Heavy Metal Immobilization

Mechanisms and Speciation in the Geoenvironment

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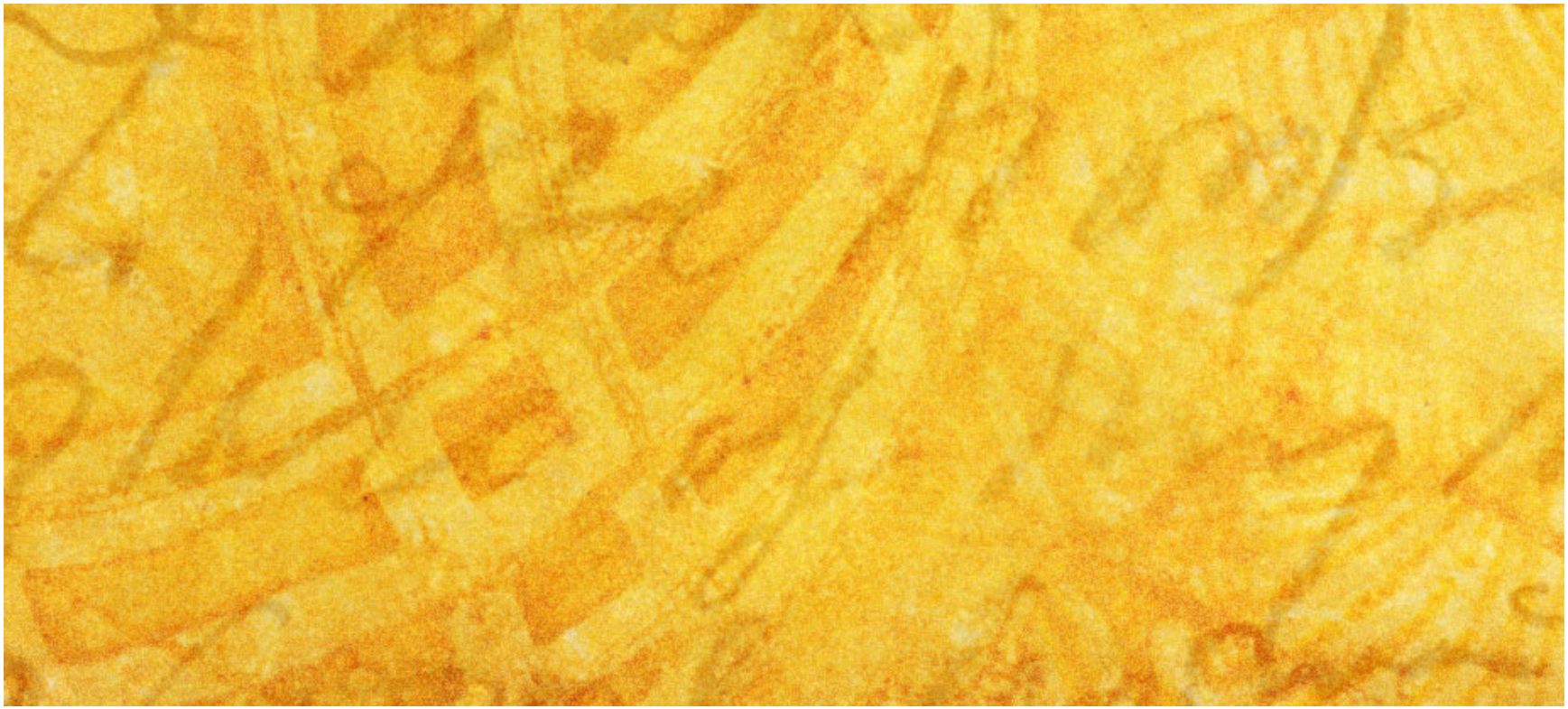


Agenda

- Why bother with heavy metal immobilization mechanisms?
- Which are they?
- Examples
- How to delineate them?
- Application context
- Bottom line (Summary and conclusions)

Significance of HM immobilization mechanisms

- Great number of contaminated sites (~500.000 in Japan, ~500.000 in US, ~ 3.000.000 in EU)
- Very high remediation cost (1-2 trillion USD only for G-20)
- Perspective: Arsenic groundwater contamination 2nd (to starvation) threat according to UNEP
- Assistance in prioritization of sites to be remediated
- Extremely costly to get it wrong!!
- Long-term remediation performance

Significance of HM immobilization mechanisms → geoenvironmental testing

- The most ***recent global shift to remediation approaches based on risk assessment***, makes it clear that total analyses (TA), Toxicity Characteristic Leaching Procedure (TCLP) and other ***conventional geoenvironmental tests are no longer sufficient*** as an adequate knowledge on the prevailing immobilization mechanisms is now required

- This underscores the significance of using ***state-of-the-art geoenvironmental characterization*** aiming predominately in obtaining a deeper understanding of the solid state ***speciation of contaminants***, and thus their ***bioavailability***, in the geoenvironment

HM immobilization mechanisms list

- Macroencapsulation and Microencapsulation
- Inclusion (crystal or amorphous)
- Sorption (adsorption vs. absorption)
- Precipitation
- Detoxification (biological or chemical)

Micro- and Macro-encapsulation

- Predominately physical mechanism
- Microencapsulation
  - Chelation (chemical) is mainly used in water decontamination applications → very rarely in soils
  - Asphalt & other non-polar organic emulsions (physical). Mainly prevent HM from dissolving in water
  - Rubber tire and Hg (Meng et al., 1998)
  - Macroencapsulation
  - Containers
  - Landfills & Impermeable Vertical Barriers

Inclusion (isomorphous substitution & amorphous inclusion)

- Mainly a Stabilization/Solidification (S/S) mechanism
- Formation of pozzolanic products (CAH, CSH, etc.) during S/S applications (cement, lime, fly ash, etc.) (Dermatas & Meng 1995; 1996; 2003)
- Isomorphous substitution → Incorporation into the product crystalline structure: Cr^{6+} substituted ettringite (Dermatas 1995, Chrysochoou & Dermatas, 2006)
- Incorporation into amorphous (gel-like) pozzolanic products: Pb in CSH gels (Dermatas et al., 2006)

Sorption

- Absorption → via cation exchange in reactive clays: Cr and Pb substituted montmorillonites (Dermatas & Dadachov, 2003)
- Adsorption: in natural environments onto mainly amorphous or fine-grained oxide and hydroxide surfaces (e.g., iron, manganese, etc.)
- Adsorption: in remediation applications onto mainly fine-grained (lately nano) active surfaces.
- Adsorption examples: As onto iron oxides (Dermatas & Meng, 2004), Pb onto TiO_2, fishbone, biochar, etc.

