Upcycling the Ashes for Sustainable Management of Soil Contaminants

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Outline

- Origin of the Stabilization Technology Development
- Background - Heavy Metal Impacts & Remediation
- Pros & Cons of Solidification and Stabilization Technology
- SRT® Mechanisms
- Performance Verification - Case Studies
- Sustainable Aspects - Revegetation & GHG Reduction
- Other Applications and Next Development

Acknowledgements

- Korea Environmental Industry & Technology (KEITI)
- NRC-IRAP
- Alberta Innovates

Bioremediation

Chemical Remediation

Stabilization & Sequestration

Thermal Extraction & Recovery

Soil Washing

Feasibility & Remediation Design

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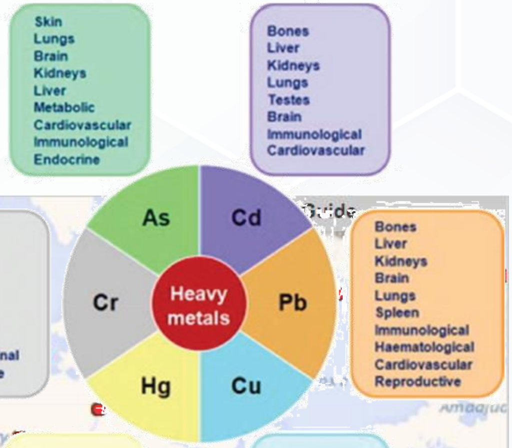
Origin

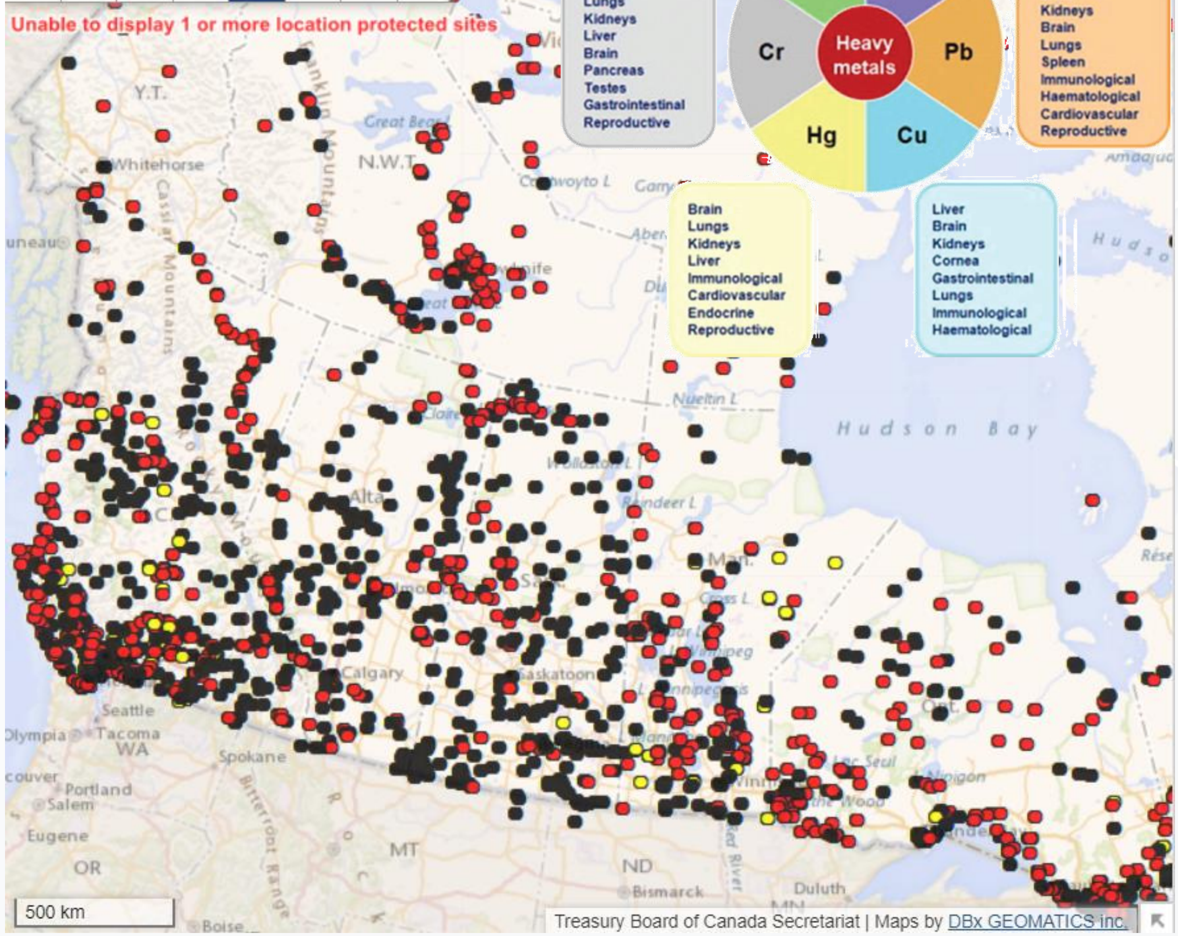
- South Korea
  - For Reuse of Leachable Heavy Metal Impacted Soil and Sewage Sludge

Background

- Heavy metals (HM) are everywhere
- > 7,000 HM contaminated sites in Canada
    - 1,572 HM impacted groundwater
    - 4,851 HM impacted soil
- Health concerns
    - Most heavy metals toxic and carcinogenic

(Masindi and Muedi 2018)



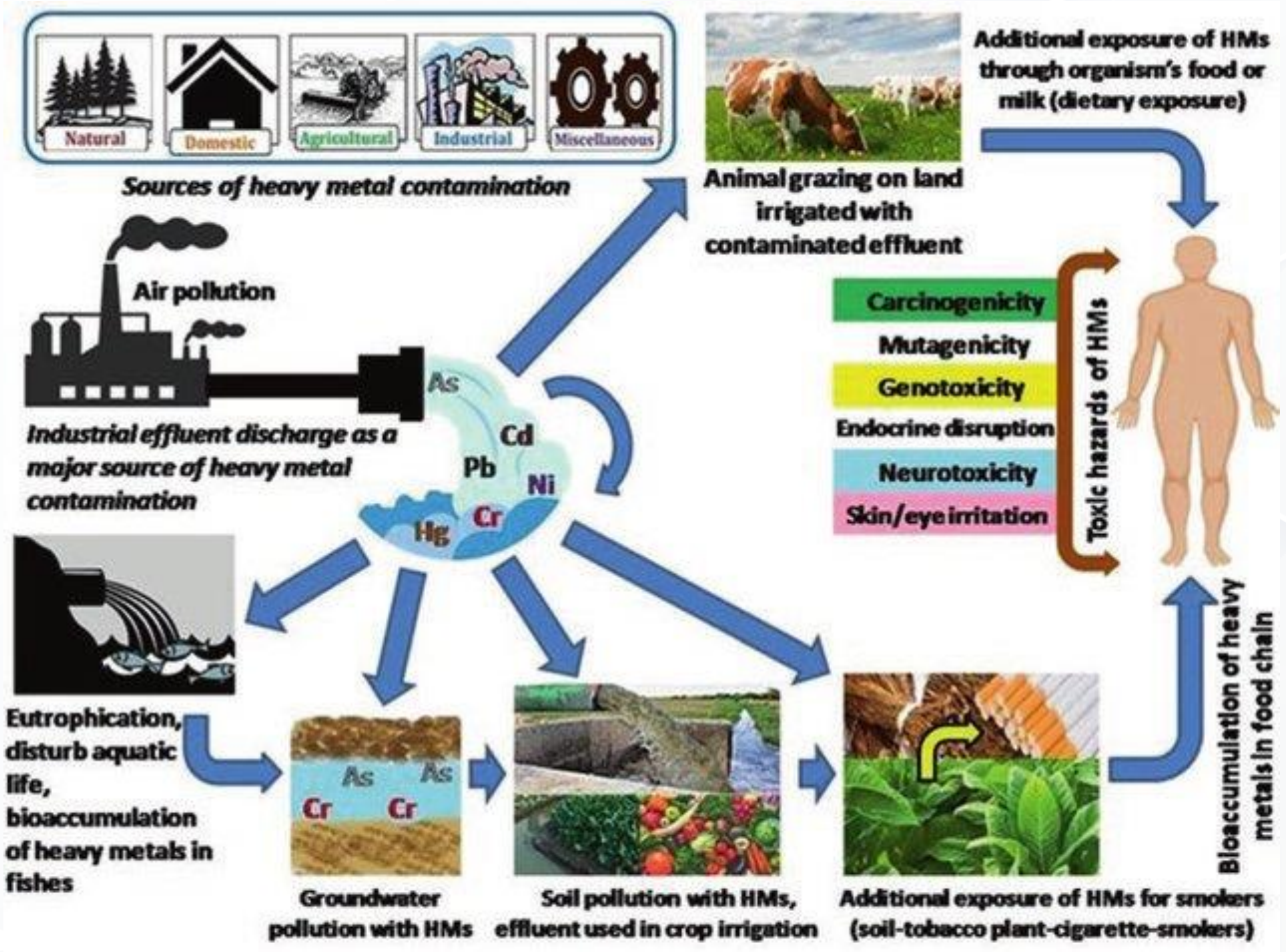


(Federal Contaminated Site Inventory)

