{Cr} = \frac{169}{431} = 0.39$

Uncontaminated (background) ground water was collected from a well upgradient from the site, and contaminated ground water from an on-site monitoring well after purging three bore volumes and filtering the ground water through a 0.45-$\mu$m pore-size nitrocellulose membrane. Unpreserved samples were analyzed for Cr(VI) within 24 hours, while samples for $\Sigma$Cr determination were preserved at pH 2 with $HNO_3$.

## Batch Test I: Determination of Adsorption Isotherms

Seven samples of background soil (50 g of both A and B) were mixed with 50 ml each of upgradient ground water spiked with 0.0, 0.5, 1.0, 2.0, 3.0, 5.0, and 6.0 mg/l Cr(VI), prepared by dissolving $K_2Cr_2O_7$ in deionized water and diluting the stock solution to the desired concentrations. The batch experiments were run under conditions (pH = 7.0, Eh = 450 mV) similar to site ground water (upgradient, pH = 7.6, Eh = 500 mV; contaminated, pH = 8.0, Eh = 440 mV). Samples were shaken for 24 hours at 25° C (U.S. EPA, 1987b), a period demonstrated to attain steady-state equilibrium, based on a kinetic study using uncontaminated soil A and Cr-contaminated (5 mg/l) ground water (Figure 1). The fluid was then filtered through a 0.45-$\mu$m-diameter nitrocellulose filter; the pH, Eh, temperature, and specific conductivity of each leachate sample recorded; and the sample acidified to pH 2 with ultrapure $HNO_3$ prior to $\Sigma$Cr analysis by EPA Method 7196.

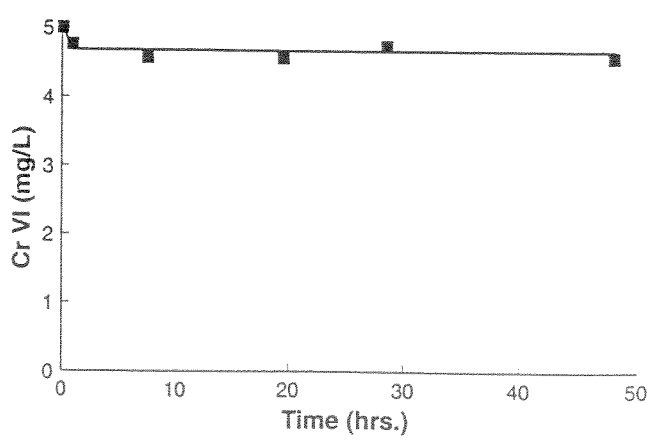


**Fig. 1. Cr(VI) solution concentration during time-dependent batch sorption test.**

### Batch Test II: Cr Fixation by Ferrous Chloride

A variety of techniques for fixation of Cr in soils have been evaluated (Beszedits, 1988), including reduction and precipitation with Fe electrodes (Moring, 1980), Fe(II) salts (Fuji, 1977; Sakakibara et al., 1979), and hydrogen peroxide (Fournier and Meyer, 1985). One of the most promising and economical methods may be the reduction of Cr(VI) by $Fe^{+2}$ (Eary and Rai, 1988), for which an optimal ratio of Cr:Fe in the hydroxide should be 1:3, i.e.,

$$0.25CrO_4^{-2} + 0.75Fe^{+2} + 2H_2O = Cr_{0.25}Fe_{0.75}(OH_3) + H^+ \quad (2)$$

While this ratio may vary in practice, the hydroxide is sufficiently insoluble (Sass and Rai, 1987) that Cr in solution was hypothesized to remain below the drinking-water standard (i.e., < 100 $\mu$g/l) at even lower Cr:Fe ratios. To test this premise, 0.26 g of reagent-grade $FeCl_2 \cdot 4H_2O$ was added to 102.7 g of soil F [188 mg/kg ΣCr; the soil containing the highest concentration of Cr(VI), 158 mg/kg] to obtain a 1:4 Cr:Fe (wt:wt) ratio, and 0.22 g of Fe salt added to 7.04 of soil F for a 1:47 Cr:Fe ratio (wt:wt), assuming the reaction stoichiometry of equation (2).

Ground water was added to each Fe-amended soil to create a 4:1 water:soil (wt:wt) slurry. Immediately after addition of the ground water, amorphous ferric hydroxide precipitated, resulting in a pH decrease from 7.6 to 6.5 (Cr:Fe; 1:4) and 5.8 (Cr:Fe, 1:47), due to release of protons [equation (2)], while the Eh remained ~ 300 mV in both cases. After a reaction period of 24 hours, the supernatant was filtered through a 0.45-$\mu$m nitrocellulose membrane and analyzed for ΣCr and Cr(VI) within 24 hours after sample collection.

### Column Tests

The soil samples were packed dry in plexiglass tubes 10 cm in diameter and 30 cm long, allowing for visual examination of the progress of the wetting front and detection of preferential flow channels along the column walls. The loading procedure consisted of filling the columns in 5-cm lifts, compacting each lift with a 2.5-kg drop hammer, scarifying the surface to prevent permeability discontinuities, and adding more material until the column was full (ASTM, 1989). Soil was retained in the columns by a 0.45-$\mu$m nitrocellulose filter, in conjunction with a plastic distribution plate at the top and base of each column. This procedure also ensured that any particulate material in the influent ground water was removed prior to passage of the water through the column, that the effluent was filtered according to standard practices, and that saturated conditions were maintained.

Clean upgradient (background) ground water (Table 3) was used to leach the soil column from base to top (to preclude the entrainment of air in pore space that occurs in top-to-bottom leaching). A constant-head (1 m) reservoir was used to deliver influent background ground water at a flow rate between 0.17 and 0.5 m per day, representative of ground-water flow rates at the site. Based on leachate collection velocities, the soil-water contact time averaged 8-24 hours in the columns. This residence time allowed attainment of steady-state Cr sorption, as demonstrated in the batch experiment (Figure 1), although dissolution of any Cr-bearing phases during the column tests could have augmented Cr effluent concentrations.

Table 3. Ground-Water Chemistry

| Parameter | Sample I.D. Background | Sample I.D. On-site well |
|---|---|---|
| pH (s.u.) | 7.6 | 8.0 |
| Eh (mV) | +500 | +440 |
| S.C. ($\mu$hmos/cm) | 852 | 1,286 |
| TDS | 637 | 834 |
| Ca | 72 | 102 |
| Mg | 26 | 39 |
| Na | 59 | 87 |
| K | 2 | 1 |
| Alkalinity ($HCO_3^-$) | 307 | 226 |
| Cl | 15 | 150 |
| $SO_4$ | 83 | 148 |
| $NO_3$-N | 16 | 18 |
| Al | <0.1 | <0.1 |
| As | 0.004 | 0.002 |
| Ba | 0.29 | 0.18 |
| B | 0.09 | 0.08 |
| Br | <0.05 | <0.05 |
| Cr(total) | <0.01 | 5.06 |
| Cr(VI) | <0.005 | 5.00 |
| Fe | <0.01 | 0.01 |
| Mn | 0.01 | <0.01 |
| P | <0.1 | 0.3 |
| Zn | 0.08 | 0.03 |

All units are mg/l except as noted.

Cumulative flow volumes, pH, and S.C. were measured, and one aliquot of each column effluent sample was acidified to pH 2 using ultrapure HCl, while the other remained unacidified, for ΣCr and Cr(VI) analysis, respectively. Initially, samples were collected at 100-ml increments, with the volumes increasing to 500 ml toward the end of the experiments as the effluent chemistry stabilized. Column pore volumes (Table 4) were calculated from:

$$PV = V - \frac{M}{(1 + W)\, G_s \rho_w} \quad (3)$$

where PV = pore volume (ml); V = volume of the column (ml); M = saturated mass of soil in column (g); W = moisture content (g water/g dry soil); $G_s$ = specific gravity of the soil; and $\rho_w$ = density of water (g/cm$^3$).

The ground-water flow rate through the columns was calculated from:

$$\text{Flow rate (cm/day)} = \frac{V_w}{nA(t_2 - t_1)} \quad (4)$$

where n = porosity; $V_w$ = fluid volume (ml) passed through column per time period; A = cross-sectional area of column (81.1 cm$^2$); and $t_2 - t_1$ = time required (days) to pass a given volume of fluid, assuming that the effective porosity is equivalent to the porosity.

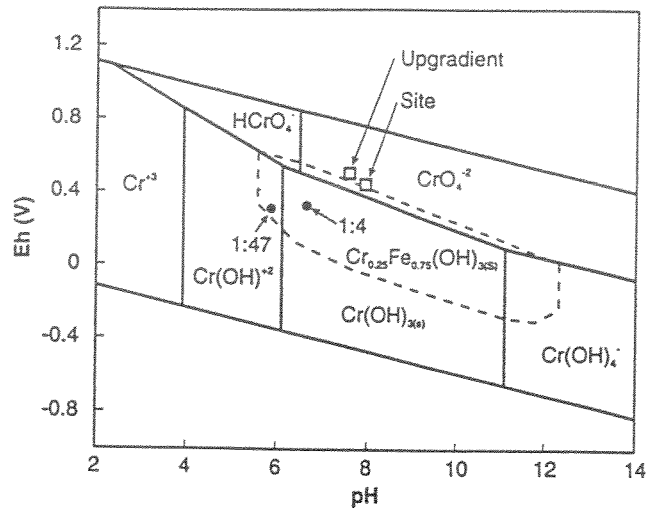


**Fig. 2. Cr Eh-pH diagram for $\Sigma Cr = 10^{-4.0}$, $\Sigma Fe = 10^{-7}$, representative of site ground-water conditions (□) based on the thermodynamic data of Schmidt (1984). The dashed lines represent the $Cr_{0.25}Fe_{0.75}Fe(OH)_3$ stability field with $Fe = 10^{-3}$, on which are superimposed the supernatant Eh-pH conditions (after spiking) for the Cr:Fe 1:4 and 1:47 fixation test conditions (●).**

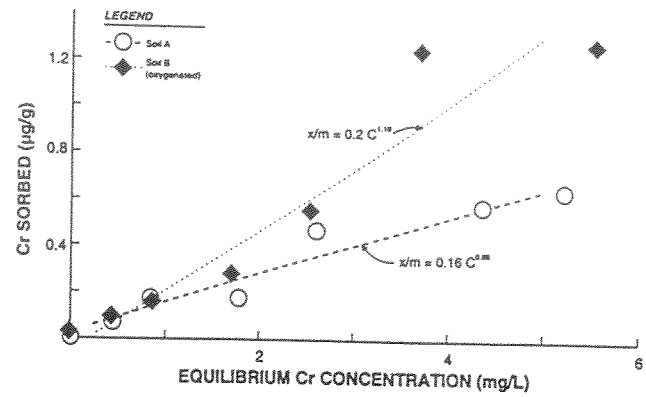


**Fig. 3. Freundlich batch adsorption isotherms for soils A and B.**

To assess the relative efficiency of columns in releasing Cr, the total Cr mass initially present in each soil column was calculated by multiplying the soil Cr concentration by the soil mass in the column. Similarly, the total mass of Cr, Cr(III), and Cr(VI) leached from each column was determined by multiplying the Cr effluent concentration and volume for each sample interval, summing the masses over each interval, and subtracting the baseline mass (the product of the Cr concentration at steady state and the cumulative eluted volume) to obtain the treatment-specific leached mass (Table 5). Then the percentages of Cr(III) and Cr(VI) leached from the soil were determined by comparing their leachate mass with the initial soil mass of each Cr valence state.