Precipitation

- As immobilization by calcium-arsenic precipitates (Moon et al., 2004)
- Cr^{3+} immobilization as hydroxide precipitate (Dermatas & Meng, 2003; Dermatas & Moon, 2006)
- Cr^{6+} immobilization as barium chromate precipitates (Chrysochoou et al., 2006)
- Pb immobilization as pyromorphite precipitate (Chrysochoou et al., 2007; Dermatas et al., 2008)

Detoxification

- Chemical Reduction of Cr^{6+} to Cr^{3+}(Dermatas et al., 2006; Moon et al., 2007; Chrysochoou et al., 2008)
- Biological reduction of Cr^{6+} to Cr^{3+}(Chrysochoou et al., 2011)
- Extracellular reduction of uranium via Geobacter conductive pili as a protective cellular mechanism (Cologgi et al., 2011)

HM immobilization mechanism delineation

- Done in the lab but sampling (i.e., field) is important
- Determination of geochemical contaminant speciation is the key
- ***Heavy metal remediation application*** inadequacies are mainly traced to a ***failure to qualitatively and quantitatively*** recognize the ***contaminant speciation*** regime
- ***Contaminant speciation***, i.e., the physicochemical state at which the contaminant exists, ultimately dictates the degree of ***contaminant immobilization*** and thus ***its release and bioavailabilty*** into the geoenvironment (USEPA 1999a; Dermatas et al. 2006b

What is contaminant speciation

- Chemical form of contaminant
  - Valence
  - Crystalline structure/amorphicity
  - Chemical formula
- Physicochemical association between contaminant & soil-water
  - Sorption (extraction tests and isotherms; both problematic)
  - Solid solution, i.e., crystal or amorphous inclusion (XRPD; SEM-EDS; EPMA)
  - Sediment hydraulic properties (*not* speciation but still needs to be considered)

Contaminant speciation importance

- Reliably evaluate public health risk associated w/ HM contamination
- Delineate mechanisms of contaminant release and ultimate fate under specific exposure environments
- Bioavailability=f (release potential)=f (speciation)
- Provide with context to leaching/release/extraction tests
- Provide with reliable basis for geochemical & groundwater modeling to be relevant (realistic)
- Provide with reliable environmental forensics context

State-of-the-art geoenvironmental characterization

- Traditional geotechnical analyses (e.g., particle size distribution, γ, w/c)
- Physicochemical analyses (e.g., pH, TA)
- Controlled pH extraction tests (***TCLP***, Synthetic Precipitation Leaching Procedure, ***SPLP***, Sequential Extraction Test (***SET***), etc.) ***coupled with***
- Quantitative mineralogical analyses (***X-ray Powder Diffraction, XRPD*** combined with ***Rietveld Quantitative Analysis, RQA***)
- Micromorphological (Scanning Electron Microscopy-Energy Dispersive Spectroscopy, SEM-EDS and/or Electron Probe Micro-Analysis, EPMA) and other contaminant speciation analyses (***X-Ray Absorption Near-Edge Structure, XANES*** and/or ***Extended X-ray Absorption Fine Structure, EXAFS*** or other newly developed techniques) should be used once a more in-depth assessment is required

traditional

State-of-the-art

Contaminant Speciation-Based Assessment

- ***High fines content → availability of soil sorption sites → contaminant immobilization***
- ***Amount of fines ≠ amount of clay*** → other minerals (feldspars and other non-clay and non-reactive fines that would likely not significantly affect contaminant leaching) may contribute to the fine fraction (Mitchell, 1993).
- Soil mineralogy (XRPD) → verify and quantify the presence of active clays and amorphous and/or poorly crystallized metal oxides and hydroxides that would contribute to contaminant immobilization (Dermatas et al., 2006a) → ***XRPD complements conventional particle size distribution testing***
- ***Contaminant speciation analyses*** can be, and usually are, ***much more intricate*** then the simple example provided. They may ***involve sophisticated quantitative and/or qualitative tools*** such as ***XRPD with RQA***, SEM-EDS, ***XANES***, ***EXAFS***, etc.
- ***Contaminant speciation*** → reliable ***input to geochemical models*** (e.g., PHREEQC and MINTEQ), to evaluate whether the system is at equilibrium or transient and to create different scenarios and project how contaminant speciation and availability, will change with time → ***sustainability***

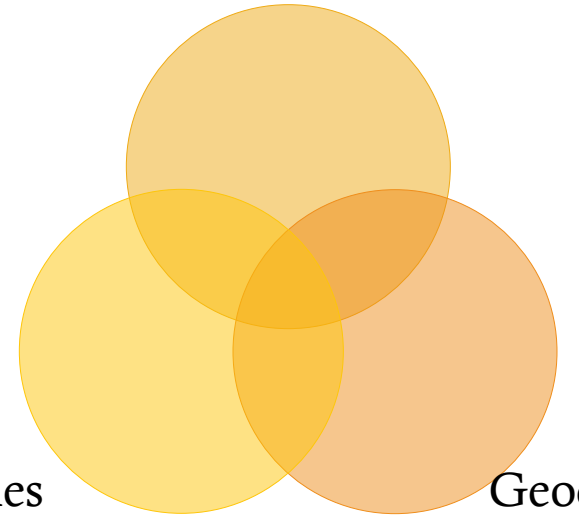
Methodology to determine sustainable treatment

Material characterization

Mineralogical (qualitative and quantitative X-ray Powder Diffraction, Scanning Electron and optical microscopy)

Chemical (pH, total analyses, Acid Neutralization Capacity)

Geotechnical (water content, density, swell testing)



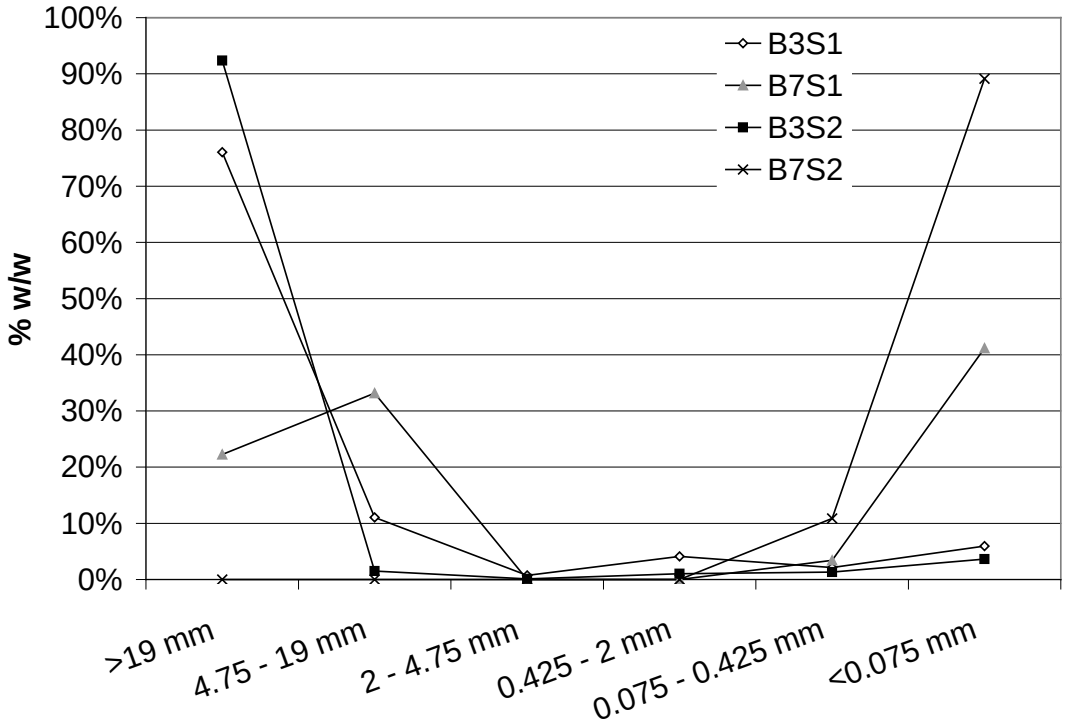
Treatability studies

Bench- and pilot- scale (Cr(VI) reduction with various agents, Cr(VI) stabilization with Ba)