Background

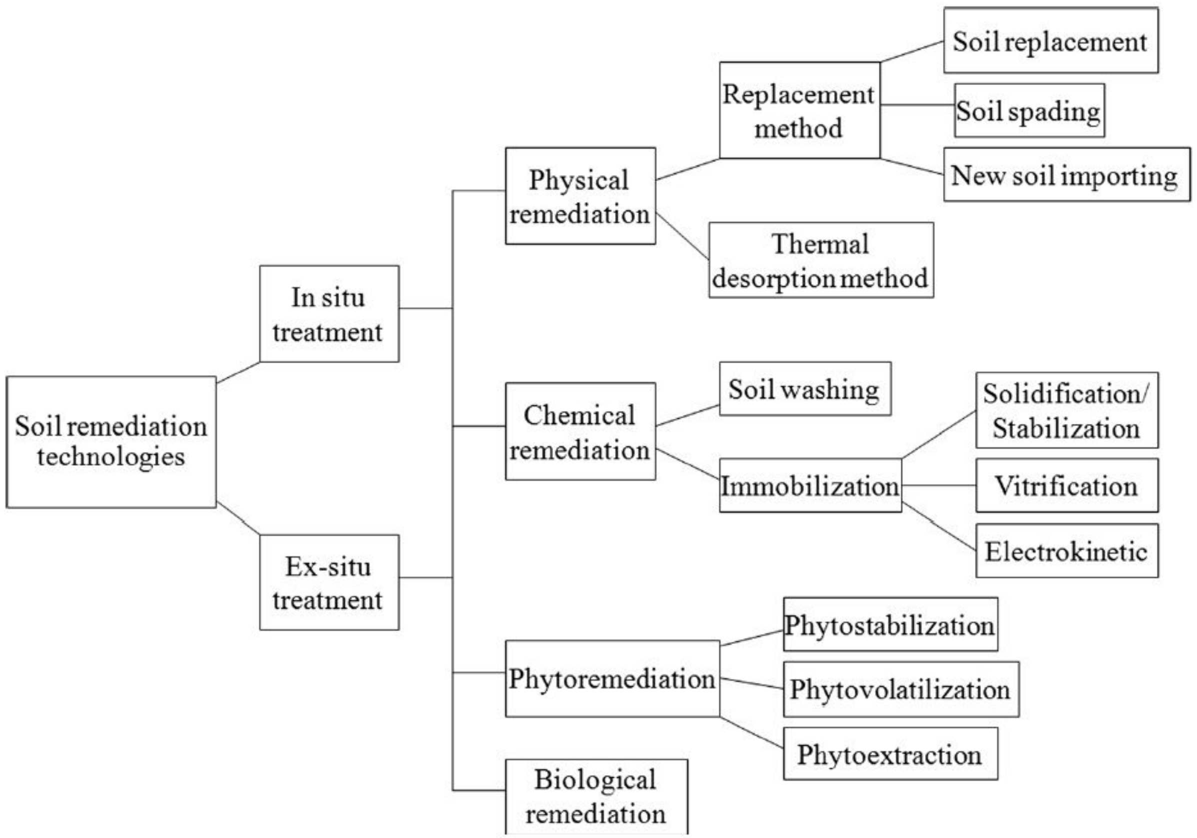
- Major Sources of Heavy Metals
  - Agriculture
    - Fertilizer, manure, irrigation, sewage sludge
  - Industry
    - Wastewater, manufacturing, power plants
    - Wood preservatives (e.g. CCA)
  - Mining
    - Ore extraction, smelting, tailings

- Exposure Pathways
  - Air, (ground)water, soil

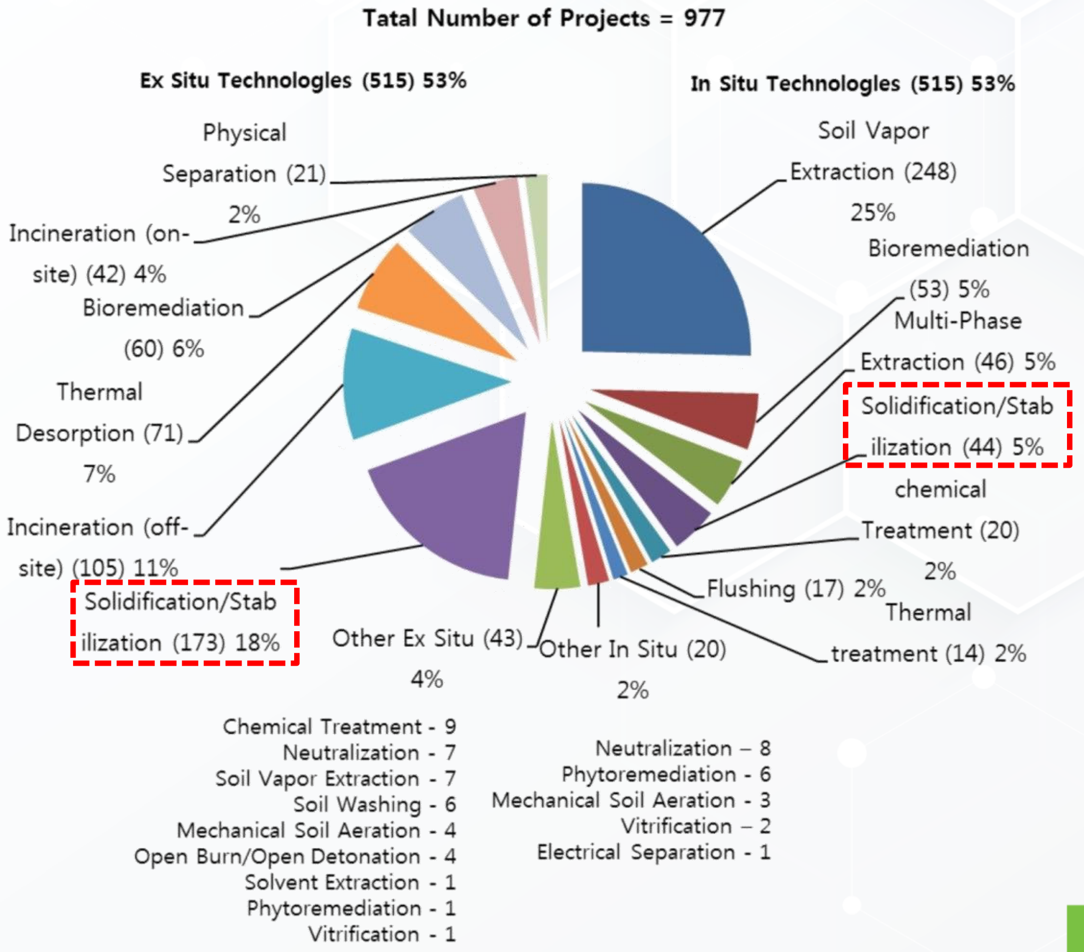


(Saxena et al. 2019)

Heavy Metals Treatment Methods



(Derakhshan Nejad et al. 2018)



(Treatments applied in USEPA Superfund Innovative Technology Evaluation Program)

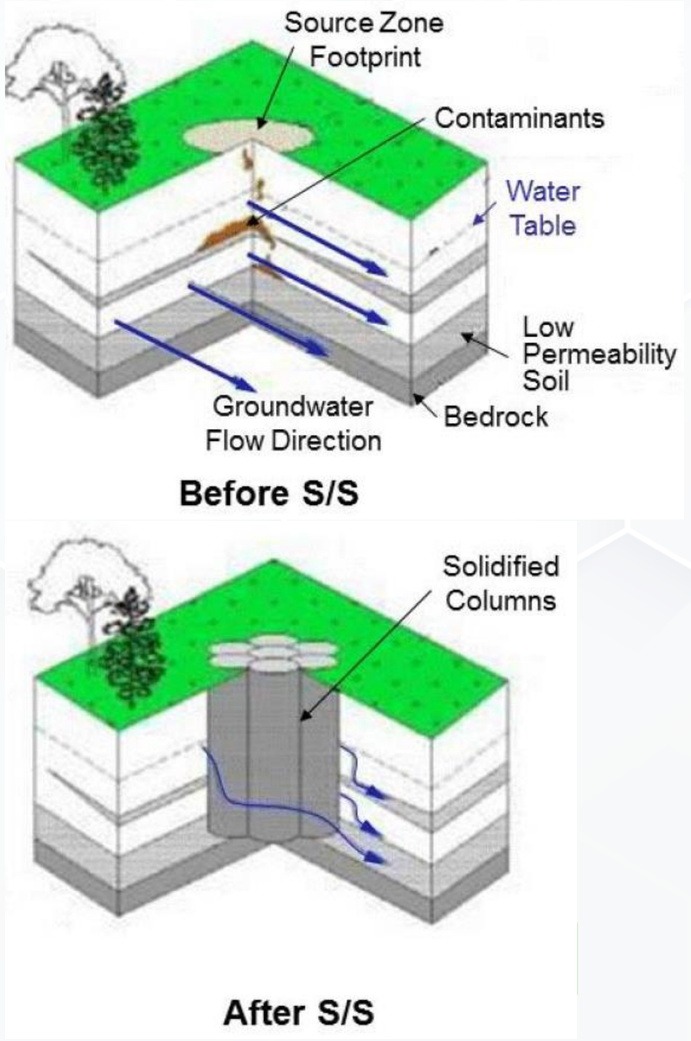
Solidification/Stabilization (S/S)

