PHOSPHORUS AND CARBON CAPTURE FROM SYNTHETIC MUNICIPAL WASTEWATER BY CARBONATE APATITE PRECIPITATION

by

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Abstract

The world's 7 billion inhabitants depend on chemical fertilizers to meet the growing demand for food. The phosphorus used in fertilizer is sourced from ancient sedimentary deposits of Phosphate Rock (PR), largely in the form of carbonate calcium phosphate, called carbonate apatite, which resembles bone. PR is non-renewable and Canada's reserves are extremely limited; currently, all 1,400,000 tonnes of phosphorus products used annually are imported. This project investigates a novel method to recycle phosphorus from municipal wastewater in a form that will enable its reuse as a fertilizer, through a reaction with $CaCO_3$ from limestone and waste CO_2 (g). This will contribute to the nascent circular nutrient economy within Canada. A review of the current state of phosphorus and nutrient recycling is presented, including a plan for establishing the Canadian Nutrient Platform.

A series of inorganic phosphate (PO_4^-, or P_i) solutions was prepared to simulate the concentrations found in Ottawa's municipal wastewater, between 2.5-30 mM P_i. These solutions were mixed with $CaCO_3$ solutions that were highly supersaturated through a carbon capture technique. Batch tests successfully reduced the [P_i] and [Ca^{2+}], as measured by colorimetry, and precipitate formed. These results were subsequently repeated in a continuous stirred lab-scale reactor. These precipitation products were characterized using Scanning Electron Microscopy, Raman Spectroscopy, X-Ray Diffraction, and carbon coulometry to measure carbonate content. This analysis confirmed the presence of both P_i and CO_3 in a bone-like, carbonate apatite. Although other technologies are being explored to recycle phosphorus from wastewater streams, this is the first indication that it may be possible to precipitate a carbonate apatite by mixing two waste streams, municipal waste water and CO_2 (g), with cost-effective $CaCO_3$.

Acknowledgements

This thesis would not have been possible without the support of my husband Eric, and the curiosity and energy of my children, Clive and Vesper (aka the Lab Mascots).

I will always be thankful for the friendship, laughter, and many, many hours of talking about big ideas with Lu Gao, as she also worked toward her Master's. I am so excited for your PhD adventures ahead, wherever they may take you.

Essie and Divya, my intrepid undergrads, always kept me on my toes with their fantastic questions and hard work - thank you and good luck finishing your studies!

And of course, this project would not have been possible without the enthusiasm and wisdom of my supervisor, Dr Sidney Omelon. Your invitation to try "just a little project" changed my life, and I could never have imagined how much I would learn, both personally and professionally, as I worked on this project. Thank you.

Author's Note

This thesis began as a humble, one-semester project with the goal of investigating the supersaturation limit of calcium phosphate. As the literature review progressed, this simple question revealed itself to be a tiny component of a wicked, global problem – wicked in the sense that there is no easy definition of the scope of the problem, let alone attempting to identify the stakeholders and understand the nuanced relationships between them, in order to begin to work toward potential solutions. It also became clear that regardless of whether or not it was possible to answer the original question posed, a technical contribution toward resolving the problem would be utterly irrelevant without understanding the landscape of players who could and should be engaged in addressing technical, political, and societal solutions.

As I realized this, two seemingly unrelated events occurred. First, I learned that the building I was supposed to work in during the summer semester (the Louis Saint-Laurent building) had burnt down, so I was effectively out of a real job until the fall. Second, I found a pamphlet for a new program being offered – the Specialization in Science, Society, and Policy – which was only available for thesis students. The math was simple: I switched from M.Eng to M.A.Sc as quickly as possible, and signed up for the specialization.

One year later, the chance encounters (and one electrical fire) that brought me back to school - and to this project in particular - seem almost impossible to believe. However, considering how much I have learned and feel that I have been able to contribute to advancing the research toward resolving this problem, I could not imagine that there was anything else I could possibly have been doing with my time that would have been remotely as productive or as rewarding.

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ABBREVIATIONS

ACP	Amorphous calcium phosphate
Ca x P	Approximation apatite's K_{sp}, i.e. $[Ca^{2+}] \times [P_i]$
CAp	Carbonate apatite
CFAP	Carbonate fluorapatite
CSTR	Continuous stirred tank reactor
DCPD	Dicalcium phosphate dihydrate (also called brushite)
ddH_2O	Deionized, distilled water
ECA	Environmental Compliance Approvals
HAP	Hydroxyapatite
IAP	Ion activity product
K_{sp}	Solubility product
MAP	Monoammonium phosphate OR magnesium ammonium phosphate (struvite)
OCP	Octacalcium phosphate
P_i	Inorganic phosphate ion (orthophosphate), $(PO_4)^{3-}$
Poly-P	Polyphosphate
PR	Phosphate rock, or phosphorite
ROPEC	Robert O. Pickard Environmental Centre; Ottawa's wastewater treatment plant
SEM	Scanning electron microscopy
TP	Total phosphorus
XRD	X-ray diffraction
WWTP	Wastewater Treatment Plant

CHAPTER 1

INTRODUCTION

1.1 Motivation

Over the last 50 years, the world's population has more than doubled to over 7 billion people (US Census.) This growth has been possible in large part due to advances in agricultural techniques, including the use of chemical fertilizers (Smil 2002, Tilman 2002). Fertilizers are a global industry worth an estimated US$ 200 billion in revenue in 2015 (International Fertilizer Industry Association 2016). They are essential in replenishing nutrients to intensely farmed soil, specifically nitrogen, phosphorus, and potassium. The demand for phosphorus fertilizer has increased at much the same rate as the human population (Figure 1.1) from which it can be inferred that the food needed to support this population depends on access to phosphorus. What is less well known, however, is that Phosphate Rock – the primary source of phosphorus for fertilizer – *is a non-renewable resource*. And although the timelines are under debate (Cordell 2011, Elser 2014), the world is approaching 'peak phosphorus.' Thus, in the long-term, the supply of phosphorus will be a food security issue (Cordell 2009, UNEP 2011, Elser 2014, Ulrich 2016).

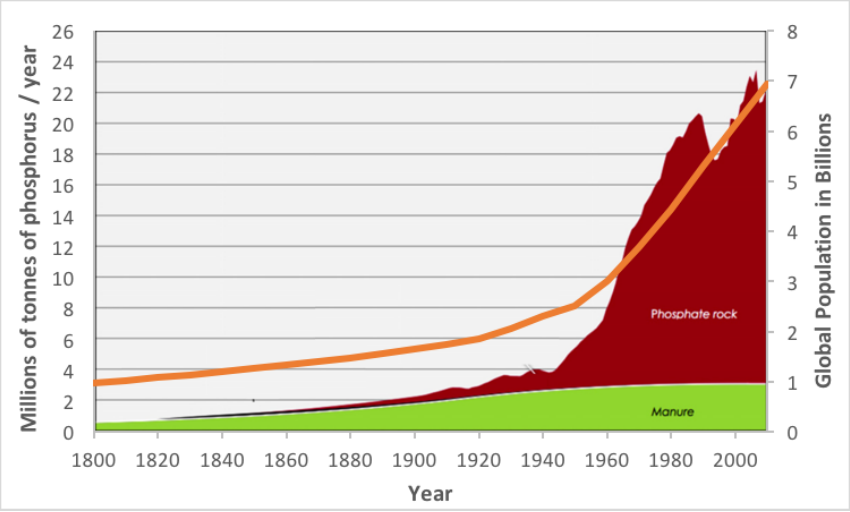

Figure 1.1: Increase in human population (billions) with increase in use of phosphorus fertilizer (millions of metric tonnes) (Adapted from Cordell and US Census Data)

Phosphate Rock (PR) (also referred to as phosphorite) is the raw sedimentary material extracted and processed for use in chemical fertilizers. The majority of known deposits in North America formed over a geological timescale from authigenic deposits created by benthic microorganisms (Schulz 2005), and the conditions required to mineralize this organic material are very specific in terms of water flow and depth (Riggs 1979, Compton 1992). Initial studies of PR formation indicated that life forms were probably responsible (Kazakov 1937). The resulting PR consists of the mineral that is of interest to phosphorus fertilizer producers: francolite, which is a carbonate fluoro-calcium phosphate, or *carbonate fluorapatite* (McConnell 1950). This thesis will narrow the focus to carbonate apatite; this is because the presence of carbonate increases apatite's solubility (Jahnke 1984), while the fluoride ions are removed during processing (Butosov 2013).

At the same time as this non-renewable PR is being depleted at ever increasing rates, the use of phosphorus throughout the food cycle is very inefficient, as illustrated in Figure 1.2. A meagre one fifth of the phosphorus entering the food system is a component of the food that is consumed (UNEP 2011). Further, the majority of the 3 MT of phosphorus absorbed from food ends up in human waste because humans require very little phosphorus – between 0.7 – 1.2 g / day (Cordell 2012, SCU 2013). This means that a technology targeting the phosphorus in human waste could potentially recycle up to one fifth of the total phosphorus requirement, from the food cycle as it exists today. Considering that the infrastructure to collect and dispose of human waste already exists within the majority of large cities, this "point-source" of phosphorus waste should simpler to manage than the losses distributed throughout the rest of cycle (Butusov 2013).

Efforts are underway to increase the efficiency of the food cycle and to reduce the "non-point source" losses of phosphorus, through agricultural education initiatives such as the 4R Nutrient Stewardship Framework developed by the fertilizer industry worldwide (Johnston 2014). The 4R approach encourages farmers to use fertilizers judiciously, by applying the "right source, at the right rate, time, and place." The thinking is two-fold: by using less fertilizer (but using more effectively) farmers can decrease their costs, and less fertilizer used will mean lower flow of nutrients into waterways. This kind of systemic change in attitude toward fertilizer use, regardless of the motivation is financial or environmental, will be essential in reducing waste of phosphorus and other nutrients in agricultural run-off (Cordell 2011).

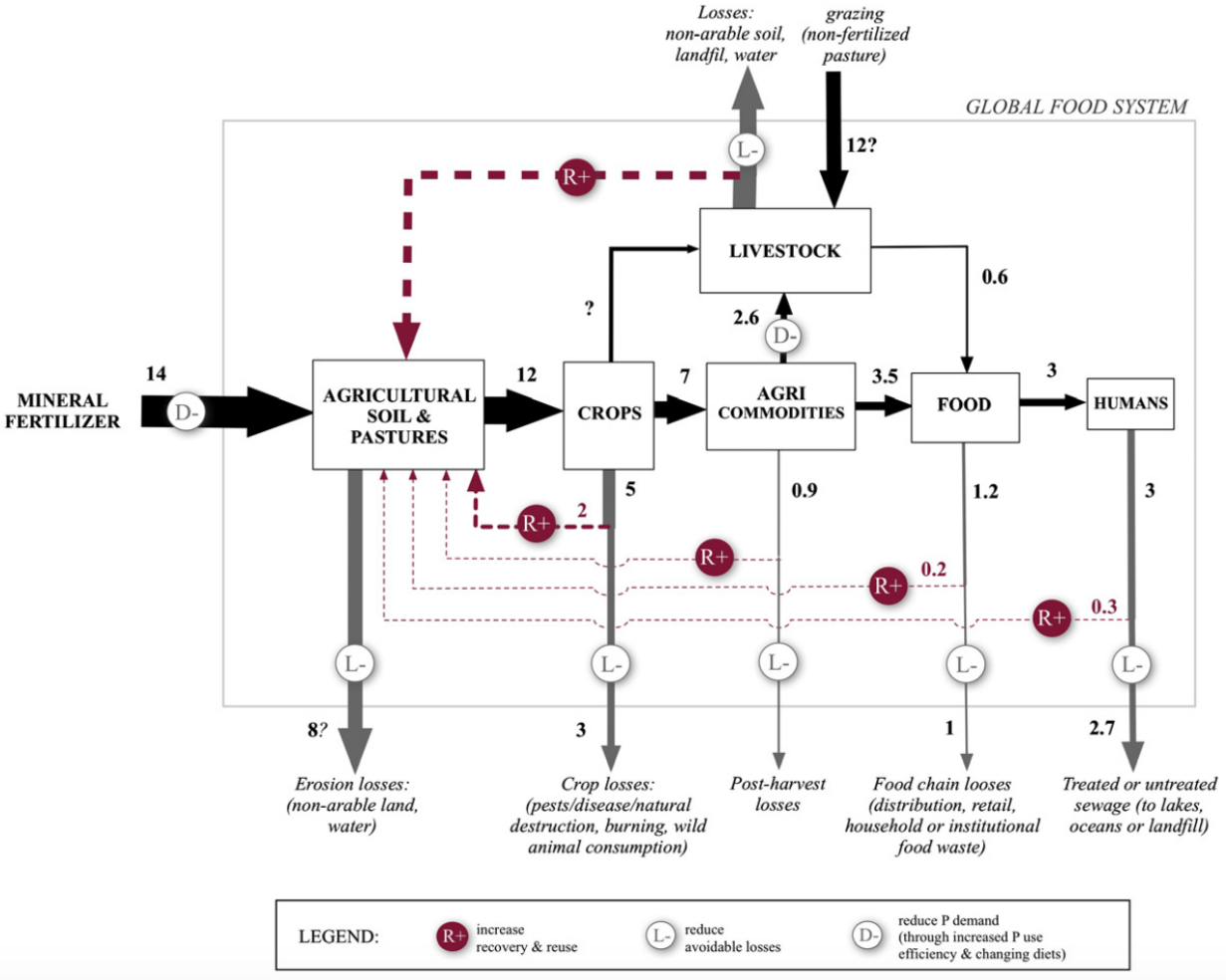

Figure 1.2: Overview of phosphorus use and losses within global food system (Cordell 2011)

Phosphorus lost throughout this cycle often ends up in watersheds, thereby increasing the phosphorus load on aquatic ecosystems and therefore the risk of eutrophication. This is an acute problem in Canada, where vast farming operations increase the likelihood of phosphorus run-off from farmlands and animal manure entering waterways (AAFC 2016). This has led to spectacular seasonal algal blooms, most notably in Lake Erie and in Lake Winnipeg (ECCC 2016, Ulrich 2016). While algal blooms may present a nutrient-rich biomass that has the potential for reuse as fertilizer, the damage to aquatic ecosystems, in addition to the large size and unpredictable movement of the blooms within waterways, means that it is not currently feasible to simply "scoop up" the algae for processing. Recent research into the use of algae as a source of biofuel and recycled nutrients relies on the careful cultivation of algae under optimal

growing conditions (Rosch 2012, Alba 2013), at a rate that allows for cycling between growth and recovery.

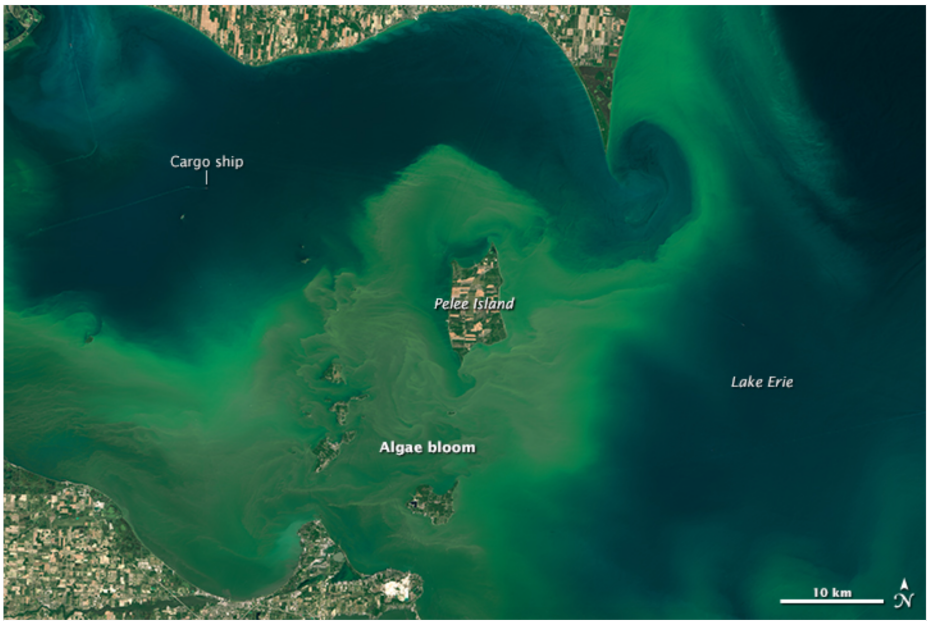

Figure 1.3: Algal blooms in Lake Erie as photographed by NASA in 2015 (NASA 2015).

The 'phosphorus problem' is thus an imbalance between short term overuse causing environmental damage, and long-term supply which will play a significant role in food security. Comparisons can easily be drawn with the well understood (though still widely debated) energy sector over the use fossil fuels and the production of carbon emissions. However, unlike energy, there is not an alternative - such as wind or solar power - that we can turn to. Phosphorus is an element, and despite the many efforts of alchemists throughout the ages, stable elements cannot be created through any known means. The total amount of the element phosphorus on this planet is finite by definition, and it is concentrated in PR in only a few locations that can be economically mined. Therefore, in order to ensure that there is sufficient and affordable phosphorus available to feed generations to come, solutions for the short-term environmental problems must look not only to *capturing* this element, but doing so in a chemical form that can be *recycled* back into the food system.

This thesis examines one specific stream of the phosphorus cycle, municipal wastewater, and tests a novel method to precipitate the phosphorus out of a synthetic stream. Current methods typically employ the chemical precipitation of phosphorus with either soluble iron or aluminum salts. Chemical precipitation is very effective for removing phosphorus from wastewater as insoluble iron phosphate or aluminum phosphate (Smil 2002). Unfortunately, the phosphate salts produced are not suitable for use as P-fertilizer due to their high metal content and low solubility (Bache 1963, Sedlak 1991). The method herein tested is different for two reasons. First, it substitutes low-cost calcium carbonate for soluble iron and aluminum salts, testing the hypothesis that such a precipitate would more closely resemble the carbonate apatite found in PR. Second, it captures carbon by diverting CO_2 (g) into the calcium stream, which both increases the dissolved calcium concentration ($[Ca^{2+}]$) in the solution as well as contributing to the carbonate content of the product. In effect, this project turns two waste streams into a potentially valuable commodity.

1.2 Thesis Objectives

Several objectives were set in order to determine if the hypothesized method was feasible, both from a technical and from a practical perspective. They are organized into three categories: Process, Product, and Application.

1.2.1 CATEGORY A: PROCESS VARIABLES

1. Supersaturation. The initial objective of this project was to map the supersaturation zone of solutions of varying concentrations of calcium and phosphate, generated by tap water saturated with calcium carbonate, and inorganic phosphate concentrations found in municipal wastewater treatment plants with anaerobic digester units. This would identify the possible operating range of such a carbonate apatite precipitation process. The initial attempt to meet this objective failed, thus necessitating the second objective.
2. Solubility of $CaCO_3$. This objective sought to determine if it would be possible to use carbonate equilibria to increase the dissolved calcium and carbonate concentrations. This could potentially be achieved by making use of the available carbon dioxide produced at municipal wastewater treatment plants with anaerobic digestion processes that co-generate electricity. This strategy would also consume another available waste (carbon

dioxide) that is generated on-site. The carbon dioxide concentration generated by the co-generation power plants is unknown, but the carbon dioxide in flue gas from natural gas power plants is known to be ~ 7%, and coal-fired power plants is ~15% (Songolzadeh 2014). In order to determine if this strategy might lead to sufficient increase in solubility, a flow of 100% CO_2 was tested. A second part of this objective was to investigate the use of low cost, natural limestone screenings, in addition to laboratory-grade $CaCO_3$.

3. Seeding. In parallel, a seeding source was anticipated, and biological carbonate apatite was a candidate waste material. Biological apatite (such as found in bone mineral) is similar to phosphorite rock in chemistry and mineralogy (McConnell 1952). Inorganic biological apatite was prepared and characterized as a seed material for PR crystal growth in a crystallizer. Knowing crystal growth theory, optimal crystallizers precipitate new material on seed crystals because this requires a lower supersaturation, better crystallizer control, and larger crystal products for optimal solid/liquid separation. The effect of biological apatite seed material on batch PR crystallization was studied. Note that this work was discontinued with the unexpected discovery of quality carbonate apatite seed from the homogeneous nucleation experiments.

1.2.2 CATEGORY B: PRODUCT

4. Characterization. The precipitates were characterized to assess their potential for use as a synthetic PR feed for phosphorus fertilizer production. Several techniques were used, including scanning electron microscopy (SEM), Raman spectroscopy, carbon coulometry, and X-ray diffraction (XRD). These techniques allowed for determination of phosphate speciation, carbonate content, and crystallinity.

1.2.3 CATEGORY C: APPLICATION

5. Reactor. The final technical objective was to set up and run a continuous stirred tank reactor (CSTR) to precipitate carbonate apatite from a calcium-carbonate rich stream, and a synthetic inorganic phosphate stream that is representative of a phosphate source from municipal wastewater treatment plants. This served to confirm that solids formed in a reactor were similar to the precipitates formed in batch tests. This would be the first step toward defining the anticipated future work of introducing the process into an existing

municipal wastewater treatment plant. The initial set up was presented at the Faculty of Engineering's 2017 Design Day competition, and was awarded the top design project out of the 99 competitors.

6. Policy. This project had an additional objective of defining the contours of Canada's phosphorus policy, which is inextricable from the wider topic of nutrient recovery and the circular economy. This additional work was tackled because the project would be of little practical application without the context of the existing rules, economics, and attitudes surrounding the concept of creating value from waste. Global nutrient recovery is seen as an existential problem in many circles, yet is not widely practiced; this objective sought to begin to understand the reasons why.

1.3 Thesis Organization

This thesis opens with a discussion in Chapter 2 of the 'big picture' historical, economic, and political aspects of the phosphorus cycle in which this problem resides. This provides an understanding of the competing interests that must be considered when seeking to implement change in both attitudes and of technology. In Chapter 3, the discussion shifts to the technical background, reviewing basic and advanced concepts of crystallization and the chemistry of calcium, carbonate, phosphorus, and water. The literature review also outlines previous methods tested to precipitate apatite, as well as an overview of wastewater treatment and existing phosphorus recycling technologies.

The experimental and analytical methods are presented in Chapter 4; the unsuccessful attempts and steps taken to overcome obstacles are also mapped out. A detailed discussion of the experimental results and implications follows in Chapter 5, aligned with how the results support each of the overarching objective categories.

Chapter 6 considers the way forward for Canada, suggesting agencies that should be engaged as well as what policy instruments could be implemented to take steps toward lasting change. Finally, the primary scientific findings are summarized in Chapter 7, along with a brief overview of the potential scientific and policy implications, and future work to be undertaken.

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US Census Data

CHAPTER 2
SOCIAL AND POLITICAL CONTEXT

2.1 Introduction

Over the last decade a significant body of work investigating the global phosphorus cycle has been generated (Pellerin 2013). The consensus is that phosphorus must be managed carefully, although the motivations diverge amongst the various stakeholders. Those interested in 'nutrient management' are concerned about running out of this non-renewable resource and imperiling global food security. This is because economic and scientific studies have underlined that the raw material used to produce phosphorus fertilizers, carbonate apatite, is crucial to long-term global food production (UNEP 2011). The environmental impetus is twofold; the risk of eutrophication of waterways, as well as the avoidable carbon footprint associated with the transportation and processing of a large fraction of raw phosphorus for fertilizer that does not contribute to food that is finally consumed. Still other groups are primarily interested in improving the human rights of the inhabitants of Western Sahara, in which large phosphorus reserves are located. Though these many parties may have different perspectives on the urgency of implementing phosphorus recycle technology, all parties agree that wasted phosphorus flowing into waterways and landfills must be reduced.

Modern phosphorus use is not efficient; it is essentially linear (Figure 2.1), with losses at each stage, from phosphorite extraction to fertilizer application, that result in sources of environmental pollution. At the same time, these losses represent an opportunity to recover and recycle phosphorus back into the soil, thus closing the historic loop.

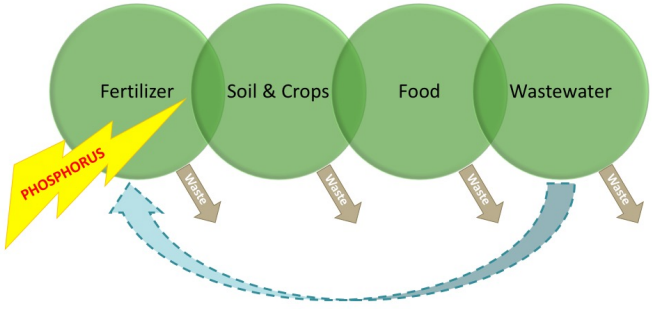

Figure 2.1: Simplified modern phosphorus cycle.

In order to effectively manage these streams, however, the regional flows of phosphorus must be understood, and matched with economical recycle solutions. In Canada, several dispersed groups have studied pockets of this cycle (Ulrich 2009, Metson 2015) but a holistic picture of the national phosphorus cycle has not been assembled and quantified (Trudeau 2014). These many nodes of activity indicate the presence of the interest and expertise needed to analyze a wider Canadian phosphorus system and identify the conditions to take action. However, for a number of reasons, these projects have yet to crystallize into a concerted, national effort. To understand the 'missing ingredient' we look to the Netherlands as a case study.

2.2 Dutch case study - success and obstacles

The Dutch Nutrient Platform, a group of initially over 20 companies, universities, government authorities and NGOs (Science Communication Unit 2013), published the Phosphate Value Chain Agreement in October of 2011(European Sustainable Phosphorus Platform (ESPP) 2011). This group was an early adopter of the concept of the circular economy, or "Cradle-to-Cradle" management of resources. By identifying and engaging key players throughout the entire cycle, they were able to thoroughly analyze economic and environmental considerations of recycling phosphorus. This in turn ensured that the various partners were involved throughout the processing cycle in a streamlined and efficient manner (Smit 2015).

Despite significant progress toward capturing and recycling phosphorus at different stages of the phosphate value chain around the world, the EU's legal framework surrounding nutrient recovery has been described as limiting "due to legal barriers for the integration of waste material" (Kabbe 2016). This means that even when phosphorus has been recovered in a form that meets the requirements for an absence of pathogen and contamination levels, the sale of such a recycled product was not permitted. However, this impediment has motivated a revision of the EU's fertilizer regulation as one of the initiatives within the circular economy package, that is currently underway (European Commission 2003/2003, 2015).

2.2.1 Comparison between Canada and the Netherlands

While progress toward recycling phosphorus in the Netherlands is valuable as a case study to inform Canada's way forward, there are many geographical, cultural, and environmental differences that must be considered. Policy diffusion cannot be applied blindly; it is most

effective when there are sufficient similarities between that policy's country and environment of origin, and the country interested in adopting it (Cairney 2016). The following is a brief discussion outlining pertinent differences and similarities.

2.2.2 By the numbers

Geography is the most obvious driver of differences between the two countries, as summarized in Table 1 (CIA World Factbook 2016). Canada's landmass dwarfs the Netherlands, whose population density is two orders of magnitude greater. The Netherlands has a greater relative area of water and is more urbanized. These factors may contribute to a generally higher awareness of aquatic issues and willingness to direct tax dollars to rectify the problem, as symptoms would be more visible, and the population more directly affected.

	Population	**Total Area (km^2)**	**Density (ppl / km^2)**	**Water Area (km^2)**	**Urbanization**	**"Water" density (ppl / km^2 water)**
Canada	35,362,905	9,984,670	4	891,163	81.8	40
Netherlands	17,016,967	41,453	411	7,650	90.5	2,224

Table 2.1: Comparative statistics: Canada and the Netherlands (CIA World Factbook 2016)

Canada, on the other hand, has a very dispersed population with respect to both total landmass as well as water area (i.e. has a less 'dense' tax base). This dispersion is even more pronounced considering its high rate of urbanization, and suggests that Canada may have a more difficult time diverting funds from densely populated cities to remote waterways and farmland. On the one hand, recycling phosphorus from the human waste stream may be simplified due to relatively high rates of urbanization and thus the large treatment plants in urban centres. The corollary to this, however, is that farming tends to take place away from cities, meaning that the phosphorus load in rural areas is disproportionate to the population. This theory is lent further weight when considering the high profile efforts in support of Lake Erie (in cooperation with the United States under the 2012 Great Lakes Water Quality Agreement), one of the Great Lakes that is located in one of the most densely populated areas of Canada, as compared to the attention paid to other waterways despite significant environmental degradation (Ulrich 2016, Binational

2017). Thus, Canada's vast geography will prove to be a significant challenge to improving the efficiency of phosphorus use and recovery.

2.2.3 Phosphorus availability

Perhaps the greatest factor contributing to a culture of phosphorus recycling (as opposed to capture and disposal) is the lack of availability of raw phosphorus in the EU (SCU 2013). Over the next three years, the FAO forecasts a deficit of phosphorus in West and Central Europe, and virtually all of the phosphorus needed by this continent is already being imported (FAO 2016.) This concern was explicitly highlighted as motivation for action in the 2011 Dutch Value Chain Agreement (ESPP 2011, UNEP 2011).

The situation in North America is currently not as dire; in the short term (up to 2019), a modest surplus of phosphorus is forecasted (FAO 2016). It is important to note that this surplus refers to Canada and the United States as an aggregate; Canada still imports all phosphorus either as raw PR or in fertilizer form. Looking beyond the 2019 forecast, however, active mines in the US (Potash Corp 2016), and the planned mines in Canada (USGS 2016) are expected to be depleted within 30 years. This means that although North America currently has a comfortable supply, this is only temporary. Another factor that makes a difference in Canada's role on the global nutrient community is its reserve of potassium (K) in the form of potash.

2.2.4 Potash: the Ace up Canada's sleeve

The three essential nutrients the are delivered by fertilizer are nitrogen, phosphorus, and potassium, hence the "N-P-K" values displayed on all bags of fertilizer. Canada is the world's largest producer and exporter of potash for agriculture, with one third of the global reserves reside within its borders (ibid). Just like phosphorus, potassium is essential for agricultural productivity (USGS 2015), which is 1.6 % of Canadian gross domestic product (CIA World Factbook). Furthermore, with the recent merger of the Canadian companies Agrium and PotashCorp, the world's number 1 producer of potash, and the number 2 producer of nitrogen fertilizer (CBC 2016). This means that as raw PR becomes more scarce, Canada will be in a position to use its potash and nitrogen resources to negotiate for access to phosphorus.

However, relatively little community, academic or governmental attention has been paid to potassium, as its runoff does not cause the same degree of damage to the environment as

phosphorus. Furthermore, while potash is as essential to food security as phosphorus, the size of the deposits and their distribution around the world mean that the long-term supply to global markets is more stable. Based on the relative rates of consumption for agricultural application, phosphorus will become the 'bottleneck' nutrient long before the potassium is depleted. This overall supply-and-demand surplus of nutrient resources is likely contributing to Canada's slow progress in addressing the myriad of issues surrounding phosphorus; there are other, more pressing concerns in the consciousness of citizens (and thus politicians) than the risk of fertilizer (and food) prices increasing sometime in the coming decades. This is a luxury not afforded to EU citizens, or indeed much of the developing world (UNEP 2011).

However, it can easily be argued that issues surrounding phosphorus, and food security at large, are intimately linked to the same causes that contribute to climate change. A significant amount of fossil-fuel energy is required to extract, transport, and process massive quantities of minerals around the world that are used to create the phosphate fertilizers required to feed the planet (NZWC 2016; CCME 2012). This means that when food waste is decreased, the burden of greenhouse gases associated the entire system that grew that food could also be avoided - *in addition to* preventing the gasses produced by rotting food. Thus, the statement given by Prime Minister Trudeau on climate change should by rights also apply to food security:

"Canada can and will do more to address the global challenge of climate change. We will do so because the science is indisputable, and tells us that our planet is already changing in ways that will have profound impacts on our future. And we will do so because it's the right thing to do, for our environment and our economy, and as part of the global community. … Canada is back."
Prime Minister Justin Trudeau, 30 November 2015, COP21

Thus, although Canada's own short-term supply of nutrients for agriculture is relatively secure, the position of leadership described by the Prime Minister at COP21- as well as the perspective taken from a moral higher ground - demands that we actively seek to reduce wasted nutrients.

2.2.5 Regulations

Unlike the EU, Canada's policies are much more permissive regarding use of processed waste as fertilizer. The Council of Canadian Ministers of the Environment (CCME) conducted a

review in 2010 to study the regulations surrounding recycle nutrients from human waste; one of the explicitly stated concerns in this report was the long-term supply of phosphorus (CCME 2010.) A follow-on report was produced in 2012 that clarified how and where processed human waste can be re-used (CCME 2012), including links to the pertinent Canadian Food Inspection Agency (CFIA) requirements. This report went so far as to recognize that removing phosphorus from wastewater in way that allowed 'beneficial re-use' was preferable to methods that would lead to disposal of phosphorus end-products. While this puts Canada in the enviable position of generating policy to allow and encourage nutrient recycling, it is not yet economical to do so. The current cost of phosphorus recycling technology means that the resulting phosphorus product is not competitive on the market (Oleszkiewicz 2015).

2.2.6 Policy networks

The EU, led by the Dutch "Nutrient Platform" has a robust phosphorus community which actively shares successes and setbacks in a manner that enables individual countries to learn from each other (Nutrient Platform NL 2016). Policy networks are described as "the relationships between actors responsible for policy decisions and the 'pressure participants' such as interest groups, or other types or levels of government, with which they consult and negotiate." (Cairney 2016). This depiction is more than fitting for the many different players involved in the EU, across industry, academia, government, and other interest groups. A key ingredient in the success of this EU network may be the European Sustainable Phosphorus Platform, which has proven to be a key facilitator in connecting these various groups, and providing a stable conduit to strengthen connections and enable productive collaborations.

The Canadian counterparts of these organizations have yet to coalesce around this complex nutrient efficiency and recycling issue. The nodes existing across Canada typically cluster around academic institutions or specific bodies of water, but they lack as yet a central point of cohesion. Just as Canada's size may seem to contribute to increasing the distance between the phosphorus problem from the average citizen, it also makes it more difficult for scientists and policymakers to find each other in order to share ideas. As suggested by Cordell (2012, 2014), identifying these stakeholder groups, their role and their motivations will assist in recognizing trends or possible candidates to galvanize a larger, coordinated Canadian effort.

2.3 Analysis of Canadian phosphorus players

This section focuses on various players involved in phosphorus cycling within Canada. It seeks to both categorize the stage of the cycle that is of most interest, as well as understand the underlying motivation (Figure 2.2). The players and corresponding phosphorus value stage(s) are presented in Figure 2.3.

2.3.1 Industry

Phosphorus Rock (PR). Within Canadian industry, there are relatively few actors involved in raw PR extraction and/or processing. Valued at $36 billion dollars, the merger of Agrium Inc. and Potash Corp. will result in the world's largest producer of potash, and second largest producer of nitrogen-based fertilizer, that also produces phosphorous fertilizer (CBC 2016). Phosphorus processing is relatively expensive compared to potash and nitrogen, and as such it contributes approximately 11% to each the overall profit margin of both companies (Agrium Inc 2016; Potash Corp 2016).

Although there are no currently active PR mines in Canada, three phosphorus mines are being developed, and are expected to become operational within the next two years. Considering, however, that Canada has 0.1% of the world's phosphorus reserve, the output of potential mines is virtually negligible on a global scale (USGS 2015; USGS 2016).

Wastewater. The only business currently selling phosphorus recovery technology in Canada is Ostara, which was founded at UBC (National Research Council (NRC) 2012). There are currently two operational plants in the prairie-region of central Canada, although the company has had far more success in selling its technology in Europe and the US than in Canada (PREX map.) The phosphorus product that is recycled from municipal wastewater treatment plants is marketed as CrystalGreen®, and meets the fertilizer specifications of the Canadian Food Inspection Agency (CFIA). However, due to its relatively high price compared to standard chemical fertilizers, and its limited supply, it is not widely available. However, the struvite fertilizer that is produced has a market that is eager to purchase it (Mavinic 2017). This means that there is still capacity within the market to accept recycled nutrients, and that the fact that it is recycled from wastewater does not seem to deter potential customers. The barrier to entering the market thus seems to be cost rather than regulations prohibiting its use, as in the case of the EU. A 2012 report from the Council of Canadian Ministers of the Environment (CCME)

acknowledged that there are many benefits to applying recycled nutrients to the soil, as long as they met hygienic standards required of fertilizers by the CFIA (CCME 2012). However, there is still some uneasiness with using recovered nutrients; a 2010 article with the misleading title "Straight from the Sewer" did not help to encourage recycled phosphorus use (Kinge 2010).

2.3.2 Interest Groups

PR. There are two groups which have repeatedly voiced concerns over the human rights situation in Western Sahara, where there are plentiful PR reserves. The Sisters of Mercy are shareholders in Potash Corp, and in a 2015 shareholder meeting they submitted a resolution requesting that a review be conducted to ensure that Western Saharans who live local to the PR deposits were being well treated. They submitted a similar request to Agrium. While both companies acknowledged these concerns, neither initiated an external review (Allen 2015).

The second, more aggressive group is known as the Western Sahara Resource Watch (WSRW). Their mission is to inform commodity traders of the situation in Western Sahara, and encourage them to halt purchases of PR until a solution has been reached to enable the local Saharawi people to exercise their right to self-determination. Their efforts in petitioning countries that purchase PR from Morocco have led to several countries, including Norway, Germany, and Australia (WSRW 2016) to acquire PR elsewhere.

Fertilizer, Crops, and Food. The International Plant Nutrition Institute (IPNI) is a global organization, but its phosphorus project is headquartered in Guelph- a Canadian city. IPNI is most interested in fertilizer use for crop growth. IPNI promotes the 4R program to reduce fertilizer waste and run-off. Although IPNI acknowledges that a sector of the scientific community is concerned about depletion of global phosphorus, it is less concerned with this long-term view, instead chooses to focus on improving current farming practices (Bruulsema 2016).

The Canadian Agri-Food Policy Institute (CAPI) is a think tank that analyzes the various policies affecting the agriculture industry, recognizing that the system is complex. They seek to bring players in the food supply chain together with researchers and government representatives, from across all Canadian provinces (Skogstad 2011.) While they are concerned about the impact of climate change on crops and food production, the scope of their interest does not extend to include PR or phosphorus in wastewater (CAPI 2016).

The National Zero Waste Council (NZWC) was founded in Vancouver in 2013, and now includes groups in Toronto, Montreal, Halifax and Edmonton. Their interest lies in preventing the avoidable waste of food and other goods by collaborating with government and businesses to enable reuse or recycling of goods, and to prevent superfluous waste production (NZWC 2016). They submitted recommendations to the Canadian government regarding strategies for reducing food waste, and the consequent reduction in carbon emissions (NZWC 2016).

Waste. The Canadian Water Network (CWN) and the Canadian Municipal Water Consortium (CMWC) are both active on the subject of phosphorus. Notably, in 2015 they commissioned a report from the University of Manitoba titled "Options for Improved Nutrient Removal and Recovery from Municipal Wastewater in the Canadian Context." This detailed report provides background not just on Canadian considerations, but also compares different and related regulations across world. One of the greatest strengths of these two networks is that they are active across the entire country, which provides a means to share ideas and collaborate on common challenges despite differences geography and regional priorities.

Complete Cycle. There are two North American groups whose mandates are across the entire phosphorus cycle; both are based in Arizona State University (ASU) (Sustainable P 2016). The Phosphorus Research Coordination Network (P-RCN) was formed in 2013, and takes a multidisciplinary approach to academic research as well as engaging policymakers. Recognizing that industry players should also be included, the P-RCN activated another group. Inspired by the success of the European Sustainable Phosphorus Platform (ESPP), the North American Sustainable Phosphorus Platform (NASPP) was announced in the January 2014 ESPP newsletter (ESPP 2014.) Since that time, the name has changed to become the Sustainable Phosphorus Alliance (SPA), though the purpose of the group continues to focus on bridging the gap between academia and industry. Neither of these groups is as active as the ESPP. Thus, there is still a gap in the North American phosphorus network. There is an opportunity to bring together Canadian researchers and institutes and take advantage of existing clusters of activity across the country to form a Canadian phosphorus policy platform.