Geochemical modeling

Visual MINTEQ (equilibrium) EQ3/6 (reaction pathway)

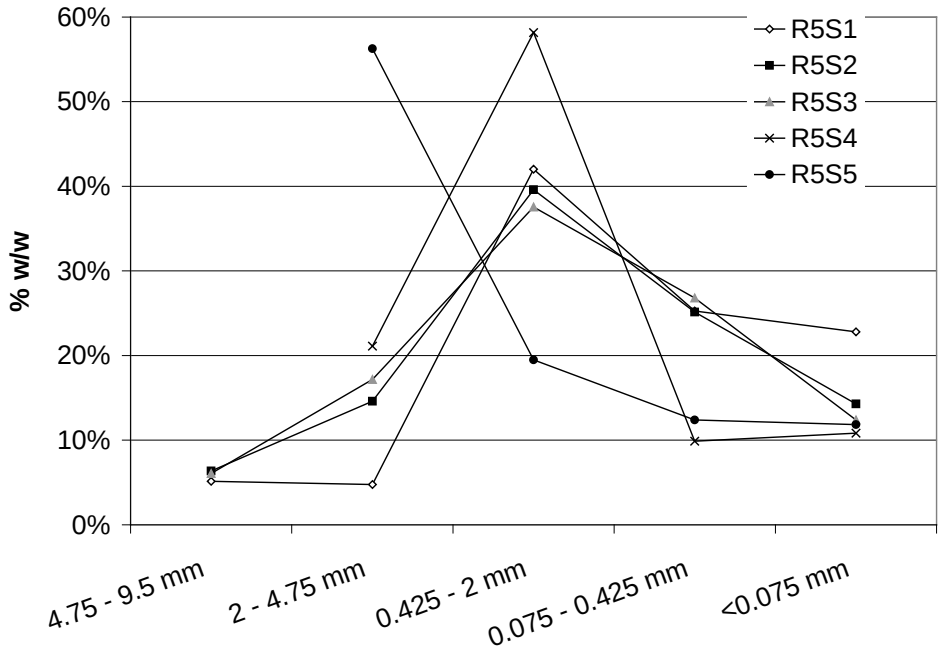
Grain-size distribution vs. total Pb analyses for firing range soils



>70% of the total Pb is present in the gravel fraction in B3 soil and >50% in the surface B7 soil

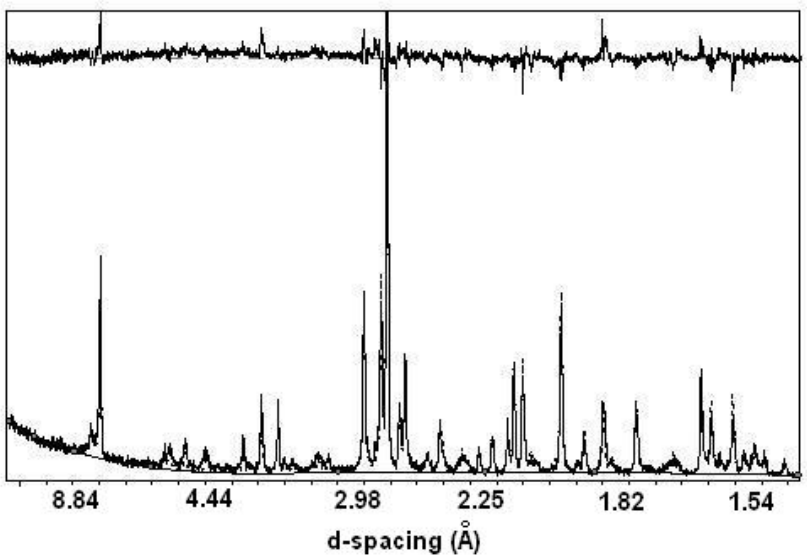
-> "cushioning" effect due to presence of clay

Grain-size distribution vs. total Pb analyses for firing range soils



- >50% of total Pb present in the fine sand and clay fractions (<0.425 mm)
- -> use of high velocity weapons leads to significant bullet fragmentation
- Use of angular sand to construct implies ricochet effects that, in turn, lead to a broad impact area surrounding the berm

XRPD quantitative analysis



Rietveld-produced XRPD pattern and residual plot for an SA7-GB sample

Rietveld method:

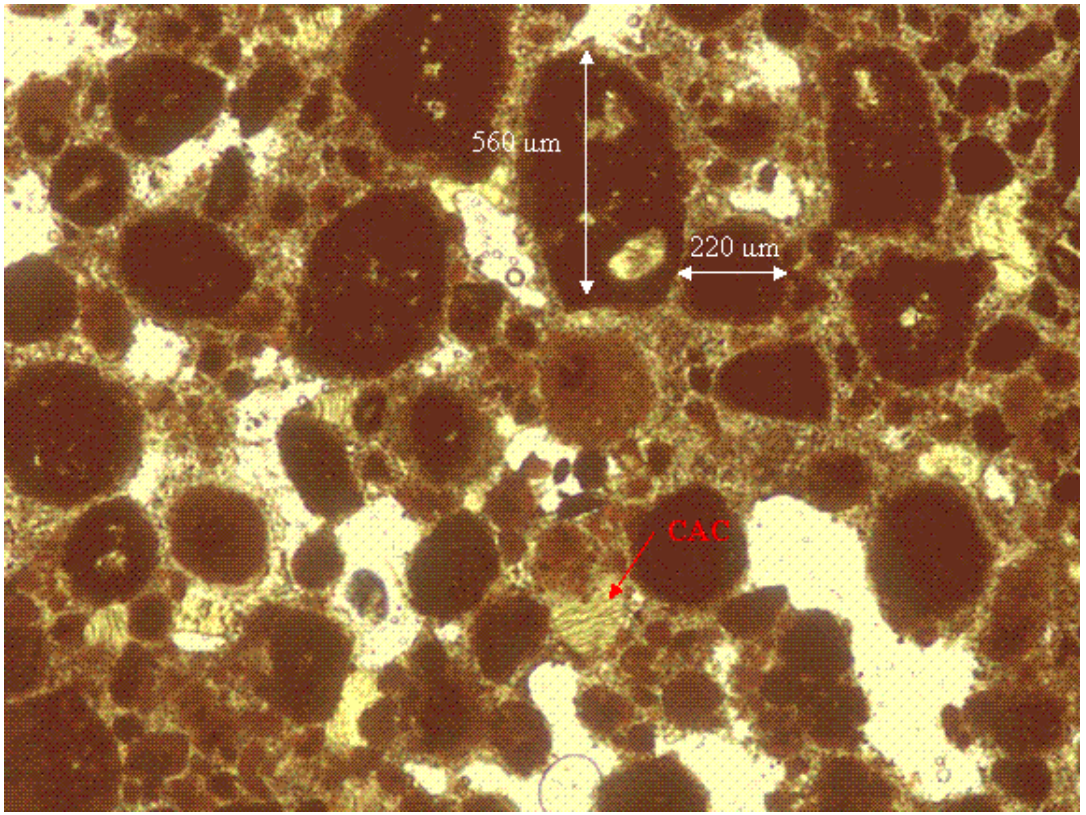
•Production of a synthetic X-ray Diffraction pattern to match the experimental as closely as possible

