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Phosphate Extractability from Groundwater Treatment Sludge is Linked to Solid-phase Ca Speciation

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Recovering phosphorus (P) from P-rich wastes offers a sustainable alternative to phosphate rock mining. One such waste with high contents of recoverable P is the iron (Fe) oxide sludge produced from Fe-based treatment of arsenic (As)-rich groundwater for drinking water production. While alkali extraction is commonly applied to release Fe-bound P, the extraction efficiency is expected to depend strongly on the sludge composition. Specifically, different calcium (Ca) species may be present at various levels in sludge depending on treatment plant properties, with each Ca species potentially influencing P release.

In this work, we investigated P extraction from groundwater treatment sludges using 1 M NaOH. The sludges were obtained from three Fe-based treatment plants with different operational properties: Holmehave, Denmark (HH); Kerte, Denmark (KT); Dhapdhapi, India (DP). We integrated temporally-resolved aqueous chemical measurements during extraction with microscale X-ray fluorescence (μ-XRF) imaging and micro-X-ray absorption spectroscopy (μ-XAS) to identify P and Ca speciation.

Our results revealed that the extracted aqueous P concentrations peaked within the first few hours for all samples (Fig. 1), which contrasted with As(V) extractability. Additionally, we found that the concentration of extracted P at later extraction stages differed among the samples, with the P concentration for the KT and DP samples decreasing markedly, which implies the formation of secondary precipitates. XAS data of P hotspots identified from μ-XRF maps of all pre-extraction sludges showed characteristic features of P sorbed to ferrihydrite (Fig. 2a), the major solid phase in the sludges. However, the spectra of all post-extraction sludges showed hydroxyapatite formation. While all pre-extraction samples displayed identical P K-edge X-ray absorption near edge structure (XANES) spectra, Ca K-edge XAS analysis revealed key differences in Ca speciation that coincided with contrasting P extractability. In particular, the HH sludge, which had the highest extractable P concentration, was dominated by organically-bound Ca, whereas calcite was present in the pre-extraction KT and DP sludges (Fig. 2b). These results suggest a link between P extractability and solid-phase Ca speciation, with the presence of calcite possibly hindering P release. Overall, this study highlights the importance of mineralogical controls in optimizing circular P management strategies.

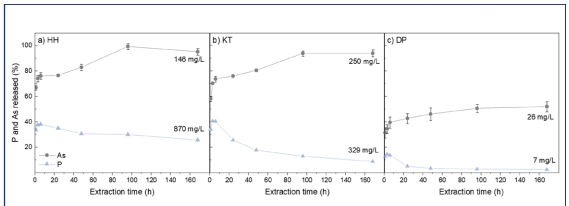


Figure 1. Extraction of P and As from groundwater treatment sludges Holmehave (HH) (a), Kerte (KT) (b) and Dhapdhapi (DP) (c) plotted in %, defined as the extracted As or P concentration normalized by the total As or P in the sludges. The final concentrations of extracted P and As (mg/L) are also given. Data points and error bars correspond to the average and standard deviation of three replicates.

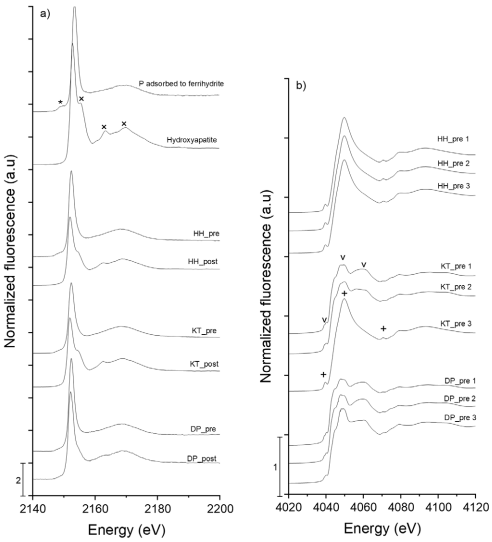


Figure 2. (a) P K-edge XANES spectra of pre- and post-extraction HH, KT and DP sludges. Only one representative P spectrum is plotted for each pre- and post-extraction sample because all spectra for these samples displayed identical features. Panel (a) also includes the spectra of relevant P-bearing reference materials for comparison. The * symbol highlights the fingerprints of P adsorbed to ferrihydrite. The x symbol is used to show features of hydroxyapatite. (b) Ca K-edge XAS data for 3 hotspots in the pre-extraction samples showing differences in Ca speciation within and among the different samples. The v and + symbols in panel b) are used to indicate characteristic spectral features of calcite and organically-bound C, respectively.