Phosphate Recovery from Aerobic Winter Municipal Wastewater by a Crystallization Process

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Introduction

Phosphate rock is a non-renewable resource used in the production of phosphorus fertilizer. With its availability declining, there is an increasing demand for alternative sources of phosphorus for phosphorus fertilizer production. A potential solution is to recycle phosphorus as phosphate from municipal wastewater. Unfortunately, to meet effluent regulations iron chloride is added to municipal wastewater, trapping the phosphate as iron phosphate and making it unavailable to plants. Work is underway to explore the possibility of precipitating carbonate apatite, a phosphorus source that can be made into fertilizer and taken up by plants, from municipal wastewater and limestone (calcium carbonate) solution. However, this process requires a way to recover phosphate by dissolving iron phosphate. The objective of this study is to explore the effects of using sodium fluoride with aerobic winter wastewater to recover phosphate and precipitate carbonate apatite. The results will be useful in the design of a larger-scale process that would produce a product with potential value to the phosphorus fertilizer industry.

Methodology

Phosphate Recovery Optimization

- Anaerobic digestate (DIG2) was bubbled with compressed air to obtain aerobic DIG2
- Sodium fluoride (NaF) was added to 15 mL tubes with aerobic DIG2 to obtain a series containing 200 mM to 400 mM NaF
- Phosphate (PO_4^{3-}) concentration was measured by a colorimetric assay with vanadomolybdate solution
- Absorbances were collected with an Epoch Microplate Spectrophotometer and BioTek Gen 5
- pH was measured with an Orion Combination Sure-Flow pH Electrode
- Reduction potential was measured with a Fisherbrand accumet Metallic ORP Combination Electrode
- Data was collected after 1 hour, 1 day, and 1 week and analyzed on Excel to determine the optimal concentration of NaF

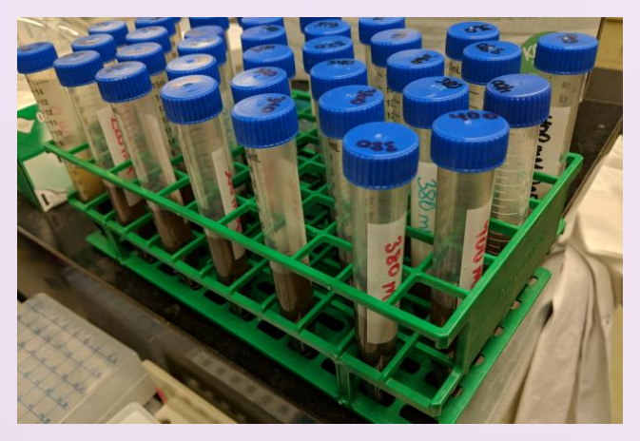


Figure 1. 200 mM to 400 mM NaF in aerobic DIG2 series.

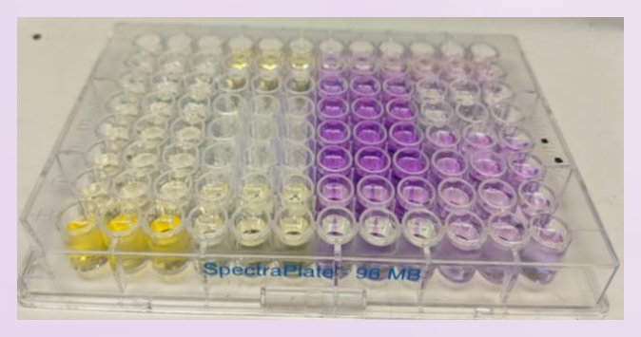


Figure 2. Phosphate and calcium assays.

Figure 3. Crystallization reactions.