•Least-square fitting algorithm for residual function

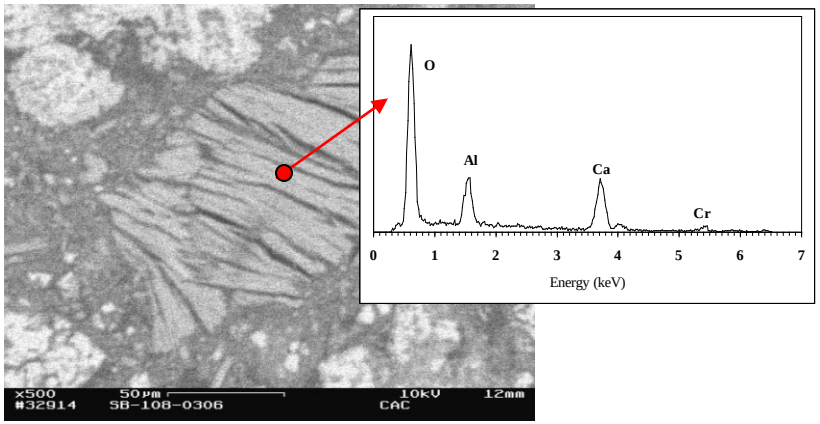
•Rarely used for multiphase systems because of pattern complexity

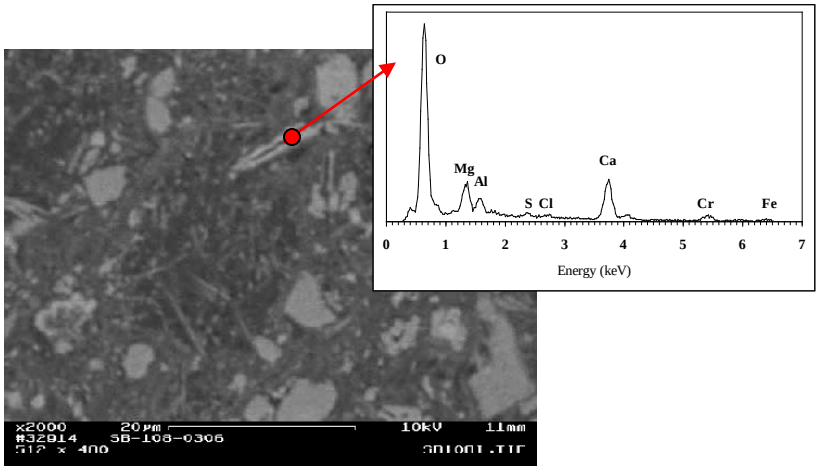
•Is the ONLY statistically reliable analysis method to determine bulk mineralogy

Optical microscopy image of GB COPR



SEM/EDX analyses





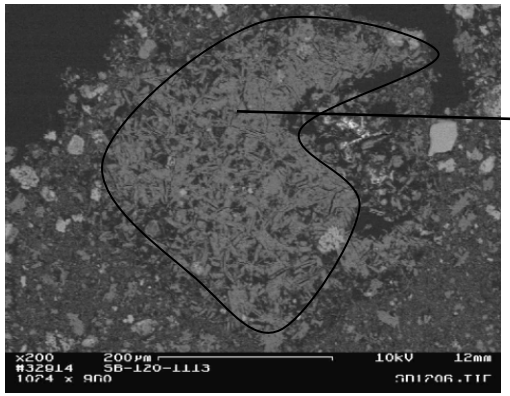
Two types of crystals identified

1. Large crystals (>20 µm diameter)
   Form mostly on rims of nodules
   Perfect basal cleavage
   Only Ca, Al and Cr in approx. 4:2:1 stoichiometry
   -> CAC

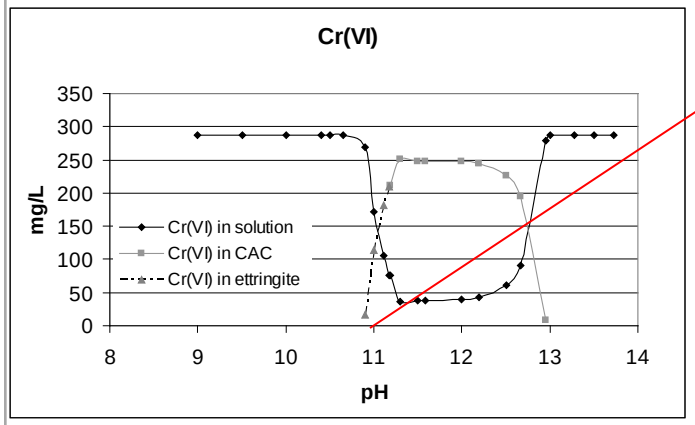
2. Small crystals in interior of cementing matrix Some with basal cleavage
   Extensive Mg for Ca substitution
   Mixed anions S (sulfate), Cl (chloride), Cr (chromate)
   -> hydrotalcite-like compound

Implications for treatment

CAC-bound Cr(VI)



CAC area
Accessible to chemicals (acid, sulfate)

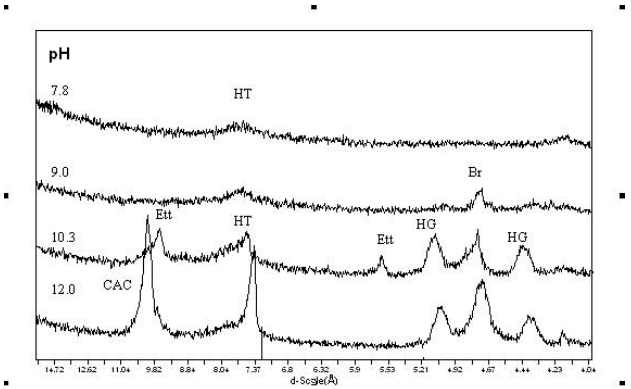


pH <11
Cr(VI) released

FASTER RELEASE

22 Modeled Cr(VI) conc in solution

Matrix-bound Cr(VI)

