Pb contamination and immobilization at shooting range sites

Xinde Cao, Deok Hyun Moon, Dimitris Dermatas, Gang Shen and Lena Q. Ma*

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

*Soil & Water Sciences Department, University of Florida

International Conference Stabilization/ Solidification Treatment and Remediation
April 12-13, 2005, Cambridge University, England, UK
High Pb concentrations are usually encountered in shooting range soils (several occurrences at up to ~ 50,000 mg/kg or 5%, highest reported ~40%)

Following projectile impact a thin layer of PbO forms immediately. Upon further exposure of Pb to moist air, PbO and stable metallic Pb can be rapidly transformed into cerussite ($\text{PbCO}_3$) and/or hydrocerussite ($\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$). Pb bioavailability may increase as a result of weathering of Pb bullets.

Other Pb transformation products are also possible as a function of anion species presence ($\text{PO}_4$, $\text{SO}_4$, etc.)
Background

- Elemental Pb and many of its compounds are toxic to both humans and animals -- decreased IQ, stunted growth for children, decreased mental ability, anemia, memory effects, high blood pressure as well as severe damages to the brain and kidneys.

- Pb is now ranked as one of the most hazardous substances on the U.S. Environmental Protection Agency (USEPA) priority list.

- USEPA screening level of total Pb in soils: 400 mg/kg

- USEPA threshold for non-hazardous waste: Pb release from the soil <5 mg/L (ppm) by Toxicity Characteristic Leaching Procedure (TCLP).

- In most cases, Pb TCLP leaching from shooting range soils is >>5 ppm (up to 1940 ppm in this study)
Background

- Pb concentrations as high as 800mg/kg were found in the shoots of Bermuda grass collected from a Florida shooting range (Cao et al. 2003)
- Migliorini et al. (2004) indicated that a significant portion of metallic Pb from spent pellets can accumulate in the predator *Ocypus olens* (Coleoptera)
- The health of individuals that work and participate in recreational shooting at these ranges may also be at risk (USEPA 2001)
- On March 29, 1993 the United States Court of Appeals for the Second Circuit ruled that Pb contaminated shooting range soils met the statutory definition of solid waste, and if not reclaimed it could be labeled hazardous waste subject to the Resource Conservation and Recovery Act (USEPA 2001).
- Therefore, controlling Pb leachability from shooting range soil media is an important step in minimizing exposure, thus effectively protecting public health and the environment.
**Background**

- **Mechanisms of phosphate-induced Pb immobilization** (chemical stabilization) ⇒ to form insoluble Pb compounds

- **Dissolution of hydroxyapatite:**
  \[
  \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2(\text{s}) + 14\text{H}^+(\text{aq}) \rightarrow 10\text{ Ca}^{2+} (\text{aq}) + 6\text{H}_2\text{PO}_4^- (\text{aq}) + \text{H}_2\text{O} \quad (1)
  \]

- **Formation of pyromorphite:**
  \[
  10\text{ Pb}^{2+}(\text{aq}) + 6\text{H}_2\text{PO}_4^- (\text{aq}) + 2\text{H}_2\text{O} \rightarrow \text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2(\text{s}) + 14\text{H}^+(\text{aq}) \quad (2)
  \]

- **Pb_{10}(\text{PO}_4)_6(\text{OH})_2 : K_{sp} = 1 \times 10^{-54} \text{ (versus K}_{sp} \text{ of PbCO}_3 = 1 \times 10^{-16})**
Study Objectives

- determine the Pb transformation mechanism in bullets spent at two shooting range soils

- assess the soil total Pb concentration and Pb leachability

- investigate the application of phosphate for immobilization of Pb in shooting range soils
Materials and Methods

- Two soil samples were studied: **ATF** indoor range soil from New Jersey; **CWR** outdoor range soil from Florida.

- For ATF soil, only the -#200 fraction was used for the study.

<table>
<thead>
<tr>
<th></th>
<th>Soil pH 1:1</th>
<th>OC %</th>
<th>Sand %</th>
<th>Silt+ Clay %</th>
</tr>
</thead>
<tbody>
<tr>
<td>ATF</td>
<td>8.6</td>
<td>0.50</td>
<td>0.0</td>
<td>100.0</td>
</tr>
<tr>
<td>CWR</td>
<td>7.2</td>
<td>0.96</td>
<td>87.8</td>
<td>12.2</td>
</tr>
</tbody>
</table>
Three types of phosphate source were applied as the stabilizer:

- Monocalcium phosphate \((\text{Ca(H}_2\text{PO}_4)_2\text{H}_2\text{O}, \text{CaP})\) mixed with ATF soil;
- Phosphate Rock (Fluoroapatite \((\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2)\ \text{PR})\) mixed with CWR soil;
- Phosphate Rock (Fluoroapatite \((\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2)\ \text{PR}) + \text{Phosphorus acid}\ \((\text{H}_3\text{PO}_4, \text{AP})\) mixed with CWR soil.
Experimental Methods