2.3.3 Academia

Participation by various universities spans the entire phosphorus cycle. There are several regional hubs where there is significant activity, as discovered by examining the home institutions of the Canadian authors of the most pertinent journal articles:

- The University of Manitoba, was involved in producing a report commissioned by the Canadian Water Network (Oleszkiewic 2015); it has also studied phosphorus through the lens of subject of phosphorus impact on Lake Winnipeg (Ulrich 2009, 2016).
- University of Guelph, home to the Food Institute whose vision is to transform global food systems (http://foodinstitute.ca). Further, the Department of Land Resource Science has been active in Africa for over 20 years (van Straaten 2002).
- Ryerson University has an Urban Water lab which hosted a daylong conference in 2014 on "Phosphorus as a Resource: Sustainable Solutions for Infrastructure, Food Security and the Environment" (Trudeau 2014). Ryerson was also commissioned by the Canadian Water Network to prepare the 2015 report "Risks Associated with Application of Municipal Biosolids to Agricultural Lands" (McCarthy 2015).
- McGill University is home to researchers who have published extensively on phosphorus recycling efforts in the US and in Montreal, and have collaborated on articles with members of the EU phosphorus network. The McGill Geography Department also has a very pertinent international project to define the concept of a "Nitrogen Footprint."
- Université Laval's Applied Biological Sciences Department has studied nutrient recovery extensively (Vaneeckhaute 2016).
- École Polytechnique (Montreal), whose Civil Engineering Department's research on phosphorus capture using apatite (a phosphate mineral) has the potential to be part of a phosphorus recycling strategy (Bellier 2006).
- University of British Columbia, where Ostara was founded ten years ago, and is also a partner with the Australian phosphorus network (Phosphorus Futures, 2016).

Each of these institutions seems to be working more or less in isolation with limited collaboration, at least as far as can be determined by examining author lists. Canadian researchers have published in partnership with scientists from the US or EU more than with each other. While this may advance their own research agendas, it does not contribute to bringing national clarity to Canada's phosphorus cycle.

2.3.4 Government

The mandates of several departments have led to participation in various aspects of phosphorus cycling, as summarized in Table 3. While there seems to be collaborations between federal and provincial counterparts (i.e. CCME), there was no clear evidence of departments working together where their mandates overlapped, such as a collaboration between Agriculture and Agri-Food Canada (AAFC) and Environment and Climate Change Canada (ECCC). In order to make any meaningful changes, their respective efforts will need to complement and reinforce each other.

Federally, ECCC has the highest profile phosphorus-specific project, and is collaborating with the United States Environmental Protection Agency (USEPA) to improve the water quality of Lake Erie. As discussed previously, Lake Erie is a geographical location where regulatory effort is currently focused, and potential instruments are being studied. AAFC is also cognizant of phosphorus use issues related to farming. Though it is tracking phosphorus risk and build up, it is only imposing voluntary corrective measures (Agriculture and Agri-Food Canada 2016b), with the intention that cost savings associated with reducing waste would be sufficient financial incentive. AAFC is also sponsoring a project and has published several papers related to responsible phosphorus use, however these are focused more on good farming practice and plant uptake than on the larger phosphorus cycle (Agriculture and Agri-Food Canada 2016a). Thus, ECCC currently has the greater Canadian role in implementing regulations and incentives.

There is no evidence that Global Affairs Canada (GAC) is specifically tracking issues surrounding phosphorus, or PR in Western Sahara. However, due to the large economic activity and significant Canadian companies in this industry, it would be naïve to assume that they are not monitoring the situation. Agrium Inc. has an agreement with the Moroccan *Office Cherifien des Phosphates* (OCP*)* to supply PR until 2020 (Agrium Inc 2016), though this agreement is not specifically mentioned in GAC's Morocco Factsheet (GAC 2015).

On a provincial level, both the Ontario Ministry of Agriculture, Food, and Rural Affairs (OMAFRA) and the Ontario Ministry of the Environment and Climate Change (OMECC) have participated in phosphorus sustainability conferences (Trudeau 2014). The primary phosphorus focus of OMECC involves the ecosystem of the Great Lakes (Wynne 2016) which again is largely Lake Erie-centric. However, after the Waste Free Ontario Act received Royal Assent in June 2016 (Bill 151 2016), the situation has changed, leading to opportunity to harness Ontario's

entire phosphorus cycle. For instance, OMECC recently launched Ontario Circular Economy Innovation Lab (CEIL) will bring together public and private sector representatives to collaborate in developing innovative ways to reduce waste and lower greenhouse gas emissions (Circular Economy Innovation Lab 2016). Potentially, these developments could contribute to connecting the many active phosphorus players in Ontario.

Ulrich (2016) made an interesting observation regarding the role of government versus non-government sectors in the case of action in the Lake Winnipeg basin, noting that "the impetus for change seems to be much stronger in the non-government sectors" (Ulrich 2016). It may be that part of the government's apprehension is due to the scope of the problem; it does not fit easily into one governmental department's mandate. Therefore it would take significant coordination and weighing of various interests, and any activity may therefore remain well outside any given mandate.

The act of uniting toward a common purpose is a powerful driver to bring a "community" together. Because the efforts required to mobilize a phosphorous community are subtler and dispersed throughout the phosphorus cycle, Canada has not yet had that "lightning rod" opportunity or event to crystallize the intentions of the many interested parties. Industry may not be taking the lead because it is not in their financial interest to do so; the cost of recycling phosphorus from wastewater is still uneconomical, and the market is not yet ready to purchase the product. The problem simply is not perceived to be particularly urgent, outside of a few very small groups of interested people. Furthermore, responsibility to resolve the issue is diluted across the country and even within government; there is not an obvious leader, nor are the solutions to phosphorous problems simple or even apparent. These disparate interest groups are all in full agreement that phosphorus must be used judiciously. The challenge in effecting Canadian change towards managing phosphorus has been to identify a common purpose and project a united front

It is salient at this juncture to discuss a workshop on "Phosphorus as a Resource: Sustainable Solutions for Infrastructure, Food Security and the Environment" which took place at Ryerson University in 2014. Canadian participants from some of the interest groups, academic institutions mentioned above, and government representatives participated, as well as members of the ESPP. A summary of these discussions was collected and published in the proceedings,

and of particular interest was the “Initial Action Plan for Engagement” (Trudeau 2014). The areas listed as requiring action are worth repeating here, as they are still pertinent:

1. lack of knowledge of the need to recognize phosphorus as a resource;
2. lack of coordination for governance, technology and research focused on recycling;
3. requirement for support of market instruments; and
4. recovery / reuse linkage to broader Nutrient – Energy – Water nexus.

These two workshops were the genesis of two valuable reports on nutrient recycling commissioned by the CWN (McCarthy 2015; Oleszkiewicz 2015). However, without the implementation of a central coordinating authority, or viable information management infrastructure to share knowledge, the effort will stagnate. In order for phosphorus recycling to regain momentum a stable platform for Canadian stakeholder engagement must be created, to provide a mechanism to collaborate and coordinate action, as well as the incentive to do so.

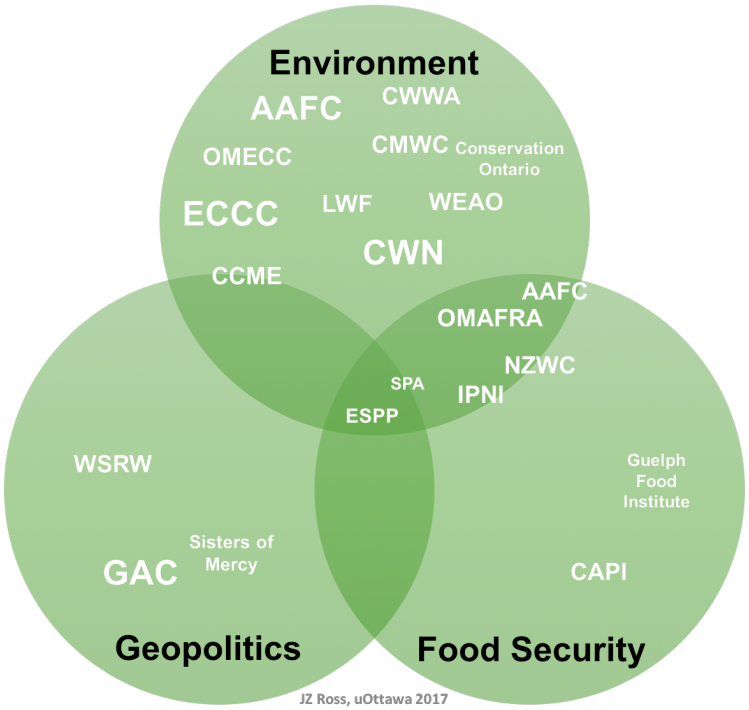

Figure 2.2: Hypothesized motivations of Canadian phosphorus players

Acronym	Full name of organization
AAFC	Agriculture and Agri-Food Canada
CAPI	Canadian Agri-Food Policy Institute
CCME	Council of Canadian Ministers of the Environment
CMWC	Canadian Municipal Wastewater Consortium
CWN	Canada Water Network
CWWA	Canadian Water and Wastewater Association
ECCC	Environment and Climate Change Canada
ESPP	European Sustainable Phosphorus Platform
GAC	Global Affairs Canada (aka Foreign Affairs)
IPNI	International Plant Nutrition Institute
LWF	Lake Winnipeg Foundation
NZWC	National Zero Waste Council
OMAFRA	Ontario Ministry of Agriculture, Food and Rural Affairs
OMECC	Ontario Ministry of Environment and Climate Change
P-RCN	Phosphorus Research Coordination Network
SPA	Sustainable Phosphorus Alliance
WEAO	Water Environment Association of Ontario
WSRW	Western Sahara Resource Watch

Table 2.2: Summary of acronyms of players within Canada phosphorus cycle

Figure 2.3: Stages of the Canadian phosphorus cycle, and which players are involved

2.4 Conclusion

Harnessing Canada's phosphorus cycle is a complex problem that must be tackled from many different fronts. Due to challenges of geography, population density, industrial and economic drivers, this problem is not perceived as urgent. To date, the only symptom of a systemic, Canadian problem with the phosphorus cycle is lake eutrophication. As such, targeting this obvious and understandable problem may be the easiest 'foot in the door' to drive improvements in the efficient use of phosphorus throughout the entire cycle. There are hubs of activity around certain academic institutions, and within government; the federal ECCC currently has the greatest relevant expertise. There are many other groups whose interests overlap, yet they have not been actively engaged to participate in a discussion of the larger Canadian phosphorus cycle. In order to effect real change in Canada, industry, academia and other groups must acknowledge their common purpose and form a supported holistic network to advance Canadian shared interests.

Fortunately, the first steps toward establishing a Canadian Nutrient Platform (CNP) are underway. The lab group is in active discussion with partners from Laval, UBC, and OMECC to create a platform to enable interested partners to learn from each other and share resources regarding nutrient recycling. Following the inaugural teleconference on 21 March 2017 (see Annex D – Appendix D2), members of the group have been working together to create a plan and request funding to help propel this valuable endeavour forward.

Figure 2.4: Unofficial CNP logo

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CHAPTER 3

BACKGROUND THEORY

The hypothesis of this project is that it is possible to precipitate a carbonate apatite from two waste streams: municipal waste water, and CO_2 (g). This would enable the recycling of phosphorus and carbon back into the food system, thus addressing the motivations raised in Chapter 2. Chapter 3 will introduce the basic science behind precipitation, and study the equilibria systems of the species of greatest interest (calcium, carbonate, phosphate, and water). It will also summarize the existing technologies for treating municipal waste, as well recycling phosphorus.

3.1 Precipitation

3.1.1 Saturation, Ion Activity Product (IAP) and Solubility Product (K_{sp})

A solution that is saturated has achieved equilibrium between a solid in the solution, and its corresponding dissociated component ions. In all cases for this thesis, the solid is a soluble salt composed of cation(s) and anion(s). This equilibrium saturation can be reached either by dissolving a solid salt, or by slowly increasing the concentration of the component ions until the corresponding solid forms. Saturation is not an absolute property, rather it varies with temperature, pH, and pressure.

IAP (sometimes shortened to AP or IP) is calculated by multiplying a solution's ideal concentrations by an experimentally determined activity coefficient which accounts for non-ideal interactions, depending on the definition, sometimes with the ion activity raised to the power of its stoichiometric coefficient (Housecroft 2001). The dissolved ionic components of an ideal ionic aqueous solution would be considered to have an activity coefficient of 1, and an ionic activity equivalent to the ionic molar concentration (Morse 1974).

For a theoretical solid salt M_aX_b dissolved in water, the dissolution would be:

$$M_aX_b\,(s) \Leftrightarrow aM^+\,(aq) + bX^-\,(aq) \qquad [3.1]$$

As the salt dissolves, its IAP could be monitored, and determined by:

$$IAP = \gamma_{M+}[M^+]^a * \gamma_{X-}[X^-]^b = (a_{M+})(a_{X-}) \qquad [3.2]$$

Once the IAP of the aqueous solution reached the K_{sp} corresponding to M_aX_b in the given conditions, the solution would be considered saturated and no additional solid would dissolve. Taking $CaCO_3$ as an example, the IAP and K_{sp} would be calculated as follows. In water, the following dissolution occurs:

$$CaCO_3\ (s) \Leftrightarrow Ca^{2+}\ (aq) + CO_3^{2-}\ (aq) \qquad [3.3]$$

The solubility product is thus calculated using the ideal concentrations of the ionic species:

$$K_{sp} = [Ca^{2+}]_{eq}[CO_3^{2-}]_{eq} \qquad [3.4]$$

If the activity coefficients of the ionic species are known, the IAP can also be determined:

$$IAP = (a_{Ca2+})(a_{(CO3)2-}) \qquad [3.5]$$

Figure 3.1 shows the solubility curve of the polymorphs of $CaCO_3$ as a function of temperature. Calcite is the most stable polymorph of calcite, and is form of $CaCO_3$ that is used throughout this thesis.

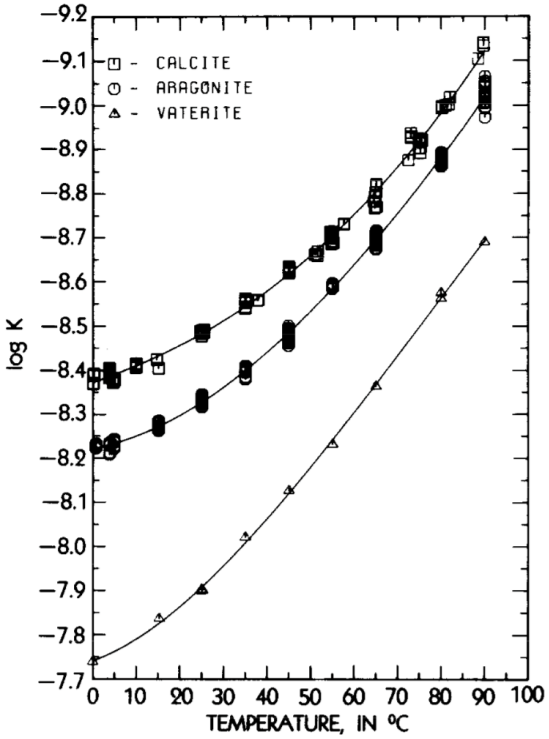


Figure 3.1. Log solubility product as a function of temperature for calcite, vaterite, and aragonite (Plummer 1982)

3.1.2 Supersaturation

The driving force behind precipitation reactions is supersaturation. As the term implies, supersaturation is the state in which a solution's IAP exceeds the equilibrium saturation.

The *degree* or *index* of supersaturation has several different definitions. Each of the definitions listed in Table 3.1 below is acceptable, however it is important to note that supersaturation values calculated using different definitions cannot be compared directly. Van Kemenade's definition will be used throughout this thesis.

	Equation	Supersaturation	Equilibrium saturation	Under saturation
Berner and Morse 1974	$\Omega_{X_xY_y} = \frac{(\alpha_{X^+})^x(\alpha_{Y^-})^y}{K_{sp}(T)}$	$\Omega > 1$	$\Omega = 1$	$\Omega < 1$
Nancollas 1974	$S = \frac{(IAP - K_{sp})}{K_{sp}}$	SI > 0	SI = 0	SI < 0
Myerson 1978	$S = \frac{\mu - \mu^*}{RT} = \ln\frac{a}{a^*}$	SI > 0	SI = 0	SI < 0
Moreno 1981	$S = \left(\frac{IAP}{K_{sp}}\right)^{1/v}$	S > 1	S = 1	S < 1
Van Kemenade 1987	$S = \left(\frac{IAP}{K_{sp}}\right)$	S > 1	S = 1	S < 1
Hartley 1997	$SI = \log\left(\frac{IAP}{K_{sp}}\right)$	SI > 0	SI = 0	SI < 0

Table 3.1: Accepted definitions of supersaturation

There are several ways that a solution can become supersaturated, two of which are illustrated in Figure 3.2 using $CaCO_3$ (as calcite) as an example. In Kawano's 2009 study, a solution that was supersaturated with respect to $CaCO_3$ was prepared by mixing a solution of dissolved $CaCl_2$ with a solution of dissolved Na_2CO_3 of the same volume and concentration. Separately, these two solutions were not saturated. However, the IAP of the resulting $[Ca^{2+}]$ and $[CO_3^{2-}]$ (shown below as point "A") exceeded the K_{sp} of $CaCO_3$ upon mixing. This would serve

to drive the 'excess' $Ca^{2+}$and CO_3^{2-} ions out of solution until point "B" was reached. This is the theory behind the experimental method that will be described in Chapter 4.

A solution can also become supersaturated without changing the concentration of the aqueous ions. Point "C" in Figure 3.2 is not supersaturated at ambient temperature. However, if it was heated to point "D" more quickly than the equilibrium of the system could adapt, it would become supersaturated. If the solution were cooled, the solution would return to its original state. If it was maintained at 90°C, then the additional $Ca^{2+}$and CO_3^{2-} ions would be driven out of solution until point "E" was reached. This same effect can be exploited by adjusting pH, because it changes the speciation the carbonate ion between HCO_3^- and CO_3^{2-}.

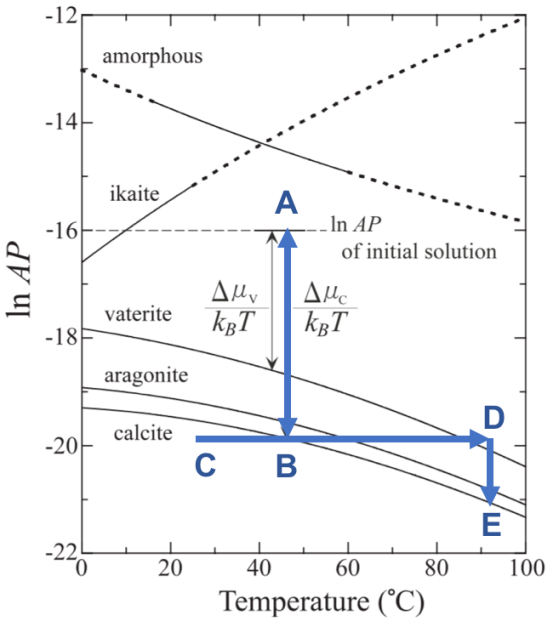


Figure 3.2: Equilibrium curves of $CaCO_3$ polymorphs as a function of temperature (adapted from Kawano 2009)

The degree to which a solution is supersaturated plays an important role in how a precipitate forms. There are four zones of saturation that are often referred to, shown below in Figure 3.3. The zones in Figure 3.3D are of greatest interest.

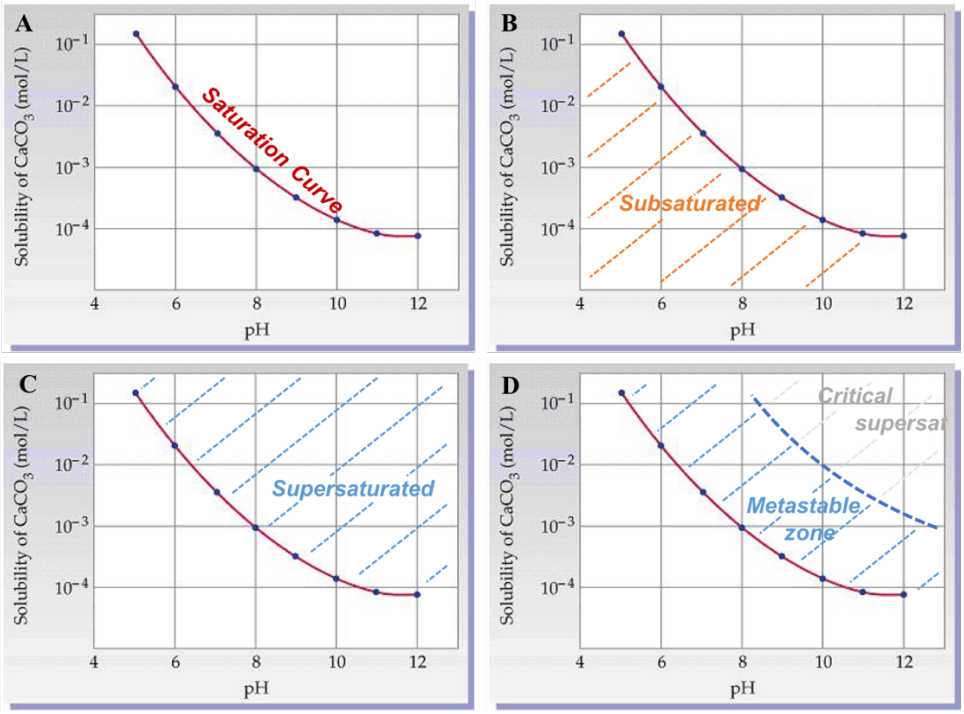


Figure 3.3: (A) Saturation, (B) Subsaturation, (C) Supersaturation (D) Metastable zone and critical supersaturation zones (Adapted from Ocean Sediment)

The metastable zone is only slightly supersaturated. In this region, solids form relatively slowly, prefer to grow on existing surfaces, and it is easier to control how they grow. For this reason, it is typically the preferred condition for large-scale precipitation. As the degree of supersaturation increases however, a point is reached at which precipitate forms almost immediately. This point is called the critical saturation limit. Above this limit, solid forms very quickly, making it difficult to control the product that is made. The mechanisms of nucleation and growth that are characteristic of these two zones are discussed in Section 3.1.3.

3.1.3 Nucleation and growth

There are three primary mechanisms by which ions precipitate out of a solution, as described by Myerson (2002).

3.1.3.1 Homogeneous nucleation. Homogeneous nucleation will occur when the chemical potential of the supersaturated state is equivalent to the chemical potential to generate a solid phase from solution, i.e. nucleation occurs. This mechanism is seen most commonly at higher supersaturation states, i.e. above critical saturation. If there are multiple species in the solid state that can nucleate from solution, that first phase to precipitate will typically be the least stable

phase (see Ostwald ripening). In the case of calcium carbonate, amorphous calcium carbonate has been seen to precipitate first, and calcite is the last to form (Figure 3.2). Often, this is not the desired mechanism of nucleation as it can lead to the production of many small particles (or 'fines'); these are very small crystalline particles that may clog a reactor or inhibit the growth of the desired species.

In a closed system, the formation of nuclei reduces the concentration of calcium and carbonate ions in solution, in turn reducing the supersaturation state of that species. At this lower supersaturation state, heterogeneous nucleation may occur. Depending on the kinetics and the method of the supersaturation decrease, foreign surfaces on which heterogeneous nucleation could occur include the reactor walls, impeller surfaces, and the air-liquid interface.

3.1.3.2 Heterogeneous nucleation. The precipitation of a solid on a surface or interface that is not the same as the precipitate is called heterogeneous nucleation. This is accomplished at supersaturations lower than that at which homogeneous nucleation occurs because the presence of a solid phase or interface lowers the energy required to form a new, solid phase. The nuclei are able to populate an existing surface rather than spontaneously form from solution.

3.1.3.3 Heterogeneous secondary nucleation, or growth. The precipitation of a solid on a surface that is the same as the precipitating solid is called heterogeneous secondary nucleation, or simply secondary nucleation. It also represents the phenomenon of crystal growth. The lowest supersaturation is required for this mechanism of solid formation, as the component ions of the solution are the same as the component ions in the solid. This mean that the lowest energy state is required to generate crystal growth. When in suspension, these solids are also called "seed," and thus it is preferable to select a seed as similar to the desired product as possible.

3.1.4 Ostwald ripening and step rule

As crystals begin to form in a solution, localized concentration gradients also develop. This leads to the transport of solute material toward larger crystals, at the expense of smaller ones. This has the overall effect of increasing the average size of crystals over time, while reducing the total number, which is known as Ostwald ripening (Myerson 2002).

A corollary of this effect is that crystals will tend to grow in an apparent step-wise manner. This is achieved by overcoming small activation energies incrementally, instead of changing energy states in one large step. Thus, the solution forms progressively more stable (and

less soluble) products over time. This sequence is sensitive to changes in temperature and pH. This has been seen experimentally, and the results from van Kemenade's study of the precipitation sequence of the calcium-phosphate system are summarized in Table 3.2 and illustrated in Figure 3.4.

Precipitating Sequences

pH	*T* (°C)	Precipitating sequence
6.7	26	DCPD = OCP → HAP
7.4	26	ACP → OCP → HAP
6	26	OCP → DCPD (→) HAP
6.7	37	DCPD → OCP → HAP

ACP: Amorphous calcium phosphate
DCPD: Dicalcium phosphate dihydrate
HAP: Hydroxyapatite
OCP: Octacalcium phosphate

Table 3.2. Precipitating sequence of calcium phosphate under different pH and temperature conditions (van Kemenade 1987)

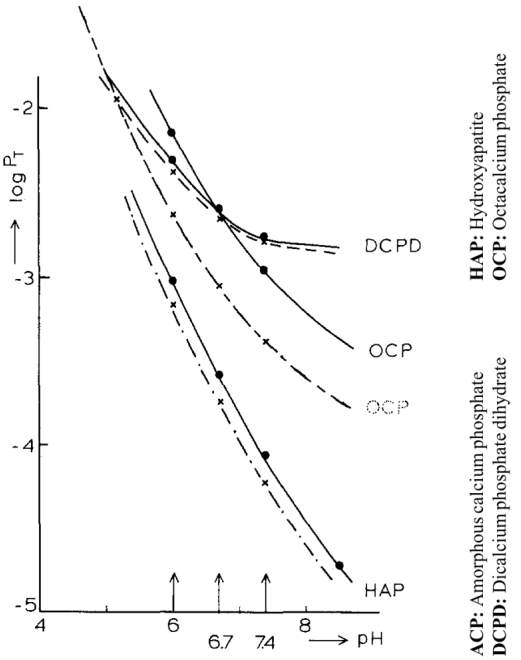
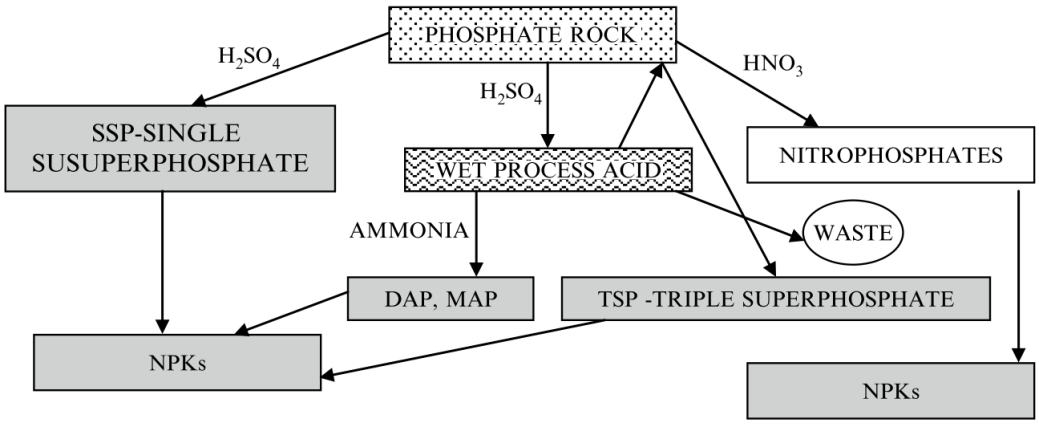


Figure 3.4. Solubility isotherms at 25°C (solid line) and 37°C (dashed line) of HAP, OCP, and DCPD against pH (van Kemenade 1987)

3.2 Chemical equilibria and speciation

3.2.1 Apatite

As indicated in the previous chapter, the product of interest to this thesis is a carbonate calcium phosphate, also called a carbonate apatite. As shown in Figure 3.5, PR is treated with H_2SO_4 to produce phosphoric acid, H_3PO_4; this is the form in which phosphorus is mixed into fertilizer (Butosov 2013). Early mineralogists named the primary mineral in PR as francolite, which is a carbonate fluorapatite of formula $Ca_{10-x-y}Na_xMg_y(PO_4)_{6-z}(CO_3)_zF_{0.4z}F_2$ (Elliott 1994). This project focuses on the CO_3^{2-} substitution rather than the F^- substitution for two reasons. First, the CO_3^{2-} ion has been shown to increase the solubility of the apatite mineral (Jahnke 1984, Schuffert 1990). PR commonly has approximately 1.4-6.3 wt% CO_3^{2-} (McArthur 1985) which facilitates the production of phosphoric acid, however higher amounts of CO_3^{2-} serve to consume excessive H_2SO_4. Second, the F^- ions react to form HF (g) during processing, and do not report to the final product (Butusov 2013). For these reasons, if a synthetic carbonate apatite can be formed, it could potentially be introduced into the existing phosphoric acid production stream.



DAP: diammonium phosphate **MAP:** monoammonium phosphate **NPK:** Nitrogen/Phosphorus/Potassium content

Figure 3.5: Overview of production of phosphorus fertilizer (Butusov 2013)

Apatite is a highly substitutable hexagonal mineral; examples of apatite are listed in Table 3.3 to illustrate the breadth of the different possible substitutes (Hughes 2015). Note that carbonate apatite and carbonate fluorapatite (francolite) are both absent from this table. This is because they are biological rather than geological apatites; they are not found in nature without a contribution of organic matter (Compton 1992, Schuffert 1998, Filippelli 2011), and are not considered to be true "minerals" (Flesicher 1995, Pan 2002).

Apatite Group	
Alforsite	$Ba_5(PO_4)_3Cl$
Chlorapatite	$Ca_5(PO_4)_3Cl$
Fluorapatite	$Ca_5(PO_4)_3F$
Hydroxylapatite	$Ca_5(PO_4)_3OH$
Hydroxylapatite-*M*	$Ca_5(PO_4)_3OH$
Johnbaumite	$Ca_5(AsO_4)_3OH$
Johnbaumite-*M*	$Ca_5(AsO_4)_3OH$
Mimetite	$Pb_5(AsO_4)_3Cl$
Mimetite-*M*	$Pb_5(AsO_4)_3Cl$
Pieczkaite	$Mn_5(PO_4)_3Cl$
Pyromorphite	$Pb_5(PO_4)_3Cl$
Stronadelphite	$Sr_5(PO_4)_3F$
Svabite	$Ca_5(AsO_4)_3F$
Turneaureite	$Ca_5(AsO_4)_3Cl$
Vanadinite	$Pb_5(VO_4)_3Cl$

Table 3.3: Examples of geological apatite minerals (Hughes 2015)

3.2.2 Calcium

The calcium ion has an oxidation state of +2, and readily forms complexes in aqueous solution. It has been found to form both inner and outer hydration layers, leading to a complex of form $[Ca(H_2O)_6]^{2+}(H_2O)_{12}$ (Dorvee 2013). This will be discussed further in Section 3.2.5. Its hydration number varies as pH and temperature, as seen in Figure 3.6.

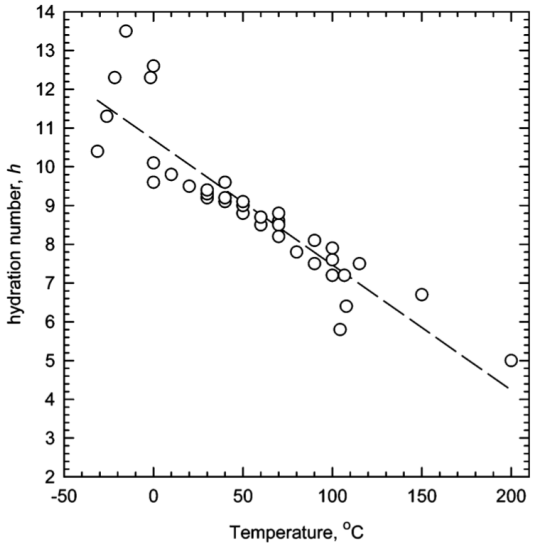


Figure 3.6. Hydration numbers against temperature (°C) (Zavitsas 2005)

Calcium interacts with phosphorus to form several different calcium phosphates. Several of the most common calcium phosphate products are listed below in Table 3.4; note that the inclusion of both calcium and phosphate in a solid do not mean that it is an apatite.

Ca/P ionic ratio	Compound	Chemical formula	Solubility at 25 ºC, –log(K_s)	Solubility at 25 ºC, g/L	pH stability range in aqueous solutions at 25°C
0.5	Monocalcium phosphate monohydrate (MCPM)	$Ca(H_2PO_4)_2·H_2O$	1.14	~ 18	0.0 – 2.0
0.5	Monocalcium phosphate anhydrous (MCPA)	$Ca(H_2PO_4)_2$	1.14	~ 17	[c]
1.0	Dicalcium phosphate dihydrate (DCPD), mineral brushite	$CaHPO_4·2H_2O$	6.59	~ 0.088	2.0 – 6.0
1.0	Dicalcium phosphate anhydrous (DCPA), mineral monetite	$CaHPO_4$	6.90	~ 0.048	[c]
1.33	Octacalcium phosphate (OCP)	$Ca_8(HPO_4)_2(PO_4)_4·5H_2O$	96.6	~ 0.0081	5.5 – 7.0
1.5	α-Tricalcium phosphate (α-TCP)	α-$Ca_3(PO_4)_2$	25.5	~ 0.0025	[a]
1.5	β-Tricalcium phosphate (β-TCP)	β-$Ca_3(PO_4)_2$	28.9	~ 0.0005	[a]
1.2 – 2.2	Amorphous calcium phosphate (ACP)	$Ca_xH_y(PO_4)_z·nH_2O$, n = 3 – 4.5; 15 – 20% H_2O	[b]	[b]	~ 5 – 12 [d]
1.5 – 1.67	Calcium-deficient hydroxyapatite (CDHA)[e]	$Ca_{10-x}(HPO_4)_x(PO_4)_{6-x}(OH)_{2-x}$ [f] (0<x<1)	~ 85.1	~ 0.0094	6.5 – 9.5
1.67	Hydroxyapatite (HA)	$Ca_{10}(PO_4)_6(OH)_2$	116.8	~ 0.0003	9.5 – 12
1.67	Fluorapatite (FA)	$Ca_{10}(PO_4)_6F_2$	120.0	~ 0.0002	7 – 12
2.0	Tetracalcium phosphate (TTCP), mineral hilgenstockite	$Ca_4(PO_4)_2O$	38 – 44	~ 0.0007	[a]

[a] These compounds cannot be precipitated from aqueous solutions.

[b] Cannot be measured precisely. However, the following values were found: 25.7 ± 0.1 (pH = 7.40), 29.9 ± 0.1 (pH = 6.00), 32.7 ± 0.1 (pH = 5.28).

[c] Stable at temperatures above 100°C.

[d] Always metastable.

[e] Occasionally, CDHA is named as precipitated HA.

[f] In the case $x = 1$ (the boundary condition with Ca/P = 1.5), the chemical formula of CDHA looks as follows: $Ca_9(HPO_4)(PO_4)_5(OH)$.

Table 3.4: Calcium phosphates and their major properties (Dorozhkin 2009)

3.2.3 Carbonate

The presence of carbonate in apatite increases its solubility (Jahnke 1984). The equilibrium system of CO_2 (g) and CO_3^{2-} (aq) is important to this study as the effects of both the CO_3^{2-} contributed by calcite as well as CO_2 in the atmosphere must be considered.

In aqueous solutions, the following reactions take place (Morse 1990):

$$CO_2\ (g) \rightleftharpoons CO_2\ (aq) \qquad [3.6]$$

$$CO_2\ (aq) + H_2O\ (l) \rightleftharpoons H_2CO_3(aq) \qquad [3.7]$$

$$H_2CO_3(aq) \rightleftharpoons\ HCO_3^-\ (aq) + H^+\ (aq) \qquad [3.8]$$

$$HCO_3^-\ (aq) \rightleftharpoons\ CO_3^{2-}\ (aq) + H^+\ (aq) \qquad [3.9]$$

These equilibria are temperature and pH-dependent, and the predominant species and its relative concentration can be predicted according to Figure 3.7 below.

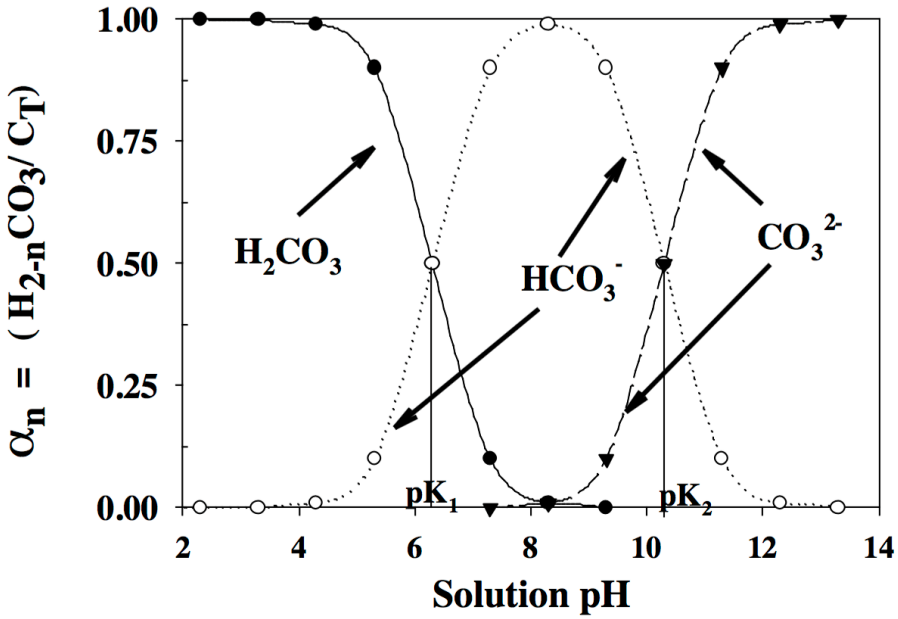


Figure 3.7. Distribution of carbonate species as a fraction of total dissolved carbonate in relation to solution pH (SSC 102 course notes)

The carbonate ion typically has a trigonal planar shape (Figure 3.8), and has been found to form complexes with water of form $[CO_3(H_2O)_9]^{2-}$ (Dorvee 2013).

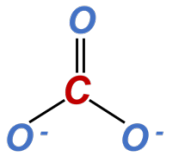


Figure 3.8: Structure of carbonate ion

3.2.4 Phosphate

Phosphorus is present in many forms in nature, but the ion of greatest interest is the orthophosphate ion, PO_4^{3-}. It is also called inorganic phosphate, P_i, and this is how it is referred to throughout this thesis. The other common form is condensed phosphate, or polyphosphate, denoted as "poly-P", which is a chain of P_i ions that must be digested in order to release the Pi ions. In wastewater treatment, the concentration of soluble P_i is tracked, as well as the total phosphorus ("TP") in solution, i.e. the concentration of both P_i and poly-P.

P_i is important because it is this form of phosphorus that is most chemically available for absorption by plants and animals. P_i has a tetrahedral structure, shown in Figure 3.9. Compared

with the carbonate ion, this may allow it to have more complex, 3-D interactions with other ions in solution. Specifically, it has been shown to form a complex of $[PO_4(H_2O)_{12}]^{3-}$ (Dorvee 2013).