- **Solidification**
  - Transforming **physical properties** of contaminated soil by addition of binding agents
  - Binding agents compact the soil matrix, change the pore volume and reduce the hydraulic conductivity
  - No active promotion in chemical changes of contaminants

- **Stabilization**
  - Transforming **chemical properties** of contaminants within the soil matrix
  - Contaminants transformed into compounds having lower water solubility, mobility and toxicity

S/S Treatment and Problems

- Cement or Pozzolan-based Binders and Stabilizers
  - Most common approach for solidification
  - Increase compressive strength and lower hydraulic conductivity/permeability
  - Limit release of heavy metals encapsulated
  - Divert groundwater flow due to low K of solidified material
  - Disadvantage in vegetation on the contaminated area and downward
  - Limited reclamation capabilities
  - Commonly 8% to >20% added
  - Poor setup in presence of organics or high moisture
  - GHG emission during cement production & S/S treatment



(ITRC 2011)

Upcycling Wastes for Valuable Products

- Patented Soil Restoration Technology (SRT®) - PCT/KR2018/002452
  - Pulp sludge or bottom ash (silicon dioxide dominant) as essential component
  - Modifiable additives upon target contaminants
    - Reducing agent for reduction multivalent heavy metals
    - Polymers for demoisturization
    - Naturally occurring materials for sorption enhancement

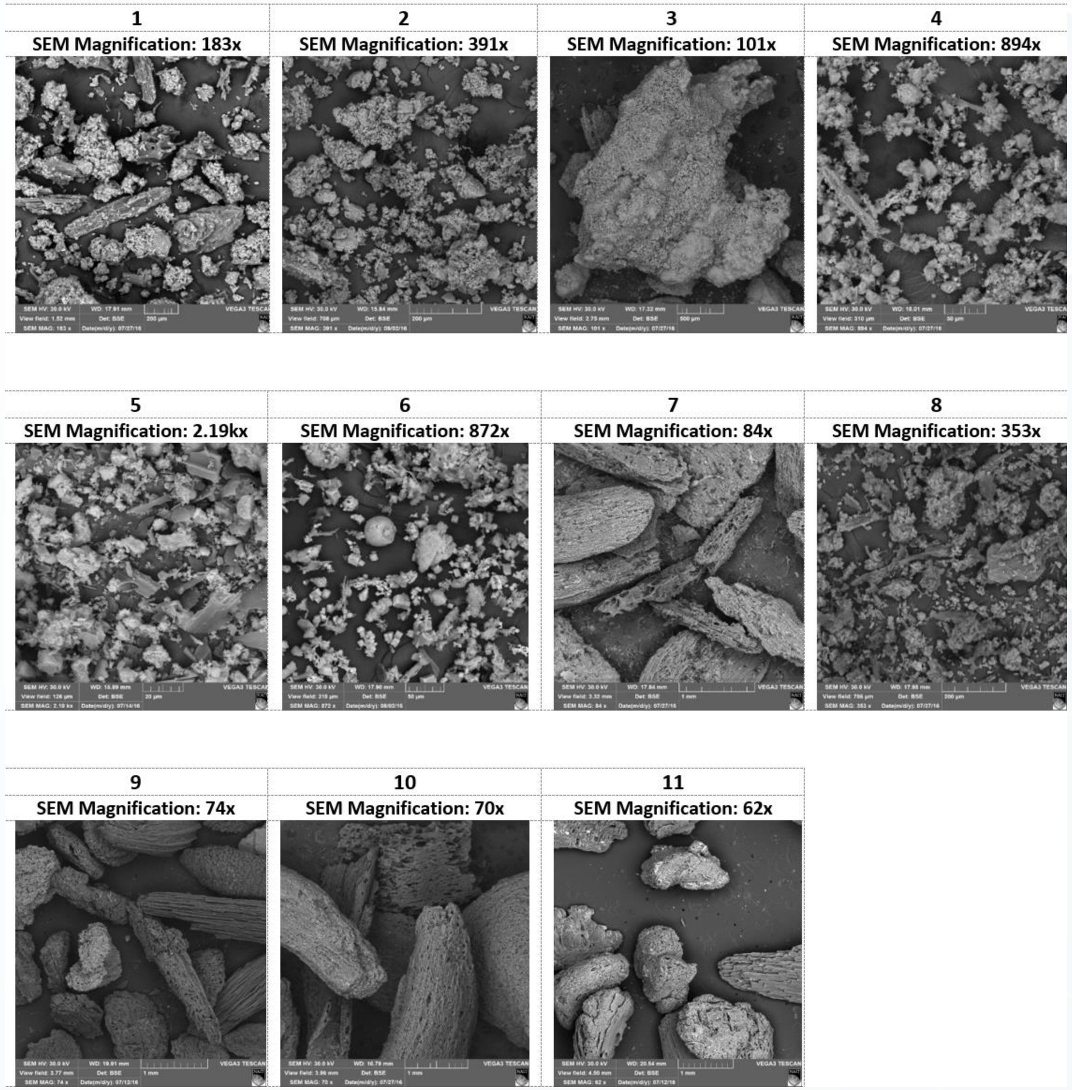
Upcycled Wastes

Additives

SRT®

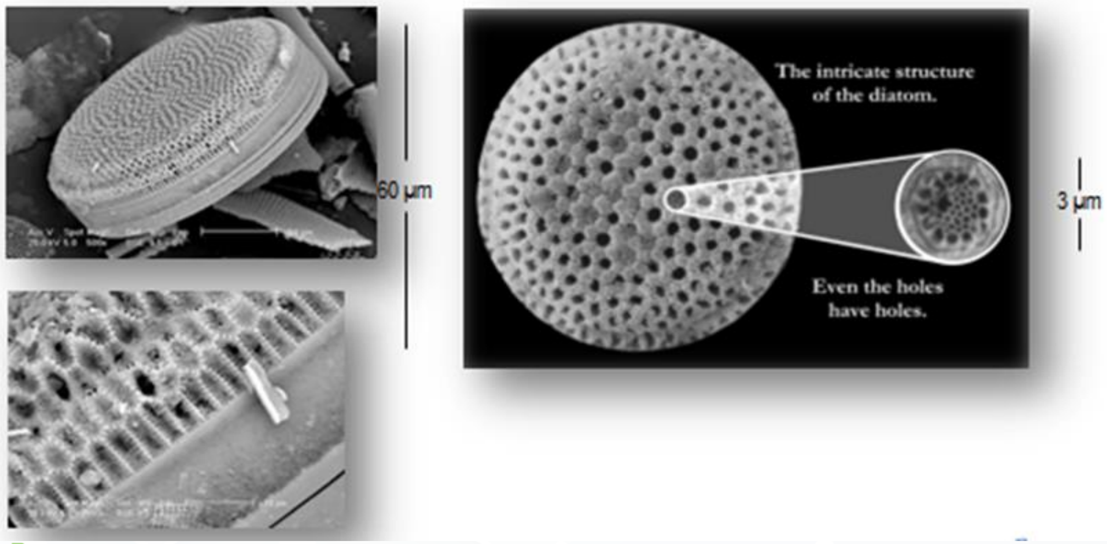
Upcycling Wastes for Valuable Products

- Not All Pulp Mill Wastes Are Equally Generated!
  - Pick most suitable material to accommodate reactions of additives and satisfy core mechanisms
  - \- Sorption
  - \- Ettringite Formation
  - \- Reduction & Precipitation