<table>
<thead>
<tr>
<th>Treatment Followed by 28 Days of Curing</th>
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<tbody>
<tr>
<td>TCLP Tests Were Conducted Following Curing</td>
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<tr>
<td>Mineralogical Studies (XRPD, SEM) Were Also Performed to Investigate Pb Immobilization Mechanisms</td>
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<tr>
<td>Chemical Analyses (Pore Water Chemistry, i.e., Anions and Metals, and Total Al, Fe, Ca and Mn in Soil)</td>
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<td>Geochemical Modeling to Determine Pb Speciation</td>
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</table>

<table>
<thead>
<tr>
<th>Treatment</th>
<th>P/Pb Molar Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>ATF with CaP</td>
<td>1.5 3 4.5 6 7.5</td>
</tr>
<tr>
<td>CWR with PR</td>
<td>2   3 4   5   --</td>
</tr>
<tr>
<td>CWR with PR+AP</td>
<td>2   3 4   5   --</td>
</tr>
</tbody>
</table>
## Results and Discussions

Total Pb levels and Pb TCLP Leaching from these two soils:

<table>
<thead>
<tr>
<th></th>
<th>Al %</th>
<th>Ca %</th>
<th>Fe %</th>
<th>Pb mg/kg</th>
<th>TCLP-Pb mg/L</th>
<th>Leachate pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>ATF</td>
<td>1.06</td>
<td>0.35</td>
<td>1.56</td>
<td>32,750</td>
<td>594</td>
<td>5.40</td>
</tr>
<tr>
<td>CWR</td>
<td>1.22</td>
<td>0.32</td>
<td>1.21</td>
<td>57,000</td>
<td>1940</td>
<td>5.15</td>
</tr>
</tbody>
</table>
Results and Discussions

Bullet Pb transformations within the two soils, based on XRPD studies:

CWR sample:
Ce, cerussite;
Hy, hydrocerussite,
Q, quartz;
Ma, massicot;

ATF sample:
Ce, cerussite; Hy, hydrocerussite, Q, quartz; Li, litharge; Pb, metallic Pb;
Al, albite; and An, anorthoclase.
Results and Discussions

Phosphate-induced Pb immobilization for ATF soil:

Pb TCLP concentrations and leachate pH in the CaP-treated ATF soil (−#200 fraction): At the P/Pb molar ratio of >3, Pb leachability decreased significantly.

![Graph showing Pb TCLP concentrations and leachate pH changes with varying molar ratios of P/Pb](image)

- 1-d Pb
- 30-d Pb
- 1-d pH
- 30-d pH
Results and Discussions

Phosphate-induced Pb immobilization for CWR soil:

Pb TCLP concentrations and leachate pH in the RP-treated CWR soil: RP alone is not effective

Pb TCLP concentrations and leachate pH in the RP+AP-treated CWR soil: effective when P/Pb ratio >3
Results and Discussions

Mineralogical investigation of the two treated soils:

XRPD patterns of ATF soil (left) treated with phosphate (P/Pb=3, 28-d curing), and the treated CWR soil (right). HyPy, hydroxyxpyromorphite Pb5(PO4)3(OH); RP, rock phosphate; Ce, cerussite; Hy, hydrocerussite; Q, quartz; Ma, massicot; Li, litharge; Pb, metallic Pb; Al, albite; and An, anorthoclase.
Results and Discussions

SEM element dot maps of the RP+AP-treated CWR soil, showing two particles, particle 1 is RP (Ca-P), and particle 2 is HyPy (Pb-P).
The $PO_4^{3-}$ dependent TCLP-Pb leaching of the CWR soil immobilized with phosphate was modeled.

In the untreated CWR soil, cerussite controlled Pb leaching.

Treatment with RP alone, cerussite still determined the Pb leaching in the RP alone treated CWR.

When combined with phosphorus acid, the RP significantly reduced the Pb$^{2+}$ activities which were supersaturated with less soluble hydroxypyromorphite indicating hydroxypyromorphite as the Pb leachability controlling mineral in the RP+AP treated soils.

The similar results were observed in the ATF soil, i.e hydroxypyromorphite determined the determined the Pb leaching in the CaP treated ATF soil (data not shown).
Conclusions

- Total levels of Pb concentration are extremely high in the two firing range soil samples → high Pb TCLP leaching
- Lead bullets spent in the shooting ranges have been partially transformed into Pb carbonates (cerussite and hydrocerussite)
- Utilization of phosphate significantly reduced the Pb leachability in the shooting range soils at P/Pb > 3.0 and ~28-d curing
- Rock phosphate (RP) treatment is not as effective as CaP and AP for Pb stabilization, due to the RP low solubility and dissolution rate
- Pb immobilization in the phosphate-treated soil is mainly related to formation of insoluble hydroxypyromorphite
Acknowledgments

- US Army, TACOM-ARDEC
  - Gregory O’Connor
  - Per Arienti
  - John Cefaloni

Thanks for your attention!!