Crystallization

- Phosphate solution was prepared by adding NaF to aerobic DIG2 to obtain a final concentration of 200 mM
- Calcium carbonate ($CaCO_3$) solution was prepared by mixing limestone fines with tap water and bubbling with 100% CO_2
- Various volume ratios of $CaCO_3$ solution to phosphate solution (50/50, 60/40, 70/30, 80/20, 90/10, and 95/5) were mixed in 50 mL centrifuge tubes to induce precipitation
- Phosphate and calcium concentrations, pH, and reduction potential were measured before mixing and 5 days after mixing
- Calcium (Ca^{2+}) concentration was measured by a colorimetric assay with *o*-cresolphthalein complexone solution
- The tubes were centrifuged and supernatant was decanted to isolate the pellets for characterization

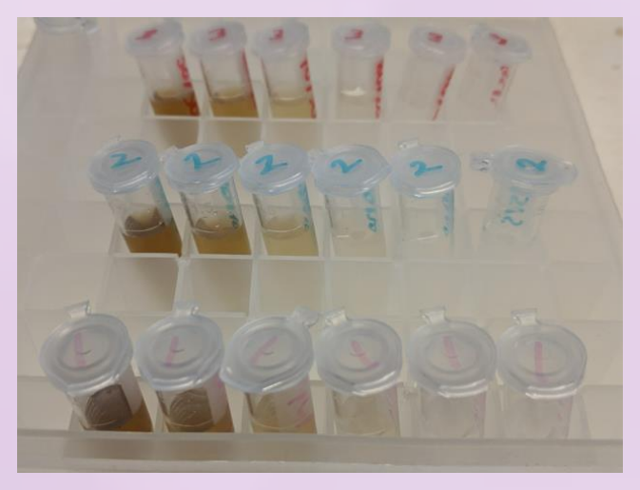


Figure 4. Samples of supernatant from crystallization.

Figure 5. Pellets from crystallization.

Characterization

- All pellets were dried in a Fisher Isotemp Junior Model Oven and characterized by Raman spectroscopy and x-ray diffraction

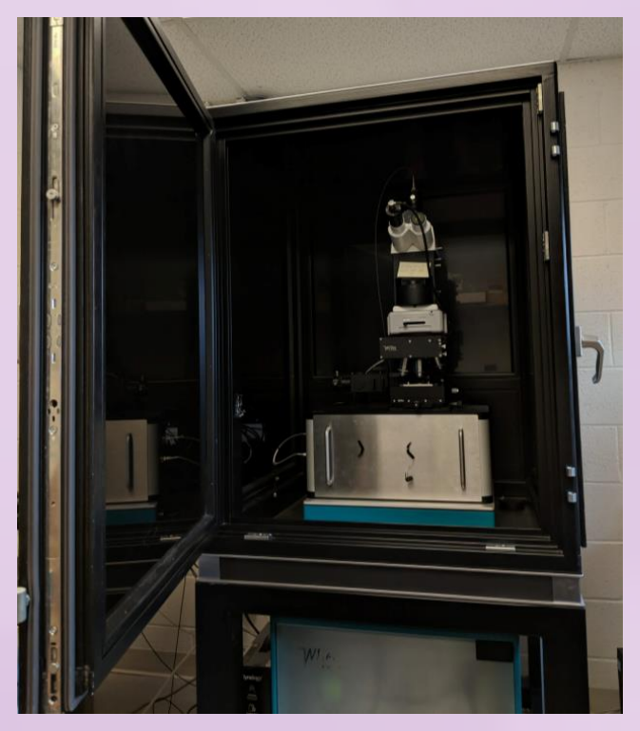


Figure 6. Raman spectrometer.

Results

Phosphate Recovery Optimization

Phosphate concentration, pH, and reduction potential were measured in samples containing 200 mM to 400 mM NaF in aerobic DIG2 after various time periods. Phosphate concentration increased, pH decreased, and reduction potential decreased with time. By the end of one week, phosphate concentration plateaued, indicating that 200 mM NaF is sufficient for phosphate recovery.