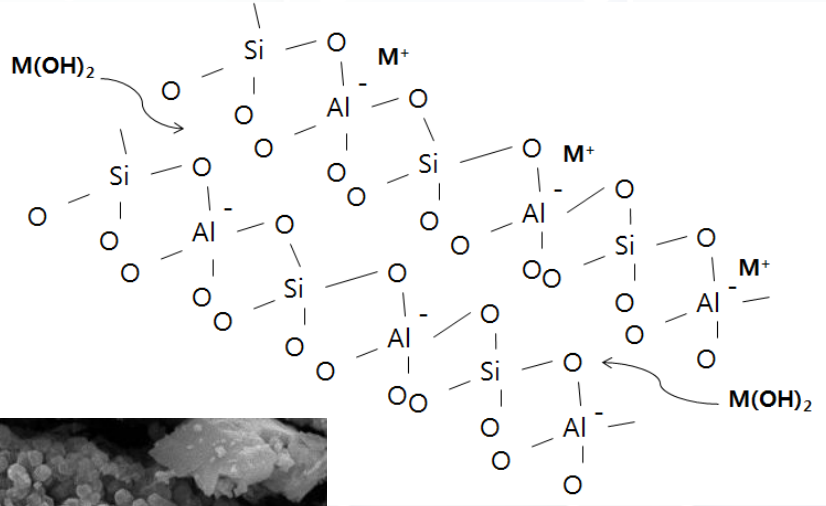


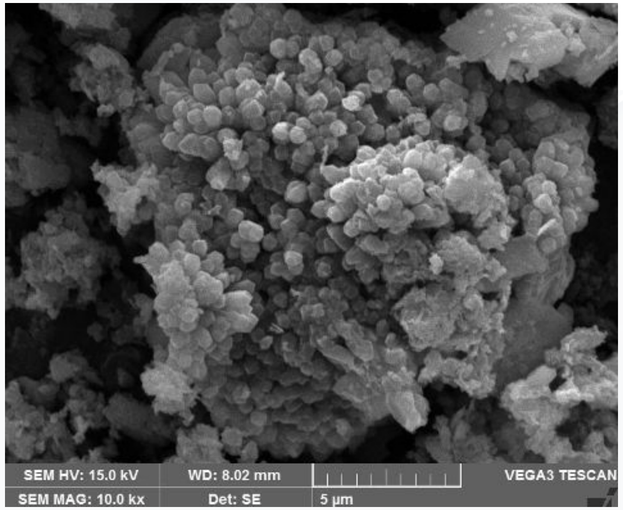
SRT® Mechanisms

- Heavy Metals Sorption on Porous Silica Dioxide
  - Formation of very hard silicon dioxide
  - Heavy metals sorbed on porous silicon dioxide
  - No or limited elution of sorbed metals



(https://imerys-filtration.com/north-america/about-us/minerals-geology/diatomite/)

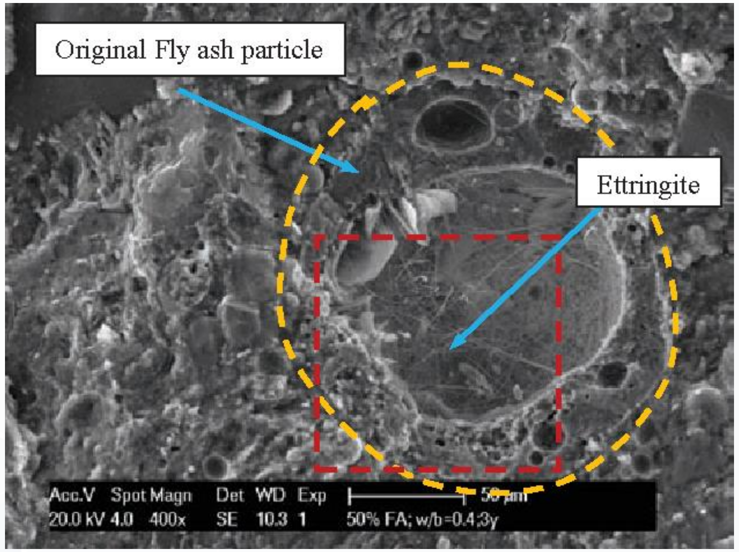




SRT® sequestering copper

SRT® Mechanisms

- Ettringite Formation by SRT® constituents
  - Silica (Si) and alumina (Al_2O_3) eluted from soil and SRT® constituents in presence of water
  - Formation of calcium silicate ($3CaO \cdot 2SiO_2 \cdot 3H_2O$) and calcium aluminate ($3CaO \cdot Al_2O_3 \cdot 6H_2O$)
  - Formation of needle-like crystal Ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$)
  - Heavy metals sorption on porous structure of Ettringite



(Yu et al. 2016)

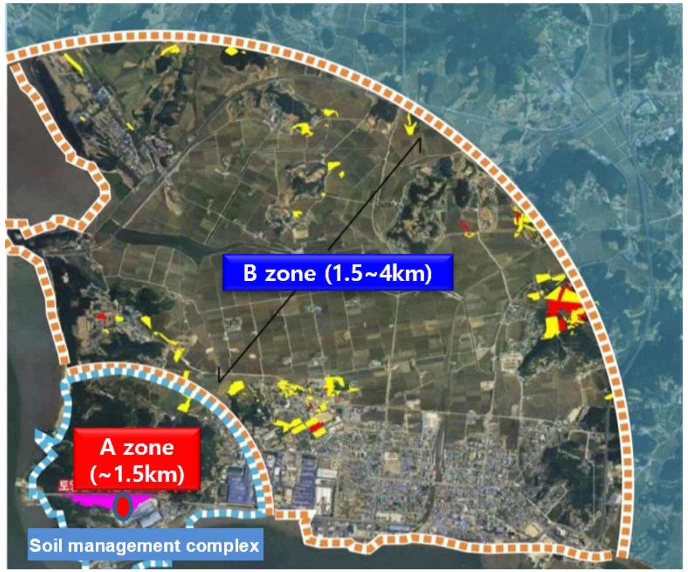
(Jun et al. 2019)

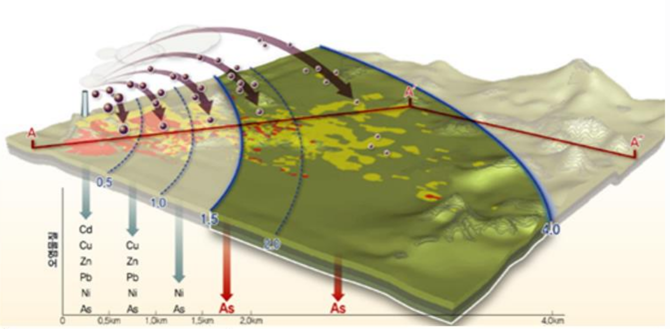
SRT® Mechanisms

- Reduction and Precipitation (example of Cr(VI))
  - Reduction of Cr(VI) to Cr(III)
    - Ferrous iron (Fe^{2+}) - additive in SRT® stabilization process as an effective reductant
    - $3Fe^{2+} + \mathbf{HCrO_4^-} + 7H^+ \leftrightarrow 3Fe^{3+} + \mathbf{Cr^{3+}} + 4H_2O$
  - Precipitation of Cr(III)
    - Calcium hydroxide ($Ca(OH)_2$) - additive in SRT® stabilization process and source of hydroxide (OH^-)
    - $\mathbf{Cr^{3+}} + 2Ca(OH)_2 + 7H^+ \leftrightarrow \mathbf{Cr(OH)_3}\downarrow + 2Ca^{2+} + H_2O$

Performance Verification

- Heavy Metals Impacted Soils from South Korean Sites





Contaminated area	A zone : 891,000㎡ B zone : 200,760㎡
Contaminated volume	A zone : 498,430㎥ B zone : 214,400㎥
Pollutants	As, Pb, Cd, Cu, Zn, Ni

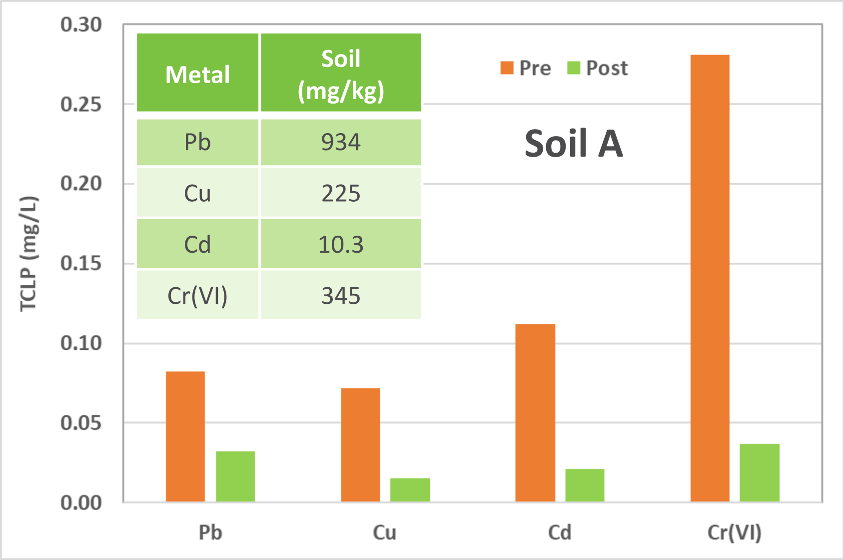
A zone(1.5km from Janghang smlter)

B zone(1.5~4km from Janghang smelter)