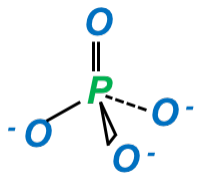


Figure 3.9: Structure of phosphate ion, P_i

Much like CO_3^{2-}, speciation and relative concentration of Pi varies as a function of pH. This is illustrated in Figure 3.10, where the effect of this equilibrium is shown both in distilled water and seawater. These conditions are both of interest because PR is primarily formed in ocean environments, whereas this thesis tests P_i dissolved in ddH_2O; future work may compare results under both conditions. Note that these equilibria are sensitive to the presence of other ions in solution. Just as the speciation to pH relationship shifted when comparing distilled water and seawater solutions, it is expected that the presence of Ca^{2+} and CO_3^{2-} will have yet another, unknown effect.

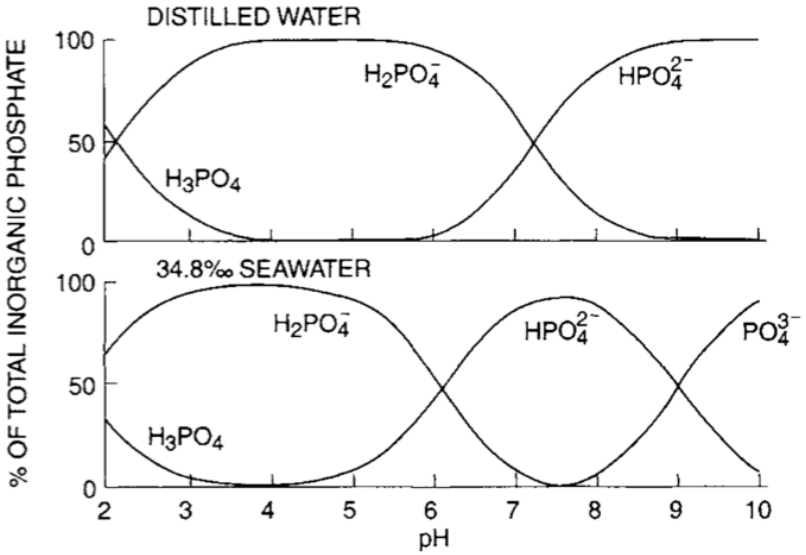


Figure 3.10. Speciation of phosphoric acid with pH (Jahnke 2000)

3.2.5 Water

Water is an important player in the relationships between Ca^{2+} - PO_4^{3-} - CO_3^{2-} because it creates hydration layers around each of these ions, reducing their activity and thus their ability to

interact in solution. The relative size and orientation of these hydrations layers is shown in Figure 3.11, as illustrated by Dorvee in 2013.

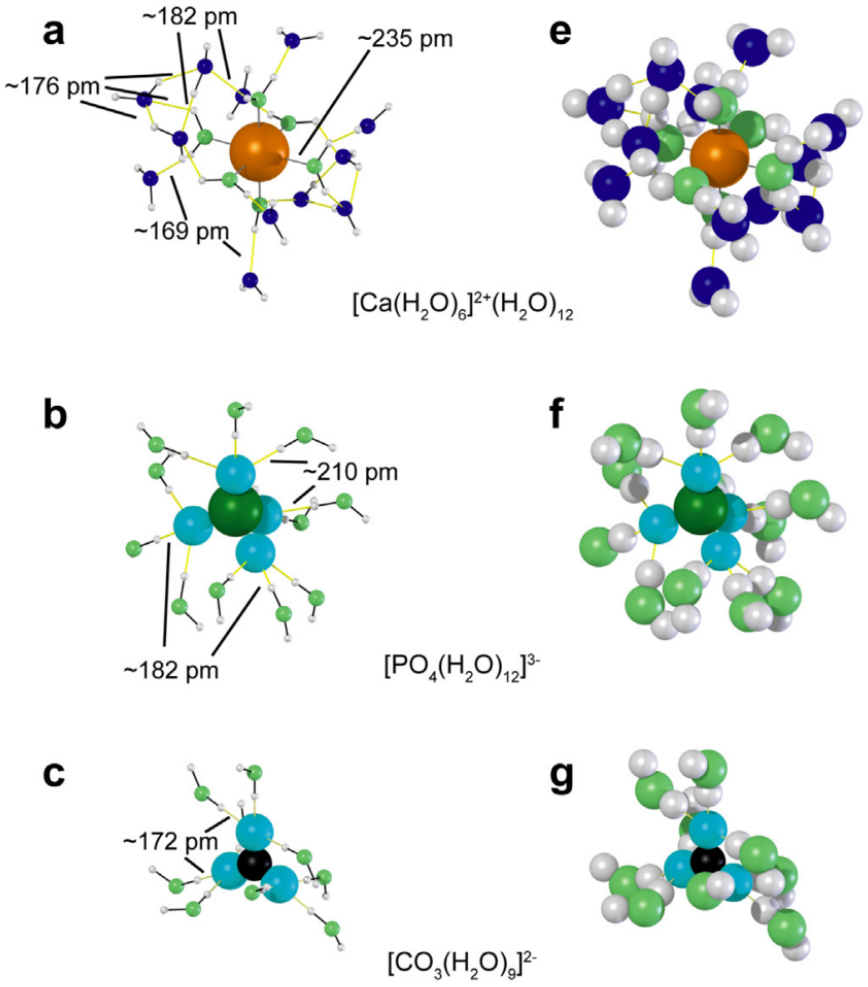


Figure 3.11: Arrangement of water around ions. Reduced-size water molecules highlight bond angles and molecular arrangements. Full sized water molecules to demonstrate space-filling and crowding by the water molecules. These configurations illustrate the momentary immobilization of water around these ions. The oxygens of the 1st layer waters are shown in light green, the oxygens of the 2nd layer waters are shown in dark blue. (Figure and caption from Dorvee 2013)

This is not to say that the presence of water prevents the precipitation reaction from taking place, however it is important to understand that it may hinder the reaction between the ions of interest at low concentrations and low supersaturations. In Figure 3.12 below, a proposed mechanism for the interaction of hydrated Ca^{2+} with hydrated P_i is illustrated.

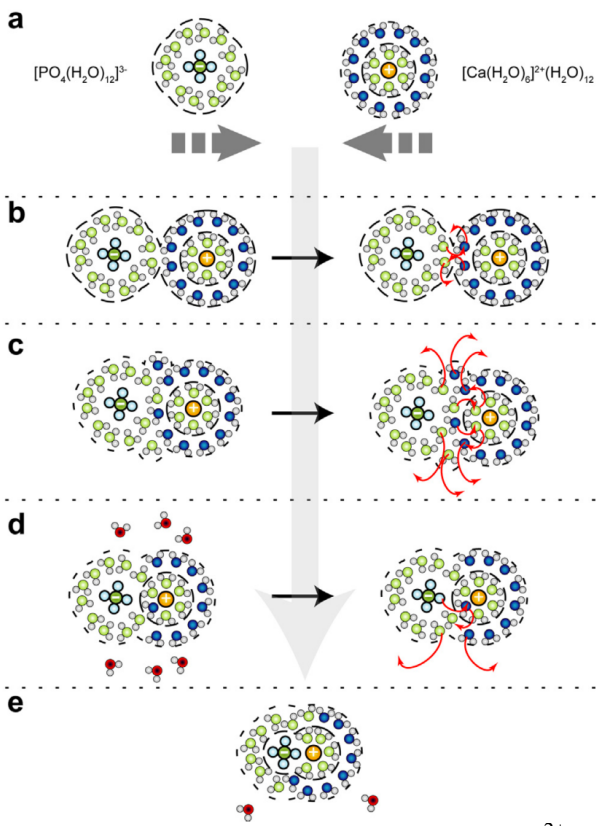


Figure 3.12: Reaction between hydrated Pi and Ca^{2+} ions, with suggested mechanism by which water is expelled (Dorvee 2013).

3.3 Synthetic apatite formation

The synthetic formation of apatite has been of interest in several fields for many years. Most commonly, the medical and dental fields explore the possibility of forming synthetic bone and tooth mineral for therapeutic applications. The chemistry of apatite has also proven important to other industries such as wastewater treatment and dairy production, where high concentrations of calcium and phosphate can lead to scaling within reactors.

This section provides an overview of mechanisms that have been tested to precipitate apatite. Existing studies were compared on the basis of parameters such as the solid produced, seed and seed density, and Ca/P ratio of reactants and products. This aided in determining suitable experimental conditions.

3.3.1 Target product and seed

HAP is the most common apatite studied, as it is the most stable species and is often used to approximate bone mineral. Seeded (Amjad 1981, Bellier 2006, Berg 2007, Campbell 1991,

Chen 2009, Hohl 1982, Koutsoukos 1981, Molle 2003, Moreno 1981, Nancollas 1974, Song 2006) and unseeded [Cui 1996, Perrone 2002, Tervahauta 2013, van Kemenade 1987] procedures have successfully proven that P can be removed from solution as HAP. Seed material added was often a small sample of the desired product (Amjad 1981 and 1984, Bellier 2006, Campbell 1991, de Rooij 1984, Hohl 1982, Koutsoukos 1981, Moreno 1981, Nancollas 1981, Nelson 1986). Several studies successfully proved the effectiveness of novel seed material such as dental enamel (carbonate apatite) (Campbell 1991, Nelson 1986), tobermorite ($Ca_5Si_6O_{16}(OH)_2 \cdot 4H_2O$) (Berg 2006), xonotlite ($Ca_6Si_6O_{17}(OH)_2$) (Chen 2009), calcite (Kotsoukkos 1981) and juraperle (a form of calcite) (Song 2006 and 2007). The density of seeding added to solution varied between 0.05 g seed / L solution, to 50 g seed / L solution. Seed was usually quantified by specific surface area (SSA), which varied greatly between species and studies. Carbonate fluorapatite (CFAP) was prepared and replicated in several unseeded studies (Jahnke 1984, Regnier 1994, Perrone 2002).

3.3.2 Methods and Materials

An important technique in precipitating apatite is the constant composition method. First developed by Morse in 1974 (though often attributed to Nancollas) it is a means to measure the precipitation and dissolution rates of species of low solubility such as calcite (Morse 1974). By maintaining a constant concentration of reactants and pH, it is possible to study these mechanisms over a longer time frame than if these parameters were allowed to drift. Further, by holding a solution at the same degree of saturation over a long period of time, it is possible to better control the precipitation reaction and thus the composition and structure of the final product. Studies sought to maintain the same ratio of Ca/P in the solution as was desired in the product (Amjad 1977, Hohl 1982, de Rooij 1984, Heughebaert 1984, Jahnke 1984, Nelson 1986, Campbell 1991, Tang 2003, Chow 2005, Pan 2013). The constant composition method will not be strictly employed during this thesis, however the theory will be applied when testing the reactor.

The majority of reviewed papers analyzed the crystallization of various apatites under physiological conditions (pH = 7.4, T=37°C) (Amjad 1981, Campbell 1991, de Rooij 1984, Hohl 1982, Ishikawa 1994, Kotsoukkos 1981, Moreno 1981, Nelson 1986, van Kemenade 1987). This project does not employ physiological conditions, as there is not the same strict requirement to

maintain the same temperature and pH throughout all stages of wastewater treatment. However, the findings are still of interest in designing the process used in this project. Virtually all of the studies prepared P_i solutions with KH_2PO_4, at concentrations ranging from 0.05 mM PO_4/L to 25 mM PO_4/L (Nancollas 1974, Freeman 1981, van Kemenade 1987, Song 2002, Molle 2005, Bellier 2006, Chen 2009, Mekmene 2009, Habraken 2013). These studies were focused on precipitating HAP without the added complication of other chemical substitutions into the lattice; as the K^+ ion has a larger radius than Ca^{2+} it is likely that any amount of K^+ in the final solid would be negligible (Perrone 2002). There were two instances of NaH_2PO_4 used to prepare the Pi solution (Neuman 1967, Minh 2012). No examples were found of the P_i source coming from Na_2HPO_4, which is what was used throughout this experiment. Na_2HPO_4 was used (in accordance with the lab protocols) for two reasons. First, a potassium ion is generally used when experimenters want to avoid undesired cationic substitutions, as it has a larger ionic radius than sodium ions; the desired apatite product in this experiment typically has many substitutions, and so it was preferable to use a sodium cation over a potassium cation. Second, the HPO_4^{2-} anion was preferable to $H_2PO_4^-$ due to its speciation in the range of experimental pH.

The most common source of Ca^{2+} was $CaCl_2$ (Amjad 1981, Kotsoukkos 1981, Campbell 1991, Song 2002, Song 2006, Chen 2009, Mekmene 2009, Sandin 2009, Zou 2016), followed by $Ca(NO_3)_2$ (de Rooij 1984, van Kemenade 1987, Ishikawa 1994, Regnier 1994, Perrone 2002). Several studies examined calcite's potential as a surface for either precipitating or adsorbing Pi from wastewater (Freeman 1981, Song 2006, Tervahauta 2014, Xu 2014.) Other studies investigated the effectiveness of apatite for this same purpose, specifically within constructed wetlands (Molle 2005, Bellier 2006). Only three instances of $CaCO_3$ being used as the primary calcium source in the precipitation of apatite were found (Clark 1954, Verwilghen 2009, Minh 2014). Clark's study was most pertinent in demonstrating that even at low exposure to CO_2, $CaCO_3$ in soil became more soluble and was likely to react with P_i within the soil. Minh compared the effectiveness of various forms of P_i salts as well as phosphoric acid when reacting with $CaCO_3$ dissolved in acid. His conclusion, that phosphoric acid was most effective for precipitating HAP, is not helpful in identifying a renewable means to make the raw material to produce phosphoric acid. Verwilghen's paper made the bold claim that $CaCO_3$ could be "conveniently" converted into HAP. None of these three studies represent a competing method.

3.3.3 K_{sp} and apatite, and the Ca x P approximation for K_{sp}

Several studies have confirmed that calcium phosphate apatites dissolve incongruently (Jahnke 1984, Perrone 2002, Tang 2003), making it difficult to agree upon a K_{sp} value. As such, another approximation is sometimes used. Originally proposed by Fleisch in 1961, the following relationship has been found to be valuable when quantifying the system of calcium and phosphate ions:

$$K_{sp} = [Ca^{2+}] \times [P_i] \qquad [3.9]$$

This definition is shortened to "Ca x P" throughout this paper. It is theorized that this relationship is valid because blood is slightly supersaturated with respect to bone mineral (a calcium-deficient carbonate apatite, $Ca_{8.1}Mg_{0.2}(PO_4)_{4.3}(HPO_4)_{0.5}(CO_3)_{1.2}(OH)_{0.3}$ (Combes 2016)), because the ions that provide the building blocks for bone are transported through the body in the blood (Dean 2015). The Ca x P approximation is used throughout this thesis because of the similarities between bone mineral and the target material of carbonate apatite, in addition to the lack of a true K_{sp} for these salts.

3.4 Wastewater Treatment

3.4.1 Activated sludge treatment (aerobic digestion)

One of the great sanitary innovations of the last century was the development of the activated sludge treatment of wastewater by Ardern and Lockett in 1914. This same theory provides the basic procedure still used today by the majority of cities in developed countries to treat municipal sewage (Oleszkiewicz 2015). The process is summarized below in Figure 3.13, with the three characteristic steps being:

1. aeration to enable aerobic digestion by bacteria;
2. sedimentation and settling of biological solids (aka 'activated' sludge); and
3. recycling solids back into aeration tank to maintain sufficient population of bacteria.

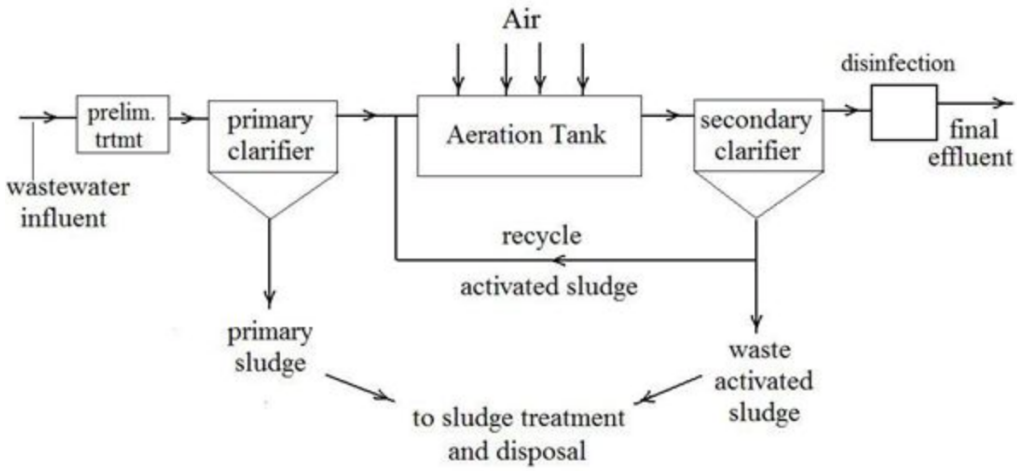


Figure 3.13: Activated sludge wastewater treatment flow diagram (Bengston)

Additional steps to target specific pathogens and chemical species are included in treatment plants of most large municipalities in developed countries. Most important to this thesis is an additional step to chemically precipitate Pi out of the effluent, by adding either iron or alum salts, which is subsequently settled and removed (Oleszkiewicz 2015).

3.4.2 Biological nutrient recovery (BNR) (anaerobic digestion)

In the 1970s, an improvement to the activated sludge treatment was developed by Dr. J. Barnard. This process saw the sludge cycled between anaerobic, anoxic, and aerobic conditions, which improved the uptake of nutrients by the bacteria within the reactor. There are several variations of this process to account for local conditions, such as seasonal temperature cycles, but the basic method is illustrated in Figure 3.14.

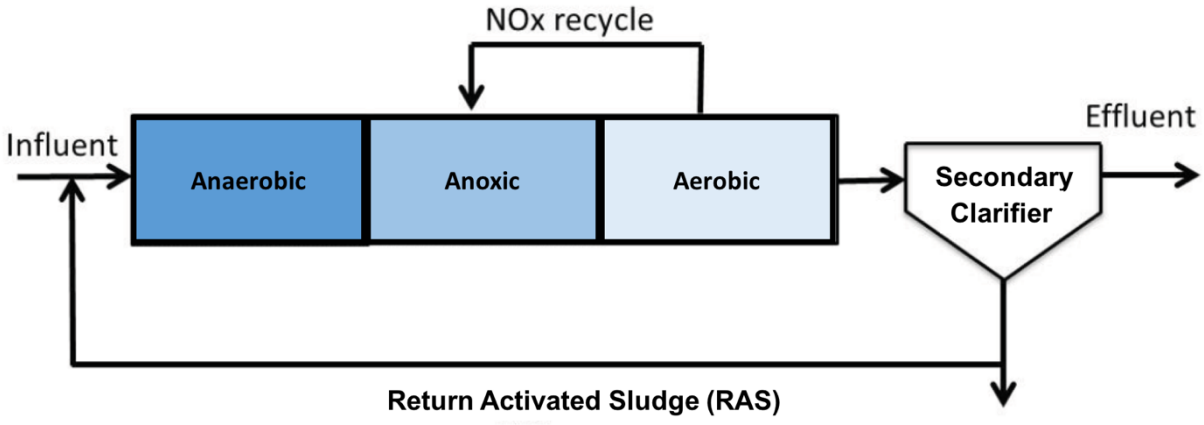


Figure 3.14: BNR wastewater treatment flow diagram (Oleszkiewicz 2015)

This technology has been adopted in several municipalities in Western Canada and throughout North America, however throughout Ontario and Eastern Canada the use of this method is the exception rather than the rule. Globally, approximately 1400 WWTPs employ the BNR method (Mavinic 2017). There are means to adapt an existing activated sludge plant to a BNR plant (as pictured in Figure 3.15). However, it may make the most fiscal sense to incorporate such a technology only when a plant is due for a life cycle upgrade. Considering that this method is a relatively recent innovation compared to the life cycle of municipal infrastructure, it is perhaps not surprising that it is not yet used at all WWTPs.

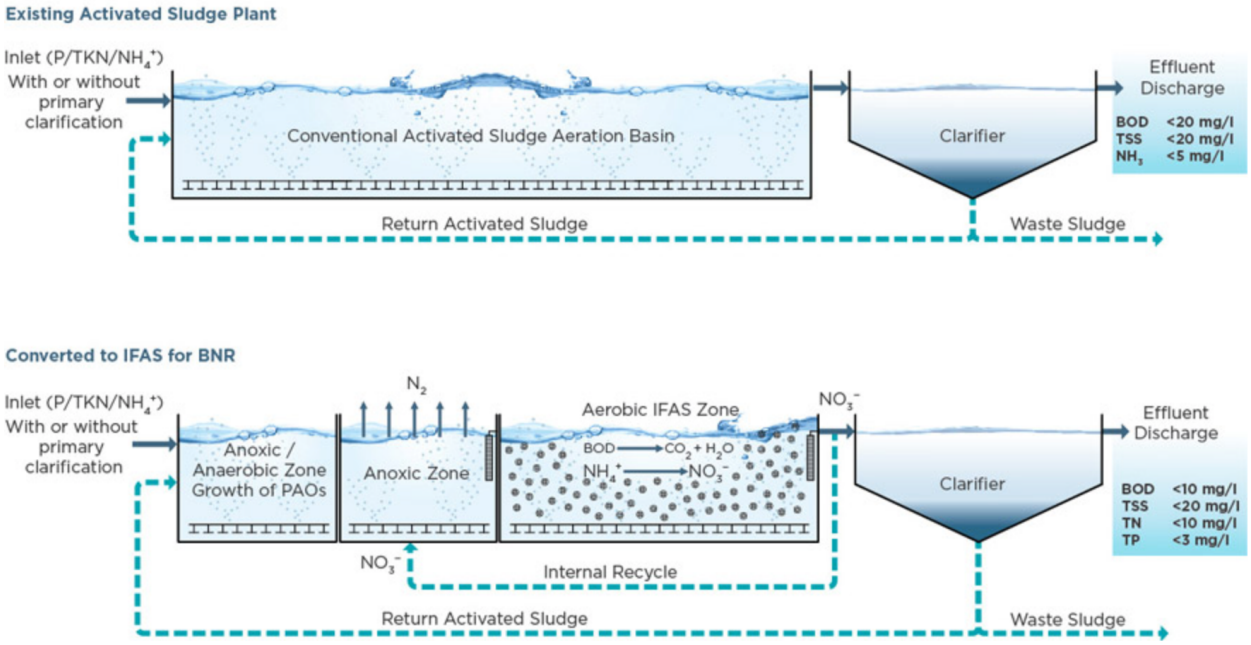


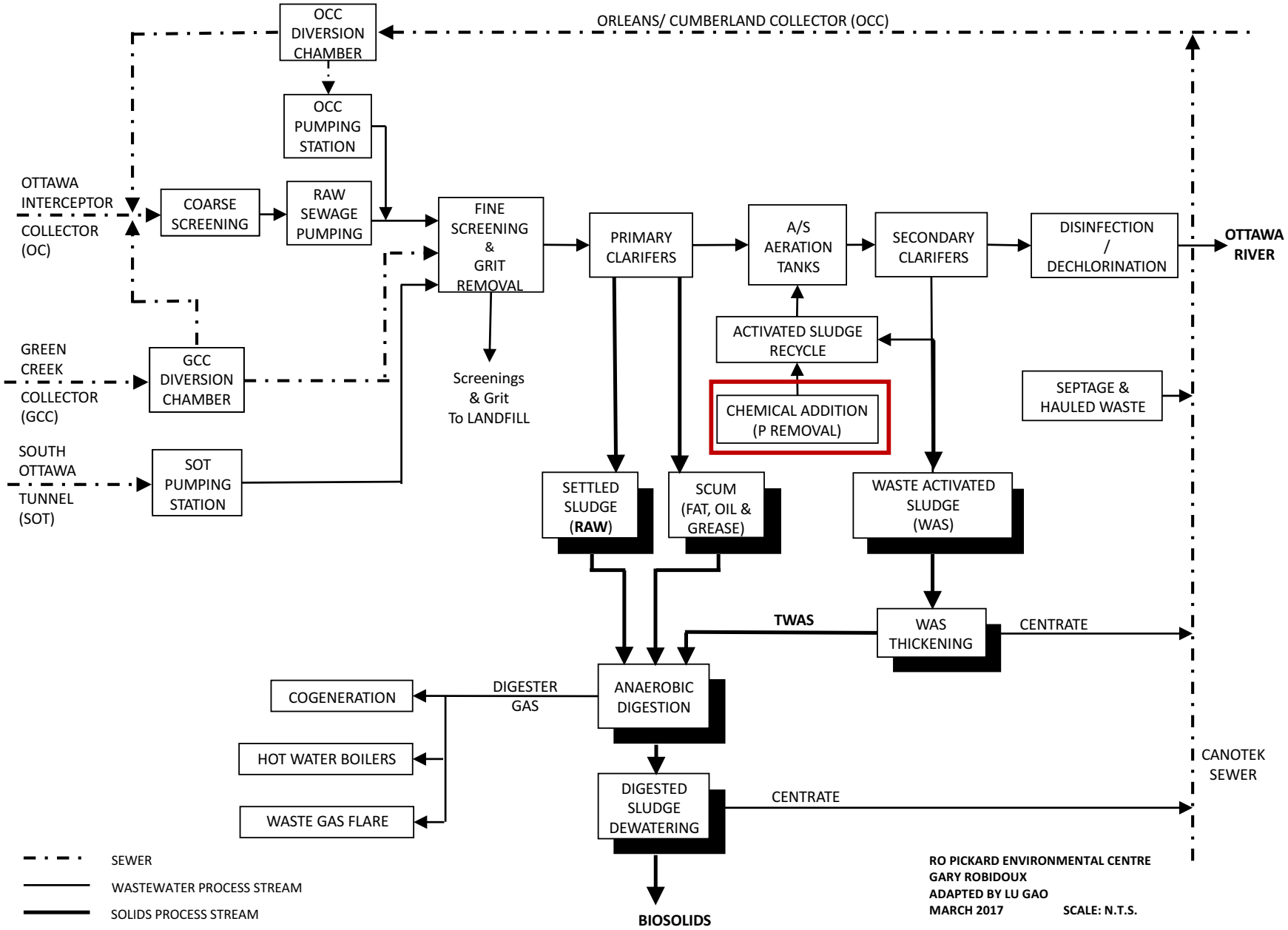
Figure 3.15: Example of activated sludge system converted to BNR (Headworks International)

3.4.3 R.O. Pickard Environmental Centre (ROPEC) – PFD and P_i Concentrations

The ROPEC is Ottawa's WWTP, collecting municipal wastewater from the greater Ottawa region for treatment before it is returned to the Ottawa River. It cleans a daily average of 390 million litres of wastewater, and produces approximately 39 dry tonnes of biosolid (ROPEC 2013). A process flow diagram of ROPEC can be found on the next page in Figure 3.16 (Robidoux 2017).

The TP standard that ROPEC must meet is 1 mg/L (0.03 mmol / L) effluent, in accordance with provincial regulations and Environmental Compliance Approvals (ECA). According to the 2015 Annual Summary Report, ROPEC was well within this limit, with an average 0.65 mg/L (0.02 mmol / L). In order to achieve this level, 1200 kg of $FeCl_3$ are added

daily to induce chemical precipitation of iron phosphate (ROPEC tour 2017). In 2015 a total of 47,012 wet tonnes of biosolids were produced, 100% of which were applied to land under the beneficial reuse program. These biosolids met provincial reuse regulations for pathogen and metal content. While this is an important step toward closing the nutrient cycle, it is important to note that only one fifth of the phosphorus present in Ottawa's biosolids is in soluble P_i form, or an average of 6,674 mg P_i /kg dry solids, compared with 31,588 mg TP/kg dry solids. The majority of the TP is likely present in a form of iron phosphate, however the iron content of the biosolids is not published, so the iron salt hypothesis cannot be confirmed.


OCC DIVERSION CHAMBER
ORLEANS/ CUMBERLAND COLLECTOR (OCC)
OCC PUMPING STATION
OTTAWA INTERCEPTOR COLLECTOR (OC)
COARSE SCREENING
RAW SEWAGE PUMPING
FINE SCREENING & GRIT REMOVAL
PRIMARY CLARIFERS
A/S AERATION TANKS
SECONDARY CLARIFERS
DISINFECTION / DECHLORINATION
OTTAWA RIVER
GREEN CREEK COLLECTOR (GCC)
GCC DIVERSION CHAMBER
Screenings & Grit To LANDFILL
ACTIVATED SLUDGE RECYCLE
CHEMICAL ADDITION (P REMOVAL)
SEPTAGE & HAULED WASTE
SOUTH OTTAWA TUNNEL (SOT)
SOT PUMPING STATION
SETTLED SLUDGE (RAW)
SCUM (FAT, OIL & GREASE)
WASTE ACTIVATED SLUDGE (WAS)
TWAS
WAS THICKENING
CENTRATE
COGENERATION
DIGESTER GAS
ANAEROBIC DIGESTION
HOT WATER BOILERS
CANOTEK SEWER
DIGESTED SLUDGE DEWATERING
CENTRATE
WASTE GAS FLARE
SEWER
WASTEWATER PROCESS STREAM
SOLIDS PROCESS STREAM
BIOSOLIDS
RO PICKARD ENVIRONMENTAL CENTRE
GARY ROBIDOUX
ADAPTED BY LU GAO
MARCH 2017
SCALE: N.T.S.

3.5 Current Phosphorus Recycling Technologies

3.5.1 Potential for P recycling

The flow of P_i through WWTPs is generally well understood. This makes it possible to estimate where P_i might be recovered throughout the process, and how much of the initial load to the WWTP could be captured (Oleszkiewicz 2015). The values reflected in Figure 3.17 are not cumulative as they refer to the potential recovery of P_i *remaining in the stream*; not all of the possible technologies will necessarily be applied, and processes downstream will only be able to recover the indicated percentage of the P_i that is present (vice originally entering system).

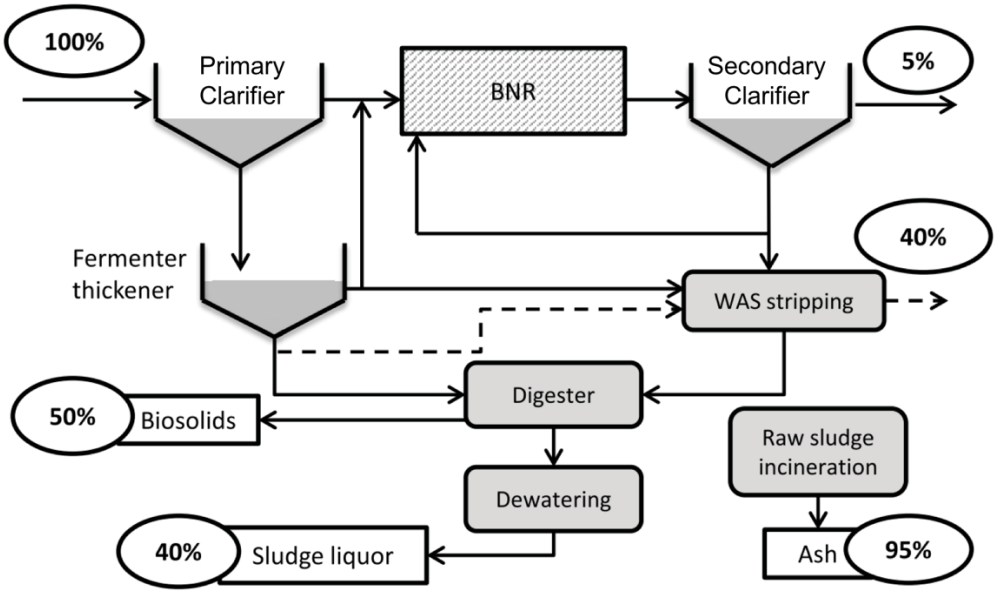


Figure 3.17: Maximum potential recovery of P_i from waste stream throughout typical WWTP (Oleszkiewicz 2015)

There are several technologies that exist to recover the P_i throughout the treatment process, and they are designed specifically to recycle phosphorus from either the biosolids/sludge, the sludge liquor, or the ash (Figure 3.18). The most successful and widely implemented methods to date typically precipitate a magnesium ammonium phosphate (MAP) commonly called struvite, $MgNH_4PO_4$, from the sludge liquor. This method is popular because it resolves the common problem of undesired buildup struvite scale within the reactor, and instead creating a product that has a market value.

If ROPEC is assumed to be an average WWTP, there are a few ways that an additional process could be incorporated in such a way that phosphorus could be recycled. First, the novel treatment could be introduced in place of the addition of $FeCl_3$; this would lead to the primary removal of phosphorus being in a form that would lend itself to reuse as a fertilizer material. Depending on the effectiveness of this treatment in practice, it would still be possible to polish the effluent with a later (and likely smaller) addition of $FeCl_3$ to ensure regulatory compliance. Conversely, it may also be effective to add a step after the initial chemical precipitation addition; this method would depend on optimization the cost of the reactants and the yield of marketable product, and would consider the decreased cost and risk associated with changing a known process.

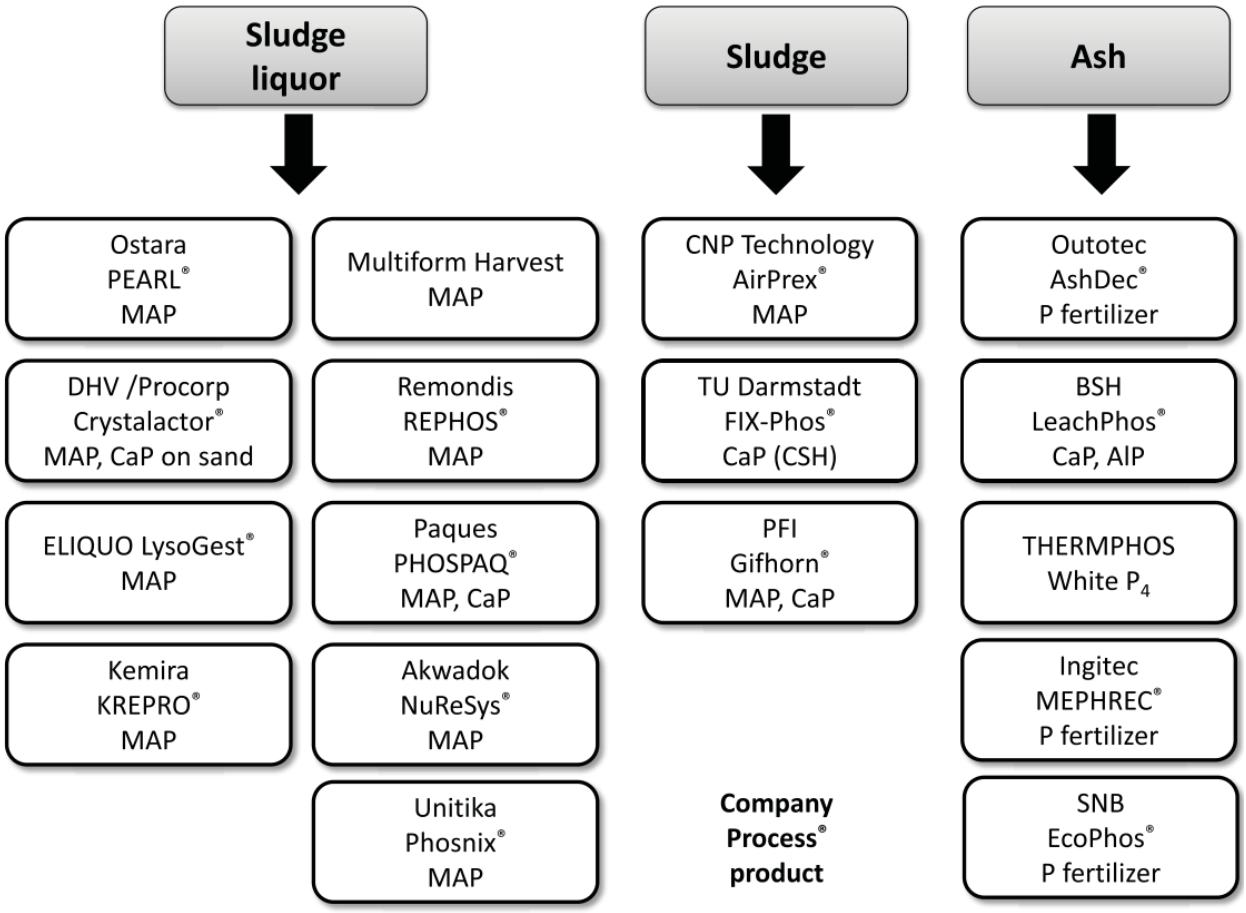


Figure 3.18: Pi recovery techniques in operation, and resulting product (Oleszkiewicz 2015)

3.5.2 Struvite precipitation

One of the most successful methods of precipitating struvite was developed at UBC by Dr. Don Mavinic and his team has grown into a global company over the last 10 years. Ostara's PEARL process can recover 80% of the phosphorus, and 20% of the nitrogen from wastewater, and this product is sold as a slow-release fertilizer (Mavinic 2017).

The process is illustrated in Figure 3.19 below, and it should be noted that it requires an anaerobic digestion step (i.e. BNR process) for it to be effective. It also requires the addition of reactants $MgCl_2$ and NaOH. For these reasons, while this method is very effective, it is not compatible with all WWTPs, either because of the treatment method used, or because of the cost and availability of the additional reactants required to control the precipitation of high quality struvite.

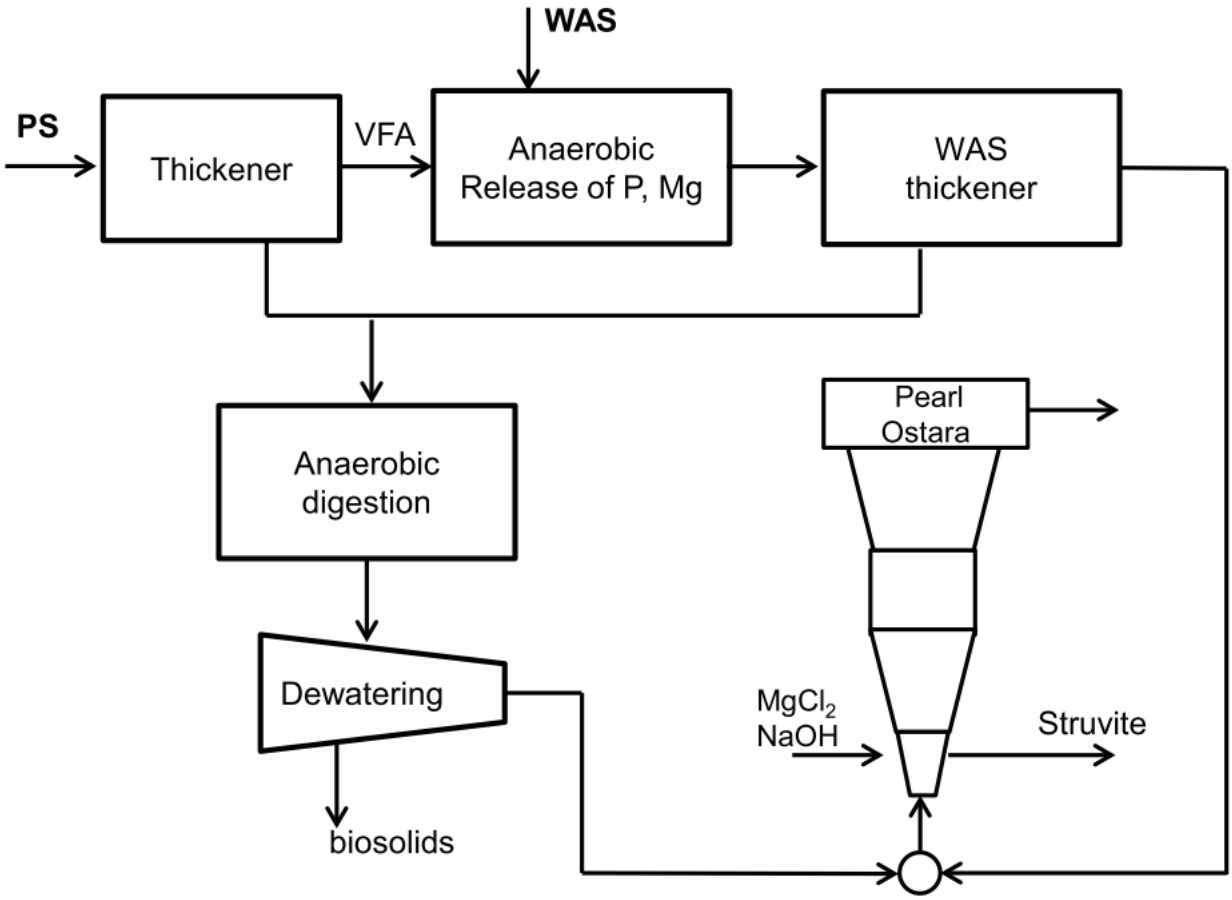


Figure 3.19: Struvite precipitation using the Ostara PEARL* process (Oleszkiewicz 2015)

3.6 Conclusion

The aqueous chemistry of the calcium-carbonate-phosphate system is complex, as the way that these ions interact changes with the conditions in which they meet. As such, this review of the pertinent theory, related studies of apatite precipitation and dissolution, and summary of applications to wastewater treatment served to inform the parameters selected for the experimental technique. The review confirmed that the method and results outlined in the next two chapters have not previously been attempted, however a prediction of how effective the method might be was not possible.