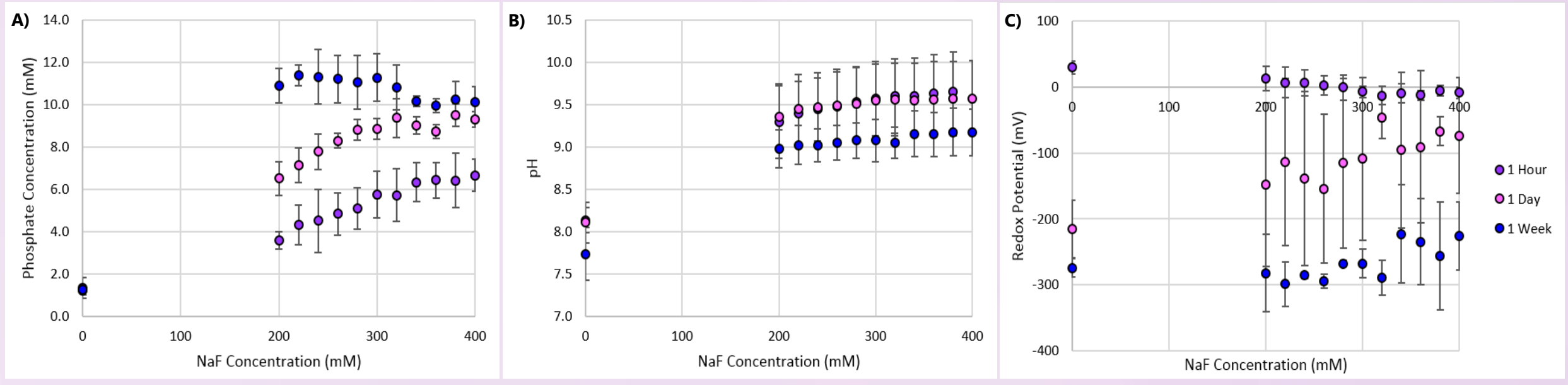


Figure 7. A) The change in phosphate concentration, **B)** pH, and **C)** reduction potential with increasing NaF concentration in samples of aerobic DIG2 one hour, one day, and one week after mixing.

Crystallization

A saturated limestone solution bubbled with 100% CO_2 was mixed with 200 mM NaF in aerobic DIG2 solution in various volume/volume ratios. The measured phosphate and calcium concentrations were lower than the theoretical concentrations in all volume ratios i.e. lower than attributable to dilution alone. Evidently, the ideal volume ratio is between 70/30 and 80/20.

