Anapaite Precipitation from Anaerobic Municipal Wastewater Treatment for Phosphorus Recovery

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Introduction: Inorganic phosphate (Pi) can be removed from municipal wastewater by iron phosphate precipitation with dissolved iron. To test if Pi precipitation from the complex composition of anaerobic digestate with calcium and carbonate was possible, dissolution of iron phosphate from anaerobic digestate solids is required. Sodium fluoride (NaF) was added to solubilize iron phosphate and precipitate iron fluoride. Pi precipitation was then tested by mixing phosphate-rich solutions with calcium carbonate solutions.

Methods: Municipal anaerobic digestate was obtained from the Robert O. Pickard Environmental Center in Ottawa, Canada. The digestate was aerated from ~-250 mV to 75 mV, and 200 mM of NaF was added, After 1 week, the digestate was centrifuged. The supernatant was aerated (pH ~9) and mixed in a range of volume ratios with a carbon-dioxide-enriched limestone solution (pH ~6), following the strategy used with synthetic wastewater and $CaCO_3$ solutions [1].

Results: Raman spectroscopy identified major peaks between ~ 943 - 960 cm^{-1}. Precipitation of amorphous calcium phosphate (955 cm^{-1}) and apatite (~960 cm^{-1}) were assigned by their ν_1 phosphate stretches. Anapaite ($Ca_2Fe^{2+}(PO_4)_2.4H_2O$) could explain the 943 cm^{-1} shift [2]. Powder x-ray diffraction of the precipitate was complex. Candidate minerals include phosphoferrite, iron (II) fluoride, apatite, anapaite, graftonite, and phosphosiderite.

Discussion: Anapaite precipitation may be possible in a reducing or slightly oxidizing environment in waters saturated with CO_2, exposed to calcite and/or dolomite in the presence of polyphosphate-accumulating, sulphur-reducing microbes. Phosphate concentrations can be increased by the action of sulphur-oxidizing bacteria [3], leading to increasing the supersaturation for anapaite in Fe^{2+}-rich environments.

References: [1] Ross *et al.* (2017) *Minerals* 7.8, 129-146. [2] Frost *et al.* (2013) *Spectroscopy Letters* 46, 441-446 [3] Goldhammer *et al.* (2010) *Nature Geoscience* 3.8, 557-561