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CHAPTER 4

MATERIALS & METHODS

4.1 Materials

In this study, ACS-grade $CaCO_3$ (as calcite, confirmed by Raman spectroscopy), and limestone screenings were the dissolved calcium ion sources. Phosphate solutions were produced by dissolving ACS-grade sodium phosphate dibasic (Na_2HPO_4) in solution.

4.1.1 Preparation of reagent solutions - phosphorus

Phosphorus solutions used throughout all experiments were prepared by dissolving sodium phosphate dibasic, Na_2HPO_4 (Sigma Batch # 108K0187) in distilled and deionized water (ddH_2O). The concentrations used ranged from 2.5 mM P_i to 30 mM P_i. All masses were weighed using the Mettler AE 200 balance in the CBY D-315 lab. At concentrations above 20 mM P_i, low heat (40-50°C) and a stir bar were required to encourage complete dissolution of the salt. These concentrations were selected as they approximate those found in the ROPEC streams that were measured by the lab group (Meouch 2016).

4.1.2 Preparation of reagent solutions – calcium carbonate

$CaCO_3$ is an ideal source for the reaction because it contains both the calcium and carbonate that are desired in the final product. It is also inexpensive and widely available as limestone. Unfortunately, it is very insoluble; previous attempts to use solid $CaCO_3$ to form a carbonate apatite product were not successful (Minh 2012). Therefore, it should not be a surprise that the preparation of the calcium solution initially proved difficult. In fact, early attempts at dissolving ACS-grade $CaCO_3$(s) in ddH_2O found that the resulting [Ca^{2+}] was lower than the natural Ca^{2+} content in Ottawa tap water, likely due to its carbonate content (City of Ottawa 2013); subsequently, all Ca^{2+} solutions were prepared using tap water. Tap water is also relevant because it could also be the water source should this process be scaled up. The attempt was further complicated by the solution's affinity for interacting with CO_2 in air, which meant that the [Ca^{2+}] varied daily as the solution was exposed to atmosphere. For these reasons, the initial attempt to meet Objective 1 failed. This finding therefore precipitated the need to explore

methods to increase the solubility of $CaCO_3$, which became the basis for Objective 2. As such, the preparation of these solutions is discussed in greater depth in Section 4.2. The successful method used is summarized here.

Carbon dioxide gas generates carbonic acid, which increases the solubility of calcium carbonate. The ability of a CO_2(g) stream, which is available at municipal wastewater plants, to increase the dissolved calcium and bicarbonate concentrations was tested. The same reactants were used in the preparation of each of the calcium solutions; $CaCO_3$ (ACS, MP Lot No. 6319K) for the synthetic solutions, and limestone screenings for the limestone solution. The initial dissolved calcium source in water was always City of Ottawa tap water from the CBY D-315 faucet. At least 1.0 g $CaCO_3$/ L was used to ensure that the solutions remained saturated even after CO_2 treatment. To prepare the synthetic Ca-CO_3 solution, approximately 1.0 g solid $CaCO_3$ was added to tap water in a 1.0 L Applikon bioreactor (0.9 L working volume) with a motor-driven agitator, and then treated with 100 % CO_2 (g) (Linde UN1013 compressed carbon dioxide). During the contact-time, solution pH was noted, and aliquots were taken for calcium concentration measurement to determine the time for the CO_2-Ca-CO_3 system to attain equilibrium, and the equilibrium calcium and carbonate concentrations.

To prepare the larger volumes of Ca-CO_3 solutions for the CSTR experiments, limestone was the $CaCO_3$(s) source. "King Brand" limestone screenings (Home Depot, Ottawa) were dried in a vacuum oven at 40-60°C and 1-5 mm Hg. Then they were sieved in an 8" nest (710 μm – 4.75 mm) and shaken for 10 minutes in an RX-29 RO-TAP. The fine filter screenings (<710 μm) were mixed with tap water in a 20 L container of tap water with an aquarium bubbler for contact with CO_2. This larger-scale limestone Ca-CO_3 solution was produced for the CSTR experiments. Gravity-settling was found to be sufficient to decant a solids-free, Ca-CO_3 solution for the CSTR experiment.

Both synthetic and limestone solutions were treated with CO_2(g) to increase the solubility of $CaCO_3$ and thus maximize the [Ca^{2+}] in solution. An AR10 pH probe was used to measure pH (see Annex B – Appendix 2) during dissolution and CO_2 treatment, and this same pH probe was used throughout all experiments. For the synthetic solutions, the CO_2(g) was delivered through the Applikon gas inlet pipe in the lid of the bioreactor, while the solution was stirred with an electric motor. 100% CO_2 gas flowrate was 0.1-0.2 L/min (measured by an Omega CO_2 gas flowmeter, model PMR1-013577) for approximately 20 minutes, or until the pH dropped to 6.5

or less. The change in $CaCO_3$ solution pH and calcium ion concentration as a function of water type (deionized and distilled water or tap water) and simulated CO_2 flue gas partial pressure (7 % for natural gas-fired power plants, 15 % for gas-fired power plants, and 100 % CO_2) was the subject of an undergraduate thesis completed by O. Meouch (Meouch 2016). Through this work it was understood that 20 minutes was required for the gas/liquid/solid phases to reach equilibrium, and the equilibrium pH was approximately 6.5. The solution was then transferred to 1.0 L glass bottle, filled to the very top to prevent CO_2 off-gassing, and sealed tightly both with a lid and Parafilm™. This bottle was left to sit overnight to allow the fine $CaCO_3$ particles to settle before use. For the larger-scale CSTR reactor tests, the limestone solution was treated using an aquarium-style CO_2 bubbler, at a flow rate of 100% CO_2 0.6 L/min for at least one hour, within a 20 L container. Further details are described below for the different experiments.

4.1.3 Seed Preparation

Seed was used to encourage crystallization especially at low supersaturation, however unseeded experiments were also conducted to determine the effect (if any) of the seed, and to allow for characterization of seed-free, spontaneous precipitate. When a seed was used, it was one of two types: defatted and deproteinized bone powder, or precipitate from a non-seeded batch experiment.

Two types of bone were used. The method used to make the bone seed was adapted from the procedure which had been used to prepare bone for carbonate measurement in the coulometer. Preliminary experiments were undertaken with previously prepared, defatted and deproteinized emu bone powder. Bovine bone was used for the majority of successful seeded tests. Bovine bone seed was prepared by cutting the bone into 1-2” pieces to increase surface area. Bone pieces were first defatted with a solvent extraction technique that used multiple exchanges of a choloform:methanol solution, followed by a methanol wash. To remove the organic components, defatted bone pieces were immersed in multiple exchanges of commercial bleach to break down and remove the collagen (mostly type I) and non-collagenous proteins. The bleaching process was undertaken for a minimum of two weeks, covered, and in the fume hood. Additional bleach was exchanged as needed to ensure bones remained immersed. Once bones were bleached, they became white due to removal of protein. Bone pieces were then dried, and crushed into fine powder. The powder was sieved using a 3” diameter nest (63 μm-300 μm) to

separate particles that were smaller than 63 μm; these were reserved for use in experiments. Emu bone seed was prepared in the same way. However emu bone was only used during preliminary batch tests because there was not enough emu bone to use for the second stage of batch experiments; emu bone results are not presented.

Two methods were used to prepare synthetic seed. The initial slurry seed was collected by mixing a 1000 mL of 20 mM Pi with an equal volume of treated $CaCO_3$ solution. The solution was left to sit for 24 hours, after which the supernatant was decanted and the remaining slurry was collected. This slurry was added directly to the reaction vessel without drying, and upon completion of the reaction was collected in the same way as the initial slurry seed. Solid seed was prepared in much the same way, but with the added step of filtering and drying the precipitate. A glass filter (Fisherbrand, G4 5.5 cm), composed of SiO_2, Na_2O and CaO (personal communication with Fisherbrand product technicians), was placed on the vacuum funnel. The product slurry was poured over the filter, and the reaction beaker was rinsed with ddH_2O to collect as much solid as possible. Early tests rinsed with excess supernatant instead of ddH_2O, until it was learned that this may lead to the precipitation of products from the solution due to drying as opposed to in the reaction vessel. That is to say, rinsing with ddH_2O served to reduce the likelihood that $CaCO_3$ would precipitate on the product as it dried, by rinsing away saturated supernatant from the surface of the solids. The filter and product were then placed on a watch glass and dried overnight in a vacuum oven at 40°C and 5 mm Hg. The filter cake was carefully removed using a plastic scraper and transferred to a glass vial until needed.

4.2 Methods

4.2.1 Preliminary batch and semi-batch tests

Preliminary tests attempted two methods to identify the carbonate apatite supersaturation zone by working with synthetic Ca-CO_3 and P_i sources. The Ca^{2+} source was a saturated solution of $CaCO_3$ in tap water, with no CO_2(g) addition, and the P_i source had a concentration of 27 mM P_i. The [P_i] was selected based on the average value found in the literature for wastewater treatment (Phillips 2006). In both cases, the reaction vessel was seeded with 1.0 g emu bone/L.

The first method was a semi-batch test in which 1 mL of Ca^{2+} solution was added to 50 mL of P_i solution, and mixed with a magnetic stir-bar for three minutes. The solution was then

allowed to settle for two minutes before a 1.0 mL aliquot was collected. The stir bar was turned on again, and another 1 mL of Ca^{2+} solution was added, and the process repeated, such that a total volume of 50 mL was maintained.

The second method was a simple batch test, in which 50 mL of Ca^{2+} solution was added to 50 mL of the P_i solution while it was mixed with a stir-bar. This was conducted concurrently to the semi-batch test of the same initial concentrations. This test sought to both observe if spontaneous carbonate apatite precipitation was observed, and to account for the loss of any product when taking the 1.0 mL aliquots during the semi-batch test. The results of this test will be summarized in this section because they were the motivation to generate a second method.

In both cases, the expected dilution was observed; no further decrease in the concentration of either Ca^{2+} or P_i was oberved outside of experimental error. There are two reasons contributing to this failure to obtain a carbonate apatite supersaturated state to produce solids by homogeneous nucleation or as grown on seed. First, there was not a high enough Ca^{2+} concentration in solution to significantly affect the [P_i], and the small decrease observed was less than the experimental error. Second, the volumes were too small to detect changes in seed mass, compared to error associated with such measurements. Scaling this method up to larger volumes may have made it possible to detect changes in [Pi] and seed and precipitate mass with confidence. However, it was clear that even if the changes could be quantified, they were too small to be of any significant value. For these reasons, a new approach for exploring the carbonate apatite supersaturation with a solution with a higher calcium concentration was created.

4.2.2 Calcium concentration increase with a carbon capture technique

The goal of this work was to add dissolved $CO_{2(g)}$ to a solution of $CaCO_{3(s)}$ in equilibrium with tap water. This would have the effect of decreasing the pH by formation of carbonic acid, which in turn would shift the carbonate equilibria in solution to favour HCO_3^- speciation. Consequently, this shift in equilibrium would increase the dissolution of $CaCO_3$ (s). This effect is illustrated in Figure 4.1.

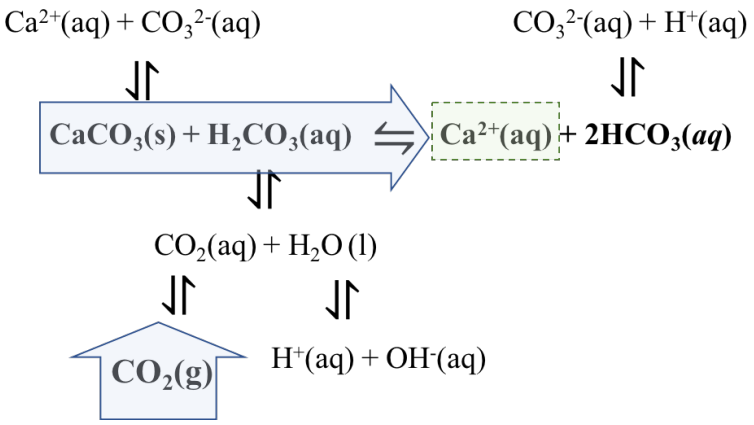

Figure 4.1: $CaCO_3$ – H_2CO_3 equilibrium system.

In order to maximize the calcium concentration in the Ca-CO_3 solution with this approach, approximately 1.0 g of synthetic $CaCO_3$ was dissolved in tap water in a 1.0 L reactor. A flow rate of 0.1-0.4 L/min of 100% CO_2 was used, as this rate was sufficient to reduce the pH without allowing excessive CO_2 to bubble straight through the solution without reacting with it. After approximately 20 minutes the solution reached the expected and steady pH of 6.2-6.5 (Meouch 2016). This increased the initial [Ca^{2+}] to the expected 4-6 mM (Meouch 2016). However, the concentration decreased with additional contact to atmosphere as the equilibrium of the (HCO_3^- ←→ CO_2) system in the solution shifted due to the lower atmospheric CO_2(g) concentration, and $CaCO_3$ precipitated back out of solution. As such, a fresh solution was prepared for each experiment; the vessel was filled to the top and the lid was secured with Parafilm™ to prevent interaction with atmosphere until the undissolved $CaCO_3$ had settled. Care was taken when transferring the $CaCO_3$ solution for each experiment; if the solid that had settled at the bottom of the flask was disturbed while decanting, it was set aside to re-treat and settle again to prevent solid $CaCO_3$ from entering the reactor.

Once the method to prepare the calcium solution was established, another calcium source was tested for the CSTR reactor experiments; natural limestone screenings. Limestone is composed primarily of $CaCO_3$ in the form of calcite as used in the initial experiments. It was selected because it is abundant in Canada, and thus relatively inexpensive. The limestone was dried in a vacuum oven at 40-60°C and 1-5 mmHg, then sieved to 710 µm to maximize its contact area and poured into a 20L container of tap water. An aquarium-style CO_2 bubbler was placed in the container, and was treated with 100% CO_2 at 0.6 L / min for approximately 1 hour.

This flow rate was selected because it is slightly in excess of what the solution could absorb at a time, as indicated by the minimal bubbling at the surface of the solution. Initial testing by the lab group found a maximum [Ca^{2+}] between 4-5 mM when preparing a limestone solution treated in this manner. Unlike the synthetic solution, the solid limestone settled very quickly. Because of this, and because the size of the container made it impractical to pour from, the solution was decanted from the top using a small beaker when needed for experiments. The same solution was used repeatedly, and was re-treated before each subsequent use by adding fresh limestone and tap water, and bubbling again with CO_2 as described to maintain a high [Ca^{2+}].

4.2.3 Batch Test Procedures

4.2.3.1 Unseeded tests. Each of the different concentrations of P_i solution was mixed with an equal volume of the Ca^{2+} solution. A sample was taken of each of the initial solutions immediately prior to mixing, and a sample was taken daily over a period of 5 days. A duration of 5 days was selected for two reasons. First, it was estimated that all ACP formed in solution would recrystallize to OCP and subsequently HAP within 48 hours (Kazanci 2006, Niu 2017), so a longer time was selected to ensure this reaction had time for completion; this would enable a comparison of the equilibrium concentrations of Ca^{2+} and P_i upon completion of the reactions. Second, the logistical scheduling of initial preparation and follow-up characterization permitted no more than one set each of a seeded and non-seeded batch each week.

The initial pH was recorded, and was noted again as each sample was taken. The pH was not controlled during these series of experiments, but was allowed to drift.

After five days, the solution was vacuum filtered to collect the solid precipitate. The liquid samples collected over the course of the experiment were analyzed at this time to measure the change in [Ca^{2+}] and [P_i]. This procedure is explained in detail in Annex B – Appendix 1.

Observations regarding whether or not precipitate was immediately visible and if scale formed on the reactor walls were noted, as this could indicate whether the reaction conditions were in either the metastable zone or at critical supersaturation.

4.2.3.2 Seeded tests. The procedure for seeded batch tests added an additional parameter to the unseeded tests. Bovine bone seed was added at either 2 g /L, 0.5 g /L, or precipitate seed

was added at 1 g /L. Based on the literature review, 0.5 – 2 g /L represented a typical range of seed densities; these were selected for the initial tests using bovine bone. After the first phase of experiments was completed, sufficient precipitate had been observed to form spontaneously and had been characterized to warrant an additional experimental phase to assess its suitability as seed material. Due to the marginal difference observed between the two seeding densities when using bone seed, a density of 1 g/L was selected for the precipitate-seeded test. The bovine bone seed was added to solutions of either 5 mM P_i or 30 mM P_i, in order to understand the effect at a relatively high and low [Pi]. The other type of seed tested was precipitate that spontaneously (homogeneously) nucleated from mixtures of Ca^{2+} and Pi solutions. This spontaneous precipitate seed was tested with concentrations of either 5 mM P_i or 7 mM P_i. The tests with spontaneous precipitate as seed were conducted after the initial tests were started. The two [P_i] selected were based on the initial performance of the seeded and unseeded batches, as well as additional information regarding the availability of P_i within the waste stream at Ottawa's WWTP (Annex C: Raw Data).

The results from the seeded tests are discussed closely in parallel with the unseeded results in Chapter 5. The structure of the results is introduced below in Section 4.2.3.3.

4.2.3.3 Organization of batch test results. The success of the batch tests will be primarily discussed in terms of the changes in [Ca^{2+}], [P_i], and pH. A great deal of information can be gleaned from these three variables, and they will be summarized in table form and shown graphically. The initial and final Ca x P values of each configuration will also be presented. This will enable an estimate of the metastable zone and the critically supersaturated region. The Ca x P values also serve as an estimate of the K_{sp} of the system. The relationship between Ca x P and pH will also be presented graphically.

The effect of the initial experimental conditions on the relative percent of P_i removed from solution will be discussed. This value will be used to estimate yield, as well the potential effectiveness of this method of wastewater treatment. Finally, the theoretical molar ratio of Ca/P in the precipitates will be calculated.

Changes in [Ca^{2+}], [P_i], and pH were monitored throughout all experiments. However, the other key reagent, CO_3^{2-}, was not followed as the reaction proceeded, despite its importance. This is because of the difficulty in measuring carbonate, and dissolved carbonate in particular. In

future work, this will be attempted. The amount of carbonate in some of the final products was measured, but this was not a parameter that was specifically controlled during the experiment. The precipitate will be characterized in a separate section.

The optimal molar ratio of $[Ca^{2+}]$ to $[P_i]$, referred to as Ca/P, and seeding parameters served to determine the initial operating range of the reactor.

4.2.4 Reactor

Based on the results from Section 4.2.3, the molar ratio of Ca/P required to operate within the metastable heterogeneous supersaturation zone was identified. The intent was to start with P_i-rich solution, add seed, and then initiate the flow of Ca^{2+} solution into the reactor and the product flow out of the reactor until within the theoretical operating Ca x P concentration. At that point, the flow of the Pi stream would be added.

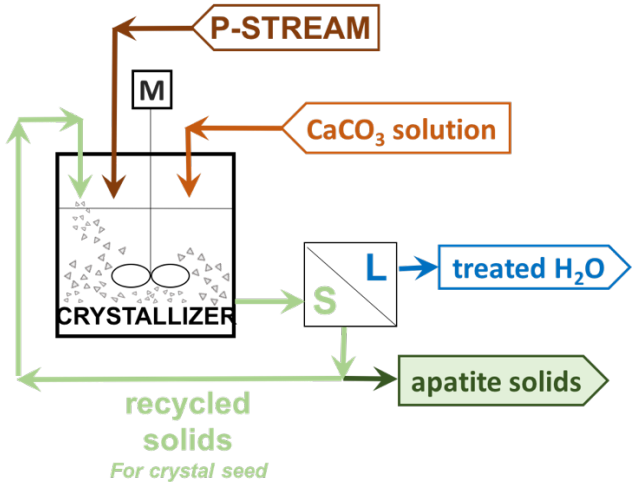

Figure 4.2: Diagram of the CSTR apatite precipitation reactor

This was achieved by first creating spontaneous seed by mixing 1000 mL of 20 mM Pi with 1000 mL of saturated Ca^{2+} solution in a 1800 mL Erlenmeyer flask. The solution was allowed to sit for a minimum of 24 hrs before collecting the seed slurry. This process created a significant amount of seed as observed by eye, which was then used for the initial reactor run. This seed was not filtered and dried, rather it was added to the reactor as a slurry. Because the supernatant was P_i rich solution that was already saturated with respect to the desired product, it was added to the reactor to form the reactor initiation state.

Ca^{2+} and P_i were metered into the system such that the mole ratio of Ca^{2+} to P_i flowing into the system was greater 1. With an influent [Ca^{2+}] of 5 mM, and influent [Pi] of 7 mM, the respective inlet flow rates were either 18 mL/min and 12 mL min, or 9 mL/min and 6 mL/min. A separate peristaltic pump was used for each stream. This had the effect of gradually increasing the saturation state with respect to Ca x P as a proxy for apatite.

A third peristaltic pump drew the product slurry from the bottom of the reactor at a rate of either 30 mL/min or 15 mL/min. This yielded residence times of 30 min and 60 min respectively. The slurry collected in an 1800 mL Erlenmeyer flask with a vacuum side arm. This provided sufficient volume in which the product could settle, and the side arm served as a weir for supernatant overflow into another flask. This initial effort was focused on testing the equipment that should be used in future projects within the lab group, as well as a preliminary indication of whether the results observed in a bench-scale batch test would correspond to those found in a basic CSTR. This means that greater attention was paid to ensuring that the inlet and outlet pumps were 'balanced' in order to maintain a constant volume within the reactor, as opposed to aiming for a strict residence time. Optimization of the crystallization reactor residence time is a topic for future work.

After the reactor run was complete, the reactor, settler, and weir overflow flasks settled overnight. Precipitate products formed in all three vessels, and they were collected and analyzed using the same methods as the batch tests.

4.3 Characterization Methods

The Category A: Process objectives were assessed using colourimetry to measure changes in [Ca^{2+}] and [P_i] over the course of the reaction. The remaining techniques used supported Category B: Product objective, by identifying the precipitates formed and determining their potential as a fertilizer nutrient source. Category C: Applications did not require the use of any additional characterization methods.

CATEGORY A

4.3.1 Colourimetry

Colourimetry was used to measure the [Ca^{2+}] and [P_i] of the liquid samples taken throughout the experiments. All samples were prepared in a 96-well, flat bottom plate made of clear polycarbonate. The samples were mixed with a colourimetric solution that would form a complex with either Ca^{2+} or P_i, and absorb light at a specific frequency. A vanadomolybdate solution was prepared to measure the [P_i] by absorbing light at 420 nm (Robinson 1971, Cheung 2002). A 0.01% O-cresolphthalein solution was used to react with the Ca^{2+} ions and absorb light at 570 nm (Schwarzenbach 1955, Cheung 2002). These solutions were prepared in accordance with SOP 9 (Cheung 2002). The Epoch Microplate BioTek Spectrophotometer 2009 in CBY D-202 was used with the Gen 5 software to analyze the samples. The detailed procedure can be found in Annex B - Appendix 3.

The colourimetric results indicating concentration were extremely valuable in assessing the effectiveness of the different experimental configurations. However, the changes in [Ca^{2+}] and [P_i] could only indicate what ions left the solution. These changes in concentration could not provide information about the form of the precipitates. For instance, it was possible that the Ca^{2+} ions all precipitated out as $CaCO_3$, or that the P_i came out of solution as an amorphous solid. Further, there was no way to determine if there was carbonate in the solid formed using this technique. For these reasons, the next section focuses on the various methods used to analyze the products formed.

CATEGORY B

4.3.2 Solubility

The samples were dissolved in 5 mL of ddH_2O, and allowed to sit for a minimum of one week to reach equilibrium. The colorimetric method was used to measure the resulting [Ca^{2+}] and [P_i]. These values used to calculate a Ca x P value, as well as the ratio of Ca/P.

4.3.3 SEM

The Phenom PRO Scanning Electron Microscopy machine in CBY D-415 was used to capture images of the precipitate at magnifications of 165x, 500x, and 1,000x. The images were scanned at 10kV and a resolution of 2048, with an exposure time of 26 seconds at full intensity. This allowed for a qualitative comparison of the products formed at different concentrations. Magnifications greater than 1,000x were attempted with mixed success, as it became very difficult to focus at greater magnifications.

4.3.4 Raman

Raman spectroscopy was undertaken with a WITec Alpha 300 confocal microscope with a 20x lens (WITec GmbH, Ulm, Germany), and was used to determine the speciation of the phosphorus and carbonate in the precipitate. Raman spectroscopy captures the inelastic scattering of Raman-active chemical bonds and allows for their identification with respect to known standard materials. For the purposes of this thesis, this technique was used to identify the calcium phosphate (Kazanci 2006) and calcium carbonate (Gunasekaran 2006) solids, as Raman spectroscopy can distinguish the different calcium phosphate minerals and calcium carbonate polymorphs. The laser source used was either 785 nm (XTRA High Power Single Frequency Diode Laser, Toptica Photonics, Victor, NY, USA), 488 or 532 nm (WITec GmbH, Ulm, Germany). Calibration was performed on the 520 nm (strongest) Raman shift of Si. Dry powdered samples were placed on a glass or quartz slide, and data was collected with an integration time of 1 second for a minimum of 45 seconds. The Raman shifts of greatest interest were 960 cm^{-1} for the P_i identification in apatite, 1070 cm^{-1} for carbonate in apatite, and 1090 cm^{-1} to determine whether $CaCO_3$ was present as calcite. Silicon, synthetic hydroxyapatite, calcite, and bone powder were used as standard materials. The resulting spectra were filtered to remove cosmic ray interference. OPUS Spectroscopy software (Bruker) (v. 6.5) was used to convert the raw data to a spectrum that was plotted with OriginPro 9.1 (OriginLab Corporation). A detailed protocol is in Annex B–Appendix 4.

4.3.5 Powder X-Ray Diffraction

Several products were analyzed with a Multiflex D3 (Department of Physics, University of Ottawa, Rigaku Americas Corp., TX, USA). This diffractometer uses copper radiation of

$CuK_{\alpha 1}$ (1.5418 A). The products were prepared on a low-background Si sample-holder, and scanned between $2\theta = 20°$-$45°$ at a rate of 1°/min (25 minutes total).

4.3.6 Carbon coulometry

A Carbon Coulometer (Model #5012) (UIC Inc., IL, USA) was used to measure the weight percent of CO_3 in the precipitate. A known mass of the sample was dissolved in 2 M perchloric acid ($HClO_4$, Sigma Aldrich), and the CO_2 (g) evolved from any $(CO_3)^{2-}$ present in the sample was quantified. The CO_2 (g) triggers a reaction between the cathode and anode solutions within the coulometer. This reaction is neutralized by applying current to the solution, and this current (i.e. the number of electrons) is proportional to the amount of CO_2 (g) that initiated the reaction. The coulometer's readout indicates the mass of the $(CO_3)^{2-}$ in the original sample, allowing a simple calculation of the weight percent. A detailed protocol can be found in the Coulometer User Manual.

4.3.7 Statistical analysis

A statistical analysis of results was conducted, to investigate the significance of the theoretical molar Ca/P of the precipitate, the precipitate's carbonate content, as well as the solubility of the precipitate. The method used was a one-way ANOVA, with a Bonferroni means comparison.

4.3.8 Units

Different disciplines of engineering commonly express related concepts using different units. In particular, moles of phosphorus per litre can also easily be characterized as mass of phosphorus per litre. These units can be converted with the knowledge that 1 mole of phosphorus weighs 30.97 g. Table 4.1 summarizes the most pertinent quantities.

mmol / L	mg / L
2.5	77
5	155
7	217
10	310
20	619
30	929

Table 4.1: Conversion between mmol/L to mg/L

4.4 References

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CHAPTER 5

RESULTS & DISCUSSION

The results are presented and discussed in support of each category of objectives. Section 5.1 examines the changes in concentrations of the solutions over the course of the batch reactions. The relationship of "Ca x P" to several variables is examined, and results of seeded and unseeded reactions are compared. Section 5.2 examines the products made during the batch reaction using several analytical techniques, and identifies which batch method parameters would be most suitable for testing in a reactor. Section 5.3 presents the reactor concentrations and analyzes the solids that precipitated within the reactor.

Note that throughout this chapter, each of the batch iterations is referred to by the $[P_i]$ prior to being mixed with and diluted by the Ca^{2+} solution. In other words, the test referred to as "10 mM P_i" would have an initial concentration of 5 mM P_i immediately upon mixing with an equal volume of Ca^{2+} solution. If seed was used, the type and density of the seeding is indicated.

5.1 Category A: Process Variables

5.1.1 Objective: Solubility of $CaCO_3$

Initial precipitation tests failed due to the low $[Ca^{2+}]$ present in solution. As such, the $CaCO_3$ / tap water solution was treated with CO_2 (g) because this is a by-product generated at the co-generation power plant onsite at the ROPEC. The lab group worked to test the extent of this effect, and the initial results were the basis of O. Meouch's 4th year thesis (Meouch, 2016). Figure 5.1 below demonstrates the $[Ca^{2+}]$ increase and pH decrease with increased gas/slurry contact time. The solution achieved a maximum Ca^{2+} concentration of approximately 6 mM within 20 minutes when treated at a flow rate of 0.15 L /min with 100% CO_2. Other gas flow rates and $[CO_2$ (g) / $N_2]$ ratios were tested, and approximately the same maximum $[Ca^{2+}]$ was reached. Once this theory was tested and the parameters were identified to achieve the maximum $[Ca^{2+}]$, the remaining experiments in support of this thesis employed the 100% CO_2 (g) stream due its faster and simpler experimental set-up.

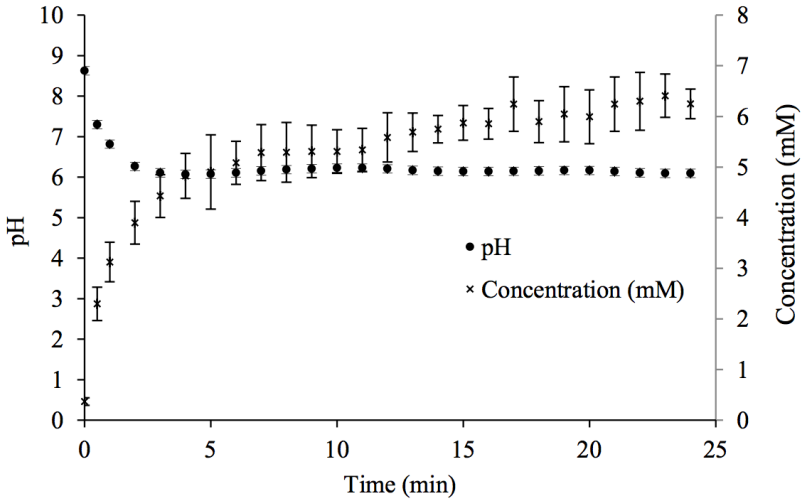

Figure 5.1: $CaCO_3$ in tap water treated with 100% CO_2 at flow rate of 0.15 L/min; corresponding change in $[Ca^{2+}]$ and pH with time (Meouch 2016)

Treating the $CaCO_3$ (s) + tap water solution with CO_2 (g) proved to be very effective for increasing the $[Ca^{2+}]$. An average of 5.5 ± 0.6 mmol/L was measured across all seeded and unseeded batch tests, as compared to an average of 0.37 ± 0.1 mmol/L that was found in solutions that were not CO_2 treated. This 14-fold increase led to a significantly higher degree of apatite supersaturation when the Ca^{2+} solution was mixed with the P_i solution for subsequent batch tests.

A compelling aspect of this procedure is that it converts a waste CO_2 (g) stream into a useful reagent. There are two potential benefits to this. First, CO_2 is a common byproduct in many industrial processes, thereby generating a readily available source of CO_2. Second, with the evolving carbon tax economy, it will benefit municipality to use CO_2 (g) that is generated within municipal processes, as opposed to releasing it into the atmosphere.

5.1.2 Objective: Supersaturation Batch Tests

Five concentrations of P_i solution were selected to approximate the values available in ROPEC streams, and to crudely model how the stream's $[P_i]$ decreases during precipitation treatment. Four repeats of each concentration were conducted, except for 30 mM P_i due to space constraints. The initial and final $[Ca^{2+}]$ and $[P_i]$ are summarized with the final pH of the solution. The percent of Ca^{2+} and P_i removed was calculated, as well as the molar theoretical ratio of Ca/P in the precipitate; these values are discussed more in sections 5.1.5 and 5.1.6. The most

important and even surprising result was that a non-negligible amount of precipitate formed spontaneously without seed.

Test	Calcium				Phosphorus				Final pH	Theoretical Ca/P of solid
	Initial mMol/L	Final mMol/L	n	% Ca removed	Initial mMol/L	Final mMol/L	n	% P removed		
2.5 mM Pi	2.89±0.43	2.07±0.24	4	17%	1.24±0.02	0.94±0.28	4	24%	7.07±0.19	1.84±0.86
5 mM Pi	2.59±0.50	1.14±0.71	4	56%	2.45±0.07	1.44±0.32	4	41%	6.95±0.21	1.47±0.23
10 mM Pi	2.68±0.40	0.36±0.20	4	87%	5.07±0.44	3.38±0.19	4	33%	7.21±0.15	1.46±0.43
20 mM Pi	2.67±0.38	0.15±0.06	4	94%	11.10±0.93	8.67±0.29	4	22%	7.34±0.18	1.08±0.19
30 mM Pi	2.40±0.18	0.05±0.01	3	98%	15.06±0.00	13.46±0.26	3	11%	7.50±0.08	1.48±0.18

Table 5.1: Summary of unseeded batch test results

The changes in concentration are shown graphically in Figure 5.2, where it becomes more apparent that the limiting reagent is different above and below $[P_i]$ = 5 mM. Virtually all of the Ca^{2+} is removed from solution when mixed with $[P_i]$ > 10 mM, while the majority of the P_i remained in solution. When the Ca^{2+} reagent was mixed with $[P_i]$ of 5 mM or less, however, significantly less Ca^{2+} precipitated from the solution. This indicates that at higher $[P_i]$, the reaction is limited by the $[Ca^{2+}]$, and significant P_i remains in solution. At lower $[P_i]$, the probability decreases for the ions to bond with one another and form a precipitate. This is an important parameter to identify because it means that while it is simple to vary the experimental $[P_i]$, the maximum $[Ca^{2+}]$ from $CaCO_3$ (s) under the conditions tested is approximately 6 mM. Thus, it may be necessary to dilute the P_i stream to achieve the optimal molar Ca/P reactant ratio of approximately 1/1, or to test whether continuous addition and CO_2 treatment of $CaCO_3$ (s) within the reactor itself may work.

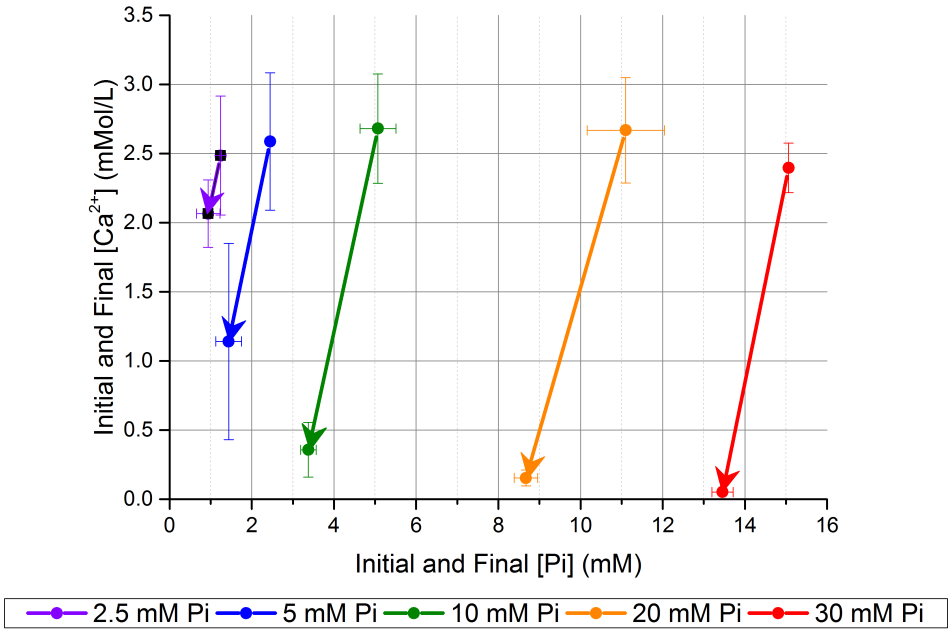

Figure 5.2: Change in [Ca^{2+}] versus change in [P_i] for unseeded tests

This approximate 1/1 ratio of 5 mM Ca^{2+} to 5 mM P_i was also of interest when identifying the metastable zone. When [P_i] was at least 10 mM before mixing, the solution became cloudy immediately upon adding Ca^{2+} to the reaction beaker. This indicated that the solution was in the critical supersaturation zone, and homogeneous nucleation was likely the dominant precipitation mechanism. With [P_i] = 5 mM, scale formed inside the beaker walls during the reaction. This would suggest that the experimental conditions for the Ca^{2+}-P_i metastable zone had been identified, and that heterogeneous nucleation was taking place.

Little to no scale was observed when the Ca^{2+} was added to a solution of 2.5 mM P_i, and very little product was visible. A decrease in both [Ca^{2+}] and [P_i] was observed, implying that the initial conditions were within the metastable zone and a small amount of Ca^{2+} and P_i did precipitate out of solution. However, due to the low concentrations involved, in addition to the small relative volume (500 mL total) it was not possible to collect sufficient solid to characterize the product.

5.1.3 Objective: Effect of Seed

The purpose of adding seed to the solution was to determine if it would increase the amount of P_i removed from the solution. Adding a seed material that is similar to the desired

product lowers the chemical potential required for precipitation to take place. This means that at low supersaturation states (i.e. in the metastable zone) the reaction can proceed further, represented by a lower equilibrium concentration of component ions, than it would without the presence of a suitable surface on which to form a solid product.

Two concentrations, 5 mM and 30 mM P_i, were selected to best allow comparison with the unseeded results. Three different seeding densities were selected; 0.5 or 2 g bone seed / L, or 1 g precipitate / L. The initial and final [Ca^{2+}] and [P_i] are summarized with the final pH of the solution. The percent of Ca^{2+} and P_i removed was calculated, as well as the theoretical ratio of Ca/P in the precipitate; these values are discussed further below.

Three repeats of the bone-seeded tests were conducted. However, the results of the first iteration were rejected due to sample preparation errors that could not be corrected. As such, n=2 for measurements of the concentrations for the majority of the seeded tests. However, pH measurements were remained valid, and all three resulting products were characterized.