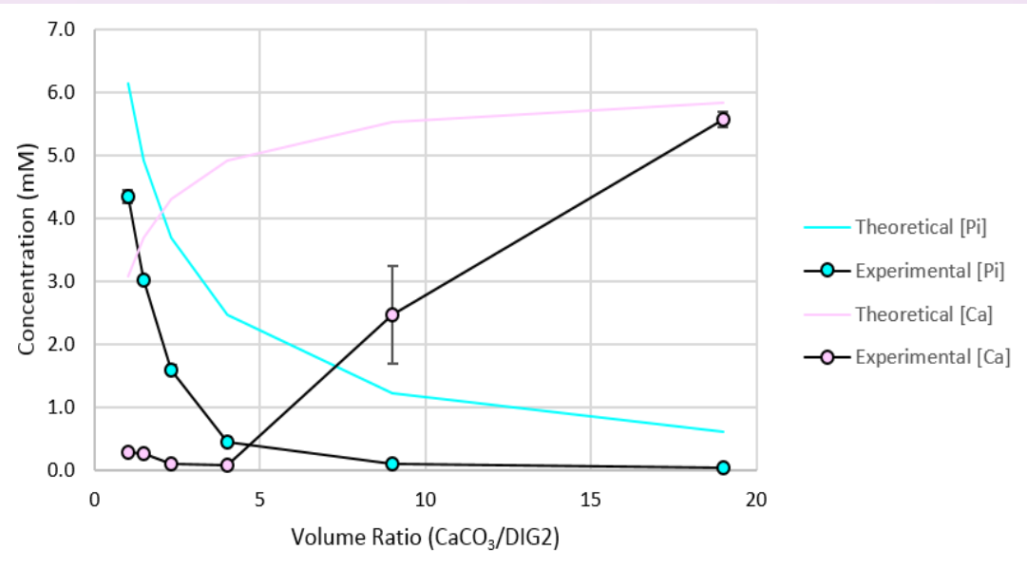
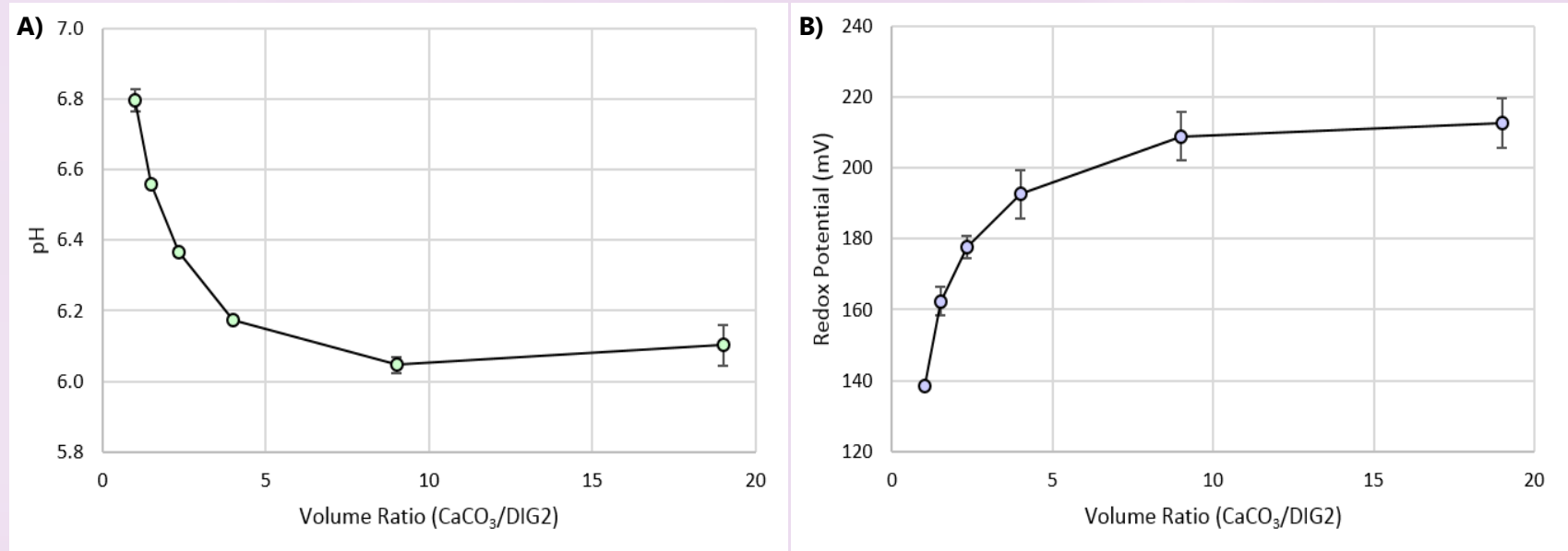


Figure 8. Phosphate (Pi) and calcium (Ca) concentrations five days after mixing the various $CaCO_3$ to DIG2 volume ratios. Theoretical concentrations are the decrease in stock solution concentrations upon mixing as a result of dilution alone.

pH and reduction potential were also measured and appeared to decrease and increase respectively with increasing volume ratio. Both curves display a hyperbolic shape.

Figure 9. A) pH and **B)** reduction potential five days after mixing the various $CaCO_3$ to DIG2 volume ratios.



Characterization

Isolated pellets from the crystallization experiment were dried and prepared for characterization. Raman spectroscopy indicated the presence of at least three different minerals or inorganic compounds with Raman shifts of 943 cm^{-1}, 950 cm^{-1}, and 960 cm^{-1}, corresponding to anapaite [1], amorphous calcium phosphate [2], and phosphate from apatite [3] respectively.

