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Recovering phosphorus from municipal anaerobic wastewater by precipitating carbonate apatite

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INTRODUCTION

Phosphorus is one of the key essential elements in modern agriculture. Along with nitrogen and potassium, phosphorus fertilizer is one of the three most common agricultural fertilizers. Carbonate apatite, an important component of phosphate rock, is necessary for the production of phosphorus fertilizer due to its higher solubility than geological apatite. However, this natural calcium carbonate phosphate mineral is a non-renewable ore. This study explores the possibility of producing carbonate apatite from phosphorus-rich municipal anaerobic wastewater sludge.

The available phosphate concentration in anaerobically digested municipal wastewater is low. To reduce phosphate concentrations of treated water that is released to the environment, municipal wastewater treatment plants add iron chloride in order to precipitate iron phosphate. It has been showed that following the addition of sodium-fluoride, inorganic phosphate is re-released in solution. This re-released phosphate is available for precipitation in this study.

Using colorimetry, those phosphate concentrations were measured and recorded for a range of sodium fluoride concentrations, from 200-400 mM NaF. After separation of solids by centrifugation, these phosphate-rich solutions were mixed with a dissolved calcium carbonate solution in a range of proportions to precipitate carbonate apatite. Final phosphate and calcium concentrations are reported. Municipal wastewater constitutes a promising source of recyclable phosphorus and could be used to replace phosphorus derived from phosphate rock for generations to come.

METHODOLOGY

Colorimetry assays

- Calcium concentration was measured with the colorimetric assay with o-cresolphthalien (pink) (Schwarzenbach).
- Phosphate concentration was measured with the vanadomolybdate colorimetric assay (yellow) (De Haas et al.)
- From the known standard concentration ladder, a standard slope of absorbance was plotted and used to determine concentrations of samples (Figure 1a: example calcium assay, Figure 1b, example phosphate assay)



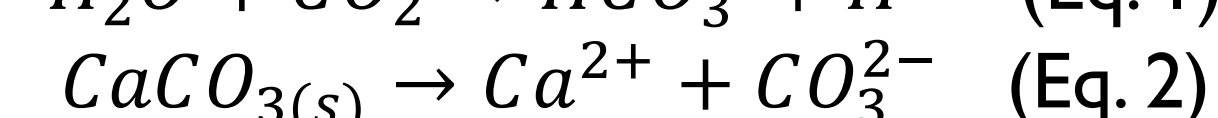
- The Epoch Microplate Spectrophotometer and Gen 5 were used to measure absorbance values.

Re-release of inorganic phosphate in solution

- The appropriate amount of NaF was added to sludge in order to create solutions ranging from 200 – 400 mM NaF

Calcium carbonate solution and batch crystallization

- Potable water was mixed with fines sieved from a bag of “limestone fines” procured from Renot Depot
- 100 % carbon dioxide gas was bubbled into the mixture for 30 minutes. This reduced the pH and enhanced CaCO_3 dissolution (Eqs. 1 and 2)



- Ca^{2+} and HCO_3^- rich solution was syphoned from the reactor and immediately mixed with the phosphate solutions at different ratios