### *Quality Control*

Sample duplicates across a range of aqueous Cr concentrations (relative percent difference for $\Sigma Cr \leq 7\%$, (n = 5); and 0% for Cr(VI), (n = 5); sample quadruplicate splits ($\sigma = 0\%$ at 0.17 mg/l); analysis of blind standard reference solutions (relative percent difference of $\leq 3\%$ between 0.5 and 6.0 mg/l); and equipment blanks (Cr < 0.01 mg/l) were collected. In addition, analytical laboratory controls were implemented [e.g., instrument calibration verification; the 24-hour sample holding-time requirement (U.S. EPA, 1988) met for Cr(VI); blank analyses; matrix spike recoveries and serial dilutions]. Replicate adsorption experiments resulted in relative percent differences of 2% at 0.5 mg/l (soil A), 1% at 2 mg/l (soil B), 3% at 3 mg/l (soil A), and 19% at 6 mg/l (soil B). These analyses demonstrated that the data met standard quality control requirements (U.S. EPA, 1988).

## Results and Discussion

### *Soil and Ground Water*

The background soil samples (soils A and B) both contained 14 mg/kg ΣCr, compared to the contaminated vadose-zone samples (C, F, and G), which contained from 49 to 188 mg/kg ΣCr. The saturated-zone soil (E) had only a slightly elevated ΣCr concentration (above background) of 20 mg/kg (Table 2). With the exception of Cr(VI), analyte concentrations were similar in the two wells (Table 3). Ground water in an on-site monitoring well contained 5.06 mg/l ΣCr, of which 5.00 mg/l was Cr(VI), consistent with the measured Eh (Figure 2), while in upgradient ground water, ΣCr and Cr(VI) were both below the method detection limits of 0.01 and 0.005 mg/l, respectively.

**Table 4. Column Geotechnical Data**

| *Column I.D.* | *Sample depth (m)* | *Column volume ($cm^3$)* | *Equivalent mass of wet soil (g)* | *Moisture content* | *Mass of dry soil (g)* | *Specific gravity of soil ($g/cm^3$)* | *Pore volume (ml)* | *Porosity* | *Bulk density ($g/cm^3$)* |
|---|---|---|---|---|---|---|---|---|---|
| A | 0.3 | 1,240 | 2,130 | 0.035 | 2,055 | 2.75 | 492 | 0.40 | 1.7 |
| B | 0.3 | 1,240 | 2,140 | 0.094 | 1,939 | 2.66 | 504 | 0.41 | 1.7 |
| C | 0.7 | 1,240 | 2,027 | 0.020 | 1,986 | 2.70 | 503 | 0.41 | 1.6 |
| D | 0.7 | 1,240 | 1,928 | 0.020 | 1,889 | 2.70 | 599 | 0.43 | 1.6 |
| E | 8.1 | 1,240 | 2,594 | 0.172 | 2,148 | 2.66 | 407 | 0.33 | 2.1 |
| F[a] | 2 | 995 | 1,179 | 0.156 | 995 | 2.78 | 327 | 0.47 | 1.7 |
| G | 2 | 1,240 | 2,523 | 0.220 | 2,043 | 2.68 | 467 | 0.38 | 2.0 |

[a] 15-cm column.

### Batch Experiments

The batch adsorption data (Figure 3) conformed best to a Freundlich isotherm, i.e.:

$$x/m = K_d C^{1/n} \quad (5)$$

where x = mass of Cr(VI) adsorbed from solution ($\mu$g); m = mass of soil or adsorbing material (g); $K_d$ = Freundlich adsorption constant (ml/g); C = concentration of Cr(VI) in solution (mg/l); and n = constant defining isotherm linearity.

Nonlinear regression analysis of the batch data resulted in $Kd_{Cr(VI)}$ of 0.16 and 0.2 (1/n = 0.88 and 1.18; $r^2$ of 0.92 and 0.96), for soils A and B, respectively. In comparison, Griffin et al. (1977) reported Langmuirean behavior over an approximately two order of magnitude range of initial aqueous Cr(VI) concentrations at pH 7, and decreasing $Kd_{Cr}$ with increasing Cr(VI) concentration, probably due to competitive inhibition for surface sites at higher Cr concentrations. In contrast, the linearity observed in our study is probably due to the lower range of Cr concentrations (representative of site conditions) used in the experiment.

Although Cr(VI) sorption to sandy soils does not appear to have been studied extensively, the lower pH in other investigations resulted in higher $Kd_{Cr(VI)}$ values (Figure 4). For example, a $Kd_{Cr(VI)}$ of 52 liters/kg at a pH of 6.8 for alluvial sands was reported by Stollenwork and Grove (1985), while in a pH 7.5 system, Henderson (1994) measured an average $Kd_{Cr}$ = 0.31 liters/kg for Trinity Sand aquifer material, probably due to the increasingly positive charge on mineral surfaces at lower pH (Dzomback and Morel, 1990).

The low $Kd_{Cr(VI)}$ measured in our study is probably due to competition for sorption sites from $SO_4^{-2}$ (83-148 mg/l; Table 3), which enhances Cr solubility (Zachara et al., 1987), and to the neutral isoelectric point pH (6-9) of Fe oxides (Drever, 1982), which constitute the principal sorbent in sandy silt. Sandy material has a greater preponderance of positively charged surfaces over the pH 5-7.5 range, compared to clay (isoelectric point pH of 2-3.5), resulting in a greater affinity for $CrO_4^{-2}$, and a higher $Kd_{Cr(VI)}$ on sand than for clay (Figure 4).

### Columns

Column A [14 mg/kg ΣCr, 0.4 mg/kg Cr(VI)], designated as a baseline control column (Table 1), was leached with uncontaminated upgradient ground water at an average flow rate of 0.5 m/day for 13 pore volumes. None of the effluent samples contained Cr > 0.01 mg/l, indicating that Cr was refractory in this soil under the prevailing column conditions.

Column B, also prepared using background soil B [14 mg/kg ΣCr, 0.8 mg/kg Cr(VI)], was initially saturated with upgradient ground water, and then flushed with contaminated ground water containing 5 mg/l Cr(VI), until this concentration was observed in the effluent (after three pore volumes). The influent then reverted to background ground water to evaluate Cr adsorption hysteresis (Figure 5a). Column B influent contained $Br^-$, added as KBr to the background ground water also at a concentration of 5 mg/l, to calculate $Kd_{Cr(VI)}$ based on the retardation factor of Cr(VI) relative to the tracer. For column experiments, the retardation factor (R) can be expressed as the ratio of the number of pore volumes required to achieve 50% of the influent concentration in the effluent for the solute of interest, compared to the tracer, i.e.,

$$R_{Cr} = \frac{\text{PV to achieve } C/C_0 = 0.5 \text{ for Cr(VI) (2.5 mg/l)}}{\text{PV to achieve } C/C_0 = 0.5 \text{ for } Br^- \text{ (2.5 mg/l)}} \quad (6)$$

where PV is the number of pore volumes, C is the effluent concentration, and $C_0$ is the influent concentration. Calculation of this ratio using the $Br^-$ and Cr(VI) data (Figure 5a) resulted in an $R_{Cr(VI)}$ of 2.1 (0.65/0.3).

$R_{Cr(VI)}$ can also be calculated using $Kd_{Cr(VI)}$ from the batch adsorption experiments using:

$$R = 1 + \frac{\rho_b Kd_{Cr(VI)}}{n} \quad (7)$$

where $Kd_{Cr(VI)}$ = distribution coefficient [0.2 ml/g for Cr(VI) in soil B]; $\rho_b$ = bulk density of the soil (1.7 g/cm$^3$ in Column B); and n = porosity (0.41 in Column B). Utilizing these data, $R_{Cr}$ = 1.8, in good agreement with the value determined from column breakthrough. No significant adsorption hysteresis (analyte tailing) was apparent (Figure 5a).

Columns C and D were both prepared using a split of shallow vadose-zone soil C [146 mg/kg ΣCr; Cr(III) = 141 mg/kg], to determine the efficacy of soil washing, with (Column C), and without in situ oxidation of Cr (Column D). Column C was leached solely with background ground water as a control column, while Column D was leached with background ground water augmented with 30 mg/l of hydrogen peroxide ($H_2O_2$), in an attempt to mobilize Cr(III) by oxidizing it to Cr(VI) (Fournier and Meyer, 1985). This concentration of $H_2O_2$ was selected based on the amount of Cr(III) in Column D soil (Table 5), the pore

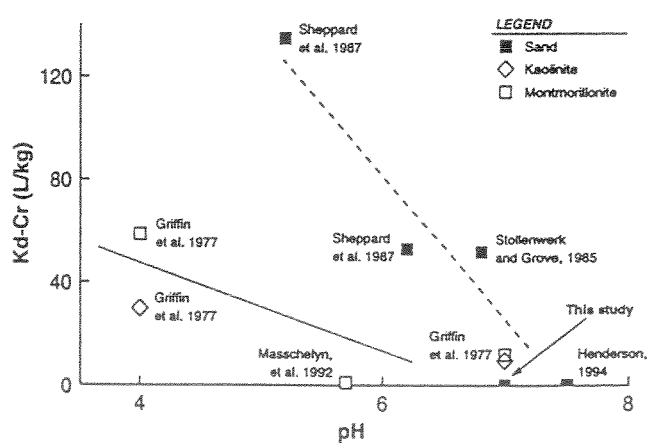


Fig. 4. Compilation of published Cr(VI) sorption data demonstrating the effect of pH and soil type on $Kd_{Cr(VI)}$. A tentatively linear relation between Kd and pH for sand (dashed line) and clays (dotted line) is shown to illustrate the trends.