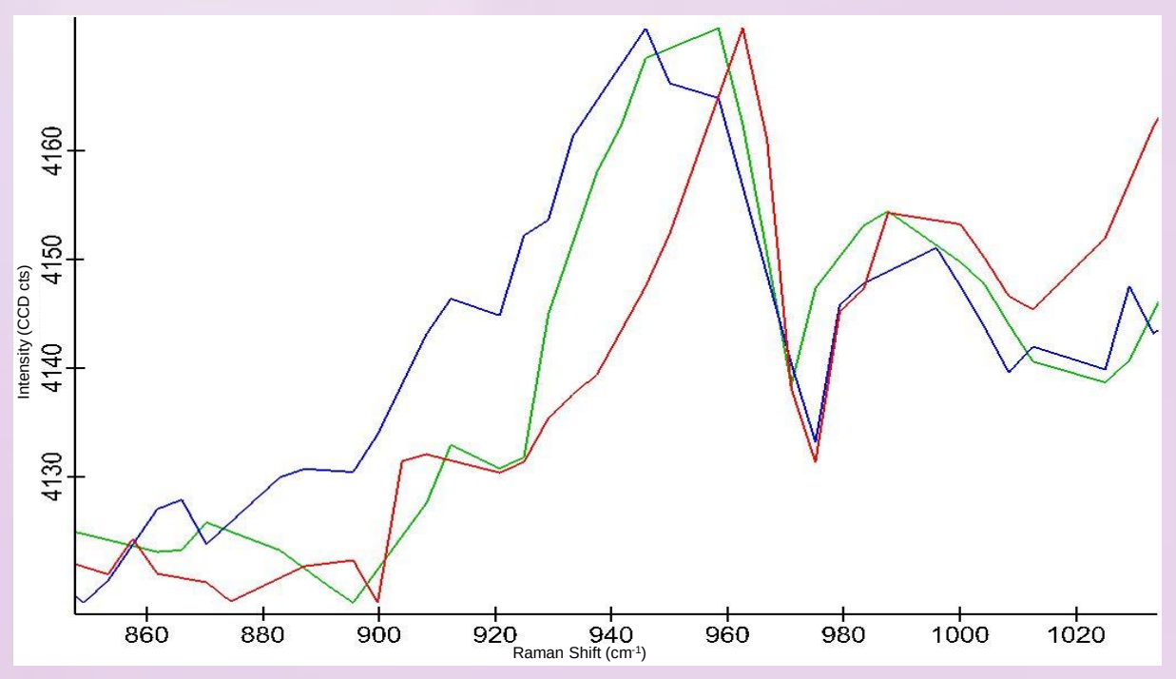


Figure 10. Raman spectrum for the 60/40 $CaCO_3$ to DIG2 volume ratio solids analyzed at three different spots.