Batch crystallization

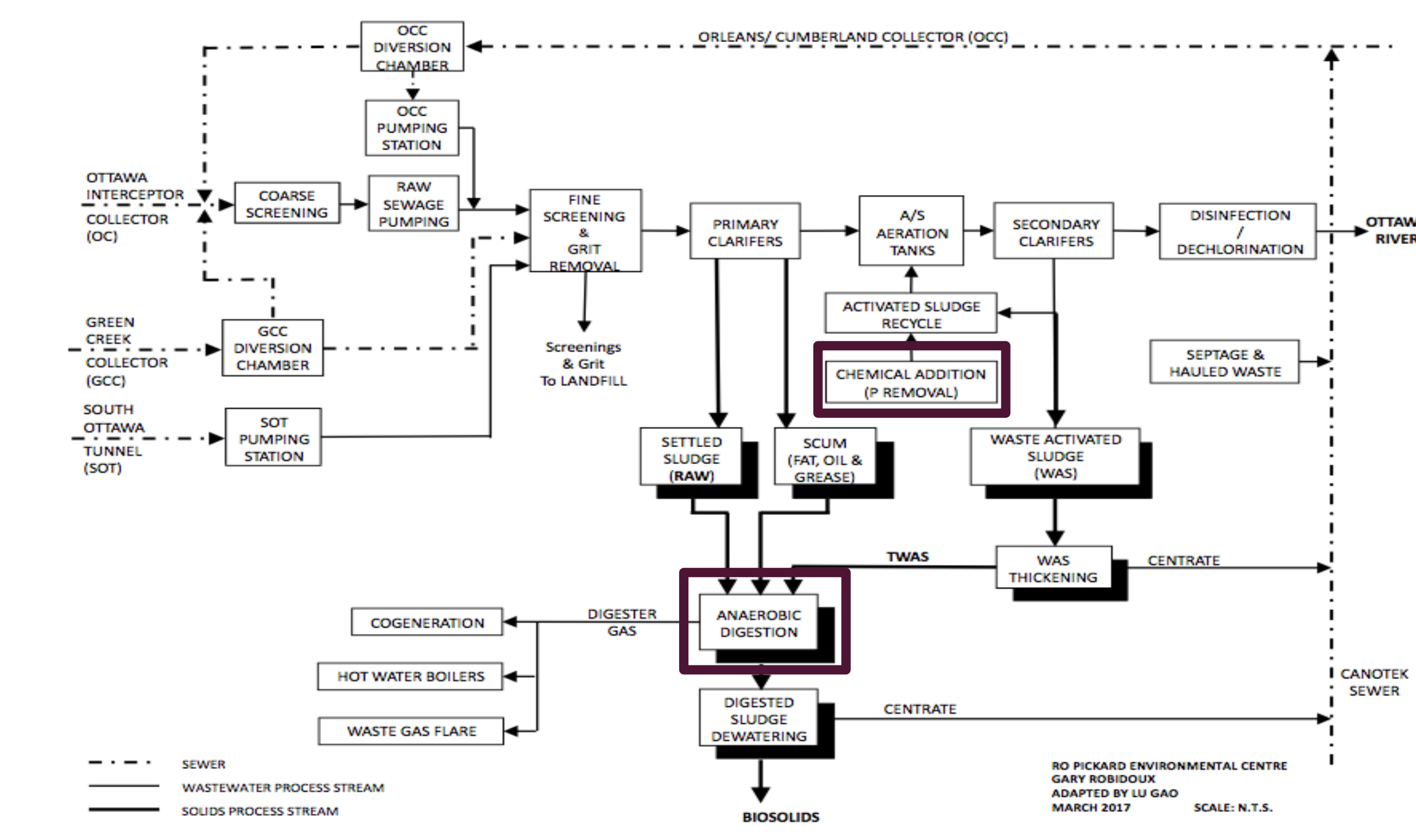
- The calcium carbonate solutions and phosphate solutions were mixed at different ratios in a final volume of 50 mL and crystallized for 9 days.



http://www.bioconservation.com/en/news/wastewater-treatment-plant-rocep-environment/wastewater-and-sewers/wastewater-collection-deodorization-plan-proiect



http://ottawa.ca/en/residents/water-and-environment/wastewater-and-sewers/wastewater-collection-deodorization-plan-proiect