Test	Calcium				Phosphorus				Final pH	Theoretical Ca/P of solid
	Initial mMol/L	Final mMol/L	n	% Ca removed	Initial mMol/L	Final mMol/L	n	% P removed		
5 mM Pi; 2 g bone	3.03	1.09	2	64%	2.53	1.11±0.39	2	56%	7.06±0.09	0.95±0.27
5 mM Pi; 0.5 g bone	3.06	1.11	2	64%	2.53	1.16±0.33	2	54%	7.06±0.09	1.44±0.11
5 mM Pi; 1 g ppt	2.96	0.26	2	91%	2.29	0.73±0.11	2	68%	7.56±0.07	1.74±0.002
7 mM Pi; 1 g ppt	2.24±0.14	0.01±0.01	4	100%	3.56	2.90±0.03	4	41%	8.23±0.05	1.52±0.07
30 mM Pi; 2 g bone	3.37	0.09	2	97%	15.13	11.09±1.33	2	27%	7.67±0.35	0.81±0.43
30 mM Pi; 0.5 g bone	3.10	0.12	2	96%	15.30	11.59±1.04	2	24%	7.55±0.09	0.86±0.37

Table 5.2: Summary of seeded batch test results.
Tests seeded with precipitate highlighted in grey.

Precipitation tests seeded with recycled precipitate appeared to be more effective at decreasing both final [Ca^{2+}] and [P_i] than the bone seed. The degree to which this was the case was unexpected. In both tests with recycled precipitate, virtually all of the Ca^{2+} was stripped from solution. This was also seen in all tests (seeded and unseeded) where the initial mole ratio of Ca/P in solution was 1/2 or greater (i.e. at higher [P_i], given a maximum [Ca^{2+}] of 5-6 mM) ; this is not surprising considering that such conditions would increase the likelihood that P_i ions

would be close enough to interact with a Ca^{2+} ion. However, the tests using recycled precipitate had an initial $[P_i]$ = 5 mM, or an initial mole ratio of 1/1. Tests with bone seed at the same $[P_i]$ only saw a 64% decrease from the initial $[Ca^{2+}]$, while the tests with the recycled precipitate had similar performance to the reactions at much higher initial $[P_i]$. This confirms that the recycled precipitate is a very effective surface for Ca-Pi crystal growth.

Although the bone seed was less effective than the recycled spontaneous precipitate in decreasing the $[Ca^{2+}]$ and $[P_i]$ in solution, it still generally proved to be superior to unseeded reactions. The changes in concentration for seeded tests are represented graphically in Figure 5.3.

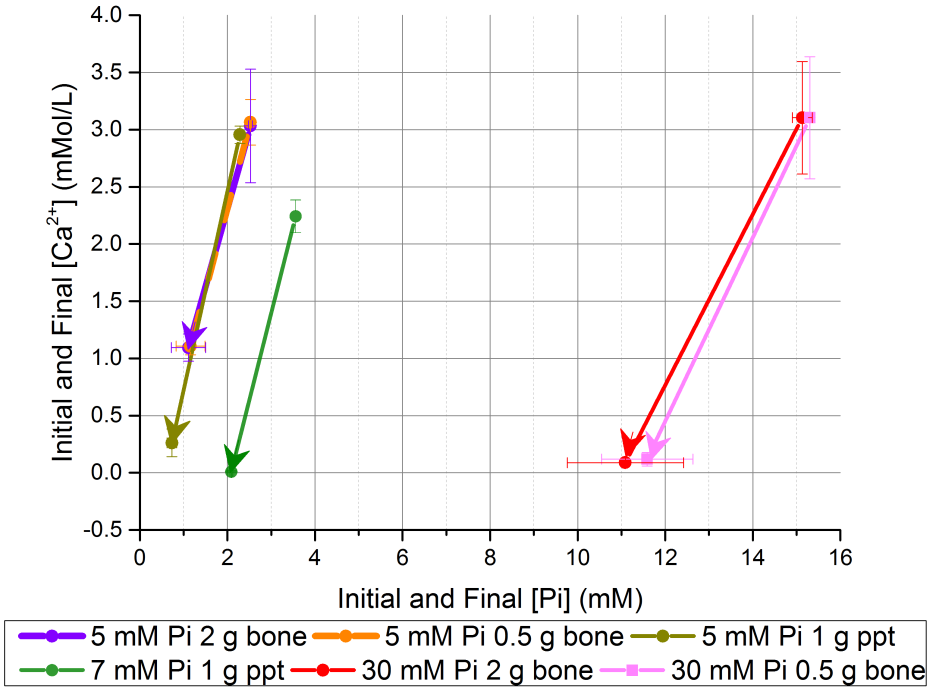

Figure 5.3: Change in $[Ca^{2+}]$ versus change in $[P_i]$ for seeded tests

At the lower $[P_i]$, the presence of bone seed showed slight improvement over unseeded tests in removing both Ca^{2+} and P_i from solution. The effect of the seeding density at lower initial $[P_i]$ was unexpected, in that appears to be negligible; the final $[Ca^{2+}]$ and $[P_i]$ were virtually the same for both seeding density values. For this reason, tests conducted after this set of results was analyzed used a seeding density of 1 g/L; this intermediate value was selected based on the availability of seed material. More rigorous testing of the optimal seed density when using the recycled precipitate warrants further attention.

As with the unseeded tests, the $[Ca^{2+}]$ limited the reaction's progress to proceed at high initial $[P_i]$. However, it is important to note that the presence of the bone seed allowed for a greater relative decrease of final $[P_i]$. Again, the seeding density appeared to have a minimal effect considering the error in measurements.

5.1.4 K_{sp} Estimation (Ca x P), relation to $[P_i]$ and to pH

As outlined in Chapter 3, the product of $[Ca^{2+}]$ x $[P_i]$, written as Ca x P, is used as an approximation of K_{sp}. It also serves as an indication of the precipitation reaction's driving force, based on the definition of supersaturation. As such, the Ca x P values of the initial and final conditions were examined, and are summarized below in Table 5.3, and Figure 5.4.

		Test	Ca X P	n
Initial [Pi] below 15 mM	o	2.5 mM Pi;	3.09±0.51	4
	f	unseed	1.90±0.48	
	o	5 mM Pi;	6.36±1.38	4
	f	unseed	1.73±1.40	
	o	**5 mM Pi;**	**7.65**	**2**
	f	**2 g bone/L**	**1.19**	
	o	**5 mM Pi;**	**7.73**	**2**
	f	**.5 g bone/L**	**1.25**	
	o	**5 mM Pi;**	**6.75**	**2**
	f	**1 g ppt/L**	**0.20**	
	o	**7 mM Pi;**	**7.98**	**4**
	f	**1 g ppt/L**	**0.02±0.02**	
	o	10 mM Pi;	13.62±2.64	4
	f	unseed	1.19±0.61	

		Test	Ca X P	n
Initial [Pi] above 15 mM	o	20 mM Pi;	29.86±6.71	4
	f	unseed	1.35±0.54	
	o	30 mM Pi;	36.11±2.69	3
	f	unseed	0.70±0.11	
	o	**30 mM Pi;**	**45.91**	**2**
	f	**2 g bone/L**	**0.99**	
	o	**30 mM Pi;**	**47.49**	**2**
	f	**.5 g bone/L**	**1.41**	

Table 5.3: Ca x P for both seeded and unseeded tests, ranked by increasing concentration. **Bold** values are for seeded tests.

Regardless of the initial Ca x P, the final Ca x P was less than 2 across all tests. It is interesting to note that unseeded tests with the highest initial Ca x P values generally produced the lowest final Ca x P values. This same trend was not observed with the seeded tests; instead, the presence of recycled precipitate led to the lowest final Ca x P values regardless of initial Ca x P. One possible hypothesis is that the presence of a relatively large amount of spontaneous precipitate has the same effect as the presence of a seed material, thus enabling the reaction to

proceed to an equilibrium state with a lower chemical potential. Alternatively, the spontaneous precipitate could reduce the solution Ca x P to a metastable state, and from this point, crystal growth could progress to the end of the test. Figure 5.4 illustrates this trend below.

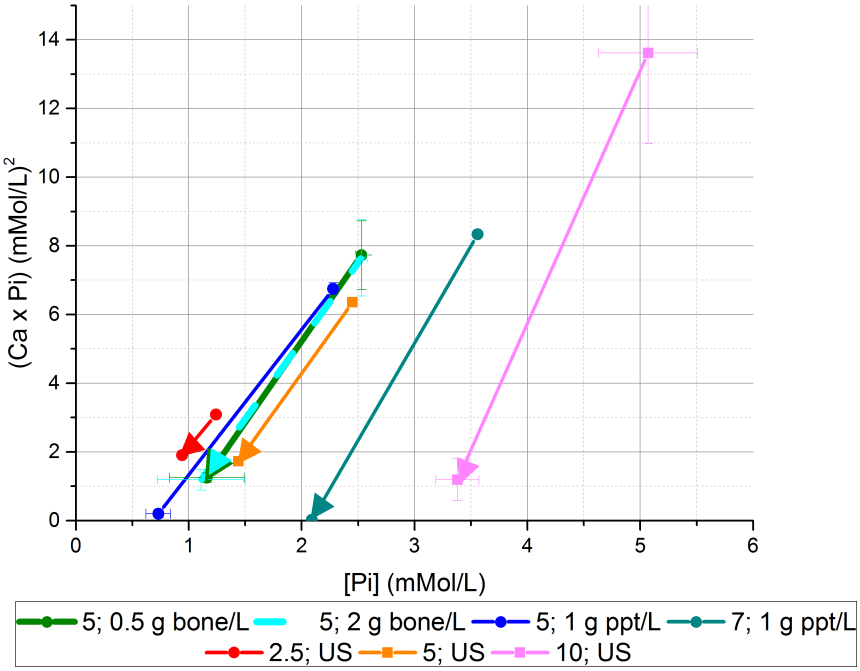

Figure 5.4A: Initial and final (Ca x P) values, versus initial and final [P_i] (initial [P_i]<15 mM)

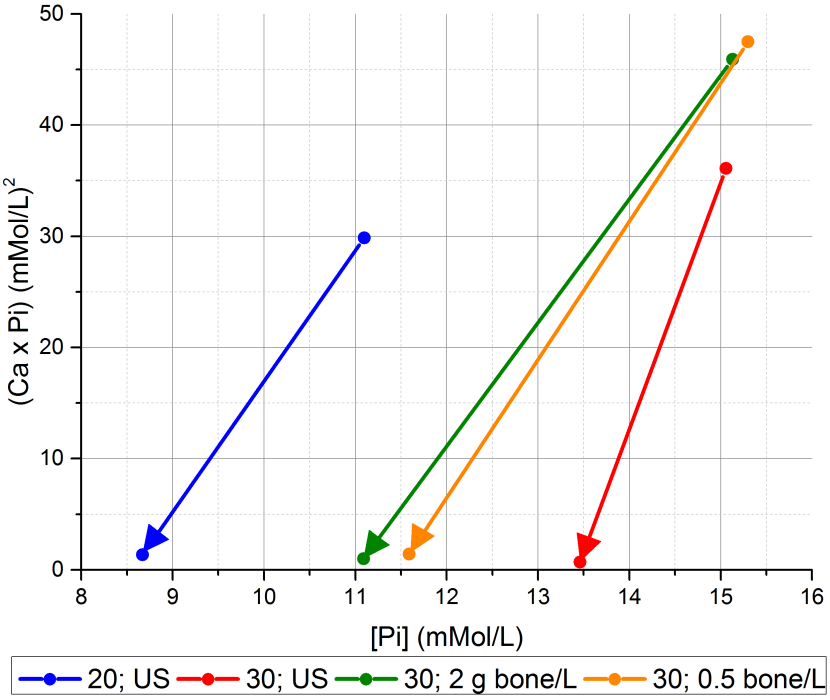

Figure 5.4B: Initial and final (Ca x P) values, versus initial and final [P_i] (initial [P_i]>15 mM)

Another trend was observed when the final Ca x P values were plotted against the final pH of the solution. The values are summarized in Table 5.4, and shown graphically in Figure 5.5.

	Test	pH	Ca x P	n
UNSEEDED	2.5 mM Pi	7.07±0.19	1.90±0.48	4
	5 mM Pi	6.95±0.21	1.73±1.40	4
	10 mM Pi	7.21±0.15	1.19±0.61	4
	20 mM Pi	7.34±0.18	1.35±0.54	4
	30 mM Pi	7.50±0.08	0.70±0.11	3
SEEDED	5 mM Pi; 2 g bone/L	7.060	1.19±0.30	2
	5 mM Pi; .5 g bone/L	7.060	1.25±0.14	2
	5 mM Pi; 1 g ppt/L	7.560	0.20±0.12	2
	7 mM Pi; 1 g ppt/L	8.23±0.05	0.02±0.02	4
	30 mM Pi; 2 g bone/L	7.670	0.99±0.14	2
	30 mM Pi; .5 g bone =/L	7.550	1.41±0.81	2

Table 5.4: Final (Ca x P) and final pH (both seeded and unseeded)

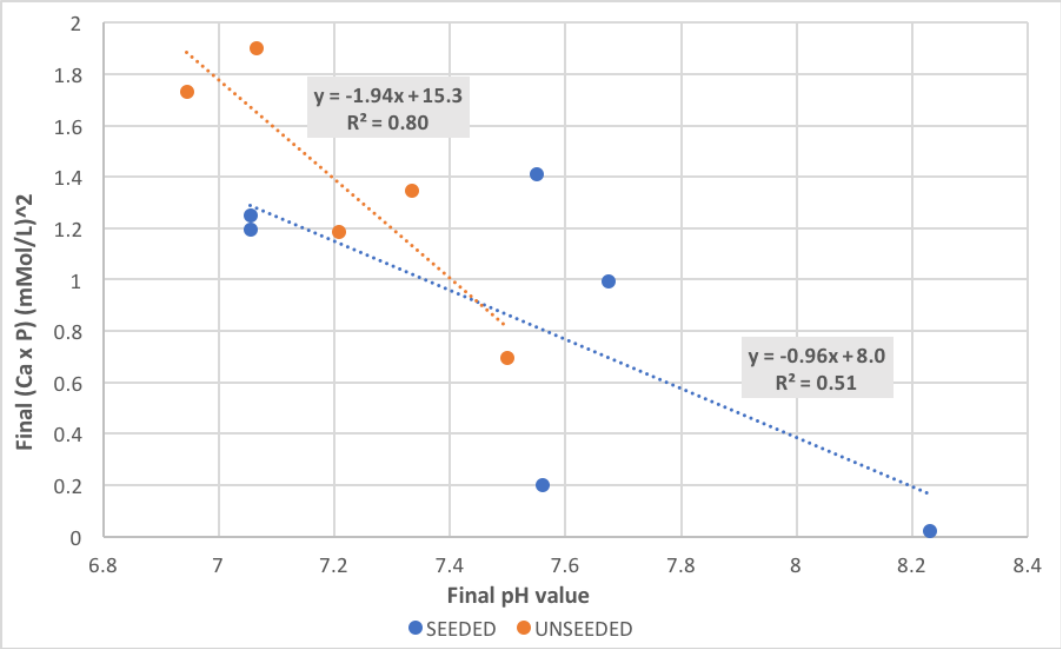

Figure 5.5: Final (Ca x P) versus final pH (both seeded and unseeded)

Across all reactions, the pH was allowed to drift, remaining close to neutral throughout the experiments. As the final pH of the reaction increased, a decrease in the final Ca x P was also observed. It is known that the speciation of phosphoric acid changes with pH, and that as pH

increases the $[PO_4^{3-}]$ also increases. However, the effect of the presence of additional aqueous species on this equilibrium is not known. This means that within this study, it is possible to confirm only that there is a correlation between pH and Ca x P, but not to draw conclusions regarding the causation or the mechanism at play.

Future work will explore the role of pH in greater detail, such as looking at whether increasing the pH of the solution will also lead to a lower Ca x P value, and thus drive a greater decrease of $[Ca^{2+}]$ and/or $[P_i]$ from solution.

5.1.5 Theoretical composition based on d$[Ca^{2+}]$ and d$[P_i]$

Knowing the final and initial $[Ca^{2+}]$ and $[P_i]$, it is possible to approximate the ratio of Ca/P in the solid precipitate formed. Assuming that all of the Ca^{2+} and P_i ions leaving solution end up in a uniform solid precipitate, the resulting Ca/P values can be calculated as follows in Equation 5.1:

$$\frac{Ca}{P} = \frac{[Ca]_o - [Ca]_f}{[Pi]_0 - [Pi]_f} \qquad [5.1]$$

The theoretical values of the products made are listed below in Table 5.5.

Test	Theoretical Ca/P of solid	n
2.5 mM Pi; unseeded	1.84±0.86	4
5 mM Pi; unseeded	1.47±0.23	4
10 mM Pi; unseeded	1.46±0.43	4
20 mM Pi; unseeded	1.08±0.19	4
30 mM Pi; unseeded	1.48±0.18	3

Test	Theoretical Ca/P of solid	n
5 mM Pi; 2 g bone	0.95	2
5 mM Pi; 0.5 g bone	1.44	2
5 mM Pi; 1 g ppt	1.74	2
7 mM Pi; 1 g ppt	1.52±0.07	4
30 mM Pi; 2 g bone	0.81	2
30 mM Pi; 0.5 g bone	0.86	2

Table 5.5: Theoretical ratio of Ca/P in products formed by each test

The mineral hydroxyapatite has a molar component ratio of approximately 10 Ca : 6 P, or a Ca/P of 1.67. Many of the batch test products have Ca/P values in that range, which is a good initial indicator that apatite was formed. Some products have a lower Ca/P value, meaning that a

greater proportion of P_i was removed from solution. Although this could mean that the product will prove to be less apatite-like, it suggests that this method is effective for removing P_i from solution. It may also mean that the product resembles bone mineral, which is a calcium-deficient apatite with a Ca/P less than 1.67 (Blumenthal 1981); the newest bone mineral Ca/P has been reported to be 1.5 (Kuhn 2008). This is important because the statistical analysis (one-way ANOVA) of the unseeded results indicate that the theoretical Ca/P of the solid is independent of the initial $[P_i]$, while in four of the five instances the calculated Ca/P was approached this same value of 1.5 within experimental error. This suggests that the system could potentially produce a similar product across a range of $[P_i]$ values, thus lowering the risk to engineers in applying these findings.

The effectiveness of P removal and recovery potential is examined in Section 5.1.6, and the products will be compared to bone mineral in Section 5.2.

5.1.6 Potential for Recovery of Phosphorus

So far, it has been shown that the precipitation method tested is effective for reducing both $[Ca^{2+}]$ and $[P_i]$. Furthermore, the precipitate formed spontaneously proved to be very effective for removing P_i from solution. It is important to note that differences between the preparation of bone seed (such as potential presence of residual chemicals, or damage to crystal structure during bleaching) may have contributed to bovine bone being less effective as a seed material. However, it should be simpler and less expensive to recycle the spontaneous precipitate for the purpose of encourage further precipitate, and as such the focus of experimentation shifted to unseeded or spontaneously precipitated tests. Finally, it is the decrease in $[P_i]$ that is of greatest interest when considering practical applications of these results.

	Test	$(Ca/P)_o$	%P removed	n
UNSEEDED	2.5 mM Pi	2.00±0.36	24%	4
	5 mM Pi	1.05±0.18	41%	4
	10 mM Pi	0.53±0.08	33%	4
	20 mM Pi	0.24±0.02	22%	4
	30 mM Pi	0.16±0.01	11%	3
SEEDED	5 mM Pi; 2 g bone/L	1.20	56%	2
	5 mM Pi; .5 g bone/L	1.22	54%	2
	5 mM Pi; 1 g ppt/L	1.29	68%	2
	7 mM Pi; 1 g ppt/L	0.66	41%	4
	30 mM Pi; 2 g bone/L	0.20	27%	2
	30 mM Pi; .5 g bone /L	0.20	24%	2

Table 5.6: Initial ratio of (Ca/P) and corresponding percent of P_i removed from solution

Because the Ca^{2+} limits the reaction, the relative amount of P_i removed from solution decreases as the initial [Pi] increases. The optimal ratio without seed is (1.05 Ca) /(1 P), and with seed it is (1.29 Ca) / (1 P). Recalling that the maximum $[Ca^{2+}]$ from $CaCO_3$ is approximately 6 mMol / L, this limit has implications for how these ratios can be achieved. Given a relatively high initial $[P_i]$ of 30 mM, the solution would need to be repeatedly treated or cycled to draw down the $[P_i]$ as the Ca^{2+} ions are depleted. Alternately, an initial mixing ratio of approximately (5 L of 5 mM Ca) : (1 L of 30 mM P_i) could be attempted in order to reach the same molar ratio.

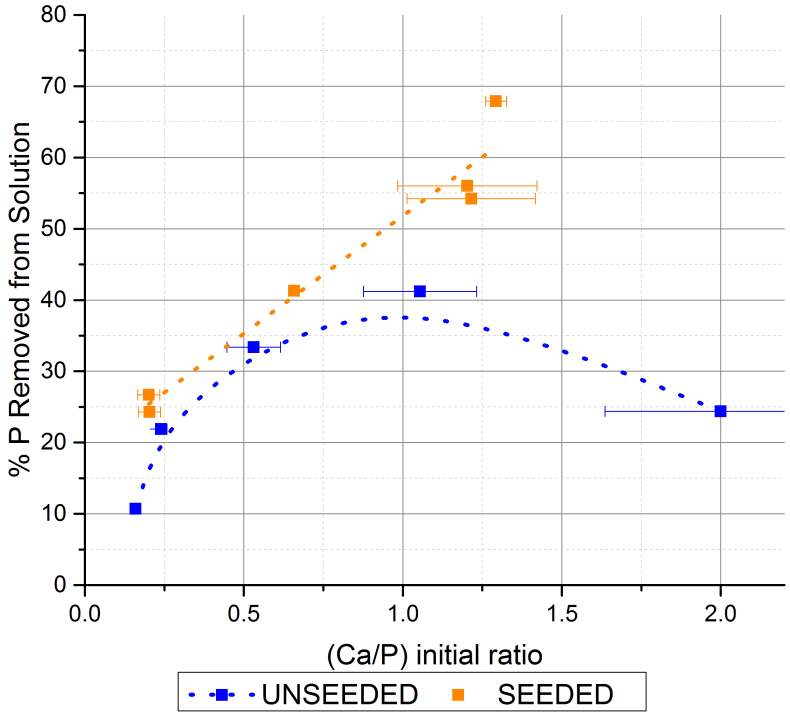

Figure 5.6: Percent of P_i recovered from solution versus initial ratio of Ca/P

5.2 Category B: Product characterization

Sufficient precipitate was formed to collect from all batch tests, with the exception of the 2.5 mM P_i iterations; possible reasons for this exception were discussed above in Section 5.1. Also, it was not possible to separate the precipitate grown on cow bone from its seed material; could falsely indicate the presence of novel carbonate apatite. For this reason, the only products tested below are those formed during unseeded tests, or in tests using pure precipitate as seed.

5.2.1 Solubility and comparison to estimated composition of product

The solubility of the unseeded products was tested, and the results are summarized in Table 5.7. The bovine bone seed was found to have a high enough solubility ($[Ca^{2+}]$ of 0.34 mMol/L, and a $[P_i]$ of 0.13 mMol/L) that its presence could potentially influence measurement of the solubility of the pure precipitate. For this reason, products that were seeded with bone were not tested for solubility because it would be difficult to determine whether the ions in solution were attributed to the product formed, or to the bovine seed. Because the recycled precipitate

was found to be an effective seed material with greater potential for industrial applications, the bovine bone solubility was not investigated in further detail.

Test	Solubility of Precipitate					Theoretical Ca/P
	[Ca] mMol/L	[Pi] mMol/L	Ca x P (mMol/L)^2	*Solubility* Ca/P	n	
5 mM Pi; 1 g ppt/L	0.24±0	0.23±0.01	0.055±0.004	1.02±0.06	2	1.74±0.002
7 mM Pi; 1 g ppt/L	0.21±0.01	0.22±0.01	0.048±0.004	0.97±0.05	4	1.52±0.07
5 mM Pi; unseed	0.16±0.02	0.16±0.02	0.026±0.006	1.03±0.15	4	1.47±0.23
10 mM Pi; unseed	0.18±0.03	0.23±0.04	0.042±0.014	0.79±0.04	4	1.46±0.43
20 mM Pi; unseed	0.18±0.02	0.51±0.12	0.094±0.016	0.38±0.14	4	1.08±0.19
30 mM Pi; unseed	0.17±0.06	0.45±0.09	0.075±0.021	0.39±0.17	3	1.48±0.18
Bone	0.34	0.13	0.044	2.62	1	n/a

Table 5.7: Theoretical Ca/P of products, versus products' measured Ca/P and Ca x P

It was anticipated that the Ca/P ratio of the ions from the dissolved products would be similar to the ratio of Ca/P that was calculated for the solid. This was not the case. For all products tested, the Ca/P was found to be lower than expected, meaning that a greater proportion of P_i dissociated than expected. However, a similar phenomenon has been described in the literature. Both Jahnke (1984) and Perrone (2002) found that carbonate apatite and similar minerals dissociate incongruently. This is part of the reason why a K_{sp} value for apatite has not been agreed upon. For these reasons, the stoichiometry of the products will not be estimated here, although solubility has been used to predict the formula of carbonate apatite in other studies (Deymier 2017).

Precipitates grown from previously homogeneously nucleated seed generated the highest average dissolved [Ca^{2+}]. A one-way ANOVA showed that the average dissolved [Ca^{2+}] from the unseeded precipitates did not change significantly with initial [P_i]. Dissolved [P_i] concentrations follow a proportional trend with increasing initial [P_i]. Statistically significant differences

between [P_i] means were noted for all groups but not between any two of the 5, 7, and 10 mM Pi groups, and between the 30 and 40 mM Pi groups (Bonferroni test). Ca/P ratios for the unseeded and precipitate-seeded experiments followed an inverse trend with the initial [P_i] from which they were nucleated, and have the same statistically significant differences as the final [P_i]. Within the margins of error, a similar trend is seen with the calculated Ca/P from the [Ca^{2+}] and [P_i] decrease in the precipitation experiments. The average calculated Ca/P values were higher than the measured solubility Ca/P values; this may result from the different solution compositions in which the precipitates were in equilibrium, and the effect of the unmeasured carbonate concentrations.

5.2.2 SEM

Scanning electron images of precipitate from the unseeded tests, as well as the products formed in the precipitate-seeded reactions, are shown in Table 5.8 on the next page. Only images taken at 500x magnification are summarized below; images captured at different magnifications, as well as the bone-seeded products, can be viewed in Annex C: Raw Data.

Based on classic nucleation theory, it was hypothesized that solids formed at lower supersaturation rates would grow to be larger in size, while the higher supersaturations would yield very fine solids. This is not what was observed. Looking initially at the unseeded products, there appears to be a trend of increasing density of the solids formed. That is to say, at 5 mM P_i, the precipitate appears 'crumbly' and few agglomerations of particles are present. At 10 mM P_i, a clear cake has formed although it appears to have a porous texture. Both 20 mM P_i and 30 mM P_i have a similar, relatively 'dense' appearance.

It is possible that the method in which the products were captured affected their final appearance. All of the solids were filtered and dried in the same manner. However, there was more solid recovered from the 20 mM P_i and 30 mM P_i experiments, leading to a thicker filter cake. It is possible that these solids were finer while in solution, but then as the drying process evaporated water, this led to another crystallization event. Unfortunately, the solids were not characterized before they were dried to confirm this explanation; it is recommended that future work include dynamic light scattering (DLS), settling tests before drying the precipitate, or dehydrating the slurry with an organic solvent, thus allowing for a measurement of the solids while still in solution.

The surface of the seeded products may provide some insight into the mechanism of precipitation. Small spheres were visible at the surface of the seeded tests (both precipitate and bone seeded). These spheres were observed to a lesser degree in the unseeded tests. Initially it was suspected that these spheres may have been $CaCO_3$ (s) that precipitated out of solution and formed at the surface of the solids during drying, as the first iterations were rinsed with supernatant as opposed to ddH_2O, as spheroidal $CaCO_3$ has been reported (Zou 2015). This could have had the effect of ions crystallizing out of solution as the water evaporated, and forming an additional solid that had not precipitated while in solution. $CaCO_3$ was suspected due to its extremely low solubility; this would also have been the simplest reason. However, when the experiment was repeated and the filter cake was rinsed with ddH_2O prior to drying, the spheres were observed. This suggested that the spheres were not created uniquely due to the drying process, but had been in the process of forming prior to being collected. As such, other possible explanations were explored.

There are several theories surrounding the nucleation pathways of calcium phosphates, many of which include the formation of an amorphous precursor, called amorphous calcium phosphate (ACP) (Posner 1980, Blumenthal 1981, Kazanci 2006, Dorozhkin 2012, Dorvee 2013, Habraken 2013, Combes 2016, Zou 2017). It is possible that this is what was observed (Figure 5.7), however further spectroscopic techniques did not corroborate this hypothesis.

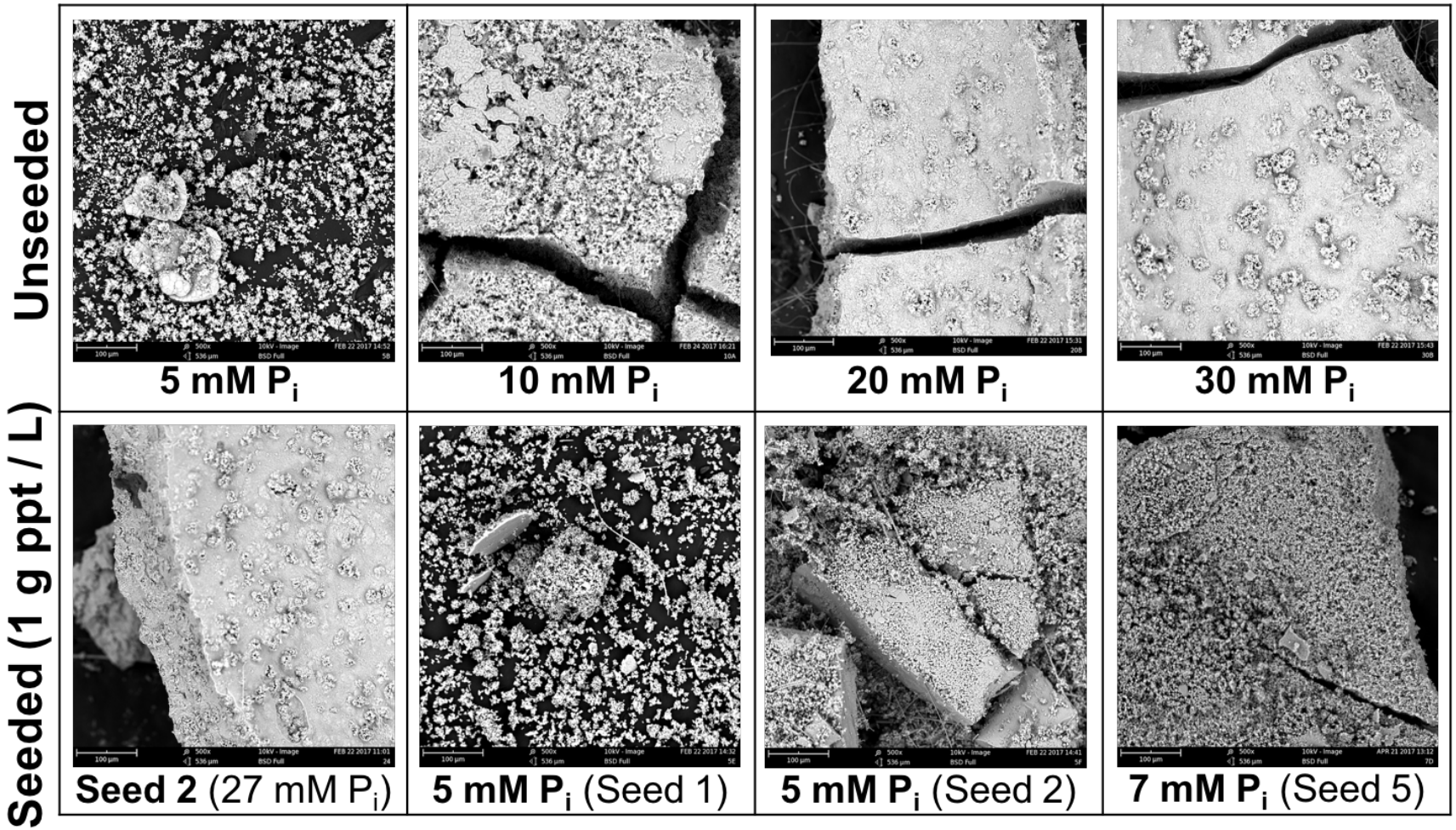

Table 5.8: SEM summary of products at 500x magnification. Top row are products of unseeded experiments, in order of increasing initial [P_i]. Bottom row shows seed and precipitates formed. Seed 2 was formed by mixing a solution of 27 mM P_i with a saturated solution of $CaCO_3$, using the same method as the unseeded tests. It was subsequently used as seed for one of the 5 mM P_i tests. The precipitates formed during both 5 mM P_i seeded tests were combined and used as seed ("Seed 5") for the 7 mM P_i tests.

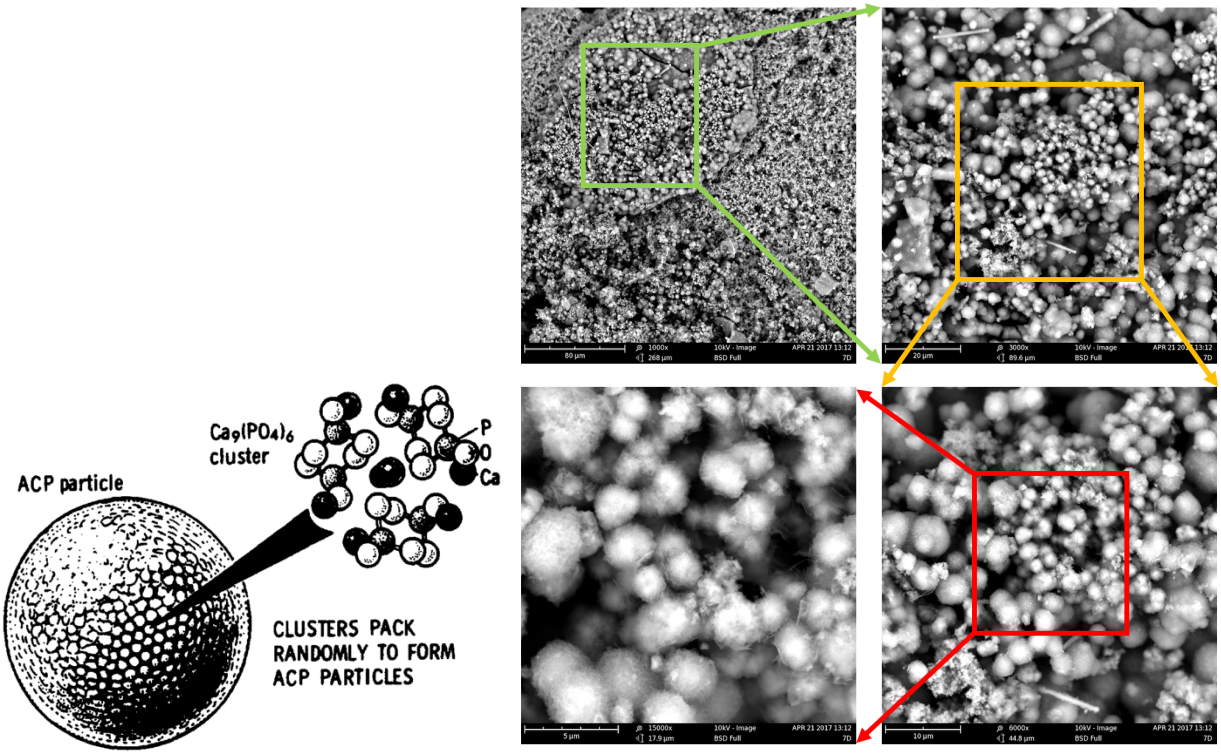

Figure 5.7: ACP clusters (Posner 1980), compared with spheres visible at increasing magnification (1000x, 3000x, 6000x, 15,000x) of product 7

These spheres suggest the presence of an interesting intermediate state, however their appearance is not sufficient to confirm whether they consist of ACP. This is because many of the other studies collected and analyzed products on a shorter time frame. Habraken's 2013 paper observed the formation of ACP spheres within approximately one hour, and they continued to change shape after forming spheres. Kazanci's 2006 paper also observed that ACP was present for approximately one hour, after which the particle began to form crystalline structures. The solids in the images above were in solution for 5 days in the case of Table 5.8, or 4 days in the case of Figure 5.7. By the mechanisms proposed by both Kazanci and Habraken, there should not be any ACP remaining after two days. Further work will need to be completed to better understand the mechanism by which it is being formed, by collecting and analyzing samples of the solid precipitate throughout the experiment.

5.2.3 Raman Spectroscopy

The unseeded solids, and solids seeded with precipitate, were analyzed using Raman spectroscopy, and compared with synthetic hydroxyapatite (HAP), synthetic $CaCO_3$ (calcite), and bone mineral. The HAP and bone were used as standards to confirm the location of the v_1PO_4 shift at 960 cm^{-1} that is characteristic of apatite, and the shift associated with carbonate substitution, the v_1CO_3 shift at 1070 cm^{-1}. $CaCO_3$ (as calcite) has a shift at 1090 cm^{-1}. This was measured in order to confirm that $CaCO_3$ was not a component of the precipitate. Immature bone mineral, or mineral containing HPO_4^{2-} as opposed to PO_4^{3-} , exhibits a v_1PO_4 shift that is closer to 955-957 cm^{-1}. Amorphous calcium phosphate produces a distinct v_1PO_4 shift ~ 951 cm^{-1}. A summary of these phosphate ion Raman shifts is in Table 5.9.

Shift (cm^{-1})	Assignment	Description
430	$v_2\ PO_4^{3-}$	Strong band
450	$v_2\ PO_4^{3-}$	Shoulder on 430 cm^{-1}
584-590	$v_4\ PO_4^{3-}$	Multiple partially resolved components
951	$v_1\ PO_4^{3-}$	Amorphous calcium phosphate (ACP)
955-957	$v_1\ PO_4^{3-}$	Bone mineral containing HPO_4^{2-}, usually immature
959-962	$v_1\ PO_4^{3-}$	Mature bone mineral, characteristic of carbonate apatite
1017-1048	$v_3\ PO_4^{3-}$	Stretching mode
1070	$v_1\ CO_3^{2-}$	B-type carbonate band (i.e. substitute for PO_4^{3-})

Table 5.9: Raman shifts assignments (Jillavenkatesa 1997, Kazanci 2006, Mandair 2015)

Raman spectra confirmed that the Ca^{2+} and P_i had precipitated in an apatite-like formation, as the v_1PO_4 shift at 960 cm^{-1} was observed across all samples. This confirmed that ACP and HPO_4^{2-} were not the dominant species present, there were not shifts 951-957 cm^{-1}. Additionally, the spectra confirmed that some CO_3^{2-} had also been incorporated into the lattice; this shift is much more subtle, and the presence of CO_3^{2-} is discussed further in Section 5.2.5.