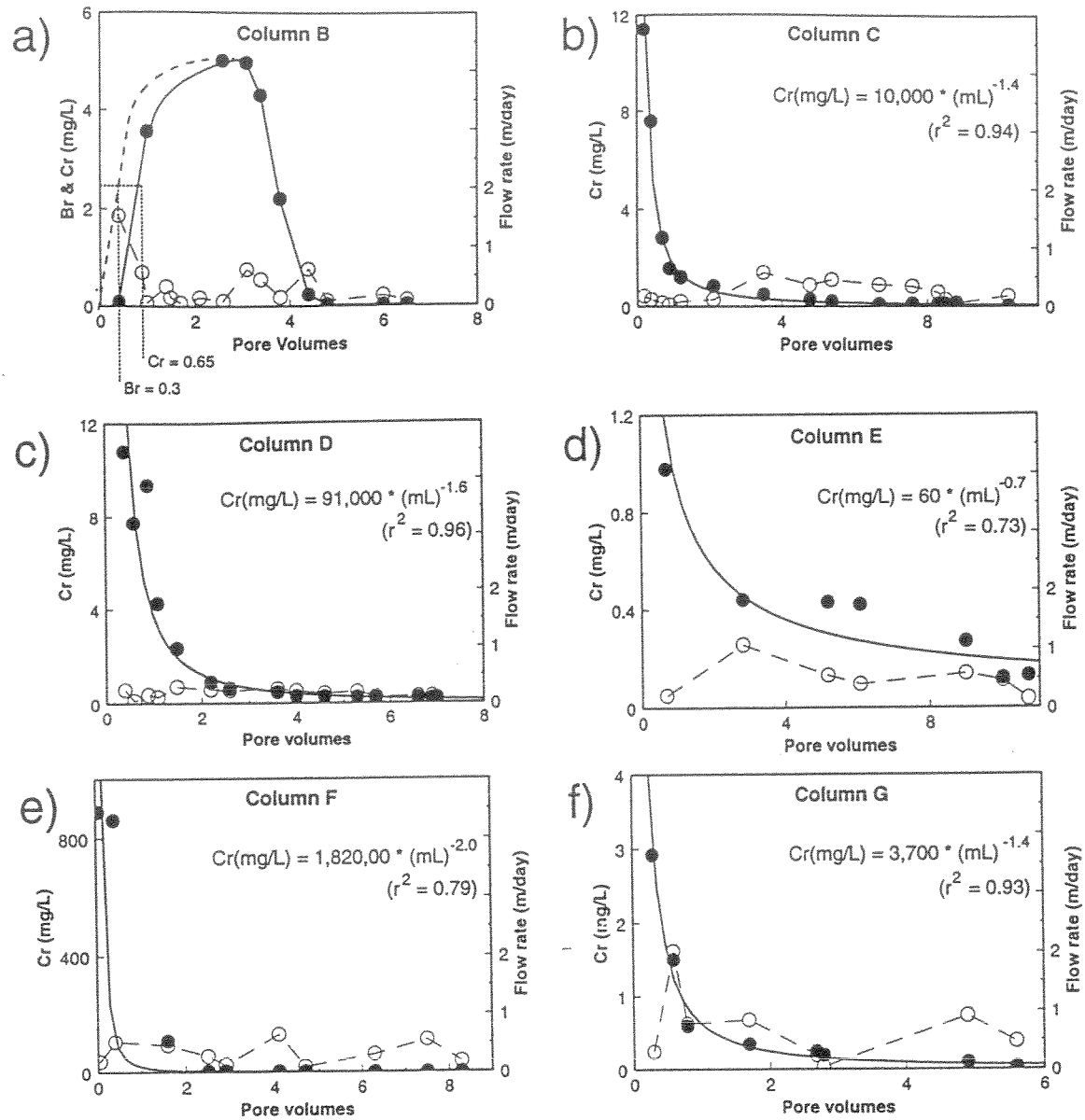


**Fig. 5. Column leachate Cr concentrations (●) and flow rates (○). Column nomenclature referenced to soil identified in Table 2. Solid line represents best-fit curve for each column, with the exception of 5a, where the curve is schematic through the data points. a): Column B, demonstrating adsorption/desorption profile for Cr(VI) and coincident Br breakthrough. Dotted lines represent $C/C_0 = 0.5$ for Br and Cr occurring at 0.3 pore volumes for Br and 0.65 pore volumes for Cr. b): Cr leachability in Column C (vadose zone soil C) in the absence of $H_2O_2$. Attainment of the MCL (0.1 mg/l) is predicted after 8 pore volumes. c): Cr leachability in Column D (vadose zone soil C) in the presence of $H_2O_2$. Attainment of the MCL is predicted after 10 pore volumes. d): Cr leachability in Column E (saturated zones soil E) with clean upgradient ground water. Attainment of the MCL predicted is after 26 pore volumes. e): Cr leachability in Column F (vadose zone soil F) with clean upgradient ground water and high soil Cr (188 mg/kg). Attainment of the MCL is predicted after 13 pore volumes. f): Cr leachability in Column G (vadose zone soil G) with clean upgradient ground water and low soil Cr (49 mg/kg). Attainment of the MCL is predicted after 4 pore volumes.**

Table 5. Column Chromium Chemistry

| *Column I.D.* | *Effluent pH range* | *Concentration total Cr (mg/kg)* | *ΣCr in soil column (mg)* | *Cr(VI) soil column (mg)* | *Cr(III) in soil column (mg)* | *% ΣCr leached* | *Cr(VI) leached (mg)* | *% Cr(VI) leached* | *Cr(III) leached (mg)* | *% Cr(III) leached* |
|---|---|---|---|---|---|---|---|---|---|---|
| A | 7.0-7.9 | 14 | 29 | 0.8 | 28.2 | <0.1 | <0.1 | <12 | <0.1 | <0.3 |
| B | 7.0-7.5 | 14 | 27 | n.c. | 27 | n.c. | n.c. | n.c. | n.c. | n.c. |
| C | 7.0-8.3 | 146 | 290 | 10 | 280 | 1.3 | 3.2 | 32 | 0.6 | 0.23 |
| D | 7.2-8.4 | 146 | 275 | 9 | 266 | 2.3 | 3.7 | 41 | 3.0 | 1.1 |
| E | 7.8-8.4 | 20 | 43 | 1.3 | 41.7 | 2.5 | 1.1 | 85 | 0.01 | 0.02 |
| F[a] | 7.7-8.6 | 188 | 187 | 157 | 30 | 83 | 154 | 98 | 0.6 | 2.0 |
| G | 7.1-7.5 | 49 | 100 | 8.6 | 91.4 | 1 | 1.0 | 12 | 0 | 0 |

[a] 15-cm column.
n.c.—Not computed, because column augmented with Cr(VI).

# ENVIRONMENTAL SOLUTIONS, INC.

By [illegible] Date 2 Apr 96 Subject Supplemental Bottom Sheet No. 1 of 10
Chkd. By EC Date 3 April 96 Fluxes and Breakthrough Times Proj. No. 95-234

## PURPOSE

Calculate leachate flux and breakthrough times for alternative lower components of the bottom composite liner, using a maximum regulatory-defined head on top of the primary (LCRS) and secondary (LDS) sumps

## APPROACH

Use the same presentation structure and assumptions, as appropriate, used in the preceding calculation of March 25, 1996 (called Addendum to Comparison of GCL+CSL and CCL). Change the head to the sum of the depths of the two sumps plus one foot as required by the Nevada Division of Environmental Protection (NDEP). This and preceding calculation both use assumptions and methods contained in Appendix I to Exhibit D of Cell 12 Design Report, Volume II, March 1996.

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# ENVIRONMENTAL SOLUTIONS, INC.

By [illegible] Date 2 Apr 96 Subject Supplemental Bottom Fluxes and Breakthrough Times Sheet No. 2 of 10
Chkd. By EC Date 3 APRIL 96 Proj. No. 95-234

ASSUMPTIONS

- Total head on the alternative lower component of the bottom composite liner equals one foot above the sumps, as required by NDEP, plus the sum of the 12 and 13 inch depths of the primary (LCRS) and secondary (LDS) sumps as shown in Attachment 1. Hence, total head = 12" + 12" + 13" = 37".
- Other assumptions are the same as in preceding calculation of March 25, 1996, except the thickness of the compacted soil layer (CSL) is doubled from 9" to 18" in the sump area as a design decision.

METHODOLOGY, GENERAL: Same as in preceding calc.

METHODS A and B " " " " "

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# ENVIRONMENTAL SOLUTIONS, INC.

By [illegible] Date 2Apr96 Subject Supplemental Bottom Sheet No. 3 of 10
Chkd. By EC Date 3April 96 Fluxes and Breakthrough Times Proj. No. 95-294

CALCULATIONS

Using Eq. 5A from the original calculation,

$$F_v = K\left(1+\frac{h}{T}\right)$$

we get

$$F_{v\,GCL/BL} = 5\times10^{-10}\,\frac{cm}{s}\left(1+\frac{39\,in.\ \frac{25.4\,mm}{in}}{7\,mm}\right)$$

$$= 7.13\times10^{-8}\ cm^3 \text{ leachate per } cm^2 \text{ sump bottom area per second}$$

Although the hydraulic conductivity of the compacted soil layer (CSL) is much greater than that of the geosynthetic clay liner (GCL),

$$K_{GCL} = 5\times10^{-10}\ cm/s \ll 10^{-5}\,\frac{cm}{s} = K_{CSL},$$

the flux through the CSL cannot exceed the flux through the GCL, hence

$$F_{v\,CSL/BL} = F_{v\,GCL/BL} = 7.13\times10^{-8}\ cm^3\,cm^{-2}\,s^{-1}.$$

$$F_{v\,CCL/BL} = 10^{-7}\,\frac{cm}{s}\left(1+\frac{39\,in\ \frac{1\,ft}{12''}}{3\,ft}\right)$$

$$= 2.08\times10^{-7}\ cm^3 \text{ leachate per } cm^2 \text{ sump floor.}$$

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# ENVIRONMENTAL SOLUTIONS, INC.

By [illegible] Date 2 Apr 96 Subject Supplemental Bottom Fluxes and Breakthrough Times Sheet No. 4 of 10
Chkd. By EC Date 3 APRIL 96 Proj. No. 95-284

CALCULATIONS (continued)

For Method A, Eq. 23 in the March 25, 1996 calculation can be used twice with two different heads $h_1$ and $h_2$ to get the following expression:

$$t_i(h_2) = \frac{F_v(h_1)}{F_v(h_2)}\, t_i(h_1) \qquad (33)$$

Using Eq. 33, we get:

$$t^A_{Cr^{+6}/GCL/BL}(h_2 = 39'') = \frac{\overbrace{2.23\times10^{-3}\ cm^3\,cm^{-2}\,s^{-1}}^{0.313}}{7.13\times10^{-3}\ \ ''}\ 2.3\ yr$$

$$= \underbrace{0.88\ yr}_{CEC_{GCL}=60\ meq/100g} \text{ to } 2.2\ yr \text{ for } CEC_{GCL} = 150\ meq/100g.$$

$$t^A_{Cr^{+3}/GCL/BL}(h_2 = 39'') = 0.313 \times 5.6\ yr$$

$$= \underbrace{1.8\ yr}_{CEC_{GCL}=60\ meq/100g} \text{ to } 4.4\ yr \text{ for } CEC_{GCL} = 150\ meq/100g.$$

$$t^A_{Cd/GCL/BL}(h_2 = 39'') = 0.313 \times 73\ yr \left(\text{for } CEC_{GCL} = 60\ \frac{meq}{100g}\right)$$

$$= 23\ yr \text{ for } CEC_{GCL} = 60\ meq/100g.$$

$$\text{to } 57\ yr \quad '' \quad '' \quad 150 \quad ''$$

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CALCULATIONS (continued)

For Method A to be applied to the CSL, Eq. 23 in the March 25, 1996 calculation must again be applied twice, but with two thicknesses $T_1$ and $T_2$ as well as two heads $h_1$ and $h_2$:

$$t_i(h_2, T_2) = \frac{T_2}{T_1} \frac{F_v(h_1)}{F_v(h_2)} t_i(h_1, T_1) \qquad (34)$$

Using Eq. 34, we get the following:

$t^A_{Cr^{+6}/CSL/BL}(h_2 = 39'', T_2 = 18'') = \frac{18}{9} \times 0.313 \times 26$ yr for $CEC_{eff} = 16 \frac{meq}{100g}$

$= 16$ yr " " "

to 36 yr " " 35 "

$t^A_{Cr^{+3}/CSL/BL}(h_2 = 39'', T_2 = 18'') = \frac{18}{9} \times 0.313 \times 52$ yr for $CEC_{eff} = 16 \frac{meq}{100g}$

$= 33$ yr " " "

to 71.2 yr. $\simeq 71$ yr " " 35 "

$t^A_{Cd/CSL/BL}(h_2 = 39'', T_2 = 18'') = \frac{18}{9} \times 0.313 \times 674$ yr for $CEC_{eff} = 16 \frac{meq}{100g}$

$= 422$ yr for " " "

to 922 " " " 35 "

For the CCL, we return to Eq. 33 to get the following:

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By [illegible] Date 2 Apr 96 Subject Supplemental Bottom Sheet No. 6 of 10
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CALCULATIONS (continued)

$$t^A_{Cr^{+6}/CCL/BL}(h_2 = 39') = \underbrace{\frac{1.33 \times 10^{-7}\ cm^3\ cm^{-2}\ s^{-1}}{2.08\ \text{"}\ \ \text{"}}}_{0.639} \times 3.8\ yr \text{ for } CEC_{CCL} = 3\ \frac{meq}{100\ g}$$

$= 2.4\ yr$ " " = " "

to $24\ yr$ " " = 30 "

$t^A_{Cr^{+3}/CCL/BL}(h_2 = 39') = 0.639 \times 7.6\ yr$ " " = 3 "

$= 4.8\ yr$ " " = " "

to $48\ yr$ " " = 30 "

$t^A_{Cd/CCL/BL}(h_2 = 39') = 0.639 \times 100\ yr$ " " = 3 "

$= 64\ yr$ " " = " "

to $640\ yr$ = 30 "

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# ENVIRONMENTAL SOLUTIONS, INC.

