A bench-scale process to remove Pb from firing range soils

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Abstract

A bench-scale process for the removal of Pb from army firing range soils has been developed. Owing to the high specific gravity of Pb (11 g/cm$^3$) and related Pb species, the conventional method for removing Pb from firing range soils entails the use of gravitational soil washing. Initial attempts to remove Pb from an indoor firing range soil by means of a spiral gravitational method were successful in concentrating the majority of metallic Pb. However, this method was not successful in reducing Pb concentrations to required regulatory levels for the bulk of the soil. The systematic study of Pb speciation in soils showed that the introduced metallic Pb particles of various sizes undergo multistage physico-chemical transformations producing a mixture of metallic Pb, Pb oxides, carbonates, hydroxo-chlorides, as well as ion-exchangeable, adsorbed and other Pb forms. Firing on the same soil over time seems to break the soil down into finer particles and compromise the protective surface layers that form onto fresh metallic lead particles. This results in the accumulation of Pb in the soils finer fractions. Quantitative phase analysis studies showed that the fine soil fractions contain considerable amounts of lead carbonates, which owing to their colloidal nature cannot be readily removed using gravitational methods. To overcome this, we have developed a bench-scale method based on dissolution of all common Pb containing phases, including metallic, oxides, carbonates, etc. Mixing the bulk soil with monobasic acid, effective separation of dissolved lead from the rest of the soil components was achieved, and then, the separated Pb was reprecipitated in the form of carbonates. According to the total digestion tests performed on the firing range soils treated by this method it was possible to reduce Pb concentrations below the required regulatory levels.
STUDY SITE LOCATION

Map showing the location of Ft. Irwin.
FORT IRWIN
OVERALL PROJECT OBJECTIVES

- Life cycle management of small arms firing ranges
  - Research and evaluation of site specific ecological and environmental risks associated with the past and present use of military ranges
  - Maintenance and/or remediation of existing ranges
  - Optimization and/or modification of remediation alternatives
  - Identification of critical design aspects for new ranges
STUDY OBJECTIVES

- Qualitative mineralogy of the soil – Optical and polarizing microscopy, XRD, SEM
- Quantitative mineralogy of the soil – Rietveld quantification
- Identification and quantification of the existing contaminants – physical states and chemical forms
- Soil washing from contaminated Pb (gravitational and chemical methods)
ENVIRONMENTAL PARAMETERS

- Climate (arid/desert)
  - Low precipitation (4-6in. per year)
  - Absence of vegetation (favors water runoff vs. infiltration)

- Soil characteristics (2 different areas)
  - a) Range 5 (active firing range)
    Berms of native sand
  - b) Goldstone (abandoned firing range)
    Berms of indigenous playa soil
    (ecologically sensitive area-endangered species habitat)
TYPICAL SAFR

* Some moderate-length ranges have fixed targets and target berms.

(USACE, 1998)
Pb contamination in SAFR

- In recent years, there has been a concern for lead contamination from SAFR.
- The type of arms SAFR are 50 caliber or less (pistols, rifles, shotguns; and machine-guns - military installations)
  - RANGE 5 (primarily M-16)
    - small diameter projectile-high velocity
    - Jacketed bullets- Cu (89-95%), Pb (max.% 0.05), and Fe (max. 0.05) and Zn (5-11%) (Battelle, 1997)
  - GOLDSTONE RANGE older facility (50 caliber and probably M1 munitions)
    - steel bullets present
Optical photo of R5S6 sample, showing relatively fresh metallic Pb piece
Optical photo of R5S6 sample, showing typical minerals assemblage, containing mostly quartz and feldspar minerals.
Optical photo of magnetic fraction of R5S6 sample containing mostly Magnetite, Hematite
Goldstone soils

Cerussite
XRD pattern of black particle containing Only Muscovite, Andalusite and quartz found in sample R5S2-4+10

XRD pattern of magnetic particles found in sample R5S2-4+10
XRD pattern of sample B7S1-400/24h-UP

XRD pattern of sample B7S1-400/24h-DOWN
Clay minerals of Goldstone soils

- Montmorillonite-15M (PDF No 13-135)
- Illite-2M1 (PDF No 26-911)
- Kaolinite-1A (PDF No 14-164)
Calculated cumulative diffraction patterns of Pb-SiO₂ mixtures (highest reflections are normalized to unity)
Theoretical calibration curve for metallic Pb concentration $I_{\text{Pb}(111)}/I_{\text{SiO}_2(101)}$ for Bragg-Brentano geometry diffractometer.