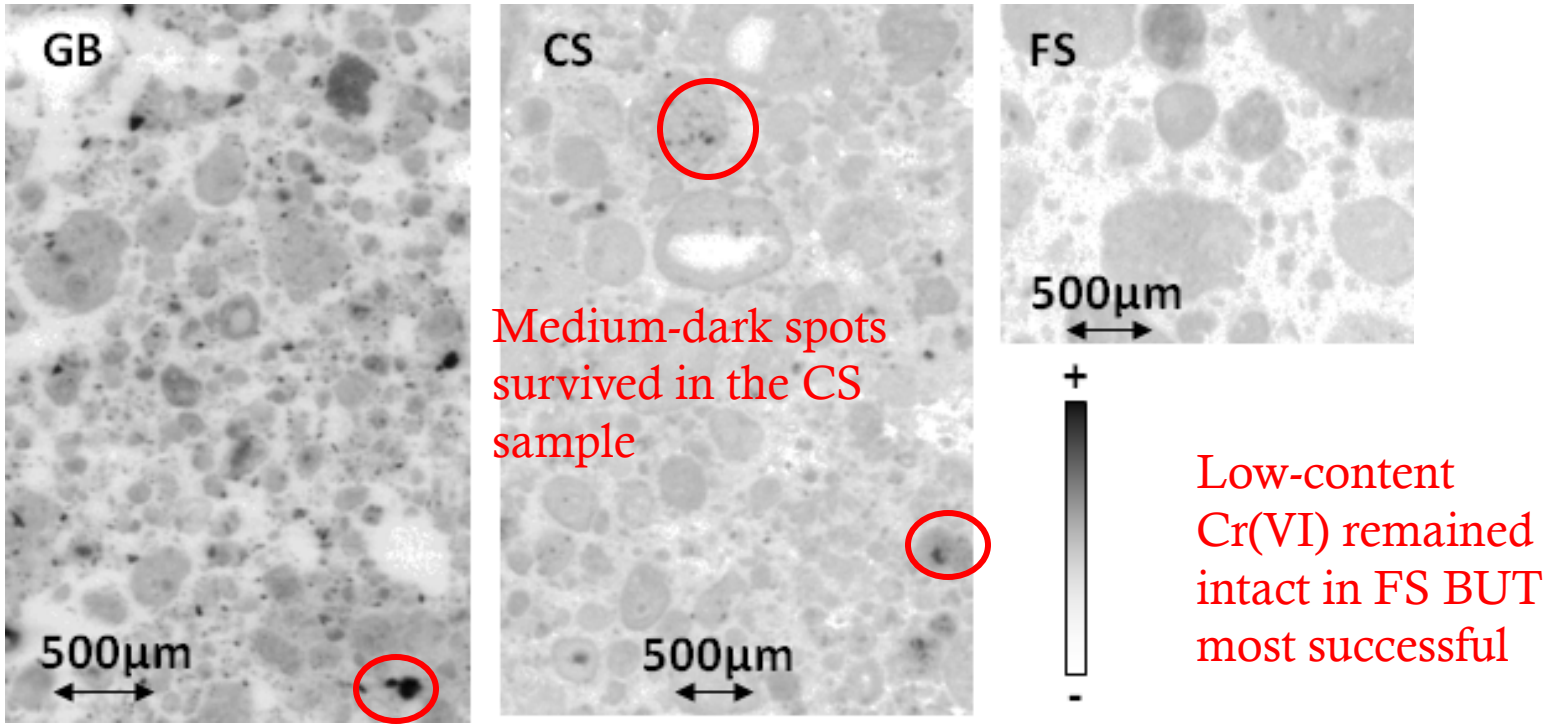


XRPD patterns of ANC residues at various pH values

Hydrotalcites are stable at lower pH values
Access to cementing matrix for acid or sulfate more difficult

SLOWER RELEASE

Cr(VI) maps using μXRF



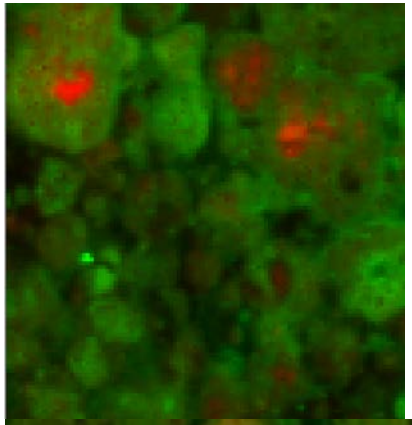
Medium-dark spots survived in the CS sample

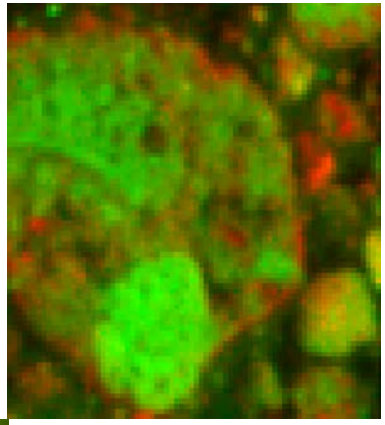
Low-content Cr(VI) remained intact in FS BUT most successful

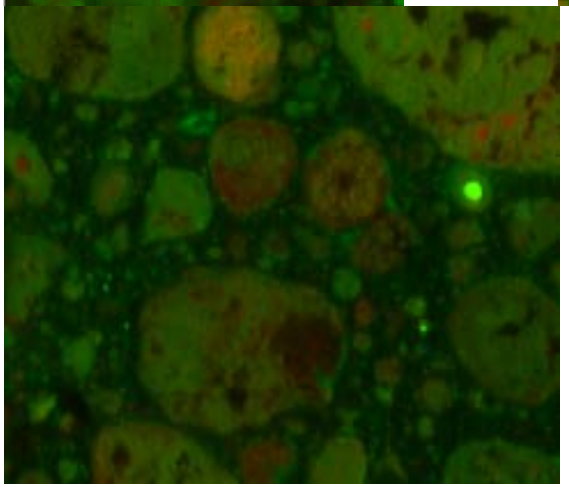
High Cr(VI) compounds (dark spots) were dissolved by both treatments
BUT significant residual Cr(VI) in both samples