By [illegible] Date 2 Apr 96 Subject Supplemental Bottom Fluxes and Breakthrough Times Sheet No. 7 of 10
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CALCULATIONS (continued)

For Method B, Eq. 26 in the March 25, 1996 calculation can also be used twice with the two different heads to get the same Eqs 33 and 34. Hence,

$t^B_{Cr^{+6}/GCL/BL}(h_2 = 39") = 0.313 \times 39\ yr = 12\ yr$

$t^B_{Cr^{+3}/GCL/BL}$ " = " $\times 2377\ yr = 743\ yr$

$t^B_{Cd/GCL/BL}$ " = " $\times 7\ yr = 2\ yr$

$t^B_{Cr^{+6}/CSL/BL}$ " $= \frac{18"}{9"} \times$ " $\times 2065\ yr = 1292\ yr \simeq 1290\ yr$

$t^B_{Cr^{+3}/CSL/BL}$ " $= \frac{18"}{9"} \times$ " $\times 124{,}559\ yr = 77{,}915\ yr$

$t^B_{Cd/CSL/BL}$ " $= \frac{18"}{9"} \times$ " $\times 378\ yr = 236\ yr$

$t^B_{Cr^{+6}/CCL/BL}$ " $= 0.639 \times 1628\ yr = 1040\ yr$

$t^B_{Cr^{+3}/CCL/BL}$ " = " $\times 98{,}214\ yr = 62{,}800\ yr$

$t^B_{Cd/CCL/BL}$ " = " $\times 298\ yr = 190\ yr$

Eqs 33 & 34 can also be used for organic constituents:

$t^B_{CHCl_3/GCL/BL}(h_2 = 39") = 0.313 \times 830\ yr = 260\ yr$

$t^B_{PCE/GCL/BL}$ " = " $\times 22{,}419\ yr = 7012\ yr \simeq 7000\ yr$

$t^B_{CHCl_3/CSL/BL}$ " $= \frac{18"}{9"} \times$ " $\times 43{,}600\ yr = 27{,}273\ yr$

$t^B_{PCE/CSL/BL}$ " $= \frac{18"}{9"} \times$ " $\times 1.18 \times 10^6\ yr = 738{,}121\ yr$

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# ENVIRONMENTAL SOLUTIONS, INC.

By EJN Date 2 Apr 96 Subject Supplemental Bottom Sheet No. 8 of 10
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CALCULATIONS (continued)

$t^{B}_{CHCl_3/CCL/BL}(h_2 = 39") = 0.639 \times 5300\ yr = 3389\ yr \simeq 3400\ yr$

$t^{B}_{PCE/CCL/BL}$ " = " $\times 143{,}157\ yr = 91{,}538\ yr$
$\simeq 92{,}000\ yr$

FINDINGS AND CONCLUSIONS

The flux of water through the engineered alternative lower component of the bottom composite liner and through the MTR, where the head is 39 inches is the following:

| POSITION | LINER | WATER FLUX ($cm^3\ cm^{-2}\ s^{-1}$) |
|---|---|---|
| BOTTOM | GCL + CSL | $7.13 \times 10^{-8}$ |
| | CCL (nondesiccated) | $2.08 \times 10^{-7}$ |

The engineered alternative has a lower flux, and hence, has a demonstrated equivalency to the MTR (assumed to be nondesiccated).

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# ENVIRONMENTAL SOLUTIONS, INC.

By EJW Date 2Apr96 Subject Supplemental Bottom Fluxes and Breakthrough Times Sheet No. 9 of 10
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FINDINGS AND CONCLUSIONS (continued)

| POSITION | LINER COMPONENT | CONSTITUENT | BREAKTHROUGH TIME (yrs) (1) STEP FUNCTION METHOD A | DISTRIBUTION COEFFICIENT METHOD B |
|---|---|---|---|---|
| BOTTOM | GCL + CSL | $Cr^{+3}$ | 35 to 76 | 79,000 |
| | | $Cr^{+6}$ | 17 to 38 | 1300 |
| | | Cd | 445 to 980 | 240 |
| | | $CHCl_3$ | NA | 28,000 |
| | | PCE | NA | 750,000 |
| | CCL (non-desiccated) | $Cr^{+3}$ | 5 to 50 | 63,000 |
| | | $Cr^{+6}$ | 2.4 to 24 | 1000 |
| | | Cd | 64 to 640 | 200 |
| | | $CHCl_3$ | NA | 3,400 |
| | | PCE | NA | 92,000 |
| | CCL (desiccated) | $Cr^{+3}$ | 5 to 10 (2) | 10 (2) |
| | | $Cr^{+6}$ | 2.4 to 10 (2) | 10 (2) |
| | | Cd | 10 (2) | 10 (2) |
| | | $CHCl_3$ | NA | 10 (2) |
| | | PCE | NA | 10 (2) |

NA = Not Applicable
(1) Times are rounded.
(2) Breakthrough of desiccated CCL cannot be delayed beyond 10 years as noted in March 25, 1996 calculation.

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# ENVIRONMENTAL SOLUTIONS, INC.

By EGW Date 2Apr96 Subject Supplemental Bottom Sheet No. 10 of 10
Chkd. By EC Date 3 APRIL 96 Fluxes and Breakthrough Times Proj. No. 95-284

FINDINGS AND CONCLUSIONS (continued)

Although the unrealistically high head causes increased flux and decreased breakthrough times to be calculated, the engineered alternative lower component (GCL + 18 inch CSL) produces longer times before leachate would break through than those for the regulatory-defined MTR lower component. For Method B, the time for each constituent to break through the engineered alternative is longer than for the MTR. For Method A, the lower and upper ends of the range of times for each constituent to break through the engineered alternative lower component of the bottom composite layer are longer than the lower and upper ends of the range for the MTR CCL, respectively. Because the CCL will probably desiccate and crack within 10 years, the difference in breakthrough times would be even larger.

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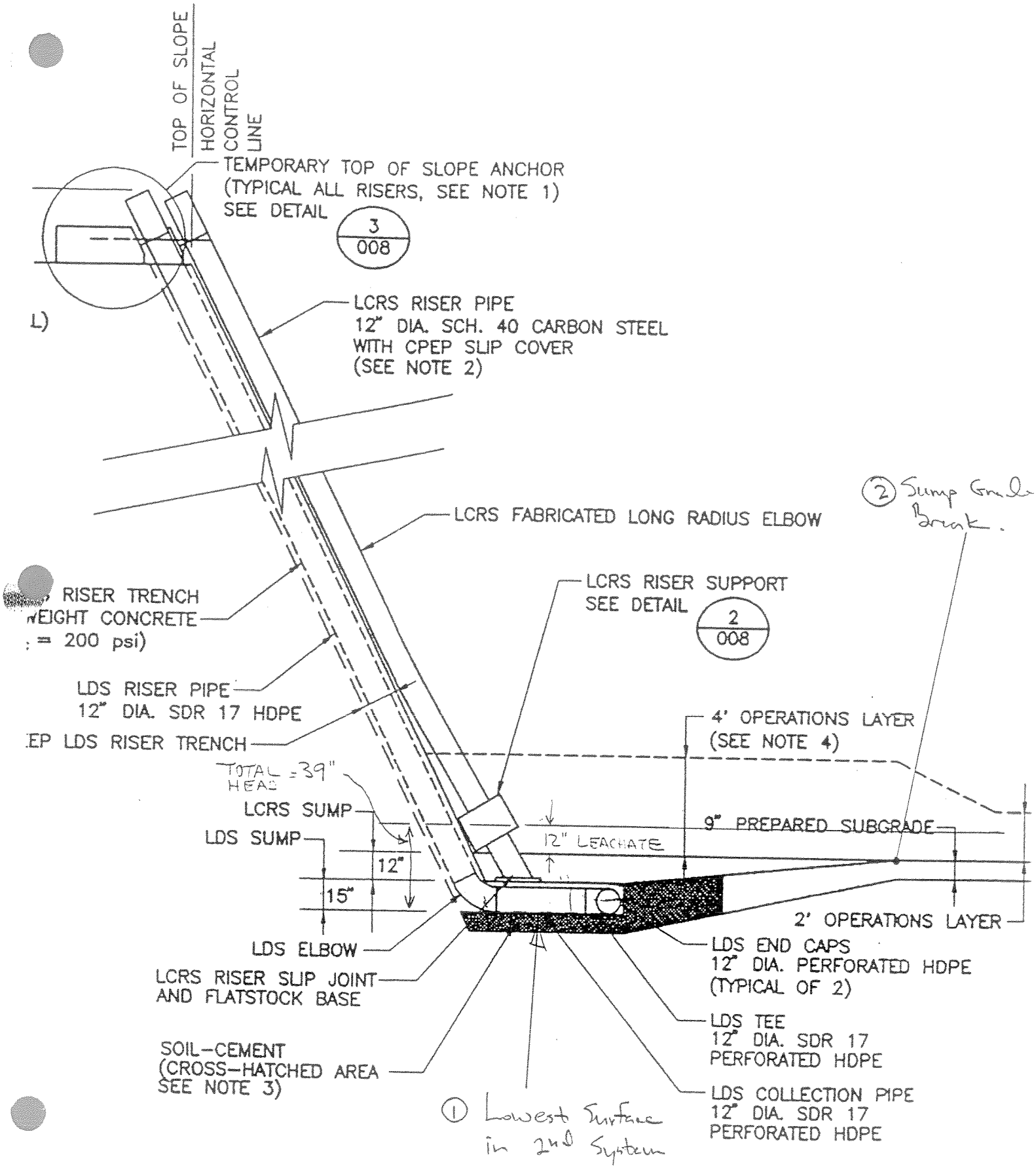
ATTACHMENT 1 Ck'd by EC 3 APRIL 96




A TYPICAL LONGITUDINAL SECTION OF SUMPS AND RISERS

ATTACHMENT 2

ERRATA
CELL 12 DESIGN REPORT, EXHIBIT D
US ECOLOGY, INC.
BEATTY, NEVADA

Please substitute the attached revised pages for their predecessors in Exhibit D of the *Cell 12 Design Report* (TRC Environmental Solutions, Inc., March 1996):

- Page D-10
- Page D-22
- Page D-38
- Page D-40
- Page D-43
- Page D-90
- Page D-108

occupied, zinc and other ionic constituents remaining in the leachate at some distance back from the leading edge can move forward, but at a velocity slower than the leachate. Method B is based on the concept of retardation of a constituent by reversible adsorption. Instead of a molecule being permanently removed from the leachate by cation exchange, the constituent molecules are temporarily adsorbed and released. The result is that the initial full constituent concentration front in the leachate becomes retarded. Instead, a gradually increasing concentration develops with distance back from the leading edge. The resulting time for breakthrough of the 50 percent concentration is calculated. Calculation results are summarized below:

| CELL LOCATION | LINER TYPE | SOLUTE CONSTITUENT | BREAKTHROUGH TIME (years) | |
|---|---|---|---|---|
| | | | Method A | Method B |
| Base | Cell 12 | Zinc | 5,000 to 11,000 | 7,900 |
| | | Chloroform | Not Applicable | 44,000 |
| | MTR (assuming undesiccated CCL) | Zinc | 100 to 1,000 | 940 |
| | | Chloroform | Not Applicable | 5,300 |
| Sideslopes | Cell 12 | Zinc | 510 to 1,400 | 180 |
| | | Chloroform | Not Applicable | 1,000 |
| | MTR (assuming undesiccated CCL) | Zinc | 230 to 2,300 | 2,200 |
| | | Chloroform | Not Applicable | 12,000 |

If the anticipated formation of desiccation cracks were to be considered for the CCL, the breakthrough times for the MTR systems would be much less than those shown in the table. For example, if a crack were to form through the clay in the 10-year period indicated by Dr. Daniel (see Section D.4.3), a direct pathway would exist. For that case, the potential breakthrough time would be only 10 years.