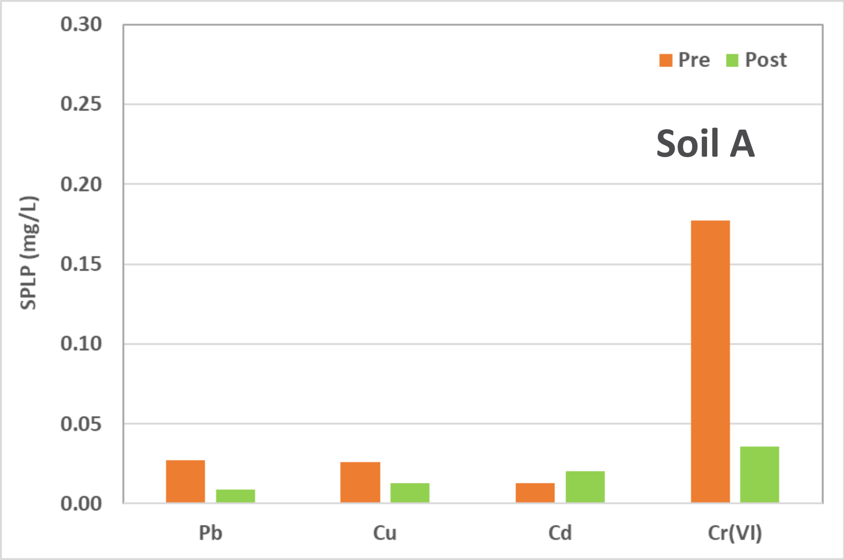
Performance Verification

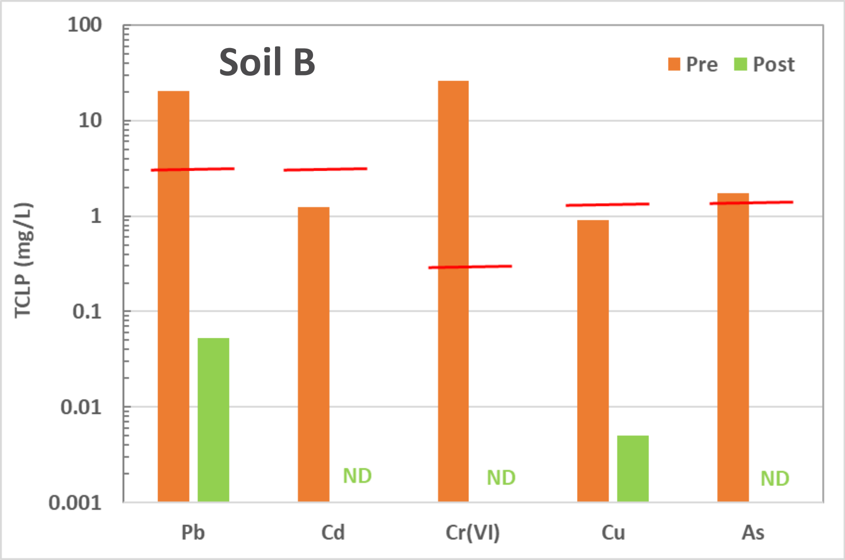
- Heavy Metals Impacted Soils from South Korean Sites
  - Leachable metals evaluated by TCLP and SPLP
    - TCLP: Toxicity Characteristic Leaching Procedure
    - SPLP: Synthetic Precipitation Leaching Procedure
  - Effectively stabilized heavy metals by addition of 5 % SRT®

*Red lines – Korean remediation guidelines



Metal	Soil (mg/kg)
Pb	934
Cu	225
Cd	10.3
Cr(VI)	345



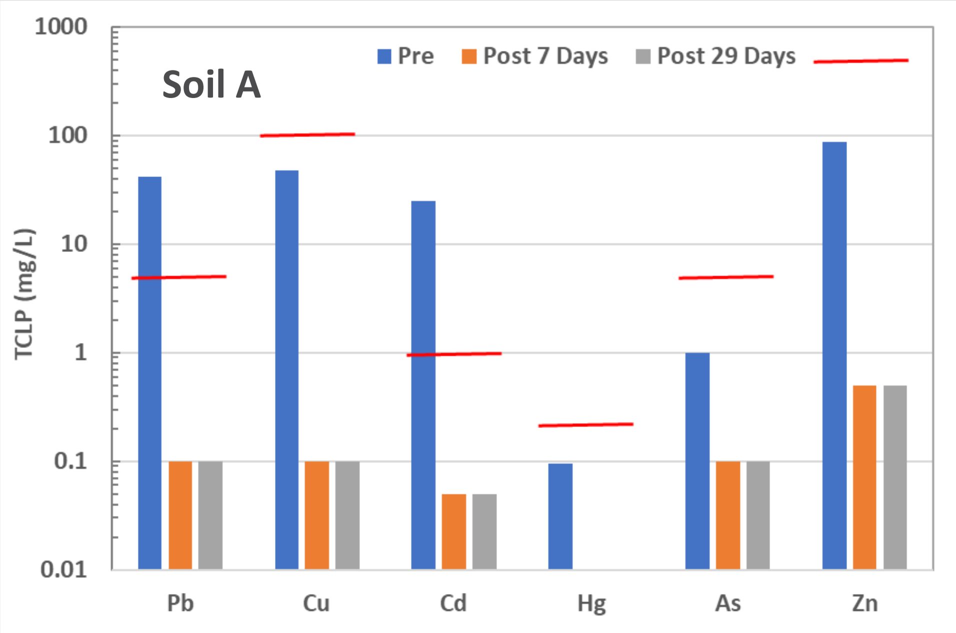


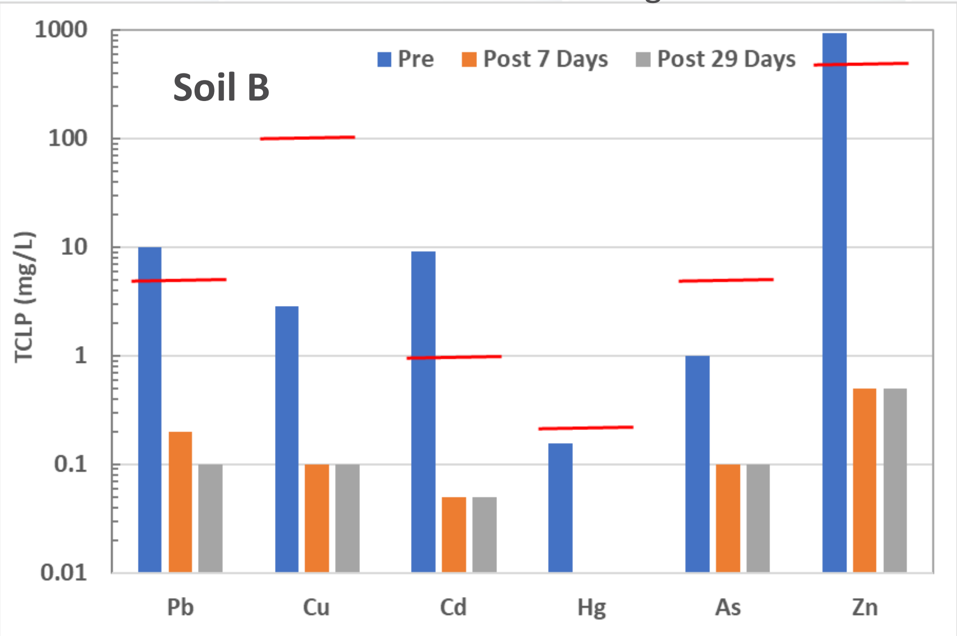
Performance Verification

- Heavy Metals Impacted Soils from a Canadian Mine
  - Highly heavy metals impacted soils
  - High leachate concentration, especially Pb and Cd
  - Rapid heavy metals stabilization with 7% SRT® addition
  - No leaching in follow-up treatment testing

*Red lines – AB Tier 1 remediation guidelines

Metal	Soil A (mg/kg)	Soil B (mg/kg)
Pb	45,100	19,900
Cu	3,090	881
Cd	799	338
Hg	-	-
As	344	572
Zn	20,500	34,000