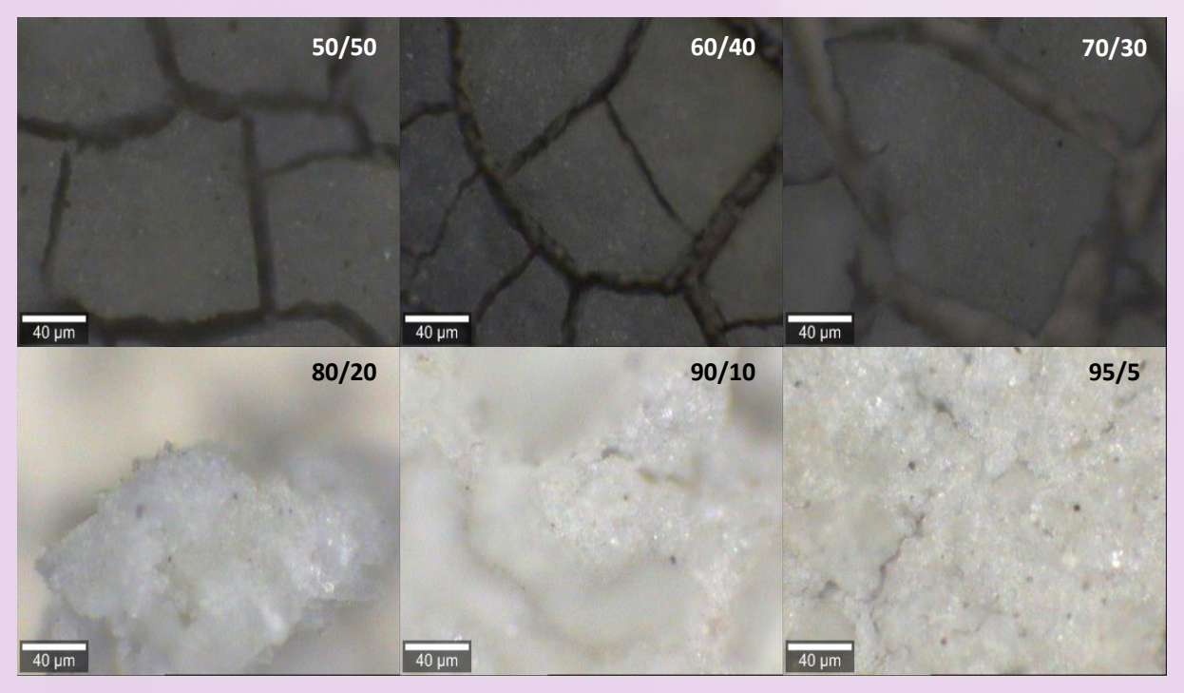


Figure 11. Raman spectrometer images of the crystals formed in each volume ratio crystallization reaction.

X-ray diffraction provided a spectrum for the crystallized solids that was compared to the known major peaks of various minerals and inorganic compounds. The best fits, indicating the presence of these compounds, occurred with anapaite, phosphoferrite, iron (II) fluoride, graftonite, and hydroxyapatite.