Cr(VI) location using μXRD

Cr6 Cr3



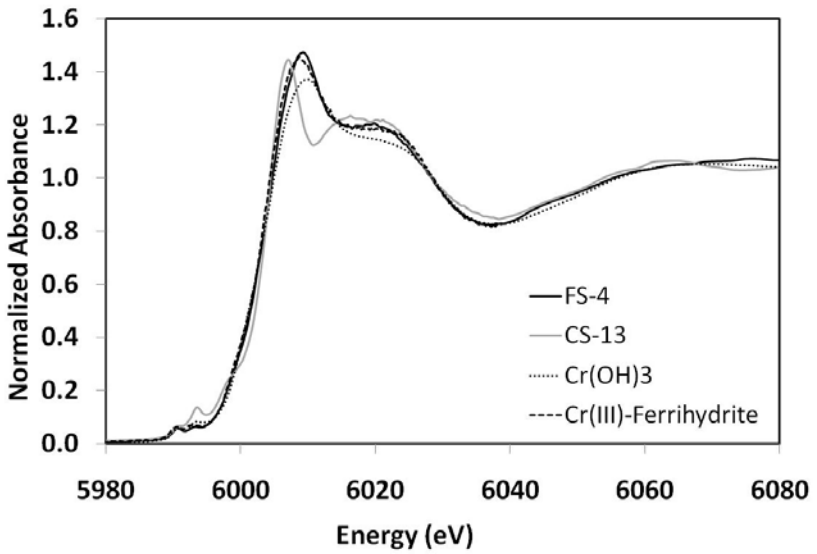




CS
Cr(VI) both on rin and interior of nodules

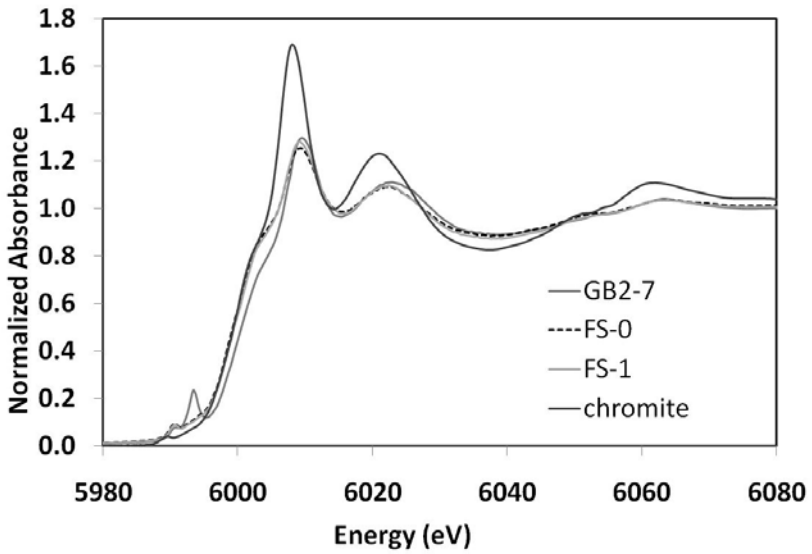
FS
Cr(VI) only in interior of nodules

Cr(III)-bearing compounds using point XANES analyses



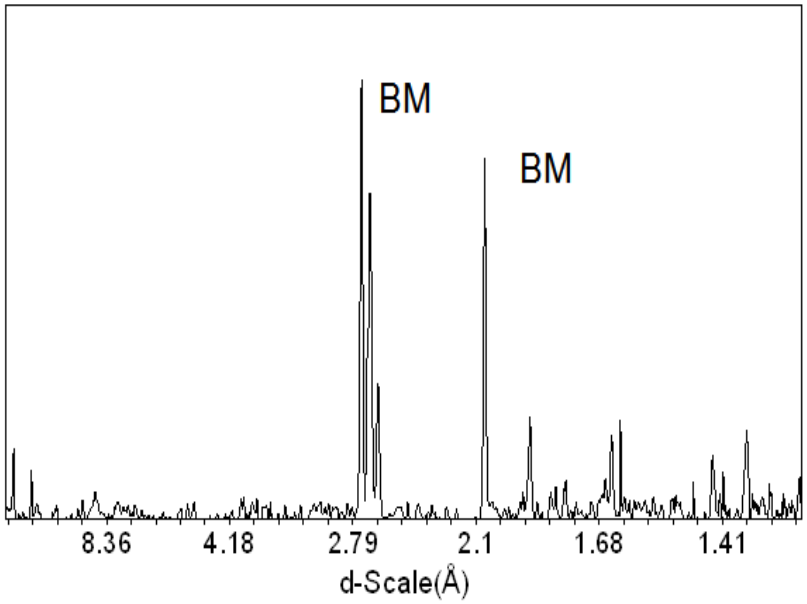
Co-precipitation of Cr(III) with Fe(III) in the FS-treated sample

$Cr(OH)_3$ in the CS sample

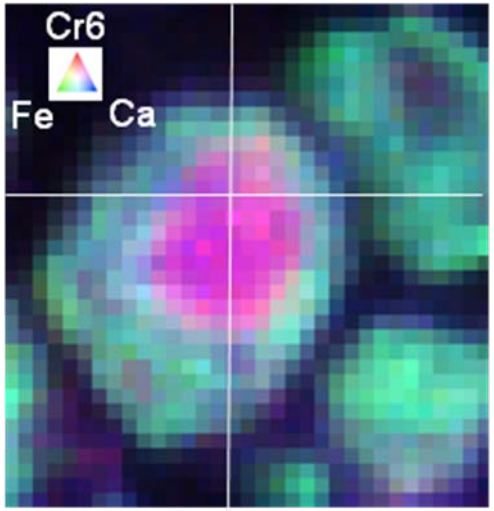


Residual chromite in all samples

Low Cr(VI) compounds using point XANES and μXRD



μXRD of FS point



Physical or chemical inclusion of Cr(VI) in parent unreacted brownmillerite

Field methods

- Sampling undisturbed/disturbed →
  - At least preserve sample-based layering profile
  - Avoid cross contamination (is this really possible without associated major cost?)
  - Limitations are cost-associated (too many samples), cross contamination, sample preservation-→ R&D opportunities
- Penetration testing (CPT, SPT, etc.)
  - Relatively inexpensive and fast provide with continuous record
  - Instrumented with sensors for non-destructive (ND) testing (similar to down-hole survey). Major limitation is mechanical disturbance of sediment

Field methods (cont'd)

- Geophysical:
  - ND, inexpensive but cannot be used alone (that's the major limitation)
  - Need more R&D to establish link between geophysical & traditional (sampling & testing)→ R&D opportunities
  - Still advocate combination of geophysical and traditional
- Other non-destructive:
  - Field XRF screening is an excellent tool
  - New laser-based (limitation of depth of penetration field; good for down-hole survey)→ R&D opportunities
  - Very high emergence rate of new technologies!! R&D opportunities

Plot of Lead Concentration From XRF Field Screening

Lab methods issues

- Sample preparation: Needs to be standardized especially for XRPD, EPMA, etc. (ASTM?)
- Material characterization analyses (traditional mostly geotech, XRPD-Rietveld, SEM-EDS, EPMA, etc.)
  - Need to accurately and reliably establish standard error involved across different samples (same medium) and then across contaminant media → Traditional QA/QC has been overcome by sample variability issues
- Traditional batch, leach/extraction tests (e.g., SET, etc.) → Problematic as contaminant speciation is altered during the test
  - Batch adsorption isotherm testing lamps sorption and precipitation together
  - SET tests are case-specific
  - Acid-based leaching/extraction tests are problematic for oxy-anion testing
  - Total analyses non-reliable either due to strong mineral associations or presence of reductant/treatment agent, etc. that would alter the contaminant speciation during the test

Lab methods issues (cont'd)

- ND (high energy → high sample penetration field (SPF); Synchrotron-based, i.e., XANES (X-ray Absorption Near-Edge Spectroscopy) or XFS(X-ray Fluorescence Spectroscopy))
  - Example AD results versus XANES results
  - Difficult to gain access
  - XFS is difficult to interpret (art form)
- Emerging ND (lower energy → low SPF; e.g., Time of Flight, Secondary Mass Spectrometer (TOF-SIMS), XPS, plus others usually laser-based → good for ONLY surface (1-10nm to molecular monolayer to sub-atomic penetration levels)
  - Need to "ground truth them" w.r.t. XANES and more traditional analyses
- A great (if not huge!) score of unresolved issues → opportunities for international R&D collaborative projects

