Simultaneous removal of arsenic and toxic metals from contaminated soil: laboratory development and pilot scale demonstration of ReMix technology

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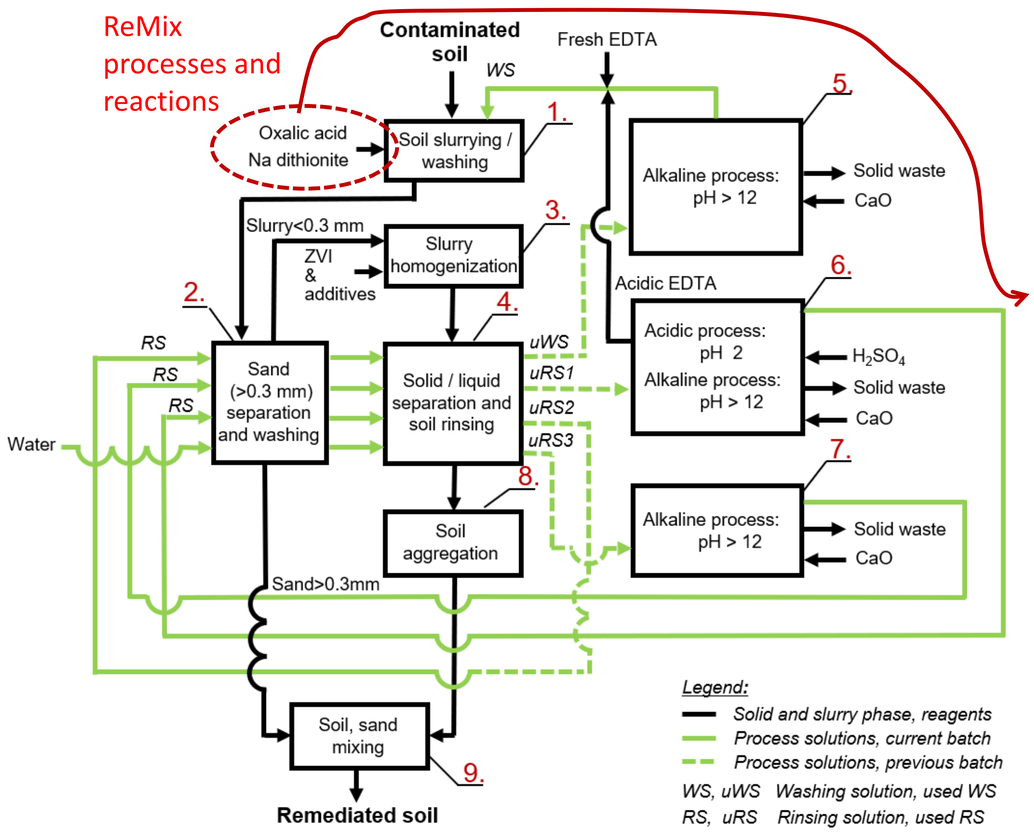
INTRODUCTION: Contamination of soils with toxic metals such are Pb, Zn, Cd, Cu, and toxic metalloids such is As is a worldwide problem. As and Pb in particular are ranked #1 and #2 environmental contaminants most hazardous for human health (ATSDR 2017). Soil chemistry of toxic metalloids and metals differs, making their simultaneous removal from soil difficult.

ReMix processes and reactions



The ReMix was developed based on a closed-loop chemical / physical platform (now called ReSoil) previously developed by Envit for the removal of toxic metals from soil by chelation with EDTA. This involves recycling process solutions and EDTA in a pH gradient of 12.5 to 2 achieved by adding quicklime and sulfuric acid, thoroughly rinsing the washed soil in a filter press, and adsorbing the remaining EDTA chelates onto the Fe-oxide hydroxide shell that develops around zero-valent iron after it is added to the soil slurry.

Chelating and transfer of toxic metals (Me) from the soil to the washing solution:

Pb-EDTA, Cd-EDTA, Zn-EDTA, Cu-EDTA…. (Me-EDTA)

Reductive dissolution of amorphous and crystalline Fe oxides and hydroxides by oxalic/citric acid and Na dithionite to release As into the washing solution as arsenite. EDTA chelation of Fe prevents precipitation of a new Fe oxide-hydroxide phase:

$$FeH_2AsO_{4(s)} \rightarrow Fe^{2+} + AsO_3^{3-} + H_2O$$
$$EDTA^{2-} + Fe^{2+} \rightarrow Fe\text{-}EDTA$$

Decomposition of Na dithionite ($Na_2S_2O_4$) and release of Na^+ and sulfide anion in solution:

$$Na_2S_2O_4 + 2H_2O \rightarrow 2Na^+ + 2HSO_3^- + 2H^+$$
$$HSO_3^- + H_2O \rightarrow SO_4^{2-} + 3H^+$$

The alkalinity (pH>12) achieved by the addition of quicklime (CaO) destabilizes the Me and Fe-EDTA chelates in the process solutions. Me and Fe are replaced by Ca, and EDTA is recycled as Ca-EDTA. Me and Fe (co)precipitate as hydroxides:

$$2Me\text{-}EDTA + Fe\text{-}EDTA + 3Ca^{2+} + 5OH^- \rightarrow 3Ca\text{-}EDTA + xMe(OH)_{2(S)} + Me_yxFe(OH)_{3(S)}$$