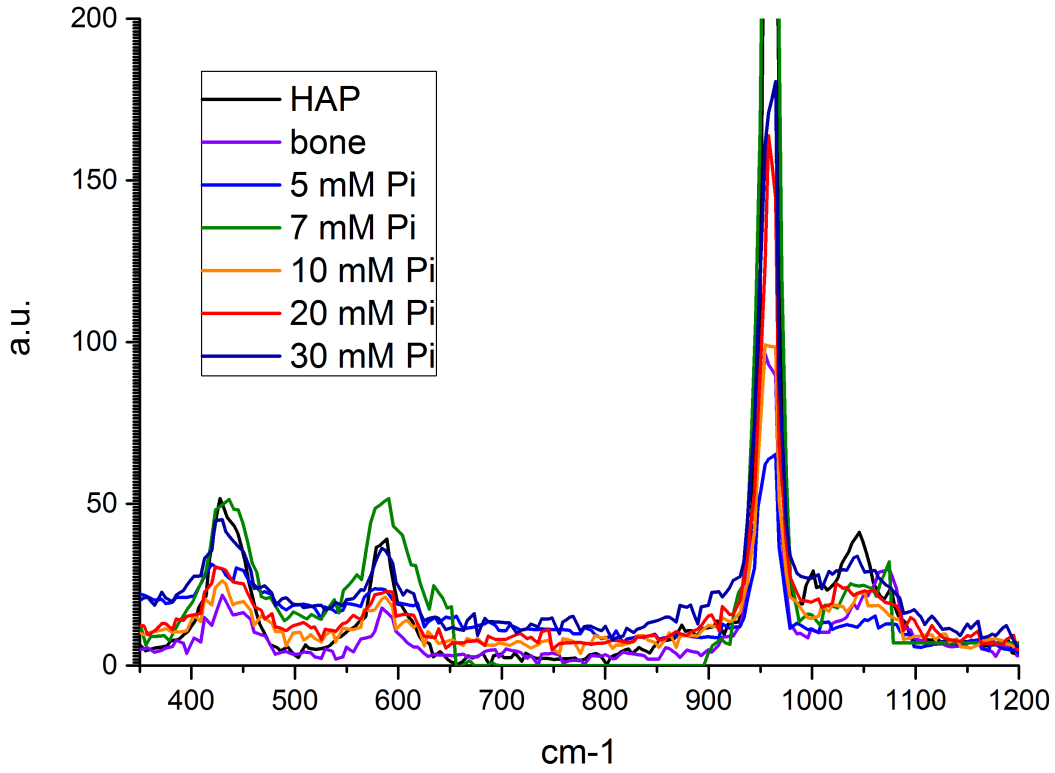

Figure 5.8: Raman shifts of unseeded products, and precipitate-product 7.

5.2.4 Powder XRD

Products were characterized using XRD to further confirm their crystallinity and mineral type. It was anticipated that the diffraction patterns would indicate that the product was similar to HAP and would be moderately crystalline. It was also recognized that it was still possible that the diffraction pattern data would indicate a different mineral form of calcium phosphate, as opposed to apatite (Figure 5.9). An amorphous calcium phosphate product would not produce a diffraction data. The results presented yet another explanation (Figure 5.10).

The peaks were not very well-defined, indicating that the structure was poorly crystalline, highly substituted and/or the crystal domains were very small. This is indicative of the biological mineral found in bone. While bone had been used as a comparison when identifying the P_i and CO_3^{2-} Raman shifts, it was not expected that the precipitates formed would resemble bone from a crystallinity perspective as well.

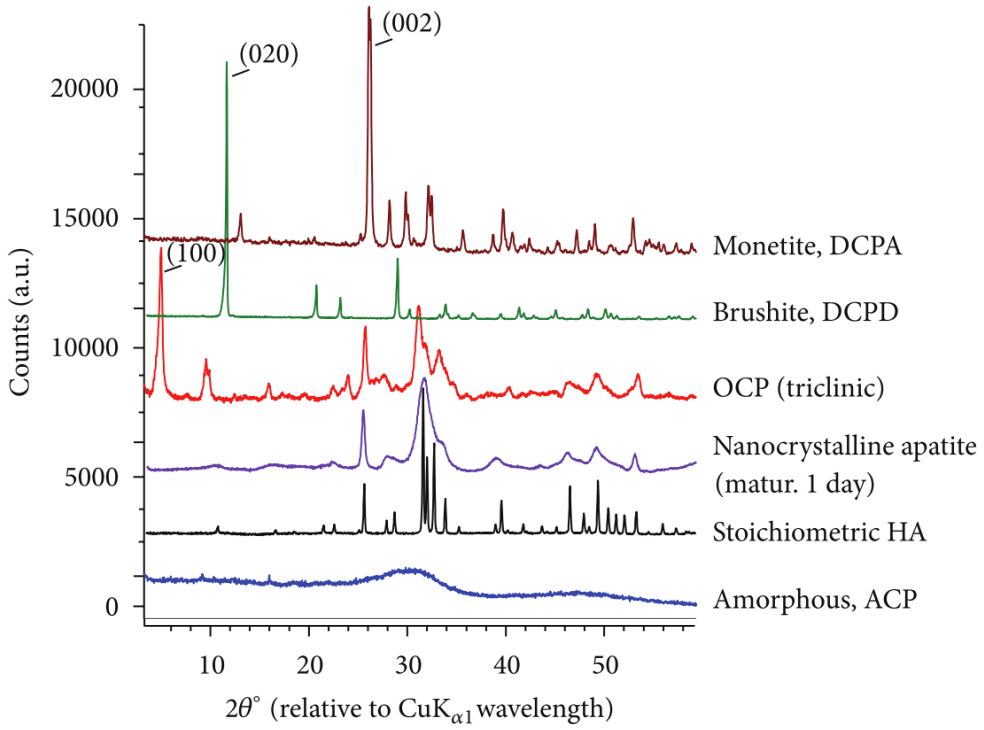

Figure 5.9: Powder XRD identification of other compounds often mistaken for apatite, compared with apatite (Drouet 2013).

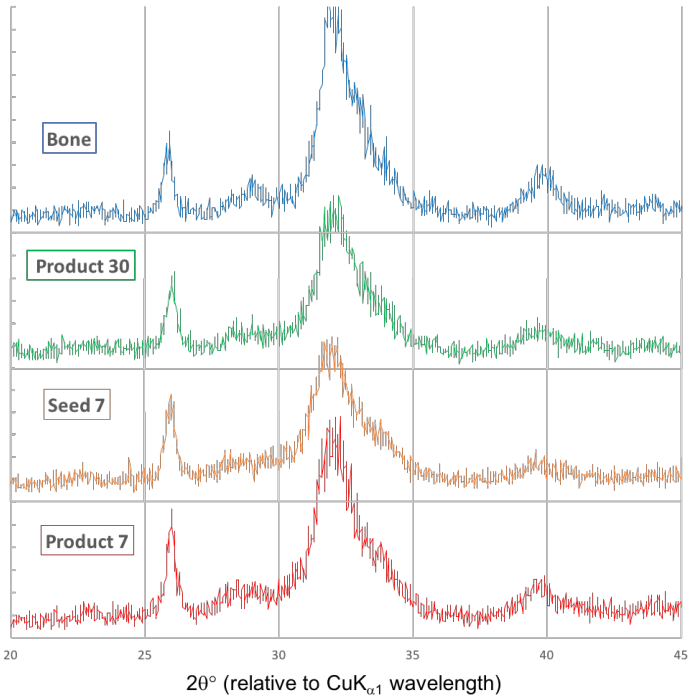

Figure 5.10: Powder XRD data of bone, Unseeded Product 30, Seed #7, Seeded Product 7.

The XRD patterns of the precipitate samples in Figure 5.10 most closely resemble the XRD pattern of the nanocrystalline apatite in Drouet's 2013 paper. Further research uncovered SEM micrograph of Drouet's nanocrystalline apatite, shown below in Figure 5.11. The author explicitly states:

"Although the observation of this type of morphology is a promising factor in favor of the precipitation of bone-like apatite, this morphology should not *be considered as an absolutely conclusive criterion."* However, considering that the XRD data rule out the likelihood that the solid is monetite or brushite (the two calcium phosphates most likely to visually resemble bone-like apatite), the similarity between the nanocrystalline apatite and Product 7 serves as further support for the explanation that the product is in fact a bone-like, carbonate-substituted apatite.

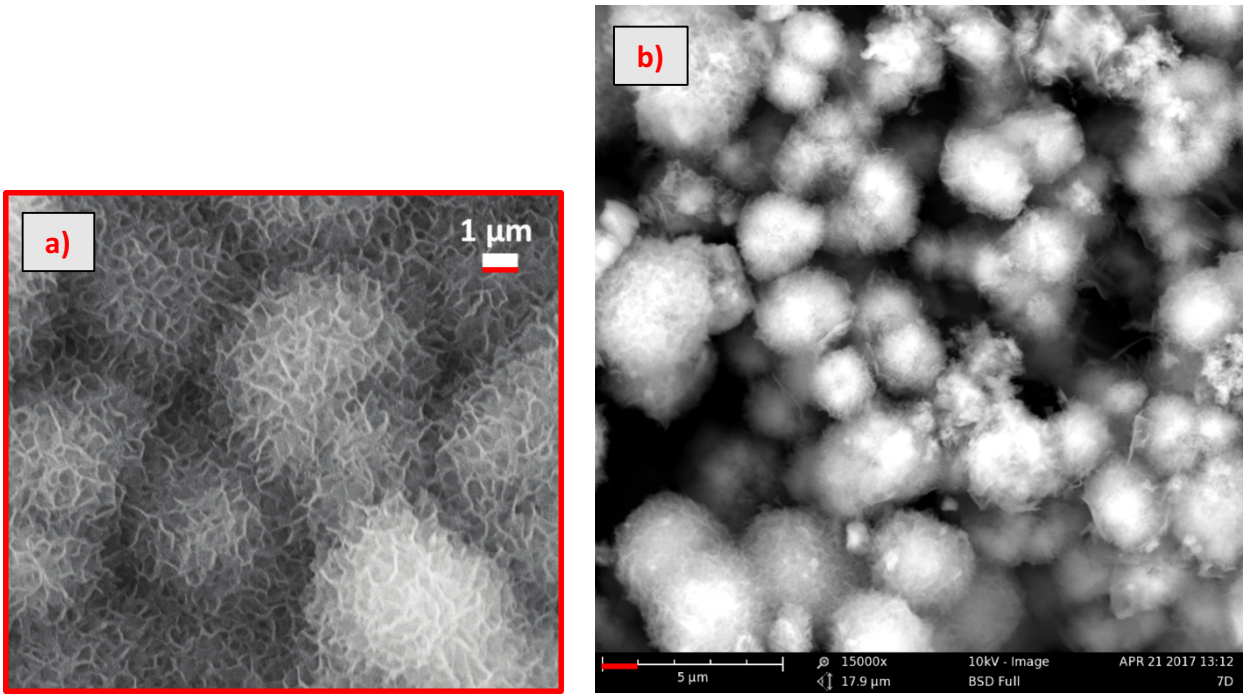

Figure 5.11: (a) SEM micrograph of nanocrystalline apatite (Drouet 2013),
(b) compared with Seeded Product 7

5.2.5 Carbon coulometry

The techniques listed above confirm that the precipitate is likely apatite, and suggest that it contains CO_3^{2-} substitutions. In order to definitively confirm this, the samples were tested using coulometry to measure the wt % CO_3^{2-} of the precipitate.

All of the unseeded samples were tested, and Seeded Product 7 was tested. $CaCO_3$ (s) was tested at the beginning and the end of each day to confirm the machine's calibration.

The samples each contained a minimum average of at least 1.1 wt % CO_3^{2-}, summarized below in Table 5.10. A correlation was observed between increasing initial [P_i], and decreasing wt % CO_3^{2-} among the unseeded products. Product 7, which was seeded with precipitate, contained the highest wt % CO_3^{2-}. Some results are within the values observed in natural francolite (1.4-6.3 wt % CO_3^{2-}, McArthur, 1985), and are lower than what is typically seen in bone (5-9 wt % CO_3^{2-}) (Penel 1998, Kuhn 2008, Mamo 2016).

Test	wt% CO3	n
5	1.95±0.08	3
10	1.21±0.43	4
20	1.13±0.14	4
30	1.10±0.04	3
7	**2.59±0.09**	**4**

Table 5.10: Weight percent of CO_3^{2-} within precipitate.
Products from unseeded experiment, except for 7 (in bold)

Knowing that CO_3^{2-} substitutions have been linked to increased solubility of calcium phosphate solids (Jahnke 1984), these values were compared with the results from the solubility tests. It was observed that although the Ca/P of aqueous ions in the solubility test generally decreased as the initial [Pi] condition increased, the [Ca^{2+}] varied very little; the change in [P_i] across each test was responsible for the changing Ca/P. Therefore, comparing the solubility [P_i] (in yellow) with the wt % CO_3^{2-} (in green) in Table 5.11 below, it was interesting to note that as the wt % CO_3^{2-} decreased, the solubility [P_i] increased. Further, the wt % CO_3^{2-} (save the 7 mM P_i sample) was found to be significantly different when analyzed using one-way ANOVA. One explanation for this (unseeded tests only) may be that the CO_3^{2-} dissolved preferentially over that of P_i. Then as the wt % CO_3^{2-} decreased, it was possible for more P_i to dissolve. This is because in bone-like apatite, CO_3^{2-} ions substitute into P_i lattice positions, which adds strain to the crystal lattice. Future work may be conducted to test this hypothesis by measuring the wt % of aqueous CO_3^{2-} during the solubility tests.

Test	[Ca] mMol/L	[Pi] mMol/L	Solubility Ca/P	wt%CO3
5	0.16±0.02	0.16±0.02	1.03±0.15	1.95±0.08
10	0.18±0.03	0.23±0.04	0.79±0.04	1.21±0.43
20	0.18±0.02	0.51±0.12	0.38±0.14	1.13±0.14
30	0.17±0.06	0.45±0.09	0.39±0.17	1.10±0.04
7	**0.21±0.01**	**0.22±0.01**	**0.97±0.05**	**2.59±0.09**

Table 5.11: Solubility of products and corresponding wt% CO_3

The presence of CO_3^{2-} substitution is important for several reasons. As stated previously, it is known to increase the solubility of apatite minerals. It is also leads to the formation of an apatite that is more chemically similar to the raw PR used for fertilizer. Deymier also recently been proved that "*carbonate substitution is sufficient to drive the formation of bone-like crystallites.*" (Deymier (2017). This provides further support for the classification of the precipitate formed as a bone-like apatite.

5.2.6 Conclusions

Based on the several characterization techniques used above, it was confirmed that the experimental methods tested were suitable for creating the conditions to precipitate a bone-like, carbonate apatite. This precipitate has the potential to be used as the raw material to be processed into phosphorus fertilizer, which will be an important commodity in ensuring global food security. For this reason, the next section explores how the process could be adapted into a reactor, and characterizes the precipitate to confirm that any changes to the experimental conditions do not adversely affect the final product.

5.3 Category C: Application

5.3.1 CSTR: Change in Ion Concentrations

The reactor was run three times at varying conditions. Knowing the initial $[Ca^{2+}]$ and $[P_i]$ of the inlet streams and the reactor, as well as the inlet and outlet flow rates, a theoretical mass balance was calculated. The purpose of this mass balance was to estimate the effect of dilution of

the Ca^{2+} and P_i streams; theoretically, if the observed [Ca^{2+}] and [P_i] were *less* than predicted, this should indicate that product was precipitating out of solution.

In all reactor tests to date, it was observed that the liquid level in the reactor vessel dropped over time. To correct this, the outlet flow rate was lowered slightly until a decrease was no longer observed. However, because of the relatively low flow rates used during these first tests, it is difficult to estimate the resulting magnitude of the error in the predicated versus actual values. For this reason, differences between the theoretical mass balance and the experimental concentrations can also be attributed to error in the flow rates. Further work must be undertaken to fine tune the reactor set-up and pump settings.

Reactor Run	Initial Reactor Condition			Inlet Values		
	[Ca2+] mMol/L	[Pi] mMol/L	Ca/P	[Ca2+] mMol/min	[Pi] mMol/min	Ca/P
1	0.668	6.774	0.099	0.077	0.068	1.13
2	0.724	4.365	0.166	0.050	0.039	1.29
3	0.310	1.362	0.228	0.038	0.018	2.16

Table 5.12: Initial CSTR reactor conditions and inlet values

The starting conditions for all three reactor runs are summarized in Table 5.12. The initial solution in the reactor was a saturated solution of Ca^{2+} and Pi. This was assumed because the supernatant of the previous run was recycled for use as the reactor starting solution for each iteration. The solution used for the first run was the solution used to prepare the initial seeding dose. The inlet ratio of Ca/P was greater than 1, which would gradually increase the supersaturation state of the reactor solution. The changes in concentration and the resulting Ca x P are illustrated in Figures 5.12.A-C.

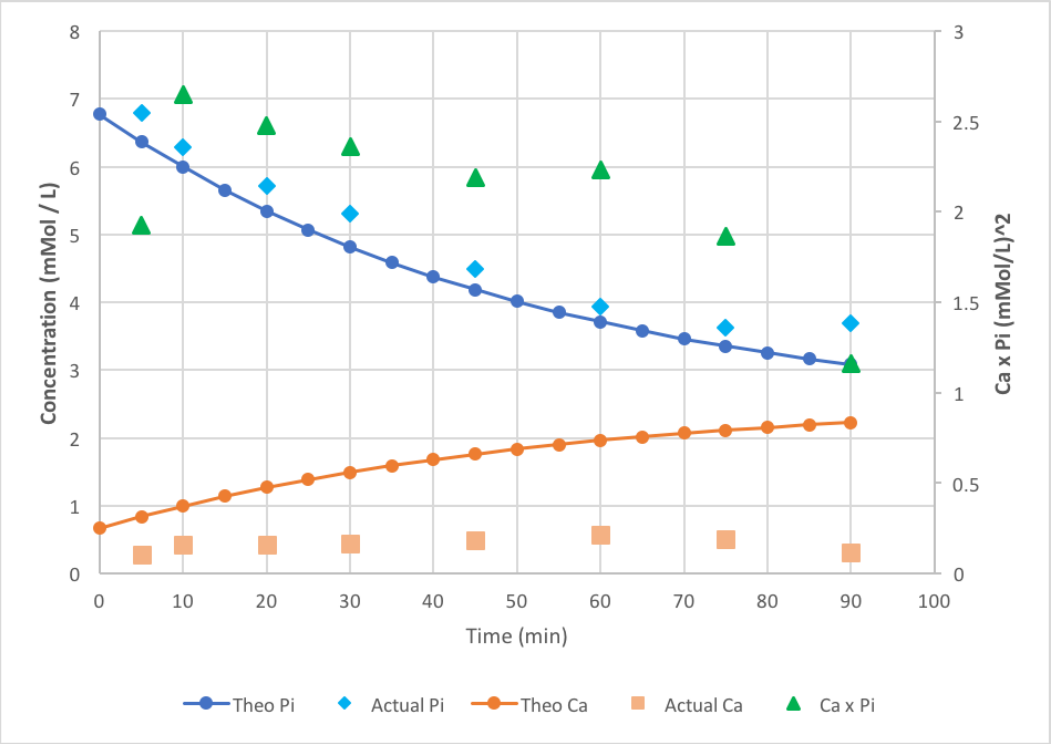

Figure 5.12A: Reactor Run 1 theoretical and experimental [Ca^{2+}] and [P_i] values

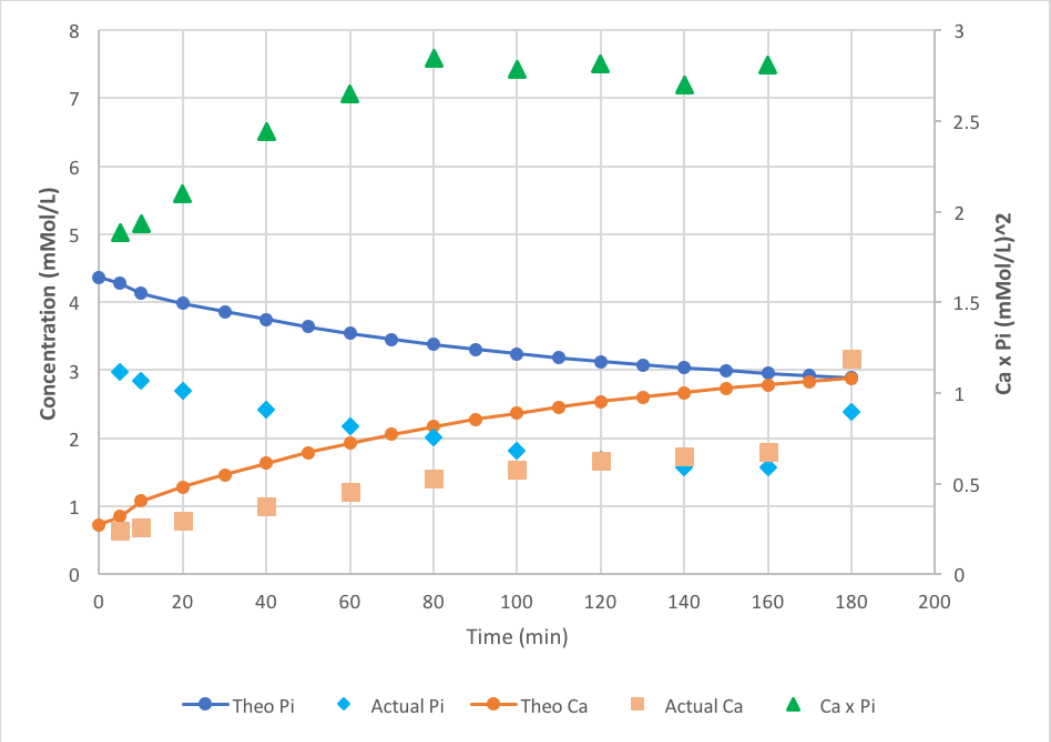

Figure 5.12B: Reactor Run 2 theoretical and experimental [Ca^{2+}] and [P_i] values

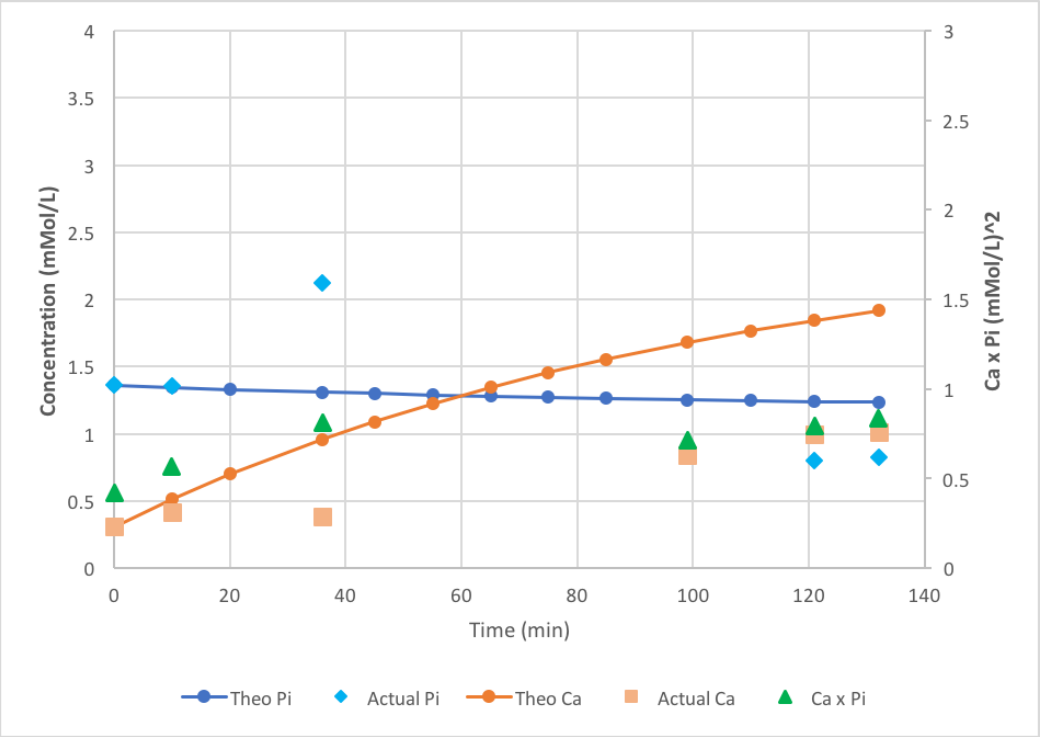

Figure 5.12C: Reactor Run 3 theoretical and experimental [Ca^{2+}] and [P_i] values

Run 1 was not run long enough to establish a steady-state Ca x P value. However, Runs 2 and 3 approached steady Ca x P values of 2.7 and 0.8 respectively.

5.3.2 CSTR Product characterization

A slurry of the precipitate was retrieved from the reactor and from the settling flask after each run. The product from each iteration was used as the seed material for the subsequent reactor run. Because of this, not all of the products from each trial were fully characterized.

Once the slurry was collected from the first two runs, a sample of approximately 5 mL was withdrawn. This sample was placed in a small watch glass, and dried overnight in the fumehood at ambient temperature and pressure. These air-dried samples were characterized by SEM and Raman spectroscopy.

The product for the third reactor run was vacuum filtered and dried overnight in the vacuum oven. This dried sample was then characterized by SEM, Raman spectroscopy, XRD,

and carbon coulometry. There was not sufficient product collected to analyze the product from the first two runs by XRD and coulometry.

5.3.2.1 SEM

Table 5.13 on the next page provides a visual overview of the products retrieved from the reactor and from the settling flask from each of the three runs. The micrographs suggest a similar morphology as the products formed during the batch tests.

It is interesting to note that although the products from each run were used to seed the following run, the overall size of the solids does not appear to increase. That is to say, there is not an obvious trend of secondary heterogeneous nucleation on products from one run to the next. However, it must be acknowledged that the micrograph sample size is very small as compared to the total population of solids formed. Conducting settling tests on the products would serve to confirm the size of the particles, and possibly identify if there is a trend toward an increase in size as precipitate is recycled as seed. Alternately, such a test may suggest whether there is a maximize size that can be reached.

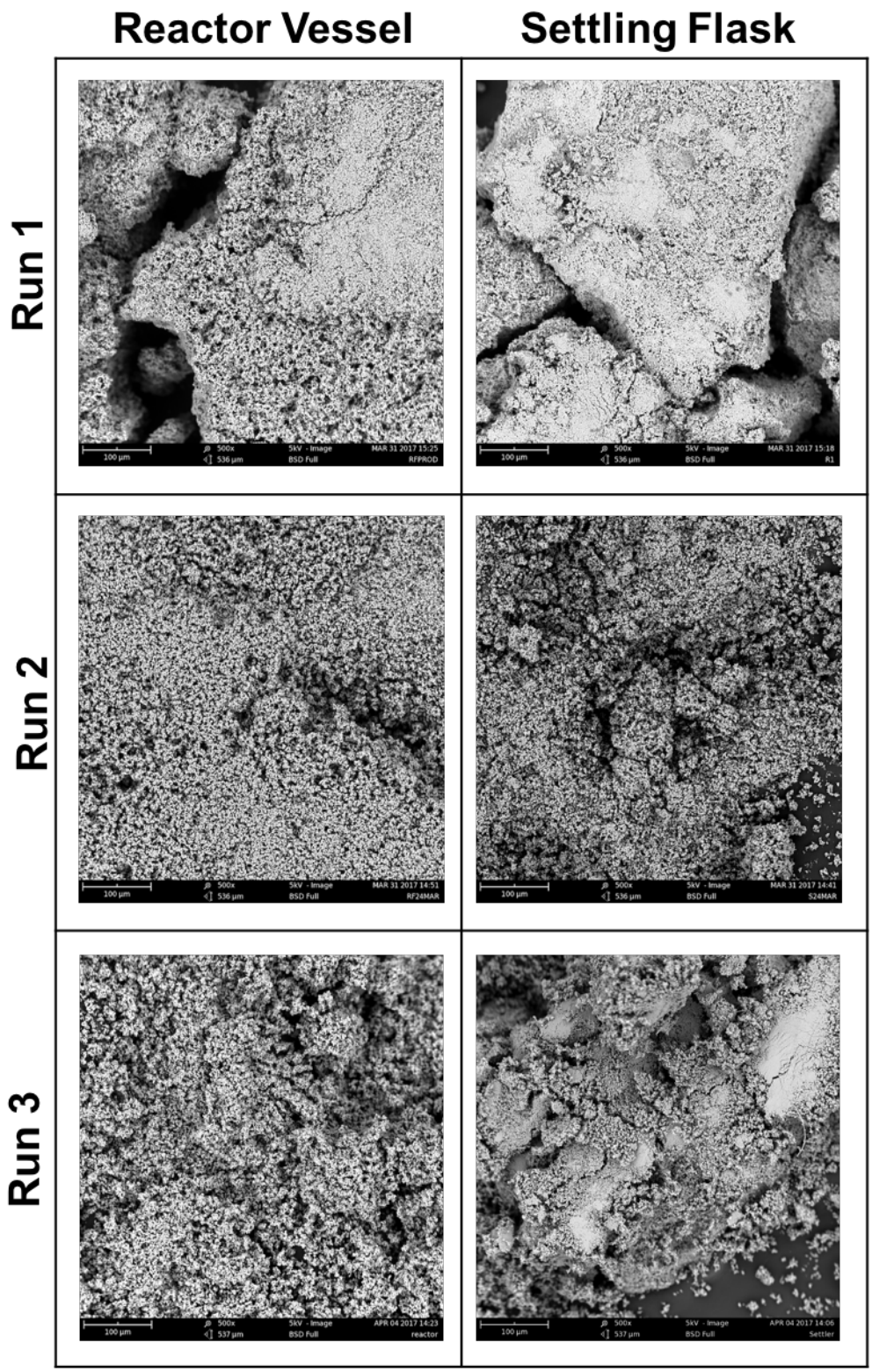

Table 5.13 SEM summary of CSTR reactor products at 500x magnification

5.3.2.2 Raman Spectroscopy

The reactor product and the settling flask product from the final reactor test were compared with bone and Seeded Product 7 using Raman spectroscopy. As anticipated, the shifts were corresponded to apatite were observed: v_1PO_4 shift at 960 cm^{-1}, and a shift at 1070 cm^{-1} (though less pronounced) corresponding to the v_1CO_3 shift due to substitution.

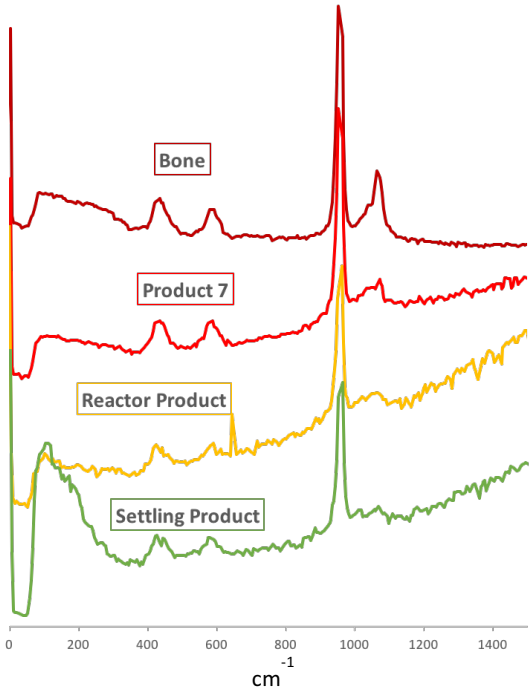

Figure 5.13: Raman spectra of reactor and settling flask precipitate.
Bone and seeded product 7 included for comparison.

5.3.2.3 Powder XRD

Only the settling flask product of the final reactor run was tested using XRD, and it was compared to bone and Product 7. Again, the peaks corresponded well with those associated with bone-like apatite.

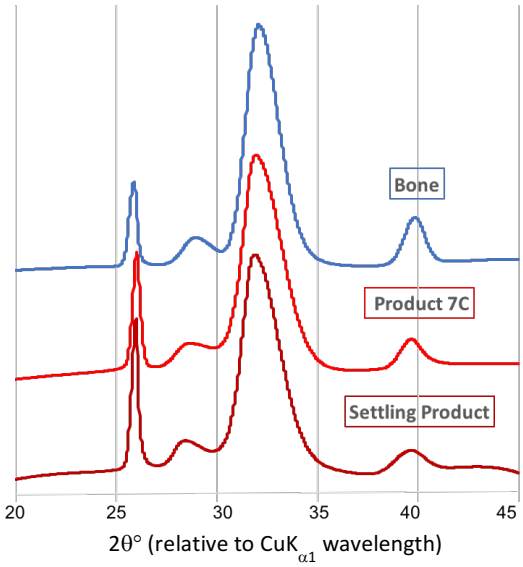

Figure 5.14: Powder XRD spectra of settling flask precipitate.
Bone and seeded product 7 included for comparison

5.3.2.4 Carbon coulometry

The reactor product showed the highest wt % CO_3^{2-} of all of the samples (both seeded and unseeded) tested. There are two factors that may have contributed to this result. First, a steady stream of fresh (Ca^{2+} + CO_3^{2-}) solution flowed continuously into the reactor. By slowly adding this solution, as opposed to adding it all at once in the batch tests, it may have had the dual effect of maintaining a lower saturation with respect to CO_3^{2-}, in addition to increasing the potential for interactions leading to precipitation between aqueous CO_3^{2-} and other ions and solids in the saturated solution. Another possible explanation is that the reactor tests used limestone as the Ca^{2+} source; the composition of this solution may have yielded a different [CO_3^{2-}] than with pure calcite.

The finding that the product from the settler had a lower wt % CO_3^{2-} warrants comment. It suggests that the solution that flowed into the settler had a lower [CO_3^{2-}]. There are three different effects that may have contributed to this. First, the initial [CO_3^{2-}] was very low, and increased slowly as fresh solution flowed into it. The solution flowing out of the reactor and into the settler would have increased incrementally at a slower rate. Second, the solution travelled from the reactor to the settler through approximately 1 m of tubing, moved by a peristaltic pump. This may have had an effect. Finally, the settler consisted of an 1800 mL Erlenmeyer flask, which was easily covered and set aside on completion of the test. The reactor vessel had the

same volume but a much larger mouth, and was not well sealed. This means that it would have been able to interact more with the atmosphere, possibly exchanging more CO_2 (g) with the air as the corresponding ions were depleted. In order to better assess this effect, future work will need to measure the aqueous carbonate content of the reaction solutions.

Test	wt% CO3
Reactor Product	2.97±0.05
Settler Product	1.91±0.01
7	2.59±0.09

Table 5.14: Weight percent of CO_3^{2-} within reactor and settling flask precipitate. Seeded product 7 included for comparison.

5.4 Summary

Upon confirming a method to increase the $[Ca^{2+}]$ in a saturated solution of $CaCO_3$ (s) in water, batch tests were successfully conducted to precipitate calcium phosphate. Batch tests seeded with either deproteinized bone mineral or with a spontaneous precipitate were conducted, and both reduced the $[Ca^{2+}]$ and $[P_i]$ in the solution. However, the recycled spontaneous precipitate was most effective seed material in terms of removing P_i from solution. Greatest removal of P occurred when the initial Ca/P ratio of the reactants in solution was 1.29; this occurred when recycled precipitate was used. Characterization of precipitate indicates that it is a poorly crystalline carbonate apatite, possibly a bone-like apatite. The initial reactor configuration was tested, and the resulting products resemble those formed during the batch tests. The only exception to this is that the wt % CO_3^{2-} of products formed within the reactor was higher than that of all other products tested.

5.5 References

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CHAPTER 6

NEXT STEPS: FROM THEORY TO PRACTICE

The initial hypothesis, that it would be possible to form a precipitate that resembled carbonate apatite from municipal wastewater, limestone, and CO_2 (g), has been proven. The real work of this project still lies ahead. The lab group's overarching goal is to promote the recycling of phosphorus and nutrients from wastewater. The actual method used to achieve this aim is less important. However, based on the low adoption rates of the technology that currently exists, it appears that sufficient financial, regulatory, and social incentives to adopt it do not yet exist.

This chapter will examine some of these barriers, and discuss how a Canadian platform could best be positioned to set the conditions to encourage increased phosphorus – and nutrient – recycling.

6.1 Recycling: Canada, and the EU

Before looking at phosphorus recycling, first consider rates of recycling of household waste. The EU has some of the most aggressive recycling targets in the world, with several countries dumping virtually no waste into landfills. The average rate of dumping into landfills has decreased from 64% in 1995 to 47% in 2004 (Figure 11), and most recently 28% in 2014.

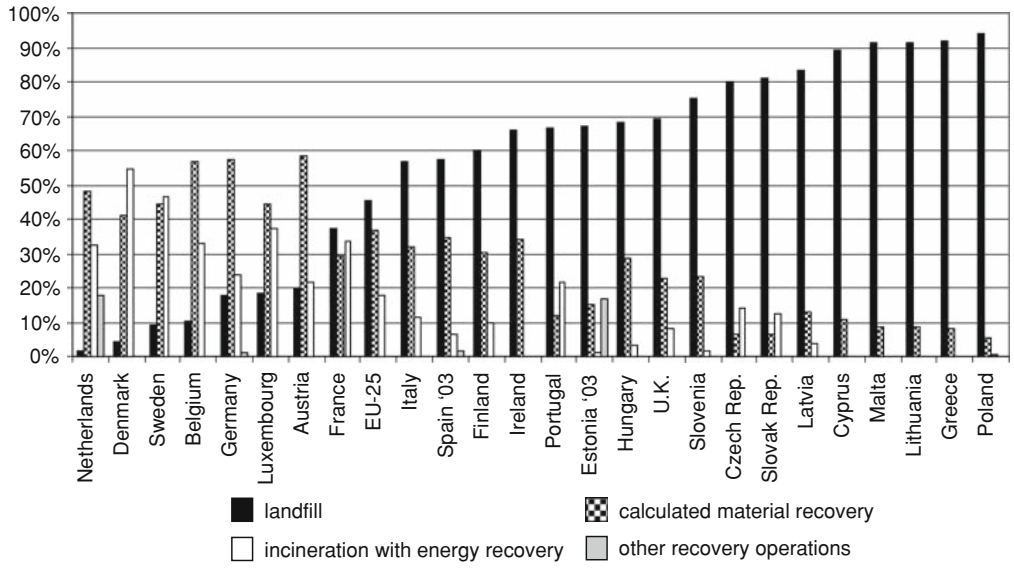

Figure 6.1. Landfill, incineration and recovery of waste in EU-25 countries in 2004. Diversion rates have continued to improve over the last decade (Mazzanti 2009).

In contrast, Canada only sees 33% of its municipal waste diverted to recycling or compost. It is the worst ranked out of 17 OECD countries for per capita waste generated; in 2008, each Canadian generated 777 kg, or 25% more municipal waste per capita than either Germany or the Netherlands.

The difference in rates of recycling between Canada and these countries is a good indication of the general attitudes toward and acceptance of recycling. Thus, the relatively low rate of diversion suggests that Canada will have a more difficult time convincing its citizens to invest tax dollars on improving infrastructure for even more recycling. This kind of shift in thinking takes time based on an individual's values and beliefs (Moser 2010).

While the large-scale recycling of phosphorus would occur at the municipal as opposed to the individual level, such a project would require political support. The actions of individuals are also important; households can divert wasted or spoiled food to municipal composting facilities, or lobby their local officials for such a service. Recent studies have shown that 'nudges' toward reminding individuals to do something based on normative values (i.e. "9/10 people in your neighbourhood compost food in the green bin") are far more effective than those based on fear (The Economist 2012). Due to the somewhat nebulous and abstract nature of the long-term phosphorus problem, it may also help to look to the psychology of climate change acceptance and adaptation for lessons learned. Unfortunately, the influence of policy, psychology, and technology development and adoption is out of the scope of this thesis and will be included in future work.

6.2 Regulations and policy tools

As discussed in Section 2.2.5, the current regulatory framework recognizes that bio-solids from municipal waste are inherently valuable. The rules surrounding the reuse of waste permit such recycling, provided that the products meet the sanitary standards established by the Canadian Food Inspection Agency (CCME 2010, 2012).

However, being *allowed* to do something is not the same as actively *encouraging* it through the use of incentives.

The responsibilities and hesitance of players within industry and government were introduced in Section 2.3.4. Due to the scope of the problem and its lack of immediate urgency, it does not fit tidily into any one government portfolio. There is little incentive for industry to

invest in developing such a technology (other than Ostara), as the cost of imported phosphorus for fertilizer is still relatively low. A detailed economic analysis has yet to be completed, comparing the cost of imported phosphate rock to the potential cost associated with the recycled apatite material, and is included in future work.