Broader unresolved issues

- Link of measurement to pathway to receptors?
- Reliability of measurement
- Sample variability & variability in general
- Point-in-time measurements → changes with time
- Public perception of risk (politics)
- See the tree but miss the forest? (COPR Ba-treatment, use of flyash or CKD or fishbone or red mud, etc. → waste combination)
- Sustainability? (Phosphates and Pb)

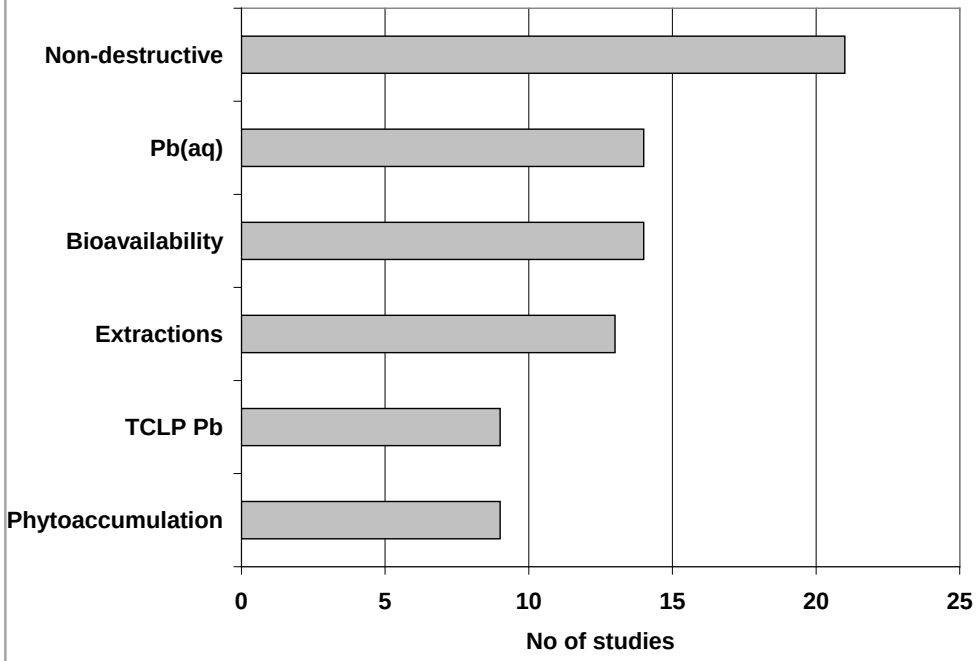
Reliability of measurement

Table 1: Total Cr(VI) in six treatment plots as measured by XANES and alkaline digestion (AD)

	Ferrous sulfate heptahydrate		Cr(VI) XANES (mg/kg)	Cr(VI) AD(mg/kg)	Ratio (XANES-to-AD)
	dosage	%w/w*			
HRM-5X			2100	1240	1.7
HRM-8X	5X	32	1848	1260	1.5
VA-5X (0-2m)	8X	51	588	154	3.8
VA-5X (2-4m)	5X	38	1685	460	3.7
PUG-5X	5X	32	1116	384	2.9
PUG-8X	8X	51	1656	421	3.9

- ***XANES analyses*** of S/S chromate waste → alkaline digestion ***(AD) results underestimated the total Cr(VI) by a factor on the order of 1.5 to 4.0***
- Reasons for this discrepancy may be that residual ferrous reduced the liberated Cr(VI) during AD and/or that Cr(VI) was not 100% released from the solid during AD
- ***Discrepancy between XANES and AD*** results renders ***AD unreliable for regulatory purposes***, when applied to ferrous-treated chromate waste (Dermatas et al. 2006d; Moon et al. 2007).

Geoenvironmental Characterization of Phosphate-Amended Pb-Contaminated Soils



Distribution of criteria and methods used to evaluate treatment performance in treatability and field studies (Chrysochoou et al. 2007)

The use of ***EXAFS*** clearly demonstrated that the ***success and sustainability of applying phosphate as a Best Management Practice (BMP)*** (USEPA, 2001) in firing range soils and other Pb contaminated solid media ***remain questionable***

EXAFS (the only reliable method to identify and quantify Pb speciation in this case) showed that ***Pb conversion to pyromorphite*** in in-situ treated soils was ***less than 45% after 32 months*** (Chrysochoou et al. 2007)

Bottom line (instead of conclusions)

- Without ***definitive knowledge of contaminant speciation and immobilization mechanisms***, remediation treatment design becomes unreliable in attaining ***long-term treatment goals in terms of performance and overall sustainability***

- There have been many cases where ***remediation treatment that appeared to be initially successful***, ended up ***failing in the near or long term*** (Dermatas et al. 2003). Moreover, lack of knowledge on immobilization mechanisms often leads to ***remediation over-treatment*** along with the associated ***waste of energy and resources***

References

- Meng, X., Hua, Z., Dermatas, D. and Wang, W. (1998), *"Immobilization of Mercury (II) in Contaminated Soils with Used Tire Rubber"*, ***Journal of Hazardous Materials,*** *Elsevier,* No. 57, Issues 1-3, January 1998, Pages 231-241.
- Dermatas, D. and Meng, X. (1995), *"Leachability Study of Cr Contaminated Soils to Assess the Long-Term Effectiveness of Remediation Technologies"*, ***Geoenvironment, No. 46***, 1995, ASCE, New York, NY, pp. 449-462.
- Dermatas, D. and Meng, X. (1995), *"A Leaching Protocol to Evaluate Flyash Reuse Potential"*, ***Innovative Technologies for Soil Remediation and Hazardous Waste Management***, 1995, ASCE, New York, NY, pp. 694-701.
- Dermatas, D. (1995), *"Ettringite-Induced Swelling in Soils: State-of-the-art"*, ***Applied Mechanics Review***, Volume 48, Number 10, October 1995, pp 659-673.
- Dermatas, D. and Meng, X. (1996), *"Stabilization/Solidification (S/S) of Heavy Metal Contaminated Soils by Means of a Quicklime-Based Treatment Approach"*, ***Stabilization and Solidification of Hazardous, Radioactive, and Mixed Wastes, ASTM STP 1240***, American Society for Testing and Materials (ASTM), Philadelphia, PA, 1996, pp. 499-513.
- Dermatas D. and Meng X. (2003), *"Utilization of Fly Ash for Stabilization/Solidification of Heavy Metal Contaminated Soils"*, ***Engineering Geology****, Elsevier*, Vol. 70/3-4, pp 377-394
- Dermatas, D. and Meng, X. (2004), *"Removal of As, Cr and Cd by Adsorptive Filtration"*, ***Global Nest (Environmental Science and Technology): the International Journal***, Vol. 6, No. 1, pp.73-80, March 2004.
- Moon, D.H., Dermatas, D., Menounou, N. (2004), *"Arsenic Immobilization by Calcium-Arsenic Precipitates in Lime Treated Soils"*, the ***Science of the Total Environment***, *Elsevier*, Vol. 330/ 1-3, pp. 171-185, September 2004.