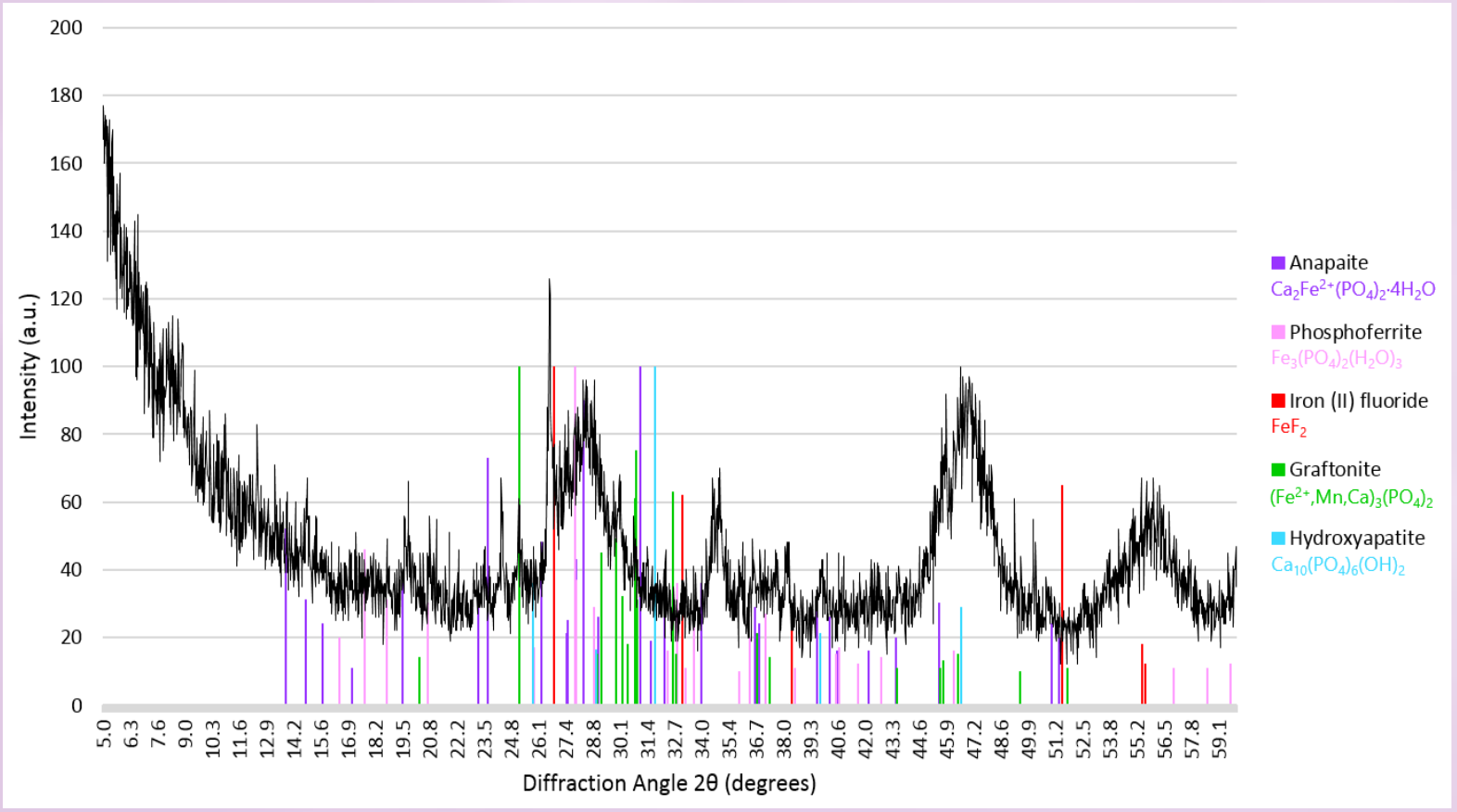


Figure 12. X-ray diffraction spectrum for the 95/5 $CaCO_3$ to DIG2 volume ratio solids compared to the major peaks of various minerals and inorganic compounds.

Discussion

200 mM NaF in aerobic DIG2 was determined to be optimal because by the end of one week all tested concentrations attained a total phosphate concentration of 10 mM to 12 mM, an increase from the initial 1.2 mM. With all concentrations releasing similar amounts of phosphate, it makes sense to choose 200 mM because it requires the least amount of NaF. By mixing various volume ratios of limestone solution with 200 mM NaF in aerobic DIG2 it was determined that phosphate and calcium concentrations decreased more than attributable to dilution alone. The decrease in phosphate and calcium concentrations suggest that phosphate and calcium were lost to the solid phase. It was determined that the ideal volume ratio is between 70/30 and 80/20 because between these ratios phosphate and calcium concentrations are low, so phosphate is precipitated out efficiently.

The formation of precipitates consisting of phosphate and calcium was confirmed by Raman spectroscopy and x-ray diffraction. Raman spectroscopy found the presence of anapaite, amorphous calcium phosphate, and phosphate from apatite. X-ray diffraction found the presence of what is likely anapaite, phosphoferrite, iron (II) fluoride, graftonite, and hydroxyapatite. The presence of these minerals or compounds make sense because the crystallization solution consists of phosphate, calcium, iron, fluoride, and water among other compounds found in municipal wastewater and tap water. Although NaF was employed to release phosphate and trap iron as iron fluoride, the presence of phosphoferrite suggests that some phosphate is stilled trapped as iron phosphate.

Conclusion

The main objectives of this investigation were to determine the optimal concentration of NaF for phosphate recovery from aerobic DIG2, the optimal volume ratio of limestone solution to aerobic DIG2 solution for crystallization, and what minerals or compounds were present in the crystallized solids. The optimal concentration of NaF for phosphate recovery was determined to be 200 mM, the optimal volume ratio of limestone solution to aerobic DIG2 solution was determined to be between 70/30 and 80/20, and the crystallized solids were characterized as anapaite, apatite, calcium phosphate, iron fluoride, and phosphoferrite among other minerals and compounds.

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