7. The more important data shown in the above table are the very long periods required for breakthrough to occur for the Cell 12 systems. Since these periods are much greater than the performance period, breakthrough would not occur. For this condition, the liners would have substantial reserve adsorption (or breakthrough time) capacity and therefore equivalence is demonstrated.

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By [illegible] Date 11 Dec 95 Subject COMPARISON OF GCL ± CSL AND CCL Sheet No. 7 of 32

Chkd. By TLP EC Date 1/31/96 2/APRIL 96 Proj. No. 95-284

ASSUMPTIONS (continued)

- Distribution coefficient ($K_d$) for zinc = ~~log~~ $\ln^{-1}$ 2.8 $\frac{cm^3}{g}$ = ~~6.3~~ 16.4 $cm^3/g$ (Dragun, 1988) (Attachment F)

- Octanol-water partition coefficient for chloroform (Attachment D)
  $K_{ow}$ $CHCl_3$ = $\log_{10}^{-1}$ 1.97 = 93

- Density of water ($\rho_w$) = 62.4 lb/ft$^3$

- Precipitation of inorganic constituents is neglected, even though it sometimes exceeds cation exchange retardation.

- Total porosities of GCL, CSL and CCL are taken as 0.75, 0.4 and 0.437 vol/vol according to HELP Model Version 3.04 Soil Types 17, 10 and 25 (Attachment C), reduced to 0.3, 0.2 and 0.2 vol/vol effective porosities on the recommendation of Daniel (1995) (Attachment J).

- Because of the lack of information on the quantitative partition of an organic constituent (e.g., chloroform) between adsorption on the surface of clay and remaining in solution in the leachate, the octanol-water partition coefficient is used as an indirect surrogate.



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# ENVIRONMENTAL SOLUTIONS, INC.

By [illegible] Date 8 Dec 95 Subject COMPARISON OF GCL + CSL AND CCL Sheet No. 23 of 32

Chkd. By TLP EC Date 1/31/96 2 APRIL 96 Proj. No. 95-284

SIDE-SLOPE LINER (continued)

$$t_{Zn/CCL} = \frac{\frac{3\,ft}{\cos 63.4^\circ} \times \frac{30.48\,cm}{1\,ft} \times 127\,\frac{lb\ CCL}{ft^3}\ 453.59\,\frac{g}{lb} \times \frac{1\,ft^2}{30.48^3\,cm^3}}{10^{-7}\,\frac{cm}{s}\left(\frac{4.9\times10^{-5}\,ft + 3\,ft/\cos 63.4^\circ}{3\,ft/\cos 63.4^\circ}\right) 1100\times10^{-6}\,\frac{g\ Zn}{l}\ \frac{1\,l}{10^3\,cm^3}}$$

$$\times \frac{3\times10^{-3}\,eq.\,Zn}{100\,g\ CCL} \times \frac{0.5\ g\text{-}mole\ Zn}{1\ eq.\ Zn} \times 65.37\,\frac{g\ Zn}{g\text{-}mole\ Zn} \times 0.01 \times 0.2$$

$= 7.41 \times 10^9$ sec = 235 yrs to 2349 yrs for CEC = 30 meq/100 g.

CALCULATIONS FOR ZINC USING METHOD B

BOTTOM LINER:

Use Eq. 22. For GCL,

$$t_{Zn/GCL} = \frac{7\,mm\,\frac{1\,cm}{10\,mm} \times \left\{0.3 + \frac{67\,\frac{lb}{ft^3}\,453.59\,\frac{g}{lb}}{30.48^3\,\frac{cm^3}{ft^3}}\left[\left(\cancel{\log^{-1}}\ \ln^{-1}\ 2.8\right)\frac{cm^3}{g}\right]\right\}}{5\times10^{-10}\,\frac{cm}{s}\left(\frac{0.1\,ft\ 304.8\,\frac{mm}{ft} + 7\,mm}{7\,mm}\right)}$$

$= \cancel{4.77\times10^{11}}\ 4.69\times10^9$ s $\doteq \cancel{5619}\ 149$ yr $\simeq \cancel{5600}\ 150$ yr

$$t_{Zn/CCL} = \frac{3\,ft \times 30.48\,\frac{cm}{ft}\left\{0.2 + \frac{127\,\frac{lb}{ft^3}\,453.59\,\frac{g}{lb}}{30.48^3\,\frac{cm^3}{ft^3}}\left[\left(\cancel{\log^{-1}}\ \ln^{-1}\ 2.8\right)\frac{cm^3}{g}\right]\right\}}{10^{-7}\,\frac{cm}{s}\left(\frac{0.1\,ft + 3\,ft}{3\,ft}\right)}$$

$\doteq \cancel{1.14\times10^{12}}\ 2.93\times10^{11}$ sec = $\cancel{36{,}000}$ 944 yr.

$$t_{Zn/CSL} = \frac{9\,in \times 2.54\,\frac{cm}{in}\left\{0.2 + \frac{108\,\frac{lb}{ft^3}\,453.59\,\frac{g}{lb}}{30.48^3\,\frac{cm^3}{ft^3}}\left[\left(\cancel{\log^{-1}}\ \ln^{-1}\ 2.8\right)\frac{cm^3}{g}\right]\right\}}{5\times10^{-10}\,\frac{cm}{s}\left(\frac{0.1\,ft\ 304.8\,\frac{mm}{ft} + 7\,mm}{7\,mm}\right)}$$

$= \cancel{9.32\times10^{12}}\ 2.45\times10^{11}$ s = $\cancel{296{,}000}$ 7757 yrs, which is large compared to $\cancel{5600}$ 150 yrs.

# ENVIRONMENTAL SOLUTIONS, INC.

By [illegible] Date 18 Jan 96 Subject COMPARISON OF GCL ± CSL AND CCL Sheet No. 25 of 32

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CALCULATIONS (continued)

METHOD B FOR SIDE-SLOPES

$$t_{zn/GCL} = \frac{\frac{7\,mm}{\cos 63.4^\circ} \times \frac{1\,cm}{10\,mm} \times \left(0.3 + \frac{67\,\frac{lb}{ft^3}\,453.59\,\frac{g}{lb}}{30.48^3\,\frac{cm^3}{ft^3}}\left[\left(\cancel{\log}\ \ln^{-1}\ 2.8\right)\frac{cm^3}{g}\right]\right)}{5\times10^{-9}\,\frac{cm}{s}\left(\frac{4.9\times10^{-5}\,ft\,\frac{304.8\,mm}{1\,ft} + \frac{7\,mm}{\cos 63.4^\circ}}{7\,mm/\cos 63.4^\circ}\right)}$$

$$t_{zn/GCL} = \cancel{2.12\times10^{11}}\ 5.61\times10^{9}\ sec = \cancel{6709}\ 178\ yrs \simeq \cancel{6700}\ 180\ yrs$$

For CCL on side-slopes:

$$t_{zn/CCL} = \frac{\frac{3\,ft}{\cos 63.4^\circ} \times \frac{30.48\,cm}{1\,ft}\left(0.2 + \frac{127\,\frac{lb}{ft^3}\,453.59\,\frac{g}{lb}}{30.48^3\,\frac{cm^3}{ft^3}}\left[\left(\cancel{\log}\ \ln^{-1}\ 2.8\right)\frac{cm^3}{g}\right]\right)}{10^{-7}\,\frac{cm}{s}\left(\frac{4.9\times10^{-5}\,ft + 3\,ft/\cos 63.4^\circ}{3\,ft/\cos 63.4^\circ}\right)}$$

$$t_{zn/CCL} = \cancel{2.62\times10^{12}}\ 6.37\times10^{10}\ sec = \cancel{83{,}000}\ 2179\ yrs \simeq 2180\ yr$$

For GCL and $CHCl_3$ on side-slopes:

$$t_{CHCl_3/GCL} = \frac{\frac{7\,mm}{\cos 63.4^\circ} \cdot \frac{1\,cm}{10\,mm}\left(0.3 + \frac{67\,\frac{lb}{ft^3}}{62.4\,\frac{lb}{ft^3}} \times 93\right)}{5\times10^{-9}\,\frac{cm}{s}\left(\frac{4.9\times10^{-5}\,ft\,\frac{304.8\,mm}{1\,ft} + \frac{7\,mm}{\cos 63.4^\circ}}{7\,mm/\cos 63.4^\circ}\right)}$$

$$t_{CHCl_3/GCL} = 3.12\times10^{10}\ sec = 990\ yr. \simeq 1000\ yr.$$



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# ENVIRONMENTAL SOLUTIONS, INC.

By [illegible] Date 18 Jan 96 Subject COMPARISON OF GCL + CSL AND CCL Sheet No. 28 of 32

Chkd. By TB EC Date 1/31/96 2 APRIL 96 Proj. No. 95-284

FINDINGS (continued)

| POSITION | LINER | CONSTITUENT | BREAKTHROUGH TIME (YRS) STEP-FUNCTION METHOD A | DISTRIBUTION COEFFICIENT METHOD B |
|---|---|---|---|---|
| BOTTOM | GCL + CSL | Zinc | 5,000 - 11,000 | 7,900 ~~300,000~~ |
| | | Chloroform | NA | 44,000 |
| | CCL (nondesiccated) | Zinc | 100 - 1,000 | 940 ~~36,000~~ |
| | | Chloroform | NA | 5,300 |
| SIDE-SLOPES | GCL | Zinc | 570 - 1,400 | ~~6,700~~ 180 |
| | | Chloroform | NA | 1,000 |
| | CCL (nondesiccated) | Zinc | 230 - 2,300 | 2,270 ~~83,000~~ |
| | | Chloroform | NA | 12,000 |

NA = Not applicable.

Note: Method A gives the break through time of the first constituent molecules, while Method B gives the later time when the concentration breaking through is half of the original concentration of the constituent in the leachate.