Courtesy G. Robidoux

Wastewater Treatment Process Flow Diagram

RESULTS & DISCUSSION

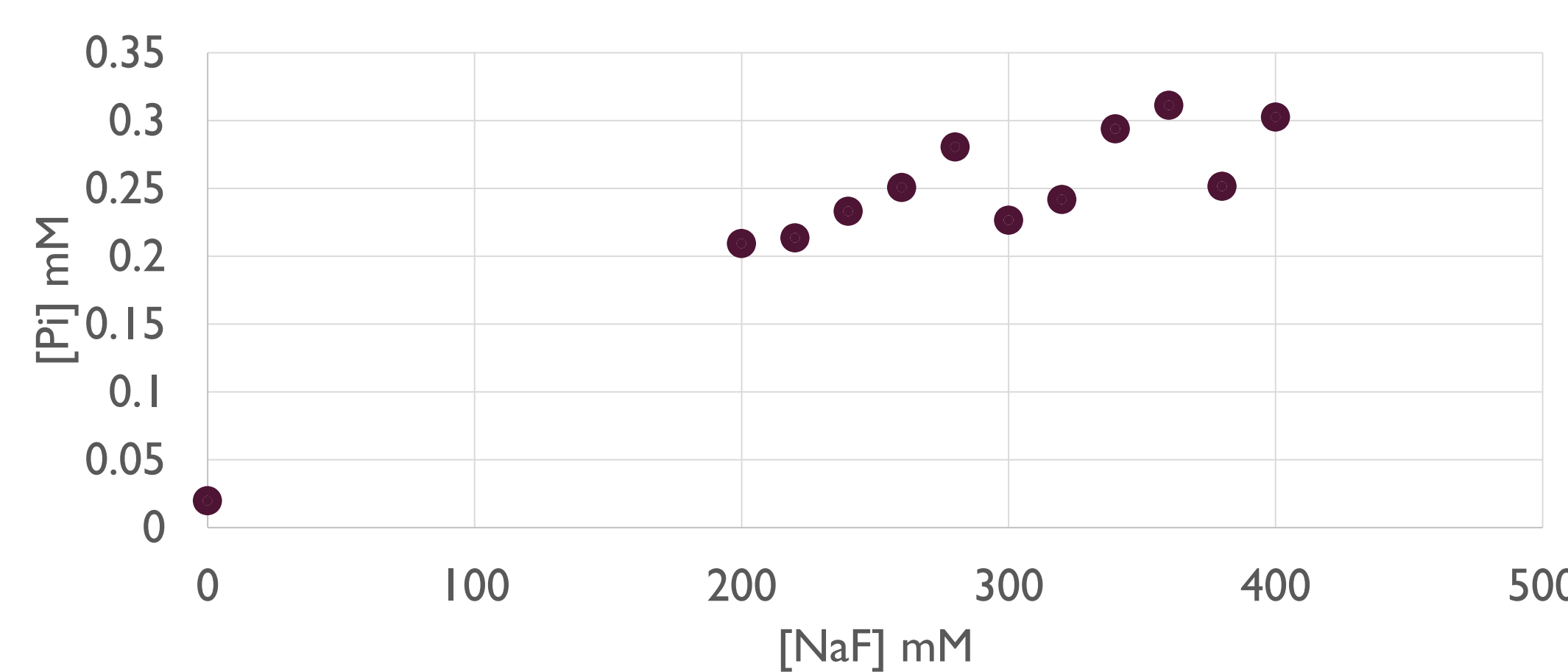


Figure 2. Phosphate concentration in mM following NaF addition at concentrations ranging from 200 to 400 mM NaF.

