Chromium (Cr$^{3+}$) Leachability from Monolithic Solids under Modified Semi-Dynamic Leaching Conditions

Deok Hyun Moon and Dimitris Dermatas

W. M. Keck Geoenvironmental Laboratory
Center for Environmental Systems
Stevens Institute of Technology

International Conference
Stabilization/ Solidification Treatment and Remediation
April 12-13, 2005, Cambridge University, England, UK
Outline

- Introduction
- Objectives
- Experimental Methodology
- Results and Discussion
- Conclusions
Introduction

- Chromium (Cr) is a naturally occurring element

- Cr is widely used in many industrial and commercial activities such as steel making, chromium electroplating, leather tanning, wood preservation and chemical manufacturing

- Cr occurs in the environment predominantly in one of two valence states: trivalent Cr (Cr\(^{3+}\)) and hexavalent Cr (Cr\(^{6+}\))

- Cr\(^{3+}\) is an essential nutrient for plants and animal metabolism at low levels. However, high levels of Cr\(^{3+}\) accumulation can be a potential carcinogen to human beings

- Cr\(^{6+}\) is more mobile and toxic than Cr\(^{3+}\). However, reduction from Cr\(^{6+}\) to Cr\(^{3+}\) can be achieved with relative ease by using metals.
Stabilization/solidification (S/S) is one of the most widely applied treatment processes for heavy metal contaminated soils.

The effectiveness of quicklime and fly ash stabilization/solidification (S/S) treatment to immobilize Cr$^{3+}$ in artificial soils was tested.

In the present study, quicklime (CaO) was used as the main S/S agent rather than using cement or hydrated lime.

The controlling leaching mechanisms of Cr$^{3+}$ following quicklime treatment was evaluated by performing semi-dynamic leaching tests.

Upon quicklime and/or fly ash treatment, there are three possible mechanisms that may be responsible for the immobilization of Cr$^{3+}$ in soils: a) precipitation b) inclusion c) sorption.
The main objectives of this study are:

- to assess the effect of surface area and cation exchange capacity (CEC) on Cr\textsuperscript{3+} release

- to determine the leaching behavior of Cr\textsuperscript{3+} in quicklime and/or fly ash treated soils by performing semi-dynamic leaching tests

- to evaluate the effectiveness of quicklime treatment and/or fly ash treatment by determining the leachability indices (LX)
Sample preparation for artificially contaminated soils

Example 1: K30L10
- Letters in the name indicate chemicals: (K:kaolinite; M:montmorillonite; C:fly ash; L:quicklime)
- Numbers after the letters denote weight fraction of the chemicals.

K30L10
- 30% kaolinite
- 10% quicklime
- 70% sand
- on top of total kaolinite and sand weight

Example 2: M5C25L10
- 5% montmorillonite
- 25% fly ash C
- 70% sand at 10% quicklime treatment level.
Experimental Methodology

- Semi-dynamic leaching tests (ANS 16.1) apparatus
According to ANS 16.1, the effective diffusivity of the leached sample ($D_e$) can be calculated by the following equation:

$$D_e = \pi \cdot \left[ \frac{a_n}{A_0} \right]^2 \cdot \left[ \frac{V}{S} \right]^2 \cdot T_n$$

where $a_n$ is the contaminant loss (mg) during the particular leaching period with index n, $A_0$ is the initial amount of contaminant present in the specimen (mg), $V$ is the volume of specimen (cm$^3$), $S$ is the surface area of specimen (cm$^2$), $\Delta t_n$ is the duration of the leaching period in seconds, $T_n$ is the elapsed time to the middle of the leaching period n in seconds and $D_e$ is the effective diffusion coefficient (cm$^2$/sec).
The effectiveness of S/S treatment can be evaluated by the leachability index. The leachability index is defined as follows:

\[ LX = \frac{1}{m} \cdot \sum_{1}^{m} \left[- \log(D_e)\right]_n \]

where \( n \) is the number of the particular leaching period, and \( m \) is the total number of individual leaching periods.
Experimental Methodology

- Model developed by de Groot and van der Sloot (1992) to evaluate type of leaching mechanism

\[
\log(B_t) = \frac{1}{2} \cdot \log(t) + \log\left(U_{\text{max}} \cdot d \cdot \sqrt{\frac{D_e}{\pi}}\right)
\]

where \(D_e\) = the effective diffusion coefficient in \(m^2/s\) for component \(x\) (lead in this study), \(B_t\) = the cumulative maximum release of the component in \(mg/m^2\), \(t\) = the contact time in seconds, \(U_{\text{max}}\) = the maximum leachable quantity in \(mg/kg\), \(d\) = the bulk density of the product in \(kg/m^3\)

- If slope \(~ 0\) \(\rightarrow\) wash-off
  \(~ 1\) \(\rightarrow\) dissolution
  \(~ 0.5\) \(\rightarrow\) diffusion
Results and Discussion