Ckd by EC 2 APRIL 96



**TABLE 4.2** Ranges for $K_d$s for Various Elements in Soils and Clays[5] (Reprinted with permission from the American Society of Agronomy, Inc., Crop Science Society of America, Inc., and the Soil Science Society of America, Inc.)

| *Element* | *Observed Range (ml/g)* | *Mean*[a] | *Standard Deviation*[b] |
|---|---|---|---|
| Ag | 10 - 1,000 | 4.7 | 1.3 |
| Am | 1.0 - 47,230 | 6.7 | 3.0 |
| As(III) | 1.0 - 8.3 | 1.2 | 0.6 |
| As(V) | 1.9 - 18 | 1.9 | 0.5 |
| Ca | 1.2 - 9.8 | 1.4 | 0.8 |
| Cd | 1.3 - 27 | 1.9 | 0.9 |
| Ce | 58 - 6,000 | 7.0 | 1.3 |
| Cm | 93 - 51,900 | 8.1 | 1.9 |
| Co | 0.2 - 3,800 | 4.0 | 2.3 |
| Cr(III) | 470 - 150,000 | 7.7 | 1.2 |
| Cr(VI) | 1.2 - 1,800 | 3.6 | 2.2 |
| Cs | 10 - 52,000 | 7.0 | 1.9 |
| Cu | 1.4 - 333 | 3.1 | 1.1 |
| Fe | 1.4 - 1,000 | 4.0 | 1.7 |
| K | 2.0 - 9.0 | 1.7 | 0.5 |
| Mg | 1.6 - 13.5 | 1.7 | 0.5 |
| Mn | 0.2 - 10,000 | 5.0 | 2.7 |
| Mo | 0.4 - 400 | 3.0 | 2.1 |
| Np | 0.2 - 929 | 2.4 | 2.3 |
| Pb | 4.5 - 7,640 | 4.6 | 1.7 |
| Po | 196 - 1,063 | 6.3 | 0.7 |
| Pu | 11 - 300,000 | 7.5 | 2.3 |
| Ru | 48 - 1,000 | 6.4 | 1.0 |
| Se(IV) | 1.2 - 8.6 | 1.0 | 0.7 |
| Sr | 0.2 - 3,300 | 3.3 | 2.0 |
| Tc | 0.003 - 0.28 | 3.4 | 1.1 |
| Th | 2,000 - 510,000 | 11.0 | 1.5 |
| U | 11 - 4,400 | 3.8 | 1.3 |
| Zn | 0.1 - 8,000 | 2.8 | 1.9 |

[a] Mean of the logarithms of the observed values.
[b] Standard deviation of the logarithms of the observed values.

For divalent cations, the order is generally[6]:

$$Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$$

In general, trivalent cations are preferentially adsorbed over divalent cations, which are preferentially adsorbed over monovalent cations.

A further analysis of the information presented in Table 4.2 will reveal that the $K_d$s measured for an individual element in soils can vary substantially; for example, the ranges of $K_d$s for Pu and Zn span four orders of magnitude. Because the magnitude of the $K_d$ is dependent upon the size and charge of the cation and upon those soil properties governing the ex-

# ENVIRONMENTAL SOLUTIONS, INC.

By [illegible] Date 5 Mar 96 18 Jan 96 Subject COMPARISON OF GCL + CSL AND CCL Sheet No. ~~28~~ 10 of ~~32~~ 10

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FINDINGS ~~(continued)~~

| POSITION | LINER | CONSTITUENT | BREAKTHROUGH TIME (YRS) STEP-FUNCTION THEORY A | BREAKTHROUGH TIME (YRS) DISTRIBUTION COEFFICIENT THEORY B | LEAKAGE |
|---|---|---|---|---|---|
| BOTTOM | GCL + CSL | Zinc | 5,000 - 11,000 | ~~300,000~~ 7,900 | 56 |
| | | Chloroform | NA | 44,000 | |
| | CCL (nondesiccated) | Zinc | 100-1,000 | ~~36,000~~ 940 | 6 |
| | | Chloroform | NA | 5,300 | |
| SIDE-SLOPES | GCL | Zinc | 200-500 | ~~2,300~~ 180 | 1 |
| | | Chloroform | NA | 340 | |
| | CCL (nondesiccated) | Zinc | 230-2,300 | ~~82,000~~ 2,200 | 13 |
| | | Chloroform | NA | 12,000 | |

NA = Not applicable.

volume of Column D (Table 4), the estimated total amount of influent (14 pore volumes), and the stoichiometry of the reaction between Cr(III) and $H_2O_2$, i.e.:

$$3H_2O_2 + 2Cr^{+3} + 2H_2O \rightleftarrows 2HCrO_4^- + 8H^+ \quad (8)$$

Effluents from both columns initially contained Cr concentrations > 10 mg/l (Figure 5b, c), which decreased rapidly during addition of the first two pore volumes of water. Calculation of mass removal of Cr demonstrated that the addition of $H_2O_2$ doubled the total Cr leached from the soil (6.7 mg ΣCr from Column D), when compared to the 3.8 mg ΣCr extracted from Column C (Table 5). However, although $H_2O_2$ application resulted in increased removal of Cr from the soil, only 2.3% of ΣCr could be leached under the conditions of this experiment.

Soil E (20 mg/kg ΣCr), obtained from the saturated zone at 8 m below ground surface, was leached with background ground water to simulate the desorption or dissolution of Cr under a pump-and-treat scenario. Based on the low $Kd_{Cr}$ determined from the batch test, pump-and-treat was anticipated to be a reasonable alternative to remediate Cr-contaminated aquifer material at the site. Effluent contained Cr(VI) only, initially > 1.0 mg/l (Figure 5d), decreasing to 0.12 mg/l after 10 pore volumes, but remaining above the maximum contaminant level (MCL) of 0.1 mg/l. The slow release of Cr(VI) was probably due to a combination of slow dissolution kinetics of Cr-bearing phases [e.g., $BaCrO_4$ or $Cr_{0.25}Fe_{0.75}Fe(OH)_3$, depending on the soil-Cr valence], and diffusion of Cr residual in dead-end pore space (Szecsody and Bales, 1989). The Column E data suggest that nonaugmented pump-and-treat techniques are not a viable aquifer remediation strategy when Cr(III) is the predominant redox species, consistent with recent field experiences (U.S. EPA, 1993; Nikolaidis et al., 1994).

Columns F (188 mg/kg ΣCr) and G (49 mg/kg ΣCr) simulated washing of contaminated soils that contained medium to high Cr concentrations and different Cr(III): Cr(VI) soil ratios with clean ground water. The effluent from Column F [84% Cr(VI) in soil] initially contained 878 mg/l of Cr(VI), decreasing to 3.2 mg/l Cr(VI) during the first 2.5 pore volumes, and to 0.06 mg/l after 8 pore volumes (Figure 5e). Column G [in which soil Cr was 9% Cr(VI)] initially leached 2.9 mg/l Cr(VI), diminishing rapidly to 0.04 mg/l Cr(VI) after 5 pore volumes (Figure 5f). Cr(III) was absent in both column effluents. Column F [84% Cr(VI) in soil] released more Cr mass (83%) than Column C (1.3%) and Column G (1%), which contained 3.4% and 8.6% soil Cr(VI), respectively, consistent with the hypothesis that Cr(VI) leaches more readily than Cr(III). These results suggest that when Cr(VI) contamination predominates, in situ flushing or ex situ soil washing may be viable remedial strategies.

A comparison of the mass and percent of Cr(III) and Cr(VI) leached from each column demonstrates that the leached Cr mass was less than the mass of ΣCr initially present in the soil, but similar to the mass of Cr(VI) in the soil (Figure 6). For example, in Column F, ΣCr in the soil was 187 mg, of which 157 mg was Cr(VI) and 30 mg Cr(III). 154 mg of Cr(VI) was collected in Column F effluent, representing 98% recovery of the soil Cr(VI), while only 0.6 mg Cr(III), representing 2% of the soil Cr(III) was leached. In Column C (soil C), where ΣCr in soil was 290 mg [10 mg as Cr(VI), 3.8 mg ΣCr [85% as Cr(VI) was leached (Table 5). However, on addition of $H_2O_2$ to Column D (soil C), 6.7 mg ΣCr [55% of which was Cr(VI)] was leached, out of 9 mg Cr(VI) and 275 mg ΣCr in the soil (Figure 6). Columns C and D were the only columns in which Cr(III) was present in the effluent, possibly due to the relatively high Cr(III) concentration in soil C (141 mg/kg) compared to the other soils (Table 2). Finally, in Column E, Cr(VI) constituted an analyzed mass of 1.3 mg in the soil, with 1.1 mg as Cr(VI) leached, out of 43 mg ΣCr.

These data suggest that, despite recent concerns over the analytical protocol used to differentiate between Cr(III) and Cr(VI), for these soils, the method appeared to accurately distinguish between Cr redox species, because the masses of Cr(III) and Cr(VI) measured using the 3060/7196 method in the soil were consistent with those measured in the leachate using method 7196 alone. In columns containing predominantly Cr(III) that were not augmented by additives in the influent (i.e., Columns A, C, E, and G), < 0.1%, 1.3%, 2.5%, and 1%, respectively, of ΣCr was leached, while in soil bearing primarily Cr(VI) (i.e., Column F), 83% of ΣCr was leached. Cr(VI) readily dissolved or desorbed from contaminated soils, while Cr(III) occurred in a predominantly nonleachable form.

Cr in column effluent was predominantly Cr(VI), decreasing with successive pore volumes below the MCL (0.1 mg/l) in Columns C, F, and G. However, Cr concentrations in leachate from Columns D (0.18 mg/l) and E (0.12 mg/l) decreased asymptotically, remaining above the MCL after 11 and 7 pore volumes, respectively. To determine when the MCL would be attained in Columns D and E, a

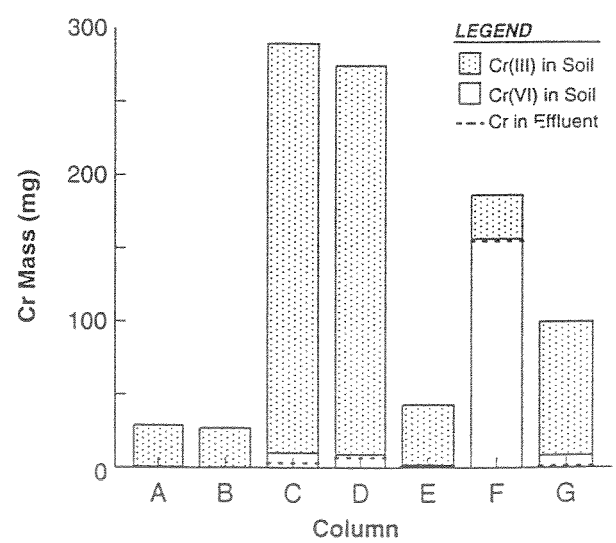


**Fig. 6. Mass of Cr leached from each column in comparison to Cr(III) and Cr(VI) mass in soil. The mass of Cr leached appears to be constrained by the proportion of Cr(VI) in the soil, suggesting that Cr(III) occurs in a refractory, nonleachable form in the other columns.**

curve-fitting program (Cox, 1984) was used. A hyperbolic function best described Cr column effluent concentrations, with the MCL predicted to be reached in leachate after 8, 10, 26, 13, and 4 pore volumes in Columns C, D, E, F, and G, respectively.

### *Batch Fixation Test*

At a Cr:Fe ratio of 1:4, soluble Cr in the supernatant was 0.02 mg/l, while the 1:47 Cr:Fe ratio produced a solution in which both Cr(VI) and Cr(III) were below the method detection limit (i.e., $<0.01$ mg/l). The higher Cr:Fe ratio (1:4) resulted in detectable Cr in solution, probably because of insufficient Fe to sequester all available Cr. At the lower Cr:Fe ratio (1:47), Fe swamped available Cr, resulting in below-detection-limit concentrations in solution. Both solutions fall in the domain controlled by $Fe_{0.75}Cr_{0.25}(OH)_3$ on a Cr Eh-pH diagram, where $\Sigma Fe = 10^{-3}$ molal (Figure 2). This theoretical model agreed with the visual observations (fine brown amorphous floc precipitating after addition of $FeCl_2$), the analytical results (low supernatant Cr concentration), and the measured postreaction Eh and pH, which fall within the $Cr_{0.25}Fe_{0.75}Fe(OH)_3$ domain (Figure 2).