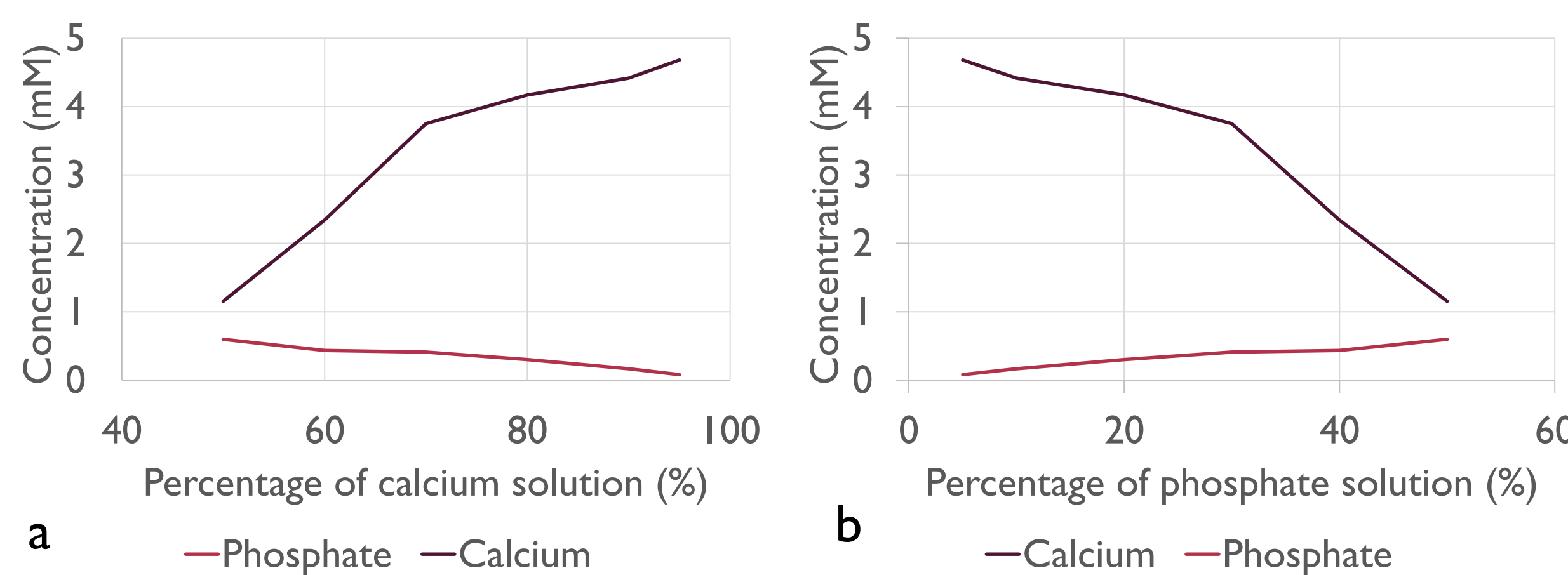
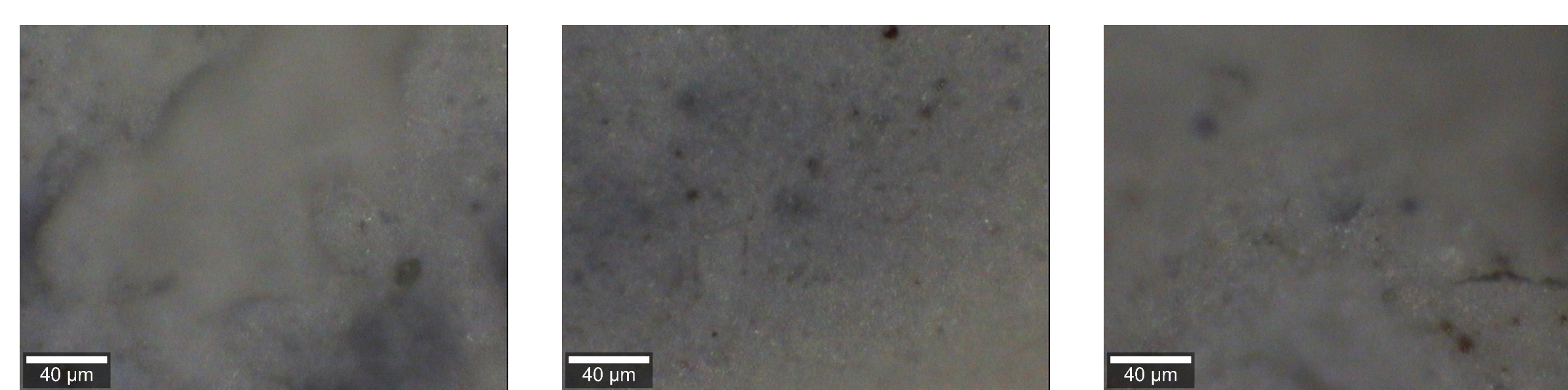


Figure 3. Calcium and phosphate concentrations in solution as the percentage of calcium (a) and phosphate (b) solution increases.