References

- Dermatas, D., Moon, D.H. (2006), *"Chromium leaching and immobilization in treated soils"*, ***J. of Environmental Engineering Science***, *Mary Ann Liebert, Inc. Publishers*, Vol. 23, No. 1, pp.75-85, February 2006.
- Chrysochoou M., Dermatas D., Moon D. H., French C, Morris J. and Kaouris M. (2006), *"Investigation of barium treatment of Chromite Ore Processing Residue (COPR) "*,***Journal of ASTM International****, ASTM, International,* Vol. 3, No.4, April 2006.
- Dermatas D., Menounou N. and Meng X. (2006), *"Mechanisms of Pb Immobilization in Treated Soils"*, ***Journal of Land Contamination and Reclamation***, 14 (1), pp. 43-56, 2006.
- Chrysochoou M. and Dermatas D. (2006), *"Evaluation of Ettringite and Hydrocalumite Formation for Heavy Metal Immobilization; Literature Review and Experimental Study"*, ***Journal of Hazardous Materials****, Elsevier*, Vol. 136, No. 1, pp 20-33, August 2006.
- Dermatas D., Shen G., Chrysochoou M., Grubb D. G., Dutko P. (2006), *"Pb Speciation versus TCLP Release in Army Firing Range Soils"*, ***Journal of Hazardous Materials***, *Elsevier*, Vol. 136, No. 1, pp 34-46, August 2006.
- Dermatas D., Chrysochoou M., Moon D.H., Grubb D.G., Wazne M., Christodoulatos C. (2006), *"Ettringite-Induced Heave in Chromite Ore Processing Residue (COPR) upon Ferrous Sulfate Treatment"*, ***Environmental Science and Technology****, ACS*, Vol. 40, Issue 18, September 15, 2006, pp 5786-5792.
- Chrysochoou M., Dermatas D. (2007), *"Application of the Rietveld Method to Assess Chromium (VI) Speciation in Chromite Ore Processing Residue"*, ***Journal of Hazardous Materials***, *Elsevier*, Vol. 141, No. 2, pp 370–377, March 15, 2007.
- Moon D. H., Wazne M., Dermatas D., Christodoulatos C., Sanchez A.M., Grubb D.G., Chrysochoou M., Kim M.G. (2007), *"Long-term treatment issues with chromite ore processing residue (COPR): Cr^{6+} reduction and heave"*, ***Journal of Hazardous Materials***, *Elsevier*, Vol. 143, No. 3, pp 629-635, May 17, 2007.

References

- Chrysochoou M., Dermatas D., Grubb D.G. (2007), *"Phosphate Application to Firing Range Soils for Pb Immobilization: The Unclear Role of Phosphate"*, ***Journal of Hazardous Materials***, *Elsevier*, Vol. 144, No. 1-2, pp 1-14, June 2007

- Dermatas D., Chrysochoou M., Grubb D. G., Xu X. (2008), *"Phosphate treatment of firing range soils: Pb fixation or P release?"*, ***Journal of Environmental Quality***, 37 (1) pp. 47-56, January 2008.

- Dermatas D., Chrysochoou M., Moon D.H. (2008), *"Geoenvironmental Characterization to Assess Waste Stabilization/Solidification Treatment Performance and Sustainability"*, ***Geotechnics of Waste Management and Remediation***, *ASCE*, Geotechnical Special Publication 177, March 2008, pp 660-667.

- Chrysochoou M., Dermatas D., Moon D.H., Christodoulatos C. (2008), *"Reductive treatment of Chromite Ore Processing Residue (COPR): lessons from a field study"*, ***Geotechnics of Waste Management and Remediation***, *ASCE*, Geotechnical Special Publication 177, March 2008, pp 748-755.

- Chrysochoou M., Dermatas D., Christodoulatos C. (2009), *"Experimental Studies on Coupled Treatment of Chromite Ore"*, ***Journal of ASTM International***, Vol. 6, No. 3, Paper ID JAI102165, available online at www.astm.org

- Chrysochoou M., Moon D.H., Fakra, S., Marcus M.A., Dermatas D. and Christodoulatos C. (2009), *"Use of X-ray Absorption Spectroscopy and diffraction to delineate Cr(VI) speciation in COPR"*, ***Global Nest: the International Journal***, Vol 11, No 3, pp 318-324, 2009.

- Chrysochoou M., Zhang X. and Amador J., (2011). Aerobic reduction of Cr(VI)-reducing bacteria in pure culture and soil, ***Soil and Sediment Contamination***, in review

- Cologgia D.L., Lampa-Pastirka S., Speersa A.M., Kellyb S.D., and Regueraa G. (2011), *"Extracellular reduction of uranium via Geobacter conductive pili as a protective cellular mechanism"*, Published online before print, doi: 10.1073/pnas.1108616108, ***Proceedings of National Academy of Sciences of America (PNAS),*** September 6, 2011

Thank you for your attention

Laboratory and field investigation methods

- Where is the money?
- Sampling, analyses and R&D altogether focused in H_2O (we drink H_2O not soil/sediment)
- Whereas the source for H_2O pollution is soil/sediment (sometimes mixed w/waste)
- H_2O testing (lab and field) is relatively straightforward when compared to soil/sediment. Soil/sediment wide variability
- Pollution prevention principle mandates an applied focus on contaminated sediments/soils
- This implies a focus (R&D) on laboratory and field methods→ present state of practice needs to be improved by overcoming testing limitations → opportunities for future international collaborative R&D
- Need to ultimately develop reliable, simple, and cost-effective lab and field investigatory tools using readily-accessible equipment

Heavy metal occurrence (sources, distribution)

- Industrial or otherwise activity vs. occurrence (mining, industrial waste, sludge amended soils, wastewater-assisted irrigation, etc.)
- Particulate vs. dissolved HM contamination
- Retention in soils
- Release from soils into the aqueous phase (mechanisms)
- HM uptake by microorganisms, trees, plants and food crops
- Likelihood of HM entering the food chain
- Hierarchical assessment of HM contamination field cases in terms of severity of possible adverse effects

Heavy metal analyses (uncertainty, traditional vs. state-of-the-art characterization)

- HM testing reliability/uncertainty
- Traditional HM analyses (total concentrations)
- Batch extraction HM analyses (Sequential Extraction Test, regulatory extraction testing, etc.)
- Non-destructive analyses (XRPD, XANES, EXAFS, etc.) → HM speciation
- Field HM monitoring and analyses (mapping)

Heavy metal remediation (mechanisms of immobilization, extraction, leaching, speciation, regulatory assessment)

- HM removal from the aqueous phase
- HM immobilization in-place
- HM extraction from the solid phase
- Mechanisms of HM immobilization
- Remediation of HM contaminated media
- HM leachability
- Long-term HM mobility and release from remediated media
- Regulatory assessment