These data are consistent with the observations of Schroeder and Lee (1975), who found that Cr(VI) was reduced to Cr(III) by Fe(II), and that amorphous ferric hydroxide fixed 90 to 99% of Cr(III) from the water phase, and with Stollenwork and Grove (1985), who demonstrated that Cr(III) or Cr(VI) in soils can react with water-soluble Fe to form a mixed hydrous Fe(III) and Cr(III) oxide mineral. Our results are also in agreement with James (1994), who demonstrated that $Fe^{+2}$ reduced soluble Cr in Cr(VI)-contaminated soil, and with the experimental data of Schwertmann et al. (1989), who demonstrated a 10 mol% Cr-for-Fe substitution in freshly precipitated goethites.

## Conclusions

In this study, the correlation between Cr(VI) soil concentrations and the mass of Cr(VI) leached from soil columns over a range of Cr(III):Cr(VI) ratios resulted in good agreement between the mass of Cr redox species in soils, and their mass in column leachate. Despite the low $Kd_{Cr(VI)}$ (0.2 liters/kg) measured for these soils, a series of batch and column tests demonstrated that pump-and-treat would require up to 26 pore volumes to reach the Cr MCL (0.1 mg/l), while $H_2O_2$ added to the influent increased the amount of leachable Cr, but reduced $\Sigma$Cr soil mass by only 2.3%. However, tests to assess in situ fixation of Cr in soils using $Fe^{+2}$ resulted in low Cr solubilities ($<$ 0.01 mg/l) probably due to precipitation of $Fe_xCr_{1-x}(OH)_3$.

Based on the results of this study, further research is warranted to evaluate in situ soil flushing in the vadose zone, ex situ soil washing, and in situ precipitation of Cr in contaminated soils and ground water. However, determination of optimal pH, additive ratio, and exact stoichiometry of the precipitating phase remain as important research topics for the in situ alternative prior to pilot-scale implementation.

## Acknowledgments

The authors thank Mohsen Mehran for providing the samples, Rick Chappell (laboratory assistance), Rick Nelson (editing), Wendy Hawkins (graphics), and Barbara Kyvik (word processing). We appreciate the thorough reviews provided by three anonymous reviewers, which led to substantial improvements to an earlier version of this paper. One of us (A.D.) appreciates the support provided by Kathy Davis.

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ATTACHMENT A.C

TRC ENVIRONMENTAL SOLUTIONS, INC.

# RECORD OF TELEPHONE CONVERSATION

| | | | |
|---|---|---|---|
| | INCOMING CALL | X | OUTGOING CALL |
| CONTACT INFO* | Jim Hancock | STAFF INFO | Chris Hansen CWH |
| TELEPHONE NO | 702/553-2203 | DATE | 22Mar96 |
| COMPANY NAME | US Ecology, Inc. | TIME | 11:45 a.m. |
| COMPANY ADDRESS | | PROJECT NO | 95-284 |
| | Beatty, NV | PROJECT NAME | AEC Beatty Cell 12 |
| | | PAGE | 1 of |

SUBJECT Representative Leachate for use in Cell 12 MTR-Equivalency Calculations

I called Jim Hancock to get some clarification on the design constituents in leachate which should be used for the Cell 12 MTR-equivalency solute breakthrough calculations. This followed a facsimile from and a telephone conversation with Zaki Naser (also of USE) yesterday afternoon, in which he stated that Cathe Pool of NDEP had requested that more concentrated leachate be used in the calculations. She had apparently sent Zaki the organics analyses summary which he then forwarded here (copy attached). After my telephone conversation with Zaki, Jim provided a metals analyses summary (copy also attached). Zaki explained that "C" sumps represent Cell 11 primary system sumps, and "D" sumps represent Cell 11 secondary system sumps. Key points of my conversation with Jim are summarized below:

- Jim checked the first five columns of the organics analyses summary sent by NDEP, and they were correct. He is comfortable that the summary is likely accurate.
- Some of the metals analyses results sent via facsimile were difficult to discern, which were clarified as shown by me on the attached Table 1.
- Samples were obtained during each sampling event from sumps which had adequate leachate volume. This explains the variability in sample points per event. Points not shown on the analyses summaries can be assumed to have been dry for the particular event. Note that organics and metals analyses were performed on different frequencies.
- The metals data was supplied only for Arsenic, Cadmium and Chromium because these are considered by USE to be the most toxic of the metals found in Cell 11 leachate. However, toxicity is not an issue for the MTR-equivalency calculations. Other than for Barium, which is naturally occurring in local soils, none of the other metals have concentrations which are substantially higher than As, Cd and Cr.
- The summarized data should be considered to be representative of Cell 11 leachate. Although there is additional data from earlier years, those data show the leachate to be generally less concentrated than in recent years. The recent years reflect an additional volume of waste in the cell. In addition, last year had above-average rainfall, on the order of 5 or 6 inches, which should result in a better leach path, more sample points and a potential larger volume of liquid in collected samples.

Attachments

*Recommended Calling

ACTION REQUIRED

cc: SMB EGW CWH Sb

# US ECOLOGY, INC.

**Beatty, NV**

## FAX...FAX...FAX...FAX...FAX...FAX

TO: Scott Brown

DATE: 3/21/96

FROM: Zaki Naser

PAGES: ~~3~~ 4
(Includes cover sheet)

MESSAGE:

TELEPHONE: 702-553-2203

FAX: 702-553-2742

US ECOLOGY LEACHATE DATA

| SUMP | D4 | D4 | C4 | D4 | D4 | C4 | D4 | D4 | C4 | C4 | D4 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| DATE SAMPLED | Sep-94 | Sep-94 | Oct-94 | Jan-95 | Jan-95 | Jan-95 | Mar-95 | Mar-95 | May-95 | Jun-95 | Jun-95 |
| PARAMETER | UG/L | UG/L | UG/L | UG/L | UG/L | UG/L | UG/L | UG/L | UG/L | UG/L | UG/L |
| METHYLENE CHLORIDE | 53 | 510 | 230 | 74 | | | | 180 | 110 | 61 | <100 |
| 1,1-DICHLOROETHANE | 24 | 48 | 180 | 36 | 35 | 86 | 130 | 130 | 130 | 140 | 160 |
| CHLOROFORM | 850 | 63 | 1100 | 580 | 600 | 2400 | | 2300 | 890 | 780 | 3500 |
| 1,1,1-TRICHLOROETHANE | 31 | 20 | 210 | 38 | 43 | 68 | 110 | 85 | 170 | 180 | 120 |
| CARBON TETRACHLORIDE | 11 | | | ND | | 39 | | 28 | <5 | <5 | 41 |
| TRICHLOROETHENE | 27 | 34 | 33 | 25 | 24 | 76 | 79 | 98 | 53 | 54 | 110 |
| TETRACHLOROETHENE | 340 | 310 | 84 | 130 | 140 | 96 | 52 | 64 | 28 | 28 | 66 |
| 1,1-DICHLOROETHENE | | 12 | | 11 | | | | | | 19 | <20 |
| CIS-1,2-DICHLOROETHENE | | 15 | | | | | | | 16 | 16 | <20 |
| ACETONE | | | | 640 | | | | | | 95 | <200 |
| 4-METHYLPHENOL | | | | | | | | 13 | | | |
| BENZENE | | | | | | | | | | | |
| 1,2-DICHLOROPROPANE | | | | | | | | | | | |
| CARBON DISULFIDE | | | | | | | | | | | |
| BROMODICHOROMETHANE | | | | | | | | | | | |
| TOLULENE | | | | | | | | | | | |
| AROCLOR-1254 | | | | | | | | | | | |
| AROCLOR-1260 | | | | | | | | | | | |
| 2,4-D | | | | | | | | | | | |
| DINOSEB | | | | | | | | | | | |
| MIBK(4-METHYL2-PENTANONE) | | | | | | | | | | | |
| DICAMBA | | | | | | | | | | | |
| 1,2,4-TRICHLOROBENZENE | | | | | | | | | | | |
| PHENOL | | | | | | | | | | | |
| MEK | | | | | | | | | | | |

US ECOLOGY LEACHATE DATA

| SUMP | C3 | D3 | C4 | D4 | C4 | C3 | D4 | C3 | C3 | D4 | C4 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| DATE SAMPLED | May-95 | JULY-95 | JULY-95 | JULY-95 | Aug-95 | Aug-95 | Aug-95 | Sep-95 | Sep-95 | Sep-95 | Sep-95 |
| PARAMETER | UG/L | UG/L | UG/L | UG/L | UG/L | UG/L | UG/L | UG/L | UG/L | UG/L | UG/L |
| METHYLENE CHLORIDE | 1200 | 1200 | 78 | | 45 | | 180 | 49 | 140 | 160(ATI) | |
| 1,1-DICHLOROETHANE | 550 | 400 | | 160 | 140 | | 130 | 130 | 120 | 44(ATI) | 130 |
| CHLOROFORM | 6100 | 7900 | 690 | 3700 | 550 | | 2600 | 900 | 360 | 800(ATI) | 460 |
| 1,1,1-TRICHLOROETHANE | | | 170 | | 93 | | 92 | | 82 | 35(ATI) | 80 |
| CARBON TETRACHLORIDE | | | | 28 | | | | 6 | | | |
| TRICHLOROETHENE | 470 | 480 | 54 | 93 | 25 | 260 | 89 | 260 | 240 | 43(ATI) | 36 |
| TETRACHLOROETHENE | 28000 | 29000 | 37 | 56 | 17 | 20000 | 39 | 13000 | 12000 | 27(ATI) | 14 |
| 1,1-DICHLOROETHENE | | | 15 | 29 | | | | 9 | | | |
| CIS-1,2-DICHLOROETHENE | 830 | 960 | 38 | | | | | 570 | | | 17 |
| ACETONE | | | 77 | | 470 | | | | | 10(ATI) | 410 |
| 4-METHYLPHENOL | | | | | | | | | | | |
| BENZENE | 230 | <200 | | | | | | 15 | | | |
| 1,2-DICHLOROPROPANE | 460 | 720 | | | | | | 21 | | | |
| CARBON DISULFIDE | | | | | | | | | | | |
| BROMODICHOROMETHANE | | | | | | | | | | | |
| TOLUILENE | 410 | <400 | 17 | | | | | 49 | | | |
| AROCLOR-1254 | | | | | | | | | | | |
| AROCLOR-1260 | | | | | 370 | | | | | 2.1 | |
| 2,4-D | | | | | 6.4 | | | | | | |
| DINOSEB | | | | | | 37 | | | | | |
| MIBK(4-METHYL2-PENTANONE) | | | | | 190 | | | | | | 160 |
| DICAMBA | | | | | | | | | | 1.6 | |
| 1,2,4-TRICHLOROBENZENE | | | | | | | | | | | |
| PHENOL | | | | | | | | | | | |
| MEK | | | | | 800 | | | | | | 390 |