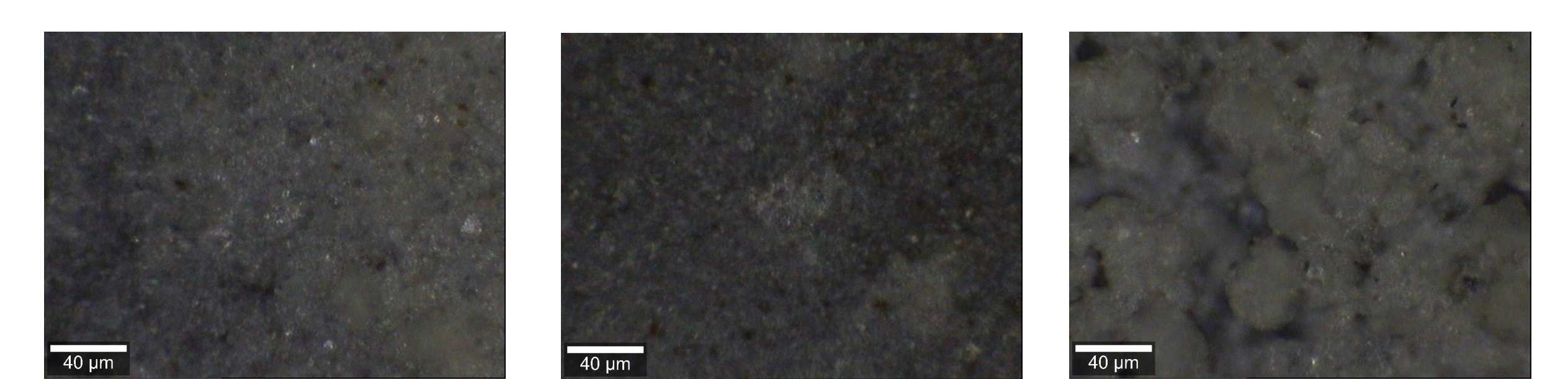


Ca:P ratio 50/50

Ca:P ratio 60/40

Ca:P ratio 70/30

Figure 4a. Light microscopy images for different ratios of calcium solution (Ca-HCO_3) and phosphate solution (NaF-treated sludge)



Ca:P ratio 80/20

Ca:P ratio 90/10

Ca:P ratio 95/10

Figure 4b. Light microscopy images of precipitates of different ratios of calcium solution (Ca-HCO_3) and phosphate solution (NaF-treated sludge)

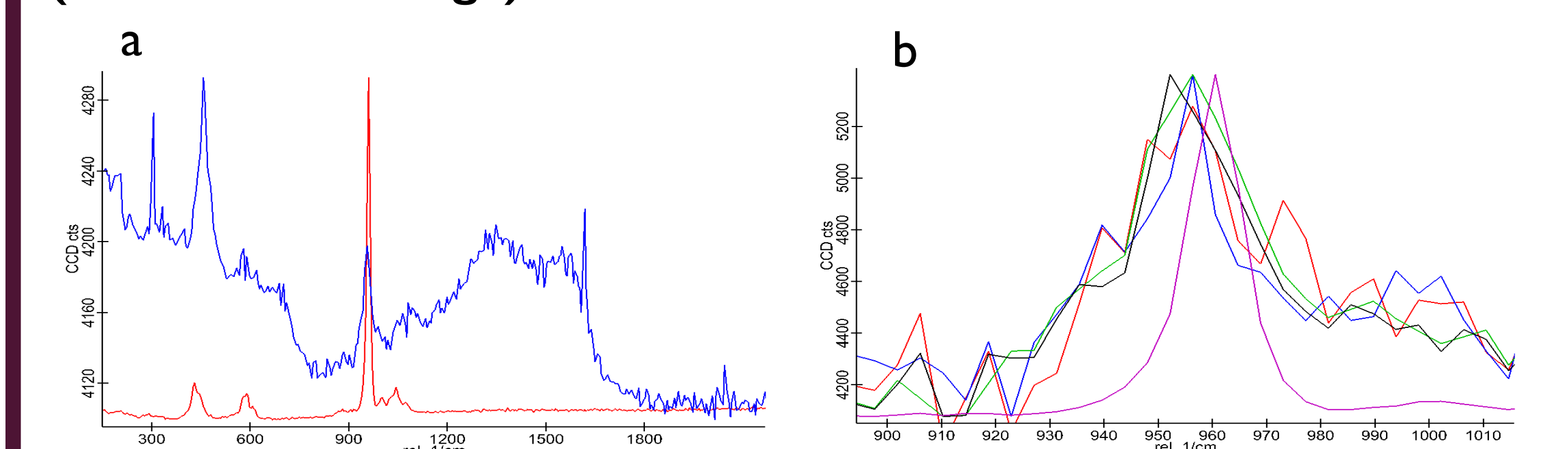


Figure 5. Raman shifts of hydroxyapatite (Hap) (a: red, b: fushia) and 95:5 experiment precipitates (a: blue, b: other colours).