Cumulative Fraction of Cr\(^{3+}\) Leached (\%\) (Untreated Samples)
## Cumulative Fraction of Cr\(^{3+}\) Leached (%) Following Test Completion

<table>
<thead>
<tr>
<th></th>
<th>Artificially Prepared Soils</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated samples</td>
<td>K15L0</td>
</tr>
<tr>
<td>Cumulative fraction of Cr(^{3+}) leached (%)</td>
<td>77.1*</td>
</tr>
<tr>
<td>Treated samples</td>
<td>K15L10</td>
</tr>
<tr>
<td>Cumulative fraction of Cr(^{3+}) leached (%)</td>
<td>0.55</td>
</tr>
</tbody>
</table>
The effect of leachant pH on Cr$^{3+}$ leachability
Logarithmic Slope Values of Cumulative Cr\(^{3+}\) Release with Time (up to 5 days)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Slope</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K15L0*</td>
<td>0.05*</td>
<td>-</td>
</tr>
<tr>
<td>K30L0</td>
<td>0.19</td>
<td>0.91</td>
</tr>
<tr>
<td>K5C25L0</td>
<td>0.61</td>
<td>0.99</td>
</tr>
<tr>
<td>M15L0</td>
<td>0.07</td>
<td>0.86</td>
</tr>
<tr>
<td>M30L0</td>
<td>0.26</td>
<td>0.96</td>
</tr>
<tr>
<td>M5C25L0</td>
<td>0.51</td>
<td>0.99</td>
</tr>
<tr>
<td>K15L10</td>
<td>0.77</td>
<td>0.95</td>
</tr>
<tr>
<td>K30L10</td>
<td>0.62</td>
<td>0.93</td>
</tr>
<tr>
<td>K5C25L10</td>
<td>0.71</td>
<td>0.94</td>
</tr>
<tr>
<td>M15L10</td>
<td>0.72</td>
<td>0.96</td>
</tr>
<tr>
<td>M30L10</td>
<td>0.77</td>
<td>0.96</td>
</tr>
<tr>
<td>M5C25L10</td>
<td>0.73</td>
<td>0.95</td>
</tr>
</tbody>
</table>

*Note: K15L0 sample was disintegrated after 7 hours of testing*
## Treatment Effectiveness Results

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mean $D_e$ (cm$^2$/s)</th>
<th>Mean $L_X$</th>
</tr>
</thead>
<tbody>
<tr>
<td>K15L0*</td>
<td>7.33E-06</td>
<td>5.1*</td>
</tr>
<tr>
<td>K30L0</td>
<td></td>
<td>6.2</td>
</tr>
<tr>
<td>K5C25L0</td>
<td></td>
<td>10.7</td>
</tr>
<tr>
<td>M15L0</td>
<td></td>
<td>7.0</td>
</tr>
<tr>
<td>M30L0</td>
<td></td>
<td>8.8</td>
</tr>
<tr>
<td>M5C25L0</td>
<td></td>
<td>10.7</td>
</tr>
<tr>
<td>K15L10</td>
<td></td>
<td>10.8</td>
</tr>
<tr>
<td>K30L10</td>
<td></td>
<td>11.2</td>
</tr>
<tr>
<td>K5C25L10</td>
<td></td>
<td>11.3</td>
</tr>
<tr>
<td>M15L10</td>
<td></td>
<td>11.4</td>
</tr>
<tr>
<td>M30L10</td>
<td></td>
<td>11.4</td>
</tr>
<tr>
<td>M5C25L10</td>
<td></td>
<td>11.9</td>
</tr>
</tbody>
</table>

*Note: K15L0 sample was disintegrated after 7 hours of testing.
Conclusions

- In montmorillonite-sand samples, the amount of clay present in the soil appears to be a significant factor affecting Cr\(^{3+}\) leachability.

- The type of clay was observed to have a considerable effect on Cr\(^{3+}\) leachability prior to treatment.

- The addition of fly ash in the untreated samples further decreased the amount of Cr\(^{3+}\) leached, in both montmorillonite and kaolinite artificial soils.

- Quicklime and/or fly ash treatment was successful in significantly reducing the mobility of Cr\(^{3+}\), thus causing only trace levels to be released.
Conclusions (cont.)

- Upon treatment, the amount of clay did not influence Cr\textsuperscript{3+} leachability in the presence of montmorillonite.
- The lowest Cr\textsuperscript{3+} leachability was observed in montmorillonite samples treated with quicklime and fly ash.
- Upon treatment, all S/S treated samples were considered acceptable for "controlled utilization".
- The leaching mechanism for untreated samples was surface wash-off.
- Following treatment the leaching mechanism was diffusion.
Acknowledgments

- US Department of Energy

Thanks for your attention!!