At the same time, As is removed from process solutions by coprecipitation with Fe hydroxide (pH>12):

$$Fe\text{-}EDTA + Ca^{2+} + 2OH^- \rightarrow Fe(OH)_{2(S)} + Ca\text{-}EDTA$$
$$Fe(OH)_{2(S)} + AsO_3^{3-} \rightarrow FeH_2AsO_{4(S)}$$

The excess oxalic acid precipitates out of the process solution as Ca-oxalate:

$$C_2O_4^{2-} + Ca^{2+} \rightarrow CaC_2O_{4(s)}$$

Hydration of quicklime binds water and enables a process without wastewater generation:

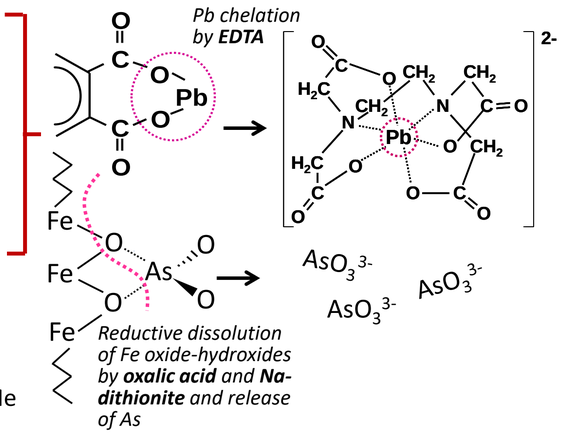
$$CaO + H_2O \rightarrow Ca(OH)_{2(s)}$$

The alkaline processes (Steps 5 and 7) recycle >90% of the EDTA. Acidifying the process solutions with sulfuric acid (H_2SO_4) to pH 2 precipitates and recycles EDTA in insoluble acidic form:

$$H_2EDTA^{2-} + 2H^{2+} \rightarrow H_4\text{-}EDTA_{(s)}$$

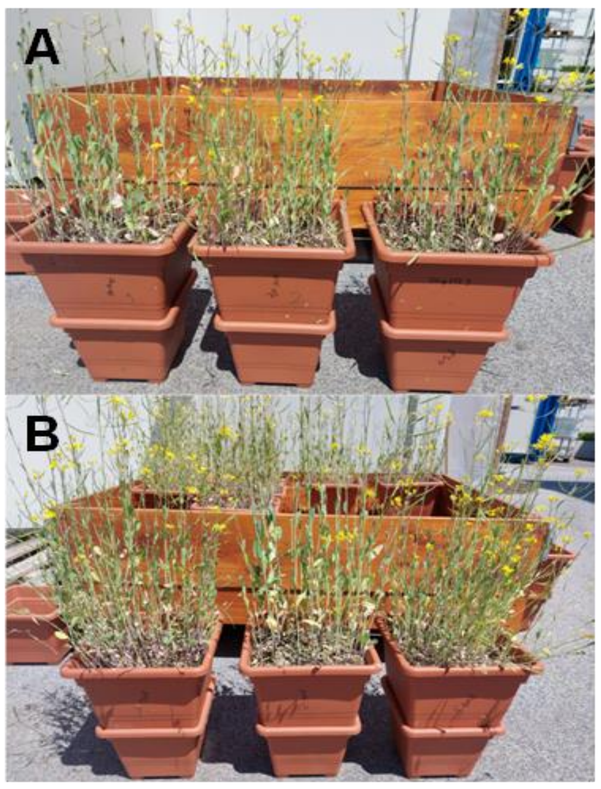
Excess SO_4^{2-} from the acidic phase and excess Ca^{2+} from the alkaline phase are removed as insoluble gypsum. This prevents the accumulation of reagents in process solutions and their deterioration in a series of batches:

$$SO_4^{2-} + Ca^{2+} \rightarrow CaSO_{4(s)}$$



RESULTS: Soil contaminated with As, Pb, Zn and Cd was washed with oxalic acid, Na-dithionite and EDTA solution. Toxic elements were removed from the washing solution by alkalinisation with CaO to a pH 12.5: As was co-precipitated with Fe from Fe-EDTA chelate formed after the soil washing. The toxic metals precipitated after substitution of their EDTA chelates with Ca. On average, 60, 76, 29, and 53% of As, Pb, Zn, and Cd were removed, no wastewater was generated and EDTA was recycled. Addition of zero-valent iron reduced the toxic elements' leachability. Remediation was most effective for As: phytoaccessibility ($CaCl_2$ extraction), mobility (NH_4NO_3), and accessibility from human gastric and gastrointestinal phases were reduced 22, 104, 6, and 51 times, respectively. Remediation increased pH but had no effect on soil functioning assessed by fluorescein diacetate hydrolysis, dehydrogenase, β-glucosidase, urease, acid and alkaline phosphatase activities. *Brassica napus* produced 1.9 times more biomass on remediated soil, accumulated no As and 5.0, 2.6, and 9.0 times less Pb, Zn and Cd, respectively.

Pilot-scale remediation unit with ReMix technology



Growth of rapeseed *(B napus*) on original (A) and remediated soil (B)

REFERENCES:

- Arteaga JFM, Gluhar S, Kaurin A, Lestan D. Simultaneous removal of arsenic and toxic metals from contaminated soil: Laboratory development and pilot scale demonstration. Environ Pollut. 2022, 294:118656. doi: 10.1016/j.envpol.2021.118656
- Patent application "Removal of arsenic, antimony and toxic metals from contaminated substrate", WO2022184903A1

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