95-10 % CaCO_3 - 5-10 % DIG2

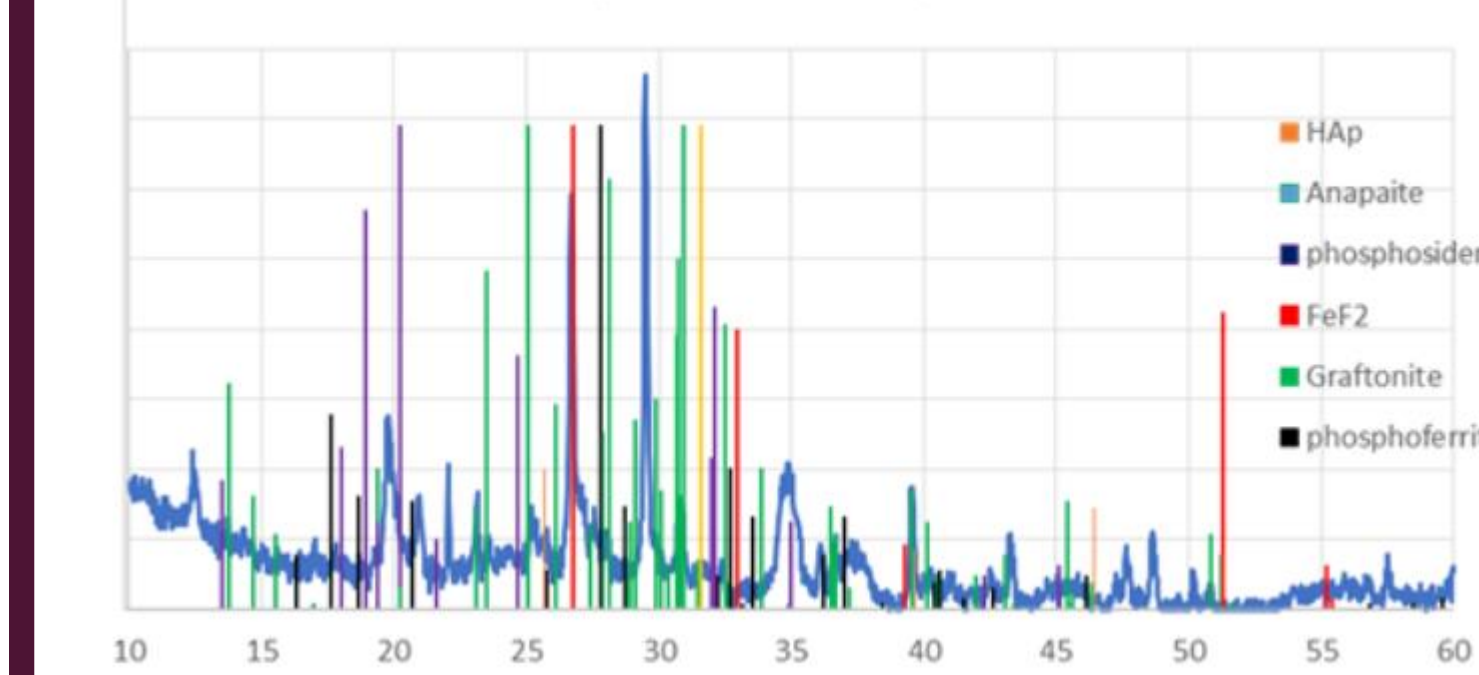


Figure 6. Powder X-ray diffraction peaks of 95/5 and 90/10 crystallization products. A large number of iron-and calcium-phosphate minerals are possible precipitates. solutions.

CONCLUSION

- By increasing the quantity of NaF added, the amount of inorganic phosphate re-released in solution plateaus
- A 200 mM NaF phosphate solution was chosen for crystallization experiments
- A reduction in calcium and phosphate concentration from what is expected by dilution indicates that precipitate containing calcium and phosphate was formed (Figures 4, 5 a, b).
- Preliminary Raman (Figure 5) and XRD (Figure 6) data suggest that a calcium iron phosphate hydrate mineral (anapatite), amorphous calcium phosphate, iron phosphate, iron fluoride and apatite precipitated from solution.

ACKNOWLEDGEMENTS

I would like to thank Dr. Omelon for allowing me to participate in this research and for guiding me throughout the project. This research project was supported and funded by the Undergraduate Research Opportunity Program at the university of Ottawa.

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