Given that industry has not taken a lead role in developing and promoting this technology, there are several policy tools that each level of government can employ. Regulations, research funding, and tax incentives are the most common tools at the federal and provincial levels. For instance, general effluent standards are identified in the federal Fisheries Act, however phosphorus levels are only set at the provincial level. An effort to harmonize these standards between provinces could be undertaken. Tax incentives or subsidies to implement recycling technology could be put in place to help lower the financial barrier and associated risk to adopting a new technology. However, the actual work of enforcing or taking advantage of these tools lies at the municipal level.

Within municipalities, the 'regulation' lever is limited as the city is typically the end-user of large-scale water treatment technology. However, municipalities are often able to build strong relationships with academic institutions, to enable the testing and later adoption of a new technology. For instance, when BNR technology was first introduced, UBC collaborated with the city of Vancouver and Kelowna to test the method and implement it at a large scale (Mavinic 2017). With these relationships already in place, Vancouver approached that same research group to help mitigate undesired struvite scaling in pipes several years later (ibid). From this project, Ostara was founded. This case study illustrates that it is in both the municipality and the university's best interest to collaborate, and that this is already taking place with respect to phosphorus cycling in larger urban centres such as Vancouver and Montreal (Metson 2015). The gap remains for smaller municipalities that do not have the proximity to an academic institution available to collaborate easily. This is where a network to link municipalities with these resources could potentially have the greatest effect.

6.3 Canadian Nutrient Platform

A Canadian Nutrient Platform (CNP) could help to connect interest groups with similarly aligned goals, and thus present a stronger front to the government when lobbying for new or improved incentives regarding nutrient recycling. By keeping each other informed of successes

and challenges, all of the groups benefit from the experience and can more efficiently streamline efforts. In many cases, it will be easier to approach the provincial level first (i.e. Ontario has already adopted the Waste-Free Act), to focus on more tangible local issues, and then to rally several provincial efforts to raise the topic to the federal level. This is because at the federal level, the reuse of biosolids is already permitted; there is not yet political will to take further action (i.e. use money and resources). Highlighting initiatives that are already underway at the provincial level, and examining how these efforts could make further positive gains in the best interest of the entire country, would serve to raise the profile of this problem and put it on the agenda.

Furthermore, bringing together these many different groups and efforts into a single, easily understood package may help to frame it as a problem that falls within the mandate of a given department (likely Agriculture and Agrifoods Canada (AAFC) or Environment and Climate Change Canada (ECCC)). A single platform both gives the effort a greater sense of legitimacy and organization, while at the same time decreasing the work required by the government to understand the problem and take action. Governments tend to be responsive to what catches the interest of the public consciousness, meaning that public awareness influences the political will to put this problem on the agenda. As such, efforts to lobby the government for change may go unheeded until the demand for change comes from outside those who perceived as being very close to the problem. A productive way to proceed in such an environment would be for the CNP to build a relationship with the departments of interest. In this way, the CNP would be in a position to recognize when an opportunity presents itself, as well as have a line of communication to help to suggest effective interventions by presenting information on efforts that have succeeded or failed throughout the country.

Phosphorus removal from municipal waste water takes place at the municipal level; therefore that is where phosphorus recycling implementation efforts should be aimed. Convincing a city to allocate time and resources on any new technology is not an easy task. For instance, in the case of Berlin, phosphorus recycling technology was only adopted after it was proven that it would significantly reduce de-watering costs (Kabbe, personal communication). Thus, emphasis should be placed on the immediate benefit to the municipality as opposed to the longer term global benefit.

The difficulty is in contacting and communicating with all of the municipalities in a meaningful way, and that is where a Canadian Nutrient Platform (CNP) could play an effective role. For instance, the Canadian Water Network initiated the Canadian Municipal Wastewater Consortium (CMWC) in 2014. One of the CMWC's goals is to increase the beneficial use of bio-solids. This organization is already involved with several municipalities, so the CNP could leverage this network and help to bridge the gap between the CMWC and other interest groups or academic institutions.

Two works in the literature stand out as frameworks to shape how nutrient recycling is defined and awareness promoted. Cordell and Neset's 2014 paper identified a means to define phosphorus (and thus food) vulnerability within a national and reginal context. This is important for Canada because the phosphorus stressors vary widely from region to region; urban density (i.e. WWTP capacity), arable farmland (i.e. agricultural run-off), and seasonal weather patterns must all be considered in a regional context when considering how to define and approach the reuse of nutrients; a national 'phosphorus flow' study would be of less value then a series of regional studies.

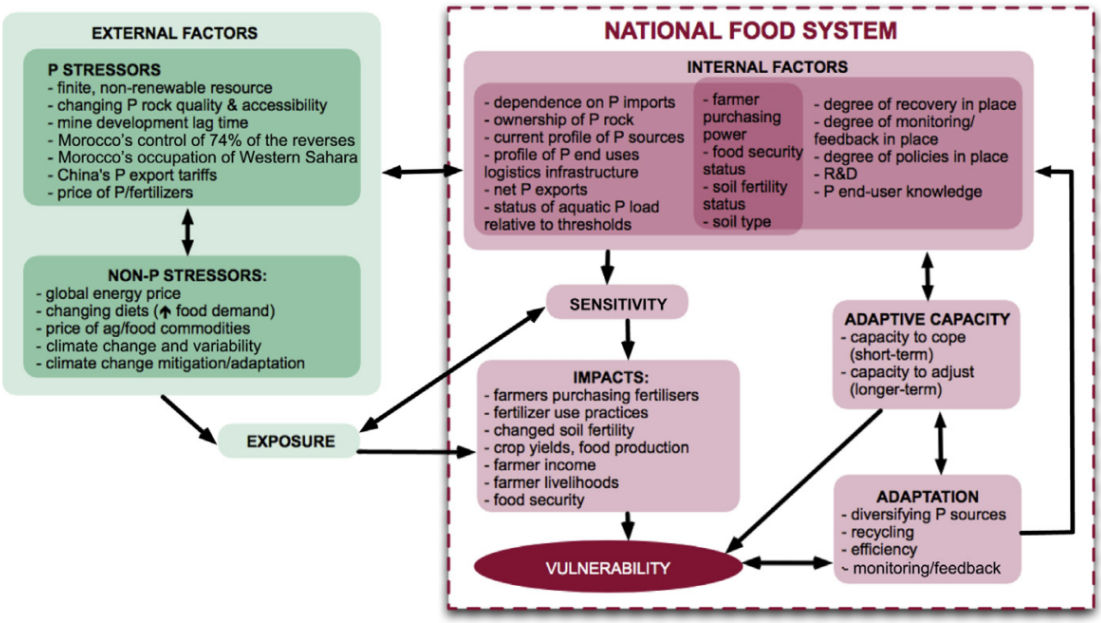

Figure 6.2: Links between drivers influencing vulnerability in the food system (Cordell 2014)

Ulrich *et al.*'s 2016 paper is valuable as it specifically identifies the challenges and progress in advocating for improved phosphorus recycling and eutrophication control, using Lake Winnipeg as a case study. One of the key take aways from this paper was identifying that *"…the impetus for change appears to be much stronger in the non-government sectors than within the jurisdictional representation…"* This statement lends weight to the idea that the CNP should position itself as a leader in bringing together the many players in this problem, as opposed to pinning all hopes on lobbying the government to take action.

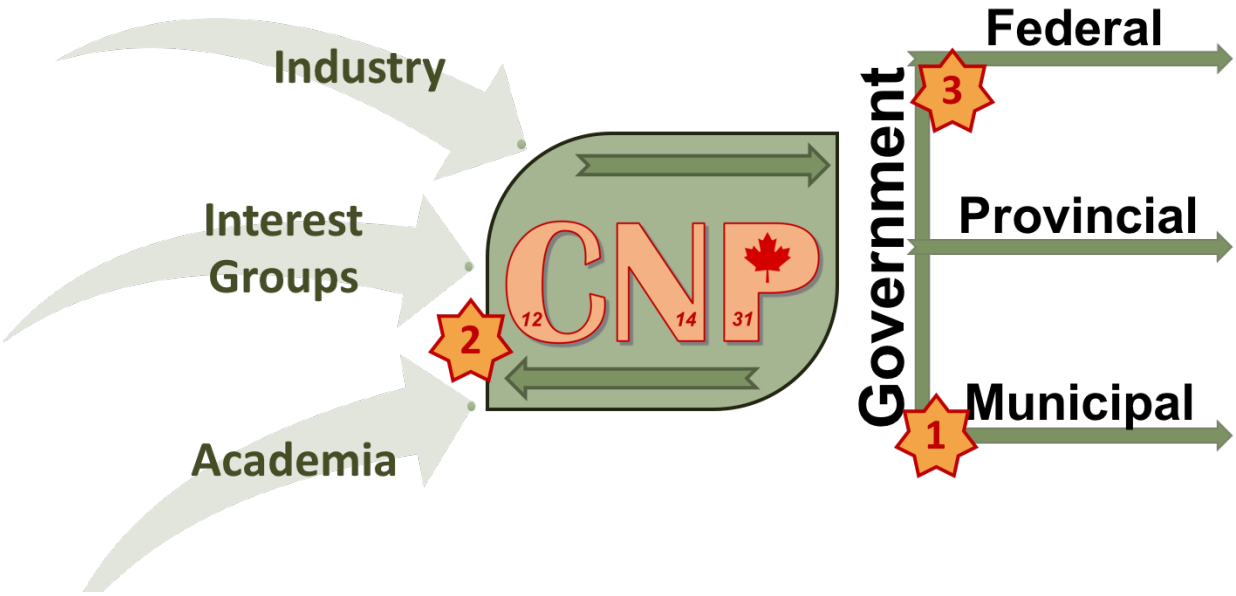

Figure 6.3: The Canadian Nutrient Platform (CNP) could serve to connect disparate groups across industry, academia, interest groups, and government

The lines of effort for the CNP are summarized in Figure 6.3 above:

1. Connect municipalities with academia or other groups that may have a technology that would benefit their local treatment process, by decreasing operating costs, enabling the production of a valuable material, or both. This will enable a greater range of technical solutions, as well as increase awareness.
2. Form a network between interest groups, academia, and industry partners with similar goals and overlapping interests. This will help to ensure that the efforts of these many different groups support each other in a coherent way (or at the very least, do not undermine and/or duplicate each other in the pursuit of the same goal).

3. Provide context and information to the many levels of government. Build this relationship so that as opportunities arise, the CNP is poised (and trusted) to suggest effective interventions by presenting information on what efforts have succeeded or failed throughout the country.

6.4 Other Applications

The recycling of phosphorus - and nutrients in general - has several other potential applications. Any instance in which humans live in an area where food is difficult to grow, the treatment of waste from food, humans, and animals should be considered. This could potentially be a niche for Canada to embrace, first by testing solutions in our North, and then applying the technology and experience to other regions.

During the 2017 Faculty of Engineering Design Day, an entire category was devoted to hydroponics, specifically with a view to enabling farming in space-constrained, soil-poor areas, such as refugee camps. There could very easily be synergies between waste recovery and food production in this context. The same concepts could potentially be applied to Canada's distant North, where the cost of flying food in to remote areas makes fresh produce prohibitively expensive (Judd 2015). Significant progress is being made toward improving farming options in the Northwest Territories through the construction of greenhouses (Hein 2016). However, with an average of only 3 months that are habitually ice-free (*for now*), this complicates not only the growing season but also limits waste treatment options (Krumhansl 2014). Despite these difficulties, Canada's North could be good test case for a circular nutrient economy to help to alleviate local food security concerns.

The International Space Station continues to recycle its water during its many years of operation (Hollingham 2015). Urine contains the majority of phosphorus that is excreted (Krahenbuhl 2016), so there is potential for it to be a valuable and relatively accessible source of nutrients for cultivation in space. This could be of particular interest when considering the possibility of longer distance space flights, such as a potential manned mission to Mars (NASA 2017).

6.5 Conclusion

The CNP is a new idea that was only recently launched, and there are several considerations to make when deciding how it should position itself for greatest effect. It will be important to have an understanding of the public perception of phosphorus (and nutrient) recycling, create a network with many interested stakeholders, and build relationships with government players. This outlook chapter frames some of the ways in which this can be achieved.

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CHAPTER 7

CONCLUSION AND FUTURE WORK

7.1 Conclusion

The six objectives, grouped into three categories, were successfully met. As the reader may recall, these objectives were:

CATEGORY A: *Process Variables*

1. Supersaturation
2. Solubility of $CaCO_3$
3. Seeding

CATEGORY B: *Products*

4. Characterization

CATEGORY C: *Application*

5. Reactor
6. Policy

The method to increase the $[Ca^{2+}]$ in a saturated solution of $CaCO_3$ (s) in water was confirmed, leading to successful batch tests of calcium phosphate precipitation. Batch tests seeded with either deproteinized bone mineral or with a spontaneous precipitate were conducted, and both reduced the $[Ca^{2+}]$ and $[P_i]$ in the solution. However, the recycled spontaneous precipitate was the most effective seed material in terms of removing P_i from solution. The greatest removal of P_i occurred when the initial Ca/P ratio of the reactants in solution was approximately 1.29, when recycled precipitate was used as seed. Characterization of precipitate indicates that it is a poorly crystalline carbonate apatite, possibly a bone-like apatite.

The initial reactor configuration was tested, and the resulting products resemble those formed during the batch tests. The only exception to this is that the weight percent of carbonate within products precipitated within the reactor was higher than that of all other products tested. An analysis of the current network of phosphorus (and nutrient) stakeholders has been conducted, and an initial action plan shared with the other members of the Canadian Nutrient Platform.

7.2 Future Work

7.2.1. Honing the current method

Throughout the study, shortcomings in the procedure and characterization methods were identified and, if not possible to correct, they were noted for future work. Below is a summary of those points, in the form of comments or research questions:

a. Desired product. Carbonate apatite, the raw material used to produce phosphorus fertilizer, requires treatment with H_2SO_4 to convert it into H_3PO_4. Can human waste be treated to form phosphoric acid directly (instead of first forming apatite) in a cost effective way?

b. Seawater medium. Carbonate apatite forms naturally in an ocean environment. Would employing seawater (as opposed to tap or distilled water) improve the method?

c. Control of pH. The role of pH should be explored in greater detail, such as looking at whether increasing the pH of the solution will also lead to a lower Ca x P value, and thus drive a greater decrease of $[Ca^{2+}]$ and/or $[P_i]$ from solution.

d. Size of precipitate and drying. It is possible that precipitates were finer while in solution, but then as the drying process evaporated water, this led to another crystallization mechanism; it is recommended that future work include settling tests before drying, and rapid drying with an organic solvent.

e. Samples during precipitation. Further work will need to be completed to better understand the mechanism by which the precipitate is being formed, by collecting and analyzing samples of the solid precipitate throughout the experiment, as opposed to characterization of only the final product.

f. Solubility of precipitate and aqueous CO_3. It was not possible to confirm why the precipitates yielded different $[P_i]$ when dissolved. One explanation for this (unseeded

tests only) may be that the CO_3^{2-} dissolved preferentially over that P_i. Then as the weight percent of CO_3^{2-} decreased, it was possible for more P_i to dissolve. Future work may be conducted to test this hypothesis by measuring the weight percent of aqueous CO_3^{2-} during the solubility tests.

g. CSTR Reactor. The peristaltic pumps used for the reactor require more detailed calibration, as the liquid level in the reactor was observed to decrease over time. Methods to recycle the stream and further decrease the steady state reactor [P_i] will also need to be explored to maximize the unit's efficiency, and optimize residence time.

h. Carbonate content and atmosphere. Solids formed in the reactor had a greater surface area exposed to the atmosphere, possibly exchanging more CO_2 (g) with the air as the corresponding ions were depleted. In order to better assess this effect, future work will need to measure the aqueous carbonate content of the reaction solutions.

i. Economic assessment. Municipalities often do not have robust budgets to allow for experimentation with untested methods of testing wastewater. Having a sound assessment of the cost of removing phosphorus from wastewater, and comparing this to the potential cost of implementing a new method would serve to decrease the sense of risk associated with trying something new. An additional assessment of the 'true cost' of imported phosphate rock would further help to identify a target operating cost at which it becomes more economic to recycle than to import the raw material. Assistant Professor David Large, Director of the Engineering Management Program at the Tefler School has agreed to enable offering such a study as a Directed Studies course to the students in the Engineering Management program.

j. Climate change case study. Convincing the public and government that climate change must be taken seriously is an ongoing campaign. There are most likely valuable lessons that have been learned – most importantly "tactics to avoid" – in terms of raising awareness and encouraging action. A thorough study of these successes and failures would be a valuable asset to the cause of nutrient recycling.

7.2.2 Scaling up

To date, only a synthetic P_i solution has been tested, and it successfully proved that the laws of physics and chemistry permitted the precipitation of a bone-like, carbonate apatite. The next step will involve inoculating the synthetic solution with material from the ROPEC to assess the effect of the other materials present in the stream, and on the precipitate. Other projects within the research group are examining means to extract P_i from the bacteria within the aerobic sludge to maximize the available P_i. The goal is to use a stream directly from the ROPEC to react with the $CaCO_3$ solution, and test this with the laboratory-scale CSTR process.

Another challenge will be preparing sufficient $CaCO_3$ solution to treat large volumes of waste stream. As alluded to in Chapter 5, it will likely be necessary to explore means to recycle the $CaCO_3$ stream and re-treat with CO_2 (g) to optimize the precipitation of carbonate apatite.

7.2.3 Science, meet society

The problem of phosphorus availability is not urgent…. *until it is*. Canadians have the luxury of massive agricultural and forest land, compared with a relatively small population. This means that the "phosphorus problem" will become a crisis in virtually every other country in the world before Canada. This is not, however, a reason to sit back and wait for those who *need* to care more to find a solution – it is an opportunity. We have the privilege of time, money, and resources to work toward a solution that can economically help to solve this problem, and contribute to global food security for generations to come.

The curse of living in a country so rich in resources is that we take them for granted. It can be difficult to convince Canadians that investing in recycling – of nutrients, of resources, of energy – is worthwhile, when we are surrounded by clean, healthy air, forests, food, and water. Positive steps are being made, such as the Waste-Free Ontario Act, but it will require a generation of effort for these measures to be accepted into the public psyche. Groups such as the fledgling Canadian Nutrient Platform (CNP) are important to help make these measures stick, and to harness the energy and efforts of various groups toward a common goal. I am proud to say that this project in some small way helped to kick-start the CNP, but there is much work ahead to ensure that it maintains momentum.

Annex A

Safety Precautions

Normal laboratory protocols of wearing nitrile gloves, lab coat, and safety glasses were adhered to at all times.

The majority of or reactants used were not harmful and required no additional measures beyond normal laboratory safety protocols. There were three exceptions in which additional measures were applied:

1. O-Cresolphthalein-complexone. Used to prepare the colorimetric solution for calcium measurements, cresolphthalein is known to be very toxic. Damp paper towel was laid down on the bench and the mass balance when this was being measured to ensure that any spill of this reactant was not able to spread.
2. Sludge samples from ROPEC. Sludge was kept in the fumehood, and any surfaces that came into contact with the container were bleached afterwards.
3. CO_2 (g) treatment. When $CaCO_3$ solutions were being prepared in the reactor, care was taken to ensure the reactor was well sealed and the gas outlet tube was evacuated into the fumehood. A minimum of two people were always in the lab when CO_2 treatment took place.

ANNEX B

Appendix B1 – Precipitation of apatite

Precipitation of calcium-phosphate apatite

Overview:

Equal volumes of a saturated $CaCO_3$ solution and a P_i solution will be mixed. There will be 4 different concentrations of P_i, each of which will be reacted with the $CaCO_3$. Samples of the initial solutions (before mixing) will be collected, and additional samples will be collected periodically as the reaction proceeds. This will allow us to determine how the concentrations of Ca^{2+} and P_i change as the reaction proceeds. The pH of the resulting solution will be monitored as well.

Preparation:

1. Collect clean glassware:
    a. 4x 500 mL reaction vessels
    b. 2x 250 mL volumetric flasks
    c. 1x 50 mL beaker for pH probe rinse
    d. 1x 50 mL beaker for ddH_2O to dilute samples
    e. 2x funnels to transfer solutions into volumetric flasks

2. Lay out equipment and other items needed:
    a. 1x stir plate
    b. pH meter (calibrate as per user manual)
    c. 4x large stir bars
    d. 12x 1.7mL sample vials
    e. 1x 1000 uL pipette
    f. 1x tape and Sharpie
    g. Parafilm

Reaction:

Repeat these steps for each of the different combinations of $[P_i]$ + $[Ca^{2+}]$ being used.

Take photos of experimental set-up and reaction flasks throughout procedure – future ref to recall details regarding the protocol used, as well as images for poster.

Day 1:

1. Measure the pH of the P_i solution.
2. Collect 1000 uL of P_i and label vial.

3. Measure 250 mL P_i and pour into reaction flask. Add stir bar. If seed is being used, add at this time.
4. Measure pH of the Ca solution.
5. Collect as much of the Ca solution as needed to fill the vial, and label. Seal vial with parafilm if not being tested immediately.
6. Measure 250 mL Ca in volumetric flask.
7. Place reaction flask onto stir plate, and initiate stirring.
8. Carefully pour Ca solution into the reaction flask. Note the time.
9. Put the pH probe into the solution.
10. Monitor pH; once seems to be stable (approximately 10 minutes), remove from stir plate.
11. Prepare vial to take a sample, by labelling and filling with 500 uL ddH_2O.
12. Approximately 1 hour after initiation of reaction, measure pH again and collect 500 uL of sample.
13. Cover flask tightly with parafilm. Set aside until the following day. Note that ideally flask would be continuously stirred to improve Ca – Pi interaction, however stir plates heat up unexpectedly with lengthy use. Further, there were not sufficient stir plates for all of the concurrent repeats taking place. As such, all flasks were left to sit, with periodic 'swirling.' If repeating this experiment with fewer flasks (or better and more plentiful stir plates),suggest increasing the amount of stirring.

Day 2-4:

1. Swirl solutions in the morning. Allow solids to settle.
2. Measure pH.
3. Take sample and dilute with ddH_2O (typically 750 uL sample to 250 uL dd H_2O). This allows for a snapshot of the concentration, rather than creating a mini-reactor inside the vial.

Day 5:

1. Follow same steps as Days 2-4 to collect sample.
2. Weigh filter and place on vacuum filter funnel.
3. Wet the filter with ddH_2O and turn on vacuum pump.
4. Carefully pour sample over filter, swirling gently to maximize transfer of solids.
5. Rinse flask with ddH_2O to assist with transfer of product onto the filter.
6. Rinse product on filter with ddH_2O to reduce precipitation of CaCO3 onto surface of product.
7. While product vacuum drying, label and measure mass of a watch glass.
8. Transfer filter and product to watch glass
9. Place in vacuum oven, heat to about 40°C at pressure between 5-10 mm Hg.
10. Allow to dry overnight.
11. Allow watch plate to cool to room temperature.
12. Weigh total mass of watch glass, filter, and product; calculate mass of precipitate formed.
13. Gently scrape filter cake form filter using plastic scraper.
14. Repeat to your heart's content.
15. Using colorimetry, measure the [Ca] and [Pi] of each of solution samples collected.

ANNEX B

Appendix B2 – Use of AR 10 pH probe

Use of AR10 pH probe

This procedure is adapted from the AR10 User Manual. In cases where this procedure requires additional clarification, refer to the User Manual.

Set up:

1. Have ddH20 rinse bottle on hand, and a beaker to rinse the probe over. Label beaker.
2. Verify solution levels inside pH probe. If top up needed, squirt Ag/AgCl reference solution into the filling hole.
3. Leave blue filling hole cover open during pH readings.
4. Ensure buffer solutions are on hand (yellow for pH 7, red for pH 4).

Initiation:

1. Set "% Slope" to 0.
2. Set Temp.
3. Switch "Mode" to "pH."

Calibration:

1. The "2 pt. STANDARDIZE" method in the AR10 USER Manual is to be followed.
2. Knowing the ambient temperature, determine the temperature corrected pH for the buffer solutions, as per the label on the bottle.
3. Rinse pH probe and blot dry (do not wipe as this may leave a charge on the bulb).
4. Immerse into pH 7 buffer.
5. Once pH reading stable, turn "Standardize" dial until the temperature corrected pH is reached.
6. Remove probe, rinse and blot dry.
7. Immerse into pH 4 buffer.

8. Once pH reading stable, turn "% Slope" dial until the temperature corrected pH is reached.

9. Remove probe, rinse and blot dry. Ready for science!

Use of probe:

1. Probe must be calibrated before use each day.

2. Probe should not be left to dry, i.e. it is either in the solution being measured, or in the storage solution.

3. Rinse and blot dry before each time it measures a new solution.

4. When no longer needed, return probe to storage solution, seal with parafilm, and turn instrument back to standby mode.

ANNEX B

Appendix B3 – Colourimetry procedure

Colourimetry procedure

Method adapted from SOP 09 (Version 5) – Elemental Chemical Analysis (Grynpas).

Ladder:

1. Prepare standard solutions (2 mM Ca^{2+}, 5 mM* and 0.5 mM Pi), prepared as per SOP 09; $CaCl_2$ and Na_2HPO_4 used to make solutions.
2. Ca^{2+} is linear between 0-2 mM; Pi is linear between 0-5 mM. Ensure ladder is prepared within these values.
3. When measuring Ca^{2+}, use a total of 80 mL sample and add 240 uL of colourimetric CPC solution. When measuring Pi, use a total of 50 uL sample and add 250 mL colourimetric vanadomolybdate solution.

Preparing the unknown solutions:

Quick Eyeball Test

1. Prepare single column of standard ladder
2. Prepare several different dilutions of unknown sample (25/50/75/100)
3. Add colourimetric solution (i.e. CPC for Ca / A-B-C vanadomolybdate for Pi)
4. Identify which standard matches unknown solution most closely. Knowing the [Ca] of the standard and the dilution of the unknown, extrapolate the unknown's original concentration.
5. Take photo of plate for future reference; test with machine (same day) if possible.

Machine

1. Carefully carry sample plate in gloved hand to D202 using service stairs; ungloved hand opens doors.
2. Turn on machine and computer; do not place plate into machine as it opens and closes while warming up.
3. Open Gen 5 software. Select "Experiment" and either Ca or Pi.
4. Press the button with the hand holding a pipette along top toolbar; fill out the layout, using the correct number of repeats (usually 3 for standards and samples, sometimes more for blank).
5. Place plate into machine's tray holder
6. Press button with the green arrow pointing into a small box
7. Name file according to date, save to 'Jess' folder.

Excel

1. While the plate is being read, prepare the Excel file (saved onto desktop, one each for Ca and Pi). Open the "Layout" worksheet and select top left corner.
2. In the Gen 5 program, pull up the "Layout." Press the Excel icon next to the drop-down menu; this will transfer the "Layout" data into the active Excel sheet.
3. Once the plate read is complete (tray will be ejected), transfer the data into the Excel file:
    a. Select "Statistics" in Gen 5
    b. Ensure the active sheet in Excel corresponds to the wavelength in "Statistics"
    c. Select Blank, then Standard, then Sample, pressing the Excel icon after each one to transfer data.
4. Save to USB and to Experiments folder.

Analysis (*see Excel file for detailed comments*):

1. For Ca analysis, make a copy of the 570 Blank worksheet and re-label accordingly. For Pi analysis, use 420 Blank. The "Blank" statistics automatically subtract the blank absorbance value from the total absorbance.
2. Look over the Std Dev associated with outliers, and cross-reference with lab book to see if there was anything noted while preparing the plate which may have affected the sample within the associated well. Do not discard outliers at this point.

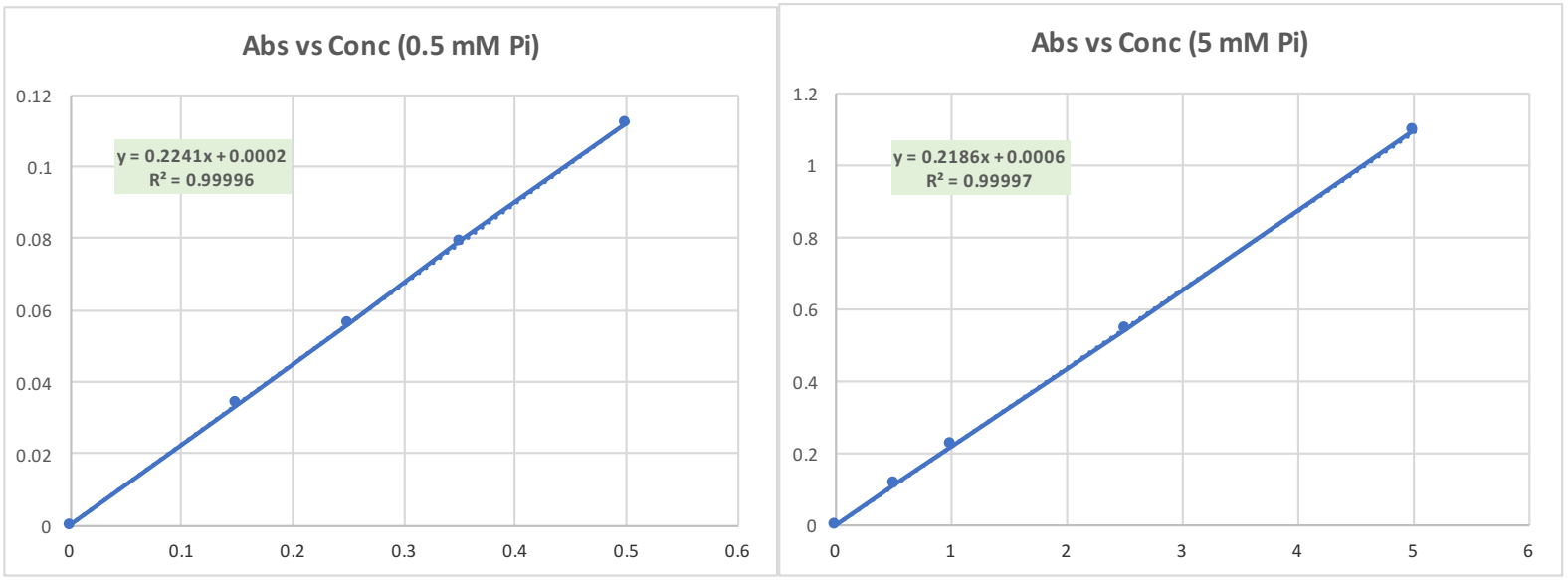
Standards curve

1. Plot a graph of concentration versus absorbance, using the values from the standard ladder.
2. Highlight the resulting line, a select "Add Trendline," then check "Display equation on chart" and "Display R-squared value on chart."
3. The equation of the resulting trendline will be used to calculate the unknown samples concentration.

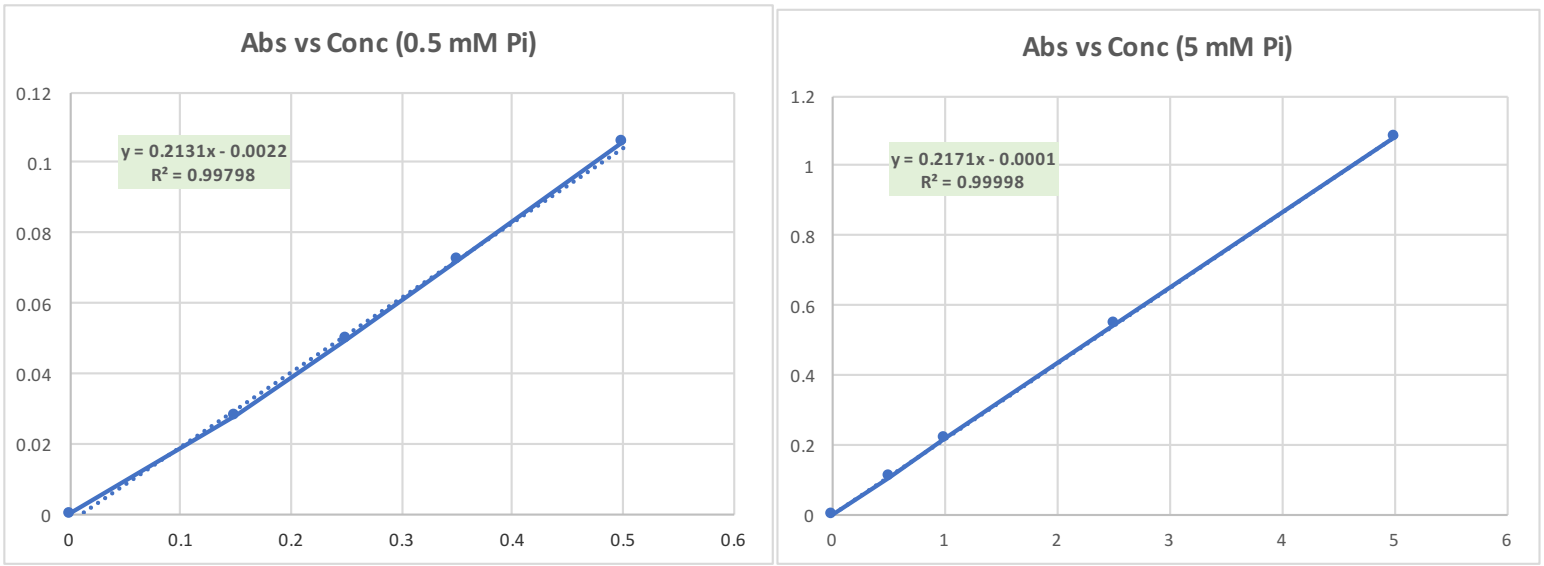
Calculation of concentration

1. Given the R-squared slope of the form $y = mx + b$ it is now possible to calculate the concentration of unknown samples.
2. Enter the absorbance as the x value, and solve for the concentration y.
3. Multiply by the dilution factor to calculate the original concentration, if applicable.

* Note that SOP 09 indicates that a standard Pi solution of 0.5 mM should be used. However, it was found that the absorbance curve for the vanadomolybdate solution is linear for a further order of magnitude, to 5 mM Pi. Two trials were conducted to explicitly test this on 16 February 2017, after which a 5 mM ladder became the standard for tests in which the final [Pi] was anticipated to be greater than 1 mM Pi. This served to minimize error associated with repeated dilutions of samples.



Test A: 0.5 mM Pi, and 5 mM Pi. Note the 5 mM Pi ladder has an additional data point for the 0.5 mM Pi solution



Test A: 0.5 mM Pi, and 5 mM Pi. Note the 5 mM Pi ladder has an additional data point for the 0.5 mM Pi solution

ANNEX B

Appendix B4 – Raman Spectroscopy

Raman procedure (v5)

PREPARATION Pre-warming the laser for 15-30min

785 nm (near IR):

Laser power box on – laser light blinks green

Wait for laser light to be stable green

Turn laser on (key ¼ turn to the right)

488 nm (blue):

Turn key ¼ turn to the right

TEST (on the software)

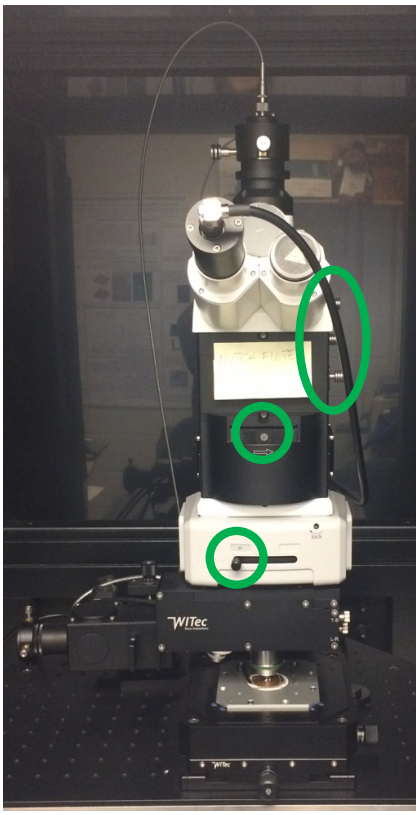
Activate on Witec Control 4 software

Wait for Oscilloscope to cool to -61 C

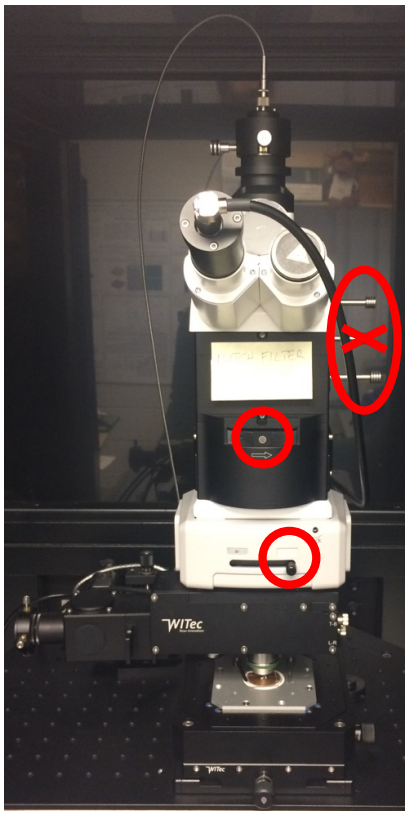
Select "Configuration" tab – Raman- Near IR 785nm OR Blue 488nm

20 x lens (green ring)

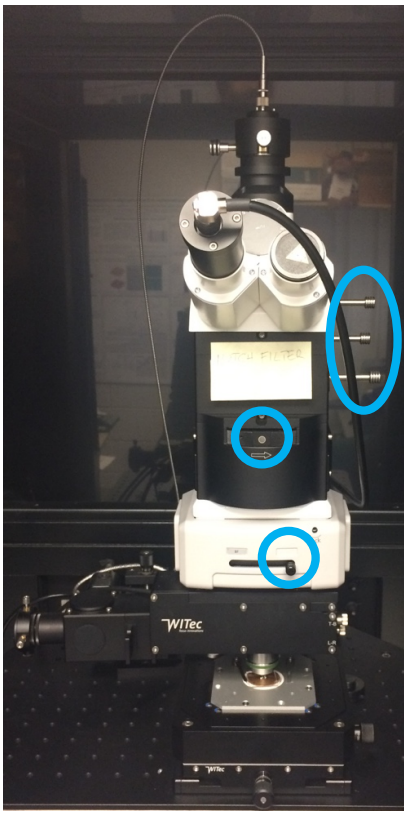
Find Si spectrum when installed; user/witec/measurements/atclient



Visible Light



Near IR 785nm 0r 532 nm



Blue Light 488nm

SAMPLE ON STAGE

Check lens under video control for the lens type (water 20x….); Pegs 1-2-3 pushed into apparatus, i.e. the 'eye' symbol, notch®, BC

Control – illumination on/off, set value around 1

*Use [+] squares to see settings

RC - set dial knob to the full left, up-arrow toggles RC: - set to microscope Z

use +z –Z to move microscope

(stage should be about 0.5-1cm for x20 objective)

*If hard to focus, trying closing the "F" aperture to improve, then focus on the sample; open "F" aperture again before beginning scan

*IF 50x or 100x objective is required, then focus x20 at first

Focus, take image (with colour graphic on the bottom right of the Video Control screen)

CALIBRATION & STANDARDS

The machine must be calibrated before each use, by scanning a silicon standard. The Si shift must be seen at 520.2±0.5 and the Raleigh peak must be within ±0.5 of 0. If these shifts are outside of these parameters, they can be adjusted by modifying the wavelength parameters on the Witec software.

Near IR (785nm):

Under Spectrograph: Set the **Spectral Center** 1600.00

Set the **grating** to either **T1: 300 g/mm BLX = 750NM** OR TX: 1200 g/mm

* Gratings will influence the optical resolution and the maximum efficiency for a specific wavelength range. If the grating is not correct, signal will be lost.

Set up the **oscilloscope parameters: Integration time 1s x 90 exposures (vary as needed)**

Pegs 1-and-3 pulled out to the right in order to set to 'camera', 785 notch®, non-BC, respectively

Close the door to the spectroscope.