Mixture containing 12.6 wt% (3.19 vol%) of metallic lead will show intensity for (111) as high as (101) peak of Quartz.
Grain size fractionation results for Fort Irwin Soil samples (wt%)

<table>
<thead>
<tr>
<th>Fractions</th>
<th>Range Five</th>
<th></th>
<th>Goldstone</th>
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<td></td>
<td></td>
<td>R5S1</td>
<td>R5S6</td>
<td>B3S1</td>
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<tr>
<td></td>
<td>A</td>
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## Mineralogical composition of Range Five soils

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### Mineralogical composition of Goldstone soils

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Lead concentration vs particle size-fractions

Pb concentration [ppm]

Fractions

- r5s6
- r5s1
- b3s1
- b7s1
Normalized concentration of Pb vs particle size-fractions adjusted according to fraction’s weight
Rietveld plot of R5S1 - 10+40 fraction

- Intensity [a.u.]
- Two theta [°]

- Observed background removed pattern
- Calculated pattern
- Difference pattern
Rietveld plot of R5S1 - 400up fraction

- Observed calibrated and background removed pattern
- Calculated pattern
- Difference pattern

Two theta [°]

Intensity [a.u.]
MATERIALS AND METHODS

- Geotechnical testing for Index properties of 7 samples from Range 5 and 5 samples from Goldstone
- Analytical testing of these samples plus those from one hand auger boring from Range 5
  - Acid digestion (EPA method 3050B)
  - Leachability test- TCLP (EPA method 1311)
  - Sequential extraction (Tessier et al. 1979)
- Mineralogical testing
  - SEM
  - XRD
Soil and water chemistry

- High concentrations of dissolved organic matter (fluvic or humic acid) can increase lead concentrations due to its chelating abilities.
- Insoluble organic matter and clays can decrease lead concentrations by adsorption or formation of stable complexes.
- Lead concentrations can decrease or increase depending on the chemistry and its effect on the redox potential and metal speciation. Lower pH’s (acid) increases lead concentrations, higher pH’s (base) decrease the lead concentrations.
- Sandy soils are less likely to bind to lead and do not retain water
- Phosphate and sulfide Pb compounds are less soluble than carbonates or hydroxides
Pb Speciation in pE-ph Diagram
SEM of cerussite forming on lead particle

Enlarged Lead particle reveals cerussite
SEM of well-developed crystals of cerussite on weathered surface of metallic lead particles
XRD of Pb core-shell particles

Range 5- Lead minerals

CR- Cerussite PbCO$_3$ (5-417)
Lt- Litharge PbO (5-561)
Q- Quartz SiO$_2$ (33-1161)
T- Tridymite SiO$_2$ (42-1401)
H- Hydrocerussite 2PbCO$_3$Pb(OH)$_2$ (13-131)
Pb- Pb metallic (4-686)
SEM-GOLDSTONE
secondary minerals

Laurionite PbClOH Crystals on Surface of Lead Particles
Goldstone XRD Pb core shell particles

Goldstone- Lead minerals

L- Laurionite PbClOH (31-680)
Pb- Pb metallic (4-686)
H- Hydrocerussite 2PbCO$_3$Pb(OH)$_2$ (13-131)
Spiral washing
### Spiral washing results

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Soil washing scheme

Dissolve Pb and Pb compounds at low pH and precipitate at high pH.
Basic reactions

**Dissolution:**
- \( \text{Pb} + 2\text{HNO}_3 \rightarrow \text{Pb}^{2+} \)
- \( \text{PbO} + 2\text{HNO}_3 \rightarrow \text{Pb}^{2+} \)
- \( \text{PbCO}_3 + 2\text{HNO}_3 \rightarrow \text{Pb}^{2+} \)
- \( \text{Pb}_2(\text{CO}_3)(\text{OH})_2 + 2\text{HNO}_3 \rightarrow \text{Pb}^{2+} \)
- \( \text{PbCl(OH)} + 2\text{HNO}_3 \rightarrow \text{Pb}^{2+} \)

**Precipitation:**
- \( \text{Pb}^{2+} + 2\text{NaOH} \rightarrow \text{Pb(OH)}_2 \)
- \( \text{Pb(OH)}_2 + \text{CO}_2 = \text{cerussite and hydrocerussite} \)
Lead extraction from Range Five soils

![Graph showing the Wt % of extracted Pb against HNO3/Soil, ml/g for two fractions: _4 fraction and _40 fraction. The graph shows a trend where the Wt % of extracted Pb increases with increasing HNO3/Soil for both fractions, with _4 fraction slightly higher than _40 fraction.]
Lead extraction from Goldstone soils

![Graph showing Wt % of extracted Pb vs HNO3/Soil, ml/g with two curves representing _4 fraction and _40 fraction.](image)
Kinetics of lead dissolution

![Graph showing kinetics of lead dissolution](image)
CONCLUSIONS

- Limited contaminant migration due to:
  - Low moisture content
  - Arid environment, flush flooding events, rapid runoff, little water infiltration
  - Formation of insoluble carbonate minerals

- XRD-analysis shows that Pb is present predominantly as:
  - Metallic Pb, cerussite and hydrocerussite in RANGE 5,
  - Metallic Pb, hydrocerussite, and laurionite in GOLDSTONE RANGE

- Gravitational methods of soil washing are not effective for lowering Pb concentration to the regulatory levels (<600ppm)

- Chemical washing of lead is an effective alternative to gravitational method