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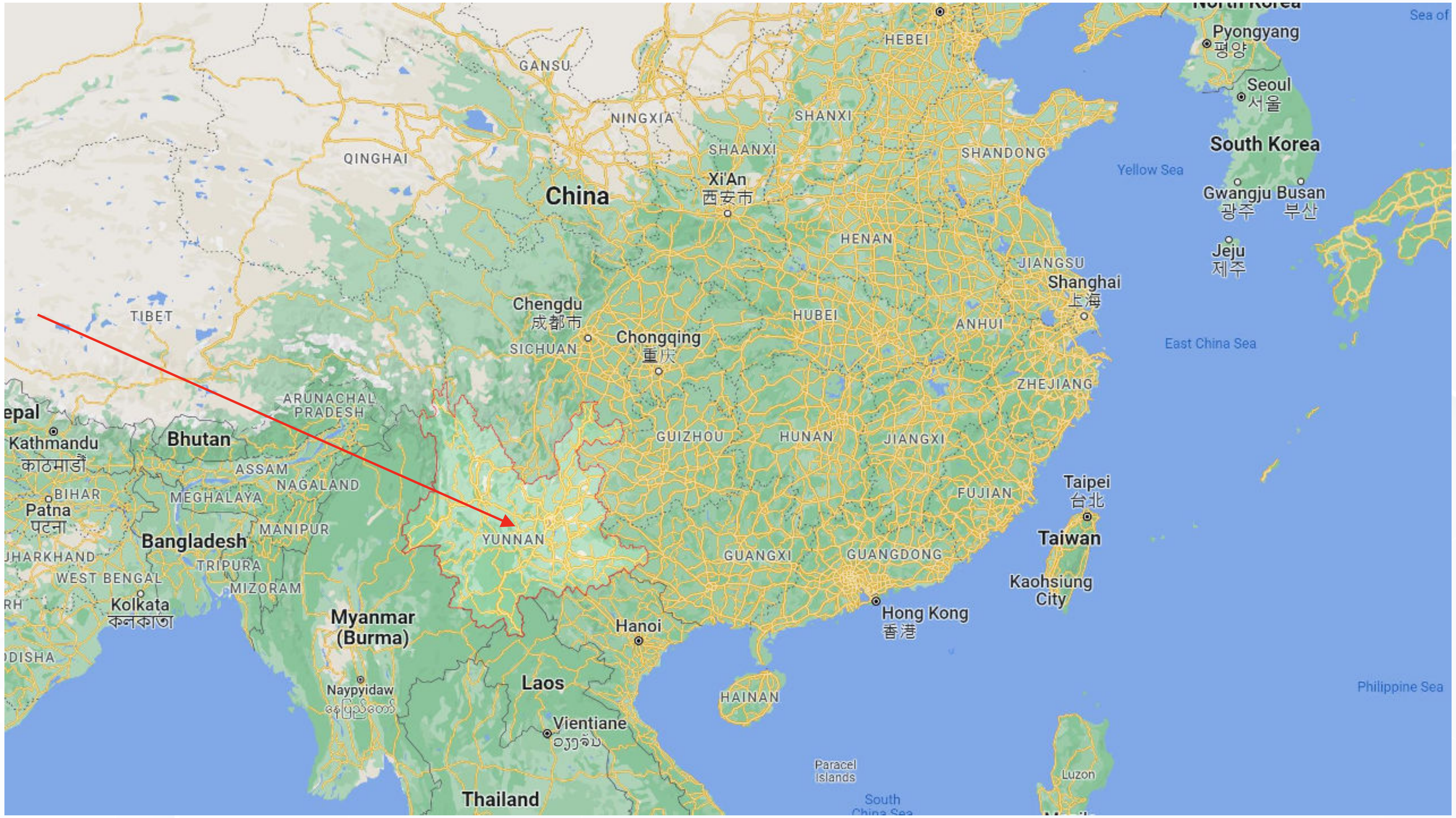
Performance Verification

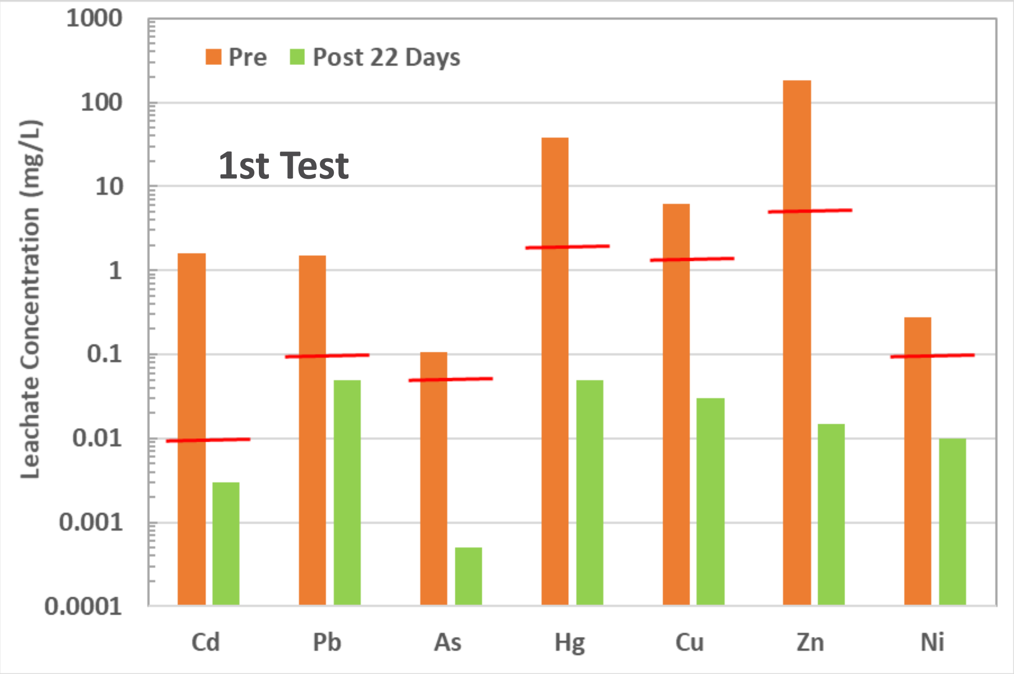
- Heavy Metal Impacted Soil from Lead Mine In Yunnan, China

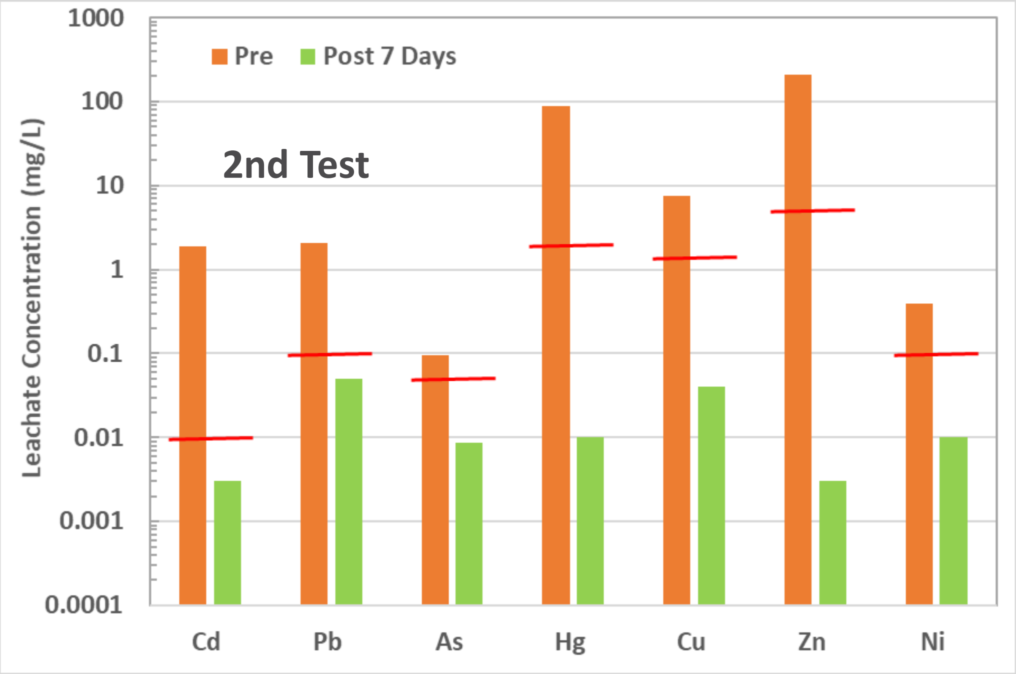


Performance Verification

- Heavy Metal Impacted Soil from Lead Mine In Yunnan, China
  - Effectively stabilized heavy metals by addition of 5 - 7% SRT®
  - No significant difference in concentration between Post 7 and 22 days results
    - Indicates primary heavy metals stabilization process within 7 days

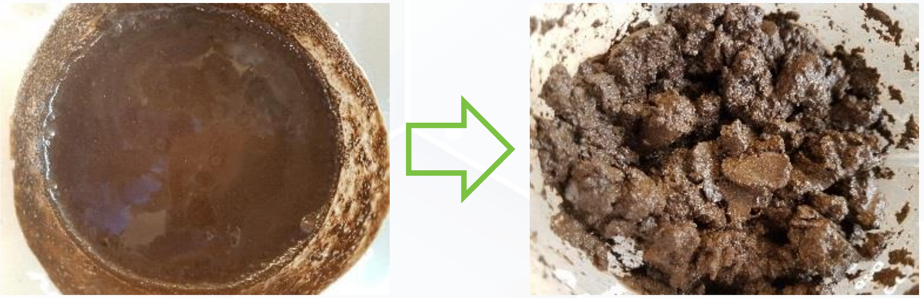
*Red lines – Chinese remediation targets