US ECOLOGY LEACHATE DATA

| SAMP | C4(ATI) | C4(SPL) | C3(SPL) | D4 | C3 | C4 | C4 |
|---|---|---|---|---|---|---|---|
| DATE SAMPLED | Sep-95 | Oct-95 | Oct-95 | Nov-95 | Nov-95 | Nov-95 | Dec-95 |
| PARAMETER | UG/L | UG/L | UG/L | UG/L | UG/L | UG/L | UG/L |
| METHYLENE CHLORIDE | 180 | 49 | 51 | 170 | 41 | 45 | 32 |
| 1,1-DICHLOROETHANE | 130 | 330 | 140 | 19 | 100 | 350 | 310 |
| CHLOROFORM | 2600 | 1200 | 320 | 300 | 300 | 1600 | 1000 |
| 1,1,1-TRICHLOROETHANE | 92 | 230 | | | | 130 | 160 |
| CARBON TETRACHLORIDE | | | 7 | | | | |
| TRICHLOROETHENE | 89 | 74 | 380 | 21 | 160 | 55 | 75 |
| TETRACHLOROETHENE | 39 | 28 | 19000 | 13 | 8800 | 19 | 28 |
| 1,1-DICHLOROETHENE | | 19 | 8 | 7 | 5 | 14 | 21 |
| CIS-1,2-DICHLOROETHENE | | 33 | 520 | | 420 | 31 | 33 |
| ACETONE | | 220 | | | | 150 | |
| 4-METHYLPHENOL | | | | | | 140 | 62 |
| BENZENE | | | 18 | | | 9 | 6 |
| 1,2-DICHLOROPROPANE | | | 21 | | | | |
| CARBON DISULFIDE | | 6 | | | | 13 | |
| BROMODICHOROMETHANE | | 8 | | | | | |
| TOLULENE | | 6 | 43 | | 13 | 6 | 5 |
| AROCLOR-1254 | 5.6 | | | | | | |
| AROCLOR-1260 | 17 | 91 | | | | 260 | |
| 2,4-D | 11 | | | | | | |
| DINOSEB | | | | | | | |
| MIBK(4-METHYL2-PENTANONE) | | 260 | | | | 280 | 120 |
| DICAMBA | | | | | | | |
| 1,2,4-TRICHLOROBENZENE | | 540 | | | | 510 | 400 |
| PHENOL | | 1400 | | | | 860 | 930 |
| MEK | | 410 | | 250 | | 360 | |

# US ECOLOGY, INC.

**Beatty, NV**

## FAX....FAX....FAX....FAX....FAX....FAX

TO: Chris Hancock

DATE: 3-22-96

FROM: Jim Hancock

PAGES: 2
(Includes cover sheet)

MESSAGE: Please find your requested information
If you have any questions please call Zahi
or myself — Thank you.

TELEPHONE: 702-553-2203 FAX: 702-553-2742

1996 MARCH FRIDAY 22

| DAT | Monitor Wells | Arsenic | Cadmium | Chromium |
|---|---|---|---|---|
| ~~JAN 94~~ Dec | MG/L | 0.017 | 0.0262 | 0.03 |
| March | 94-D-4 | 0.024 | .0074 | ND |
| June | 94-D4 | .017 | .0051 | ND |
| Sept | 94-D4 | .010 | .0031 | ND |
| JAN | 95-D4 | .014 | .0014 | ND |
| April | 95 D4 | ND | .0028 | 0.03 |
| ~~OCT~~ Sept | 95 C3 | 0.2 | 1.5 | 12/1 |
| ~~OCT 95~~ | ~~C4~~ | 0.19/0.05 | 1.1 | 5.5/0.4 |
| OCT | 95 C3 | 0.16/.05 | .0024/.0001 | 0.019/.002 |
| JAN | 96 C3 | 0.16/.05 | | |
| FEB | 96 C4 | 0.23/.05 | .012/.004 | .04/0.01 |

| EXPENSE | AMOUNT |
|---|---|
| | |

FEBRUARY

| S | M | T | W | T | F | S |
|---|---|---|---|---|---|---|
| | | | | 1 | 2 | 3 |
| 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| 11 | 12 | 13 | 14 | 15 | 16 | 17 |
| 18 | 19 | 20 | 21 | 22 | 23 | 24 |
| 25 | 26 | 27 | 28 | 29 | | |

MARCH

| S | M | T | W | T | F | S |
|---|---|---|---|---|---|---|
| | | | | | 1 | 2 |
| 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| 10 | 11 | 12 | 13 | 14 | 15 | 16 |
| 17 | 18 | 19 | 20 | 21 | 22 | 23 |
| 24 | 25 | 26 | 27 | 28 | 29 | 30 |
| 31 | | | | | | |

APRIL

| S | M | T | W | T | F | S |
|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 |
| 7 | 8 | 9 | 10 | 11 | 12 | 13 |
| 14 | 15 | 16 | 17 | 18 | 19 | 20 |
| 21 | 22 | 23 | 24 | 25 | 26 | 27 |
| 28 | 29 | 30 | | | | |

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# TRC ENVIRONMENTAL SOLUTIONS, INC.

By CWH Date 22Mar96 Subject _____ Sheet No. 1 of 1

Chkd. By ____ Date ____ Proj. No. 95-284

TABLE 1

SELECTED METALS ANALYSIS IN CELL 11 LEACHATE (1)
US ECOLOGY, INC.
BEATTY, NEVADA

| DATE | SUMP | LEACHATE ANALYSIS (mg/L) (2) | | | | | |
|---|---|---|---|---|---|---|---|
| | | Arsenic | | Cadmium | | Chromium (Total) | |
| | | Results | MDL | Results | MDL | Results | MDL |
| Jan94 | D4 | 0.017 | -- | 0.0262 | -- | 0.03 | -- |
| Mar94 | D4 | 0.024 | -- | 0.0074 | -- | ND | -- |
| Jun94 | D4 | 0.017 | -- | 0.0051 | -- | ND | -- |
| Sep94 | D4 | 0.010 | -- | 0.0031 | -- | ND | -- |
| Jan95 | D4 | 0.014 | -- | 0.0014 | -- | ND | -- |
| Aug95 | D4 | ND | -- | 0.0028 | -- | 0.03 | -- |
| Sep95 | C3 | 0.2 | -- | 1.5 | -- | 12 | 1 |
| Sep95 | C4 | 0.19 | 0.05 | 1.1 | -- | 5.5 | 0.4 |
| Oct95 | C3 | 0.16 | 0.05 | 0.0024 | 0.0001 | 0.019 | 0.002 |
| Jan96 | C3 | 0.16 | 0.05 | -- | -- | -- | -- |
| Feb96 | C4 | 0.23 | 0.05 | 0.012 | 0.001 | 0.04 | 0.01 |

MDL = Method Detection Limit
ND = Not Detected
-- = Not Analyzed or Not Provided

(1) Based on a facsimile dated 22Mar96 from Jim Hancock of US Ecology, Inc. to Chris Hansen of TRC Environmental Solutions, Inc., as clarified by a telephone conversation of that same date.
(2) Analyses through Aug95 by ATI in San Diego, and from Sep95 forward by STL in Houston.

ATTACHMENT A.D

# THE SOIL CHEMISTRY OF HAZARDOUS MATERIALS

James Dragun, Ph.D.

PROPERTY OF
ENVIRONMENTAL SOLUTIONS, INC.
c.2

Hazardous Materials Control Research Institute
Silver Spring, Maryland

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9300 Columbia Boulevard
Silver Spring, Maryland 20910

**TABLE 4.2** Ranges for $K_d$s for Various Elements in Soils and Clays[5] (Reprinted with permission from the American Society of Agronomy, Inc., Crop Science Society of America, Inc., and the Soil Science Society of America, Inc.)

| *Element* | *Observed Range (ml/g)* | *Mean*[a] | *Standard Deviation*[b] |
|---|---|---|---|
| Ag | 10 - 1,000 | 4.7 | 1.3 |
| Am | 1.0 - 47,230 | 6.7 | 3.0 |
| As(III) | 1.0 - 8.3 | 1.2 | 0.6 |
| As(V) | 1.9 - 18 | 1.9 | 0.5 |
| Ca | 1.2 - 9.8 | 1.4 | 0.8 |
| Cd | 1.3 - 27 | 1.9 | 0.9 |
| Ce | 58 - 6,000 | 7.0 | 1.3 |
| Cm | 93 - 51,900 | 8.1 | 1.9 |
| Co | 0.2 - 3,800 | 4.0 | 2.3 |
| Cr(III) | 470 - 150,000 | 7.7 | 1.2 |
| Cr(VI) | 1.2 - 1,800 | 3.6 | 2.2 |
| Cs | 10 - 52,000 | 7.0 | 1.9 |
| Cu | 1.4 - 333 | 3.1 | 1.1 |
| Fe | 1.4 - 1,000 | 4.0 | 1.7 |
| K | 2.0 - 9.0 | 1.7 | 0.5 |
| Mg | 1.6 - 13.5 | 1.7 | 0.5 |
| Mn | 0.2 - 10,000 | 5.0 | 2.7 |
| Mo | 0.4 - 400 | 3.0 | 2.1 |
| Np | 0.2 - 929 | 2.4 | 2.3 |
| Pb | 4.5 - 7,640 | 4.6 | 1.7 |
| Po | 196 - 1,063 | 6.3 | 0.7 |
| Pu | 11 - 300,000 | 7.5 | 2.3 |
| Ru | 48 - 1,000 | 6.4 | 1.0 |
| Se(IV) | 1.2 - 8.6 | 1.0 | 0.7 |
| Sr | 0.2 - 3,300 | 3.3 | 2.0 |
| Tc | 0.003 - 0.28 | 3.4 | 1.1 |
| Th | 2,000 - 510,000 | 11.0 | 1.5 |
| U | 11 - 4,400 | 3.8 | 1.3 |
| Zn | 0.1 - 8,000 | 2.8 | 1.9 |

[a] Mean of the logarithms of the observed values.
[b] Standard deviation of the logarithms of the observed values.

$\ln^{-1} 1.9 = e^{1.9} = 6.7$

$\ln^{-1} 7.7 = 2208$

$\ln^{-1} 3.6 = 36.6$

$\ln K_d(Zn) = 2.8$

$K_d(Zn) = \ln^{-1} 2.8 = 16.4 \text{ cm g}^{-1}$

For divalent cations, the order is generally[6]:

$$Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$$

In general, trivalent cations are preferentially adsorbed over divalent cations, which are preferentially adsorbed over monovalent cations.

A further analysis of the information presented in Table 4.2 will reveal that the $K_d$s measured for an individual element in soils can vary substantially; for example, the ranges of $K_d$s for Pu and Zn span four orders of magnitude. Because the magnitude of the $K_d$ is dependent upon the size and charge of the cation and upon those soil properties governing the ex-

ATTACHMENT A.E

Volume II
Solvents

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# Handbook of Environmental FATE and EXPOSURE DATA

## For Organic Chemicals


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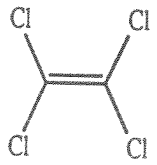
# Tetrachloroethylene

## SUBSTANCE IDENTIFICATION

**Synonyms:**

**Structure:**




**CAS Registry Number:** 127-18-4

**Molecular Formula:** $C_2Cl_4$

**Wiswesser Line Notation:** GYGUYGG

## CHEMICAL AND PHYSICAL PROPERTIES

**Boiling Point:** 121 °C at 760 mm Hg

**Melting Point:** -19 °C

**Molecular Weight:** 165.82

**Dissociation Constants:**

**Log Octanol/Water Partition Coefficient:** 3.40 [37]

**Water Solubility:** 1503 mg/L at 25 °C [41]

**Vapor Pressure:** 18.49 mm Hg at 25 °C [20]

**Henry's Law Constant:** $1.49 \times 10^{-2}$ atm-m$^3$/mole [75]

## ENVIRONMENTAL FATE/EXPOSURE POTENTIAL

**Summary:** Tetrachloroethylene (PCE) is likely to enter the environment by fugitive air emissions from dry cleaning and metal degreasing industries and by spills or accidental releases to air, soil, or water. If