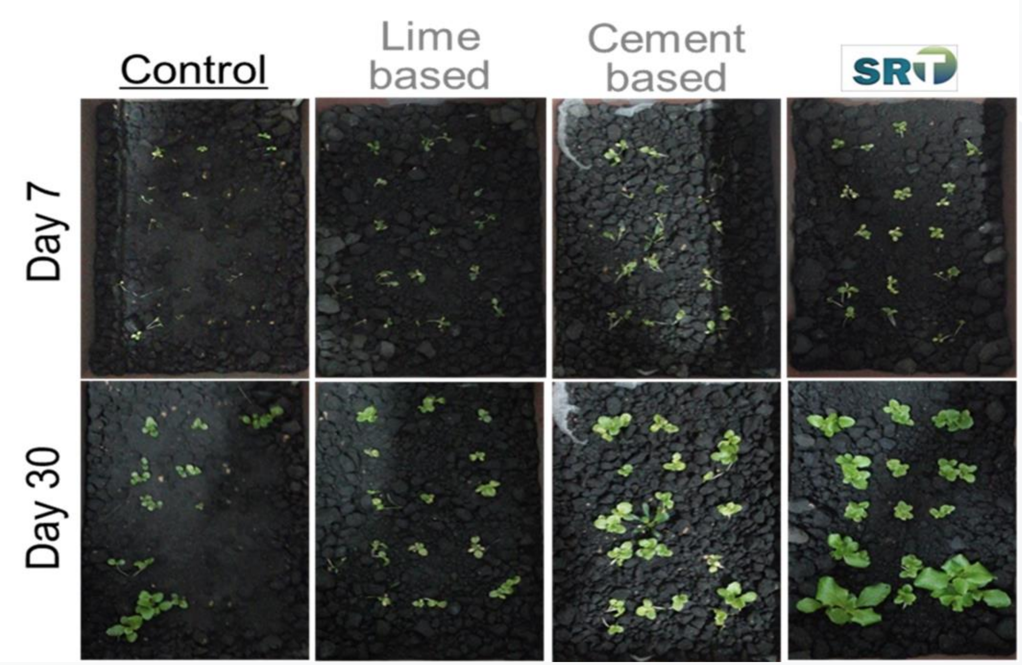
Performance Verification

- Aquatic Eco Toxicity, Hydraulic Conductivity and Vegetation Tests
  - Reduced toxic unit with SRT® application
  - No or less impact on hydraulic conductivity
  - Enhanced vegetation with SRT®
  - No significant volume increase



Metal	TU (Pre)	TU (Post)
Lead (Pb)	4.0	1.9
Arsenic (As)	6.1	2.0

Parameters	Sample A		Sample B	
	Pre	Post 7 Days	Pre	Post 7 Days
Bulk Hydraulic Conductivity (m/s)	3.48 X 10^{-5}	4.96 X 10^{-5}	1.60 X 10^{-6}	3.84 X 10^{-6}
Moisture (%)	40.0	28.2	-	-

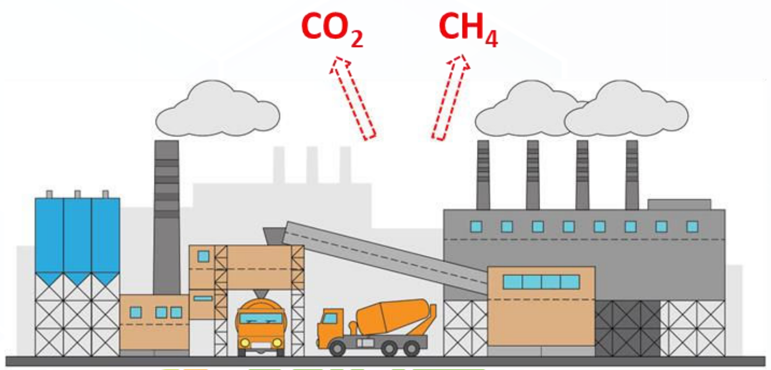


GHG Emissions Reduction

- Considerable GHG Emissions by Cementitious Products
  - GHG emissions during cement production and S/S treatment
    - 0.9 kg CO_2e/kg cement in cement production (Portland Cement Association)
    - 19.1 - 47.6 kg CO_2e/m^3 concrete-like soil structure (8 - 20 % by mass) based on 238.2 kg CO_2e/m^3 concrete during curing period
  - No or limited GHG reduction by revegetation after treatment

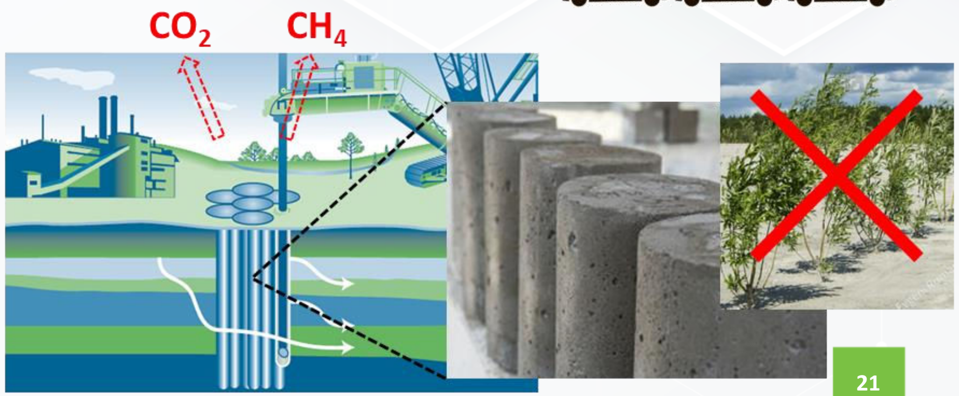
CO_2 from 200 cars

Stabilization of 1,000 m^3 soil =



Cement Manufacturing

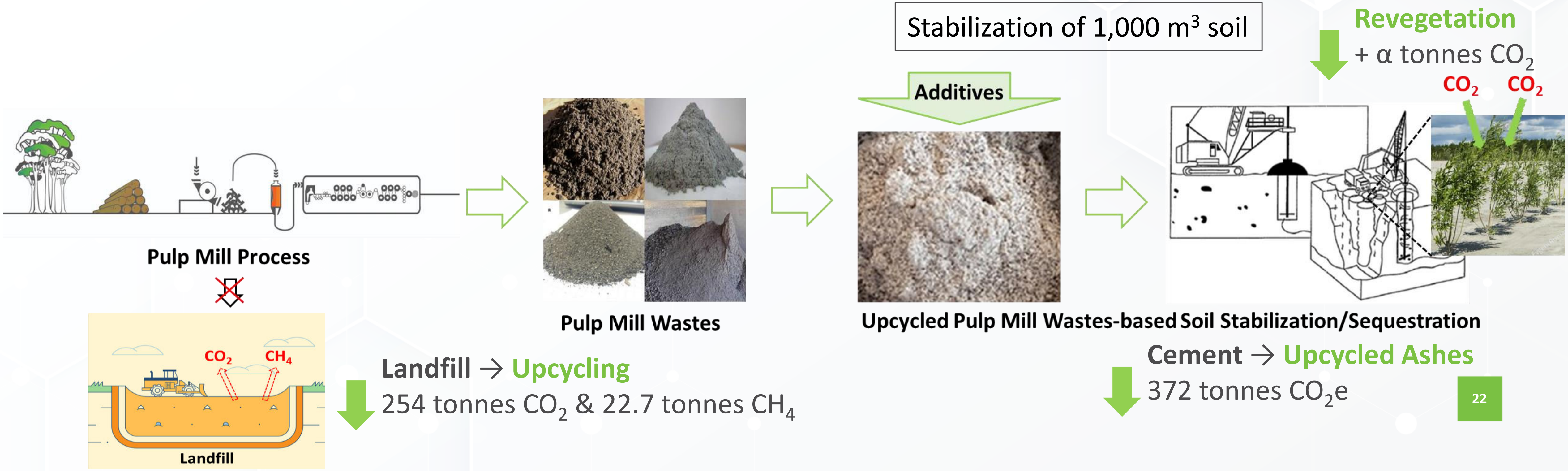
Portland Cement



Cement Based Solidification/Stabilization of Contaminated Soil

GHG Emissions Reduction

- GHG Emissions Reduction by Upcycling Pulp Mill Wastes
  - GHG reduction = less cement production + less pulp mill wastes landfilling + revegetation
    - 2.69 kg CO_2 & 0.24 kg CH_4/kg landfilled pulp mill sludge (Likon and Trebse, 2012)

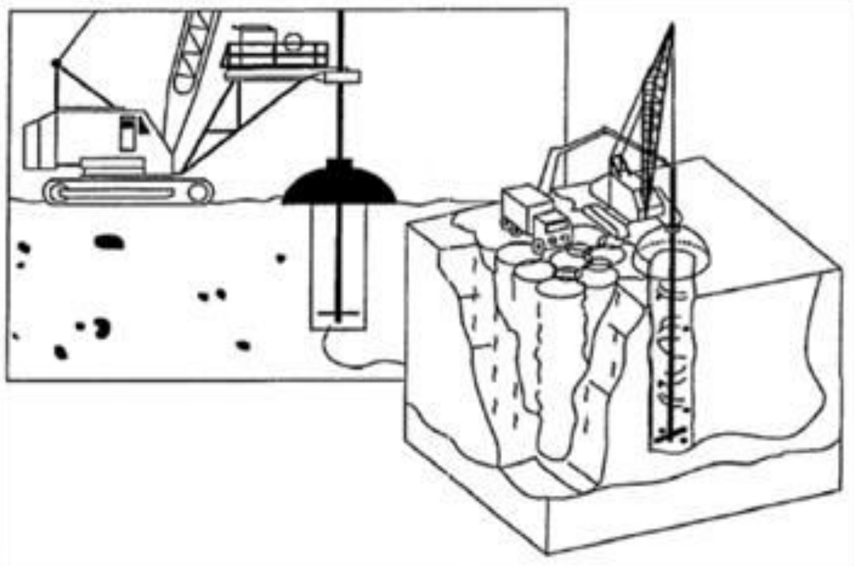


Application

- Typical Ex-situ and In-situ Applications

Ex-situ mixing

Shallow in-situ mixing



Deep in-situ mixing

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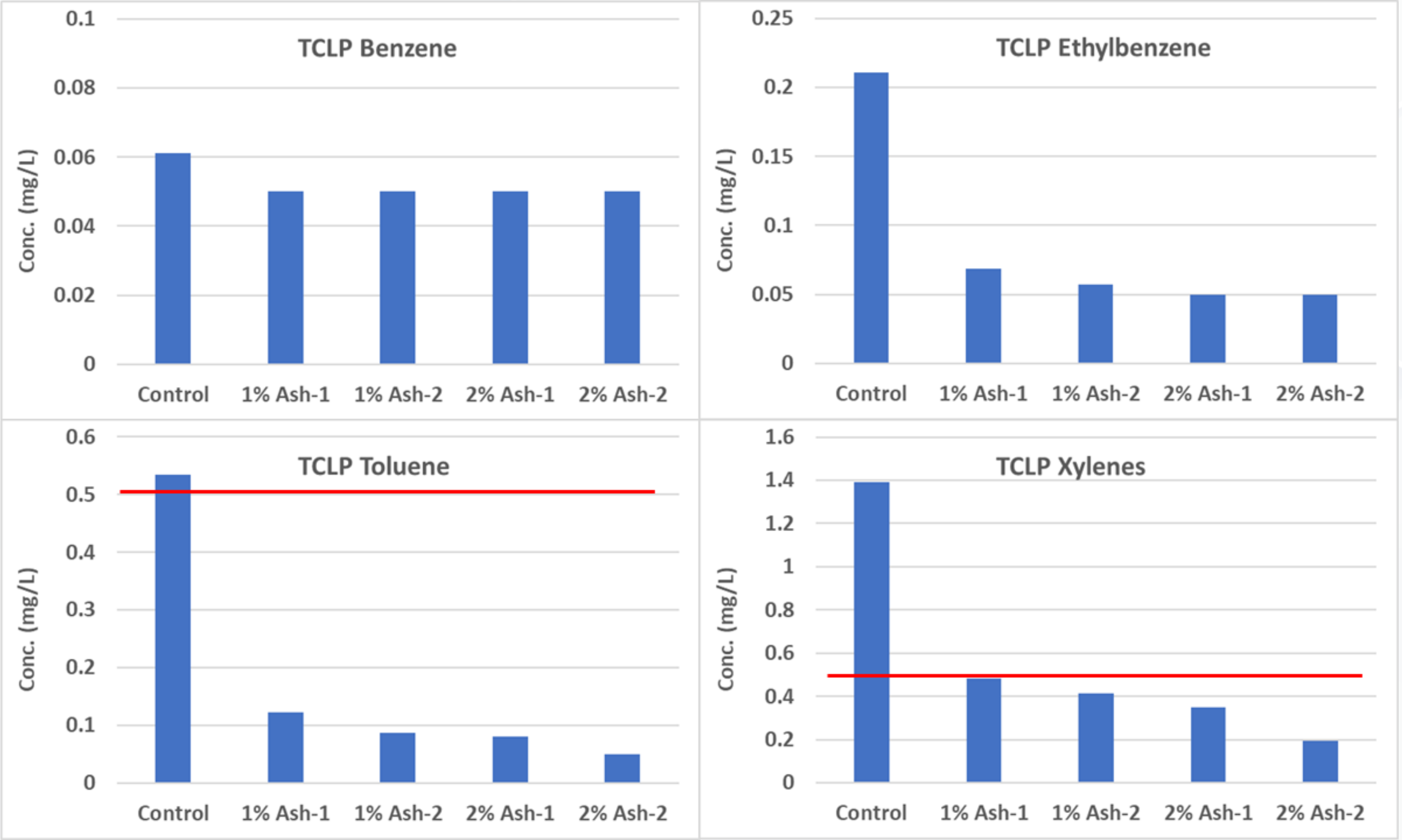
Other Application – Leachable BTEX

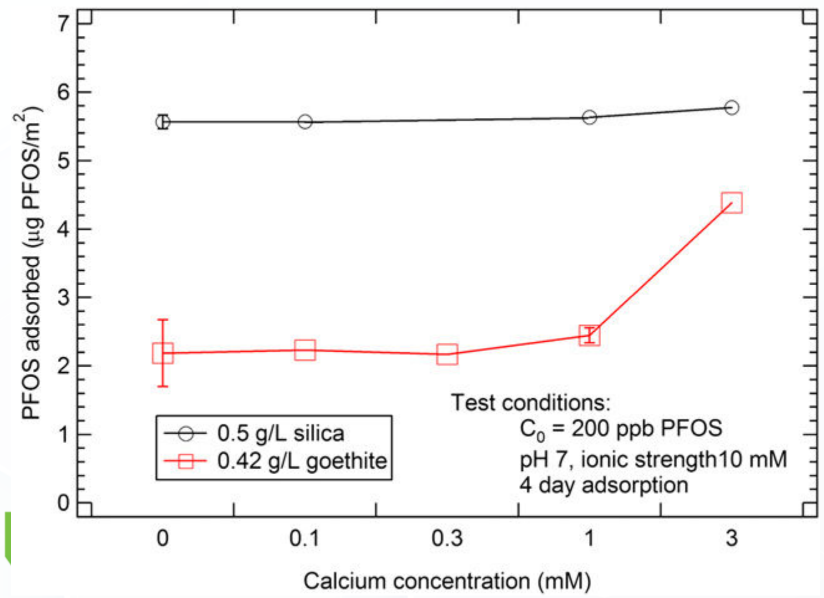
- Feasible Ash Application for Landfilling BTEX Impacted Soil
  - Significant reduction of leachable ethylbenzene, toluene, and xylenes by ash application within hours
  - All BTEX meet the guidelines (< 0.5 mg/L) after ash treatment
  - Benzene and ethylbenzene (and one of replicate for toluene) below the detection limits (<0.05 mg/L) with 2% ash application

*Red lines indicate guidelines from Alberta User Guide for Waste Managers.

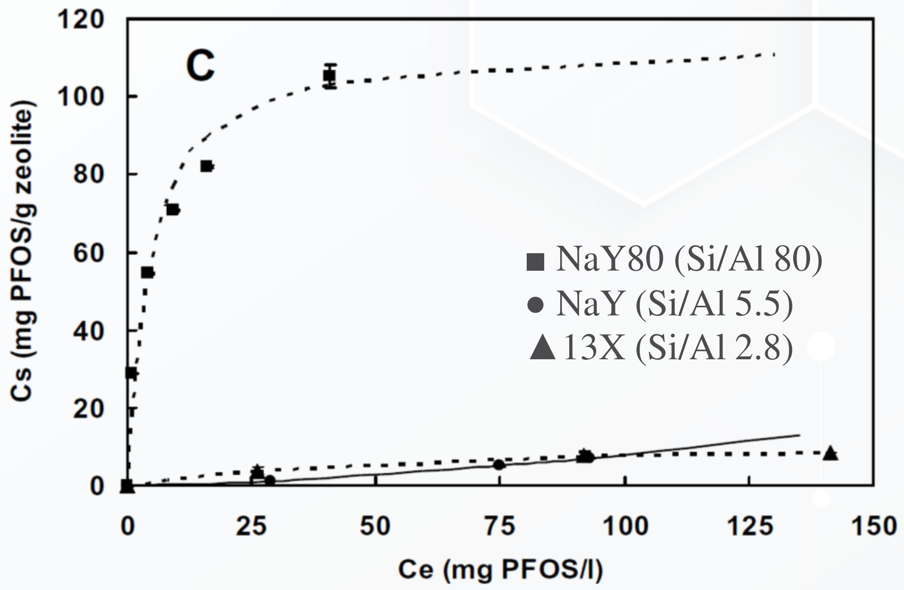


Potential Application for PFAS

- High Levels of PFOS Uptake by Natural Adsorbents
  - ~ 115 mg PFOS/g adsorbent (>90 % removal from aqueous phase)
    - Comparable to PFOS adsorption by granular activated carbon (GAC)
  - Weakly sensitive to geochemical change (i.e. pH and ionic strength)
  - Probably due to hydrophobic interaction rather than electrostatic interaction



(Tang et al. 2010)



(Ochoa-Herrera and Sierra-Alvarez 2008)

SUMMARY

- Soil Restoration Technology using Recycled Pulp Wastes and Naturally Occurring Materials
  - Effectively reduce, adsorb and precipitate metals by several physicochemical mechanisms
  - Prevent leaching contaminants after rapid binding/stabilization
  - Reduce toxicity of metals
  - Reclamation capacity after treatment
  - Stabilization potential for PFAS, hydrocarbons, and other organic contaminants
  - Limited or no GHG footprint

Reagent	SRT®	Cement	CaO	Polymer
pH	Neutral	Alkaline	Alkaline	Neutral
Permeability (porosity)	Normal	Poor	Poor	Poor
Compaction	Good	Good	Poor	Poor
Leachability	Reduced	Reduced	Reduced	Reduced

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Reference

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Questions?

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