Blue Light (488nm):

Under Spectrograph: Set the **Spectral Center** 2200

Set the **grating** to either **T1: 600 g/mm**

* Gratings will influence the optical resolution and the maximum efficiency for a specific wavelength range. If the grating is not proper, signal will be lost.

Set up the **oscilloscope parameters: Integration time 1s x 90 exposures (vary as needed)**

Pegs 1-2-3 pulled out to the right in order to set to 'camera', notch®, non-BC, respectively

Close the door to the spectroscope.

MEASUREMENT

Turn the **oscilloscope** on.

Confirm that the laser tuning knob is closed to the right.

Switch open the laser gate

Increase the intensity by ∏ attenuator until no change anymore

***Check the axes – you can change them with** Check the set-up of the y axis with list button (bottom left) of the Hardware Spectrum window; top of ~8000 for laser peak; set window ~4000

MOUSE CONTROL Right-click and hold- you see a box with many options:

Mouse Mode – Mouse Zoom in (select region) (see magnifying glass icon) is useful.

The Mouse Move (arrow) is useful for knowing the wavenumber value.

When in focus

set microscope Z control – set Zero (status)

Confirm Status box has 0 [um] for the z position

*Usually (up) **~20-50um** for visible focus

Stop oscilloscope once focused

COLLECTION

Single spectro "**Accum spectro**" (make sure time and times) *

*NOTE: Turn the right side of "Accum spectro "otherwise there is not new window of collected data jump-out. (Recommendation: **1s 90times** accumulations for eliminating noisy background)

EXPORT

Spectral data:

- ➔ Double click on spectra
- ➔ Right click on spectra image box
- ➔ ASCII to file
- ➔ Save in Data/user folder

Image:

Save visible image: open photo → save on bitmap → .JPG

AFTER DONE

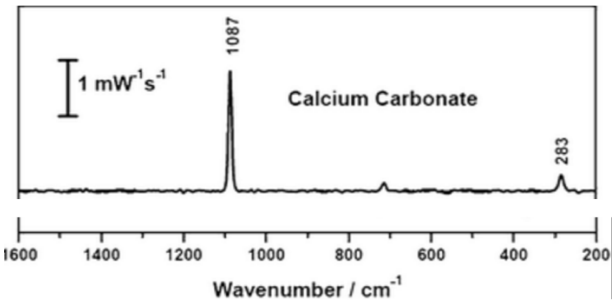
Turn the near IR laser box key 1/4 turn to the left. The key handle should be pointing straight up and down.

Last, turn off the power source that is to the left of the laser box.

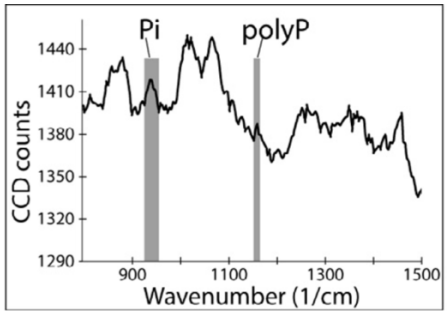
Shut down the software (unless someone else is using it after) - this takes a while because it must turn off many things in the microscope.

Reference

HAp(std) ~961nm



Left one from Google image.



Dr.Omelon's 2014 paper

Mandair 2015: Contribution of Raman spectroscopy to the understanding of bone strength

Table 1 Raman spectroscopic band assignments for bone mineral and matrix components

Raman shift, cm^{-1}	*Assignment*	*Comments*	*Reference(s)*
430	$\nu_2PO_4^{3-}$	Strong band	1
450	$\nu_2PO_4^{3-}$	Shoulder on 430 cm^{-1} band	1
584–590	$\nu_4PO_4^{3-}$	Multiple partially resolved components	1
609	$\nu_4PO_4^{3-}$	Shoulder on 590 cm^{-1} band	1
668	ν(C–S)	Cysteine	1,85
756	$\nu_4CO_3^{2-}$	B-type carbonate, very weak	1
853	ν(C–C)	Collagen proline, may include δ(C–C–H) contribution from tyrosine	1,85
872	ν(C–C)	Mostly collagen hydroxyproline	61,86
920	ν(C–C)	Shoulder, mostly collagen proline	86,87
937	ν(C–C)	Proline and protein backbone	1,85
955	$\nu_1PO_4^{3-}$	Transient bone mineral (P–O) phase, usually seen in immature bone.	6
957	$\nu_1PO_4^{3-}$	Bone mineral containing extensive HPO_4^{2-}, usually immature	6
959–962	$\nu_1PO_4^{3-}$	Bone mineral, mature	1,6,9
1003	ν(C–C)	Phenylalanine	1,87
1035	$\nu_3PO_4^{3-}$	Overlaps with proline ν (C–C) component	9,86
1048	$\nu_3PO_4^{3-}$		1,9
1060	Proteoglycan	Overlaps with lipids, collagen and components of $\nu_3PO_4^{3-}$	88
1070	$\nu_1CO_3^{2-}$	Overlaps with component of $\nu_3PO_4^{3-}$	9
1076	$\nu_3PO_4^{3-}$	Overlaps with component of $\nu_1CO_3^{2-}$	9
1176	ν(C–O–C)	Tyrosine, phenylalanine	1,85
1204	ω(CH_2)	Tyrosine, hydroxyproline	85,86
1242	Amide III	Protein β-sheet and random coils	85,89
1272	Amide III	Protein α-helix	85
1293–1305	δ(=CH)	Lipid band, sometimes seen in fresh untreated bone	1,90
1340	Amide III	Protein α-helix, sometimes called CH_2CH_2 wag	1,85
1365	Pentosidine	Overlap with lipid 1369 cm^{-1} band	1,12,13,85
1375	Proteoglycan	Representative of glycosaminoglycans	88
1446	δ(CH_2)	Protein CH_2 deformation	1,85
1585	ν(C–C–H)	Weak band, aromatic ring	1
1609	δ(C=C)	Phenylalanine, tyrosine	85
1640	ν(C=C)	Shoulder to 1660 cm^{-1} band	1,61
1660	Amide I	Strongest amide I ν(C=O) component, polarization sensitive	1,17
1690	Amide I	Shoulder, prominent with immature cross-links The band also relates to β-sheet or disordered secondary structure	45,51,91

Annex C

Raw Data and Sample Calculations

Table of contents

C1 Sample calculations and raw data for 7 mM P_i seeded tests

Colorimetric data and [P_i] calculations

This series of calculations uses values that were automatically corrected for the blank values. The standard curve is plotted as "absorbance versus concentration."

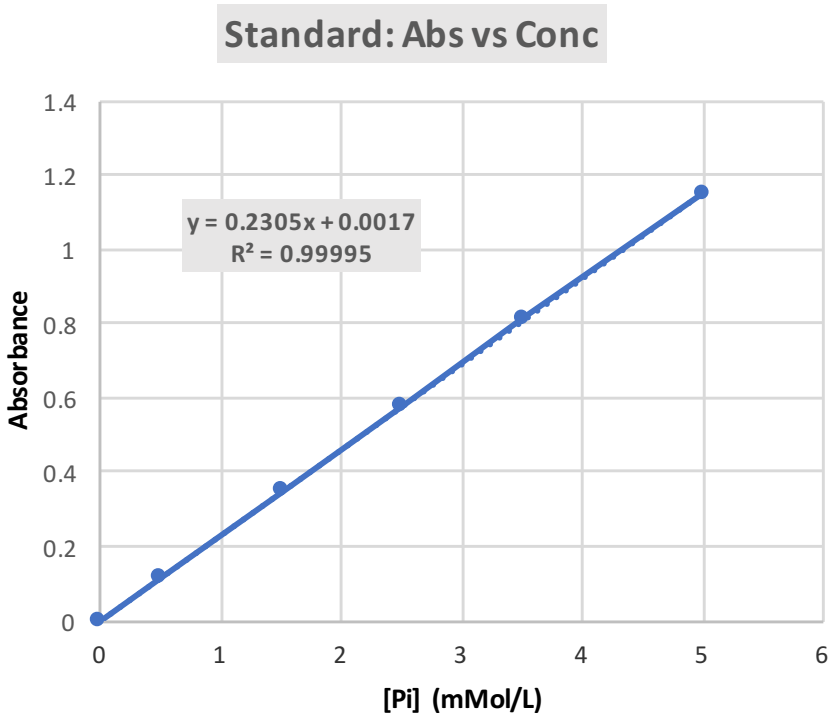
Corrected blank values:

Well ID	Name	Well	Conc/Dil	420	Blank 420	Count	Mean	Std Dev	CV (%)
BLK		A1		0.08	0.001	6	0	0.001	5.67E+16
		A2		0.08	-0.001				
		A3		0.08	0.002				
		B4		0.08	-0.001				
		B5		0.08	-0.001				
		B6		0.08	0				

Values for standard concentrations, corrected for blank:

Well ID	Name	Well	Conc/Dil	420	Blank 420	Count	Mean	Std Dev	CV (%)
STD1		B1	0.5	0.19	0.115	6	0.117	0.002	1.51
		B2	0.5	0.2	0.117				
		B3	0.5	0.2	0.116				
		C10	0.5	0.2	0.117				
		C11	0.5	0.2	0.12				
		C12	0.5	0.2	0.119				
STD2		C1	1.5	0.43	0.351	3	0.347	0.003	0.979
		C2	1.5	0.42	0.344				
		C3	1.5	0.43	0.347				
STD3		D1	2.5	0.66	0.58	3	0.578	0.002	0.269
		D2	2.5	0.66	0.577				
		D3	2.5	0.66	0.578				
STD4		E1	3.5	0.9	0.821	3	0.814	0.006	0.734
		E2	3.5	0.89	0.811				
		E3	3.5	0.89	0.81				
STD5		F1	5	1.23	1.154	3	1.15	0.003	0.3
		F2	5	1.23	1.147				
		F3	5	1.23	1.149				

Plot of standards curve from values in table above:



Absorbance values for unknown samples, corrected for blank:

Well ID	Name	Well	Conc/Dil	420	Blank 420	Count	Mean	Std Dev	CV (%)
SPL13		F7		0.9	0.824	3	0.822	0.003	0.38
		F8		0.9	0.823				
		F9		0.9	0.818				
SPL14		G7		0.44	0.362	3	0.363	0.002	0.416
		G8		0.44	0.365				
		G9		0.44	0.363				
SPL15		H7		0.44	0.358	3	0.358	0.002	0.644
		H8		0.44	0.356				
		H9		0.44	0.361				
SPL16		A10		0.44	0.358	3	0.36	0.002	0.418
		A11		0.44	0.361				
		A12		0.44	0.361				
SPL17		B10		0.45	0.371	3	0.371	0.008	2.26
		B11		0.44	0.363				
		B12		0.46	0.379				

Using the slope of the standards curve, it is possible calculate concentration of unknown samples on the microplate assay from their absorbance.

$$y = 0.2305x + 0.0017$$

In this case, y refers to the absorbance and x is the unknown concentration value. Thus, we must solve for x:

$$x = (y - 0.0017) / 0.2305$$

These concentration values must still be multiplied by the dilution of the sample to determine the original concentration within the sample.

Original sample concentration = (Concentration on plate) x (Dilution factor)

Sample	Name	Abs	Concentration on plate	Dilution	Concentration of sample
13	Initial 7 mM solution	0.822	3.5588	2	7.118
14	Final [P] 7A	0.363	1.5675	1.33	2.090
15	Final [P] 7B	0.358	1.5458	1.33	2.061
16	Final [P] 7C	0.36	1.5544	1.33	2.073
17	Final [P] 7D	0.371	1.6022	1.33	2.136

Colorimetric data and [Ca^{2+}] calculations

This series of calculations does not use values that were automatically corrected for the blank values; the blank value is subtracted within Excel. The standard curve is plotted as "concentration versus absorbance."

Uncorrected blank values:

Well ID	Name	Well	Conc/Dil	570	Count	Mean	Std Dev	CV (%)
BLK		A1		0.257	3	0.245	0.01	4.23
		A2		0.239				
		A3		0.239				

Values for standard concentrations, not corrected for blank:

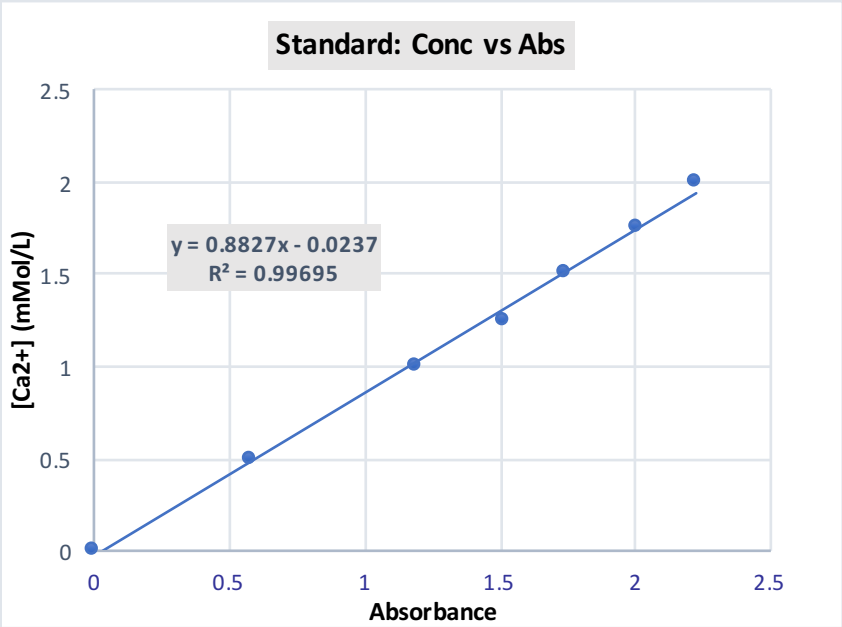
Well ID	Name	Well	Conc/Dil	570	Count	Mean	Std Dev	CV (%)
STD1		B1	0.5	0.77	3	0.821	0.045	5.43
		B2	0.5	0.848				
		B3	0.5	0.845				
STD2		C1	1	1.403	3	1.436	0.035	2.41
		C2	1	1.472				
		C3	1	1.433				
STD3		D1	1.25	1.758	3	1.755	0.009	0.492
		D2	1.25	1.745				
		D3	1.25	1.762				
STD4		E1	1.5	1.91	3	1.988	0.069	3.45
		E2	1.5	2.014				
		E3	1.5	2.04				
STD5		F1	1.75	2.262	3	2.253	0.009	0.407
		F2	1.75	2.244				
		F3	1.75	2.252				
STD6		G1	2	2.479	3	2.467	0.01	0.406
		G2	2	2.462				
		G3	2	2.462				

These values are corrected for the blank by subtracting the blank value from the standards' values:

Corrected absorbance = Absorbance – blank reading

Abs	Corrected	Standard (mMol/L)
0.245	0	0
0.821	0.576	0.5
1.436	1.191	1
1.755	1.510	1.25
1.988	1.743	1.5
2.253	2.008	1.75
2.468	2.223	2

Plot of standards curve from values in table above:



Absorbance values for unknown samples, not yet corrected for blank:

Well ID	Name	Well	Conc/Dil	570	Count	Mean	Std Dev	CV (%)
SPL12		D7		1.667	3	1.599	0.108	6.77
		D8		1.655				
		D9		1.474				
SPL13		E7		1.574	3	1.484	0.083	5.62
		E8		1.47				
		E9		1.409				
SPL21		E10		0.259	3	0.256	0.003	1.2
		E11		0.253				
		E12		0.256				
SPL22		F10		0.284	3	0.285	0.001	0.372
		F11		0.285				
		F12		0.286				
SPL23		G10		0.286	3	0.29	0.004	1.42
		G11		0.289				
		G12		0.294				
SPL24		H10		0.261	3	0.262	0.001	0.442
		H11		0.263				
		H12		0.263				

Using the slope of the standards curve, it is possible calculate concentration of unknown samples on the microplate assay from their absorbance.

$$y = 0.8827x - 0.0237$$

These concentration values must still be multiplied by the dilution of the sample to determine the original concentration within the sample.

Original sample concentration = (Concentration on plate) x (Dilution factor)

Absorbance values corrected for blank, and then concentration calculated using the slope:

Sample	Name	Abs	Abs minus blank	Conc on plate	Dilution	Sample Conc mMol/L
12	Ca (before A)	1.484	1.239	1.070	4	4.281
13	Ca (after D)	1.599	1.354	1.171	4	4.685
21	7A	0.256	0.011	-0.014	1.33	-0.019
22	7B	0.285	0.040	0.012	1.33	0.015
23	7C	0.290	0.045	0.016	1.33	0.021
24	7D	0.262	0.017	-0.008	1.33	-0.011

Note that the concentrations of 7A and 7D appear to be below 0. On closer inspection, it is observed that the absorbance values of these samples are just above the absorbance value of the blank so these values should not be discarded. When these two values were entered into the slope formula, there were effectively non-detectable due to experimental error. As such, the concentrations used throughout the remaining calculations for the "7" series took the values to be 0, or essentially a negligible amount of Ca^{2+} ion remained in the solution upon the conclusion of the experiment.

C2 EDTA test to select concentration of 7 mM P_i

Measurement of [P_i] in ROPEC digestate; EDTA used to reduce [Fe^{3+}]

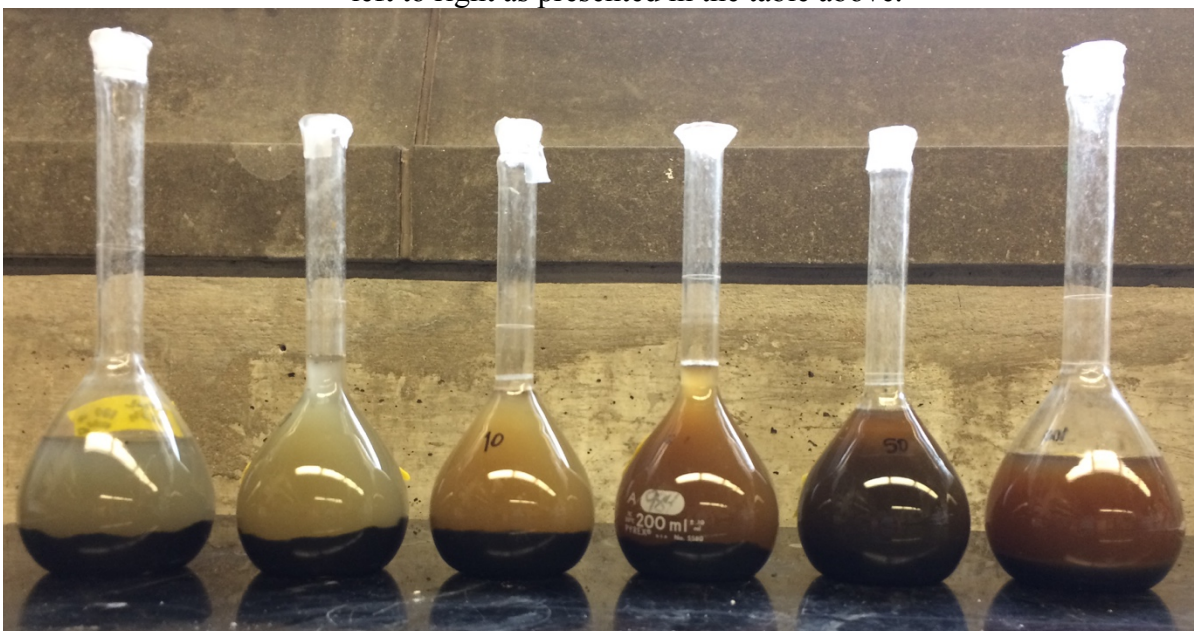
100 mL of digestate from the ROPEC was mixed with a 100 mL solution; composition of the solution varied as the table above.

The maximum [P_i] that was achieved was approximately 7 mM/L. This means that even without the benefit of additional polyphosphate digestion steps, it was possible to find this minimum [P_i]. This is how the 7 mM P_i concentration was selected for the final precipitate-seeded tests, and for the reactor tests.

EDTA solution and resulting [P_i]

SAMPLE	ABS	[P_i] (mM/L)
100% CACO3	0.072	0.306
100% H2O	0.096	0.410
10% EDTA	0.779	3.357
20% EDTA	1.476	6.366
50% EDTA	**0.342**	**7.356**
100% EDTA	**0.348**	**7.486**

Visual difference between tests of different dilutions and solutions. Flasks in same order from left to right as presented in the table above.



C3 Data from unseeded batch tests

2.5 mM Pi	Initial				Final					PROD THEO
	[Ca]o	[Pi]o	(Ca x P) o	(Ca/P) o	[Ca]f	[Pi]f	pH	(Ca x P) f	(Ca/P) f	d[Ca]/d[Pi]
A	3.081	1.236	3.808	2.492	2.366	0.521	6.80	1.233	4.539	1.000
B	2.339	1.236	2.891	1.892	2.048	1.140	7.16	2.335	1.797	3.029
C	2.464	1.236	3.046	1.993	2.083	1.021	7.06	2.126	2.040	1.774
D	2.059	1.270	2.614	1.622	1.769	1.080	7.24	1.911	1.637	1.537
AVERAGE	2.486	1.244	3.090	2.000	2.066	0.941	7.07	1.901	2.503	1.835
Std Dev	0.431	0.017	0.511	0.364	0.244	0.284	0.19	0.478	1.367	0.860

5 mM Pi	Initial				Final					PROD THEO
	[Ca]o	[Pi]o	(Ca x P) o	(Ca/P) o	[Ca]f	[Pi]f	pH	(Ca x P) f	(Ca/P) f	d[Ca]/d[Pi]
A	2.874	2.427	6.974	1.184	1.389	1.110	6.75	1.542	1.251	1.128
B	2.285	2.420	5.528	0.944	0.719	1.458	6.97	1.048	0.493	1.629
C	3.128	2.554	7.988	1.225	2.021	1.854	6.83	3.748	1.090	1.583
D	2.064	2.392	4.936	0.863	0.435	1.333	7.23	0.579	0.326	1.538
AVERAGE	2.588	2.448	6.357	1.054	1.141	1.439	6.95	1.729	0.790	1.470
Std Dev	0.497	0.072	1.384	0.178	0.710	0.312	0.21	1.402	0.449	0.231

10 mM Pi	Initial				Final					PROD THEO
	[Ca]o	[Pi]o	(Ca x P) o	(Ca/P) o	[Ca]f	[Pi]f	pH	(Ca x P) f	(Ca/P) f	d[Ca]/d[Pi]
A	2.903	4.581	13.297	0.634	0.337	3.240	7.21	1.093	0.104	1.913
B	2.305	5.234	12.063	0.440	0.331	3.496	7.18	1.156	0.095	1.136
C	3.123	5.586	17.444	0.559	0.622	3.192	7.04	1.986	0.195	1.045
D	2.394	4.880	11.682	0.490	0.143	3.579	7.40	0.511	0.040	1.730
AVERAGE	2.681	5.070	13.621	0.531	0.358	3.377	7.21	1.187	0.108	1.456
Std Dev	0.395	0.435	2.640	0.084	0.198	0.190	0.15	0.607	0.064	0.430

20 mM Pi	Initial				Final					PROD THEO
	[Ca]o	[Pi]o	(Ca x P) o	(Ca/P) o	[Ca]f	[Pi]f	pH	(Ca x P) f	(Ca/P) f	d[Ca]/d[Pi]
A	2.832	11.285	31.955	0.251	0.146	8.631	7.44	1.262	0.017	1.012
B	2.285	10.685	24.412	0.214	0.171	8.884	7.47	1.519	0.019	1.174
C	3.123	12.312	38.447	0.254	0.219	8.892	7.08	1.950	0.025	0.849
D	2.435	10.113	24.629	0.241	0.080	8.284	7.35	0.661	0.010	1.288
AVERAGE	2.669	11.098	29.861	0.240	0.154	8.673	7.34	1.348	0.018	1.081
Std Dev	0.381	0.940	6.712	0.018	0.058	0.286	0.18	0.539	0.006	0.192

30 mM Pi	Initial				Final					PROD THEO
	[Ca]o	[Pi]o	(Ca x P) o	(Ca/P) o	[Ca]f	[Pi]f		(Ca x P) f	(Ca/P) f	d[Ca]/d[Pi]
A	2.218	15.063	33.405	0.147	0.047	13.540	7.59	0.630	0.003	1.425
B	2.575	15.063	38.792	0.171	0.063	13.164	7.47	0.825	0.005	1.323
C	2.399	15.063	36.132	0.159	0.047	13.665	7.44	0.635	0.003	1.682
AVERAGE	2.397	15.063	36.110	0.159	0.052	13.456	7.50	0.697	0.004	1.477
Std Dev	0.179	0.000	2.694	0.012	0.009	0.260	0.08	0.111	0.001	0.185

C4 Data from seeded batch tests

Note: Iteration "A" of the bone-seeded tests produced [Pi] invalid results, that could not be corrected even upon re-testing. It is suspected the error lay either in the initial sample collection, or that the colorimetric solution had been contaminated. As such, only the concentrations of Iteration B and C were considered. The recorded pH values were still considered.

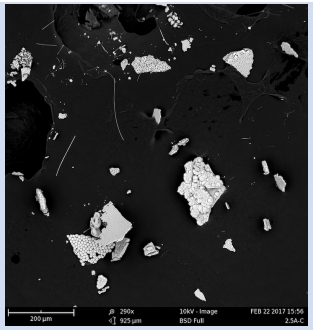
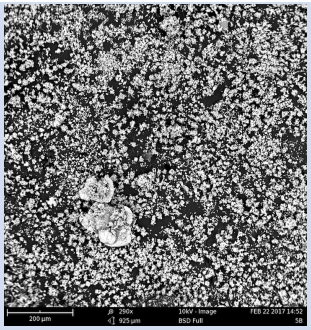
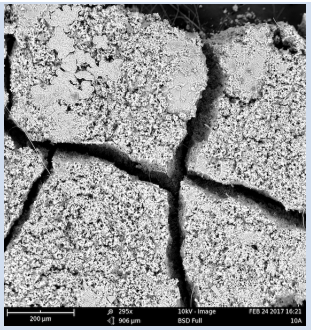
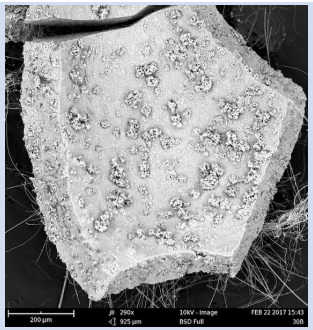
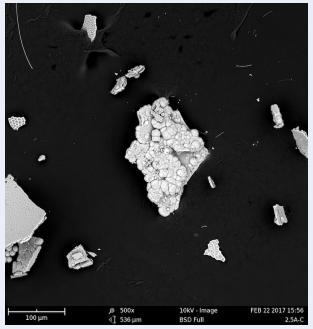
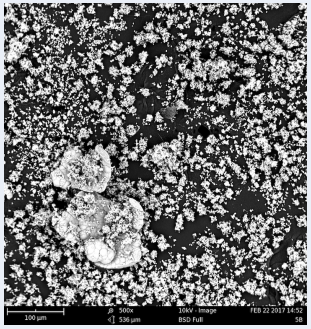
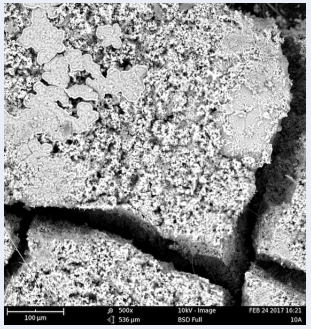
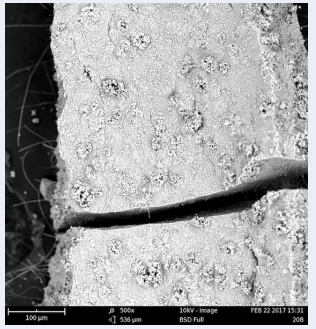
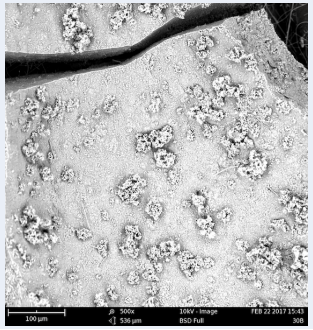
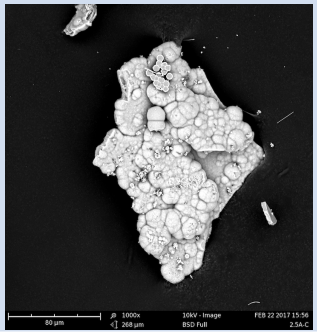
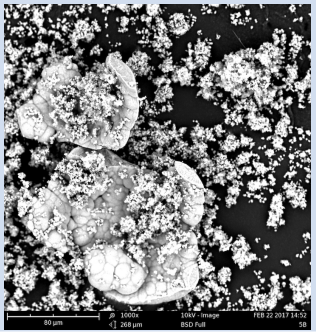
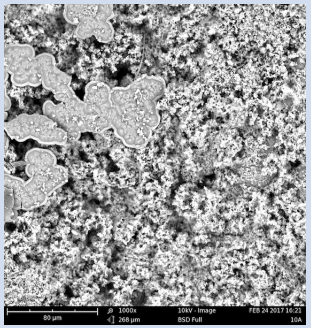
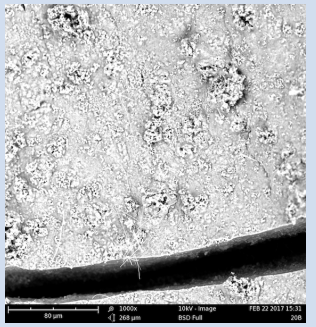
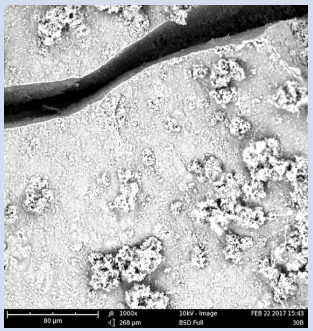
5 mM Pi; 2 g bone/L	Initial				Final					PROD THEO
	[Ca]o	[Pi]o	(Ca x P) o	(Ca/P) o	[Ca]f	[Pi]f	pH	(Ca x P) f	(Ca/P) f	d[Ca]/d[Pi]
A	1.705				0.526		7.36			
B	2.682	2.558	6.862	1.048	1.010	1.389	7.12	1.403	0.727	1.430
C	3.385	2.492	8.435	1.358	1.179	0.835	6.99	0.984	1.411	1.331
AVERAGE	3.033	2.525	7.648	1.203	1.094	1.112	7.06	1.194	1.069	1.381
Std Dev	0.497	0.047	1.113	0.219	0.119	0.392	0.09	0.296	0.484	0.070

5 mM Pi; 0.5 g bone/L	Initial				Final					PROD THEO
	[Ca]o	[Pi]o	(Ca x P) o	(Ca/P) o	[Ca]f	[Pi]f	pH	(Ca x P) f	(Ca/P) f	d[Ca]/d[Pi]
A	1.409				0.363		7.40			
B	2.744	2.558	7.021	1.073	0.967	1.389	7.14	1.344	0.696	1.520
C	3.385	2.492	8.435	1.358	1.247	0.924	6.97	1.152	1.350	1.363
AVERAGE	3.064	2.525	7.728	1.215	1.107	1.157	7.06	1.248	1.023	1.441
Std Dev	0.453	0.047	1.000	0.202	0.198	0.329	0.12	0.136	0.462	0.111

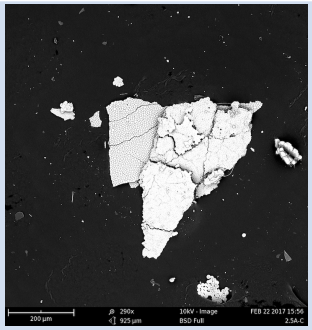
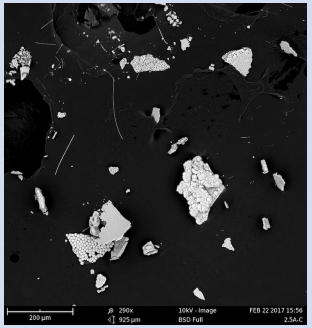
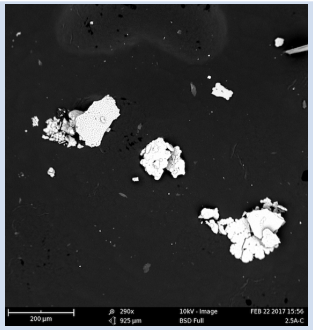
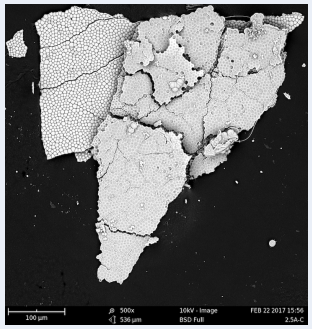
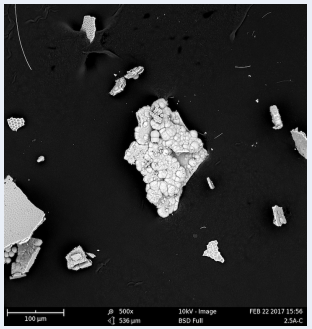
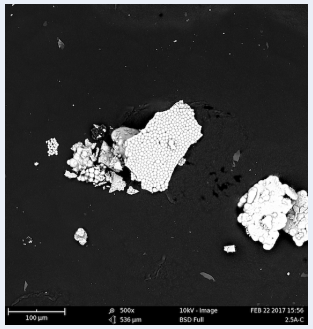
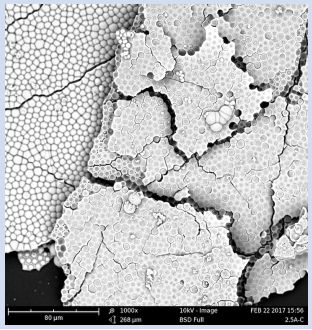
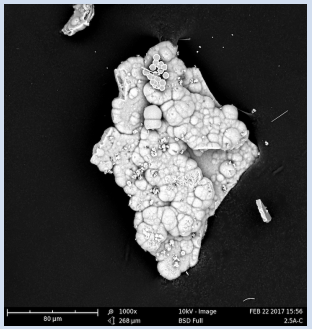
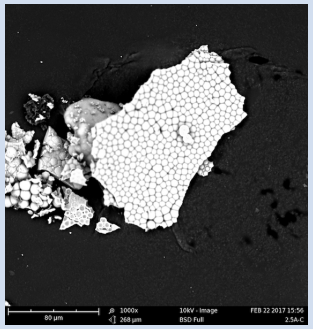
5 mM Pi; 1 g ppt/L	Initial				Final					PROD THEO
	[Ca]o	[Pi]o	(Ca x P) o	(Ca/P) o	[Ca]f	[Pi]f	pH	(Ca x P) f	(Ca/P) f	d[Ca]/d[Pi]
E	3.008	2.285	6.872	1.317	0.176	0.654	7.61	0.115	0.269	1.737
F	2.901		6.628	1.270	0.347	0.811	7.51	0.281	0.427	1.734
AVERAGE	2.955	2.285	6.750	1.293	0.261	0.733	7.56	0.198	0.348	1.736
Std Dev	0.076		0.173	0.033	0.121	0.111	0.07	0.118	0.112	0.002

30 mM Pi; 2 g bone/L	Initial				Final					PROD THEO
	[Ca]o	[Pi]o	(Ca x P) o	(Ca/P) o	[Ca]f	[Pi]f	pH	(Ca x P) f	(Ca/P) f	d[Ca]/d[Pi]
A	2.107				0.053		7.66			
B	2.690	15.295	41.147	0.176	0.088	10.150	7.65	0.896	0.009	0.506
C	3.385	14.973	50.678	0.226	0.091	12.031	7.70	1.090	0.008	1.119
AVERAGE	3.037	15.134	45.913	0.201	0.089	11.090	7.68	0.993	0.008	0.813
Std Dev	0.491	0.227	6.739	0.035	0.002	1.330	0.04	0.137	0.001	0.434

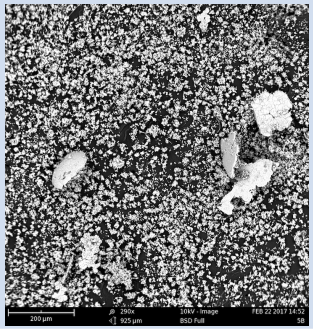
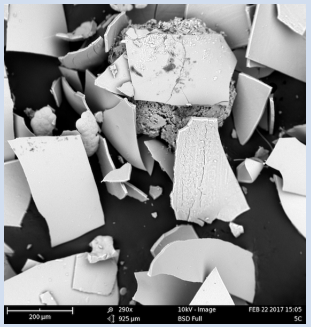
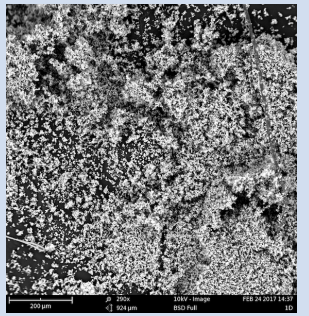
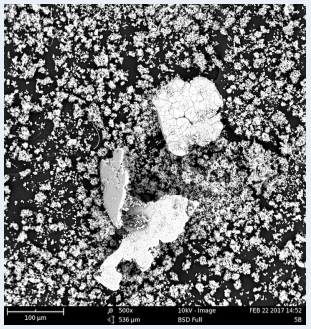
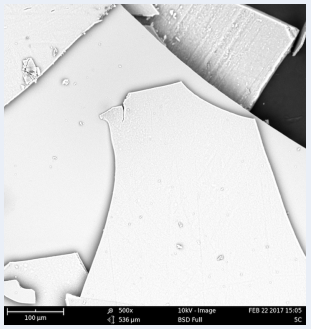
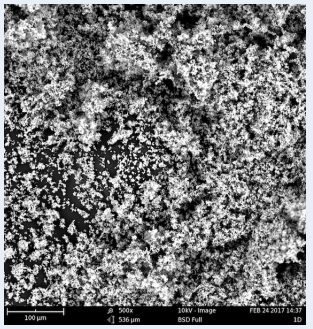
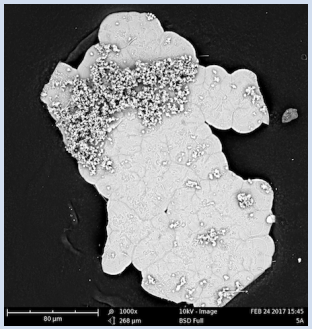
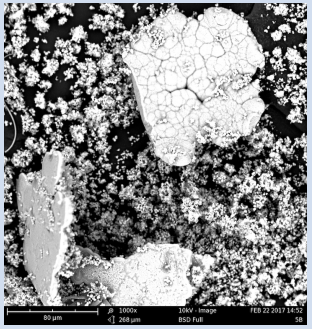
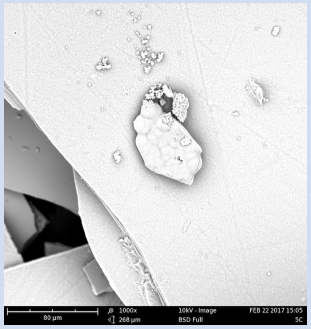
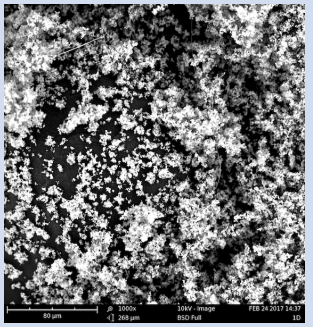
30 mM Pi; 0.5 g bone/L	Initial				Final					PROD THEO
	[Ca]o	[Pi]o	(Ca x P) o	(Ca/P) o	[Ca]f	[Pi]f	pH	(Ca x P) f	(Ca/P) f	d[Ca]/d[Pi]
A	2.109				0.057		7.62			
B	2.727	15.295	41.712	0.178	0.077	10.851	7.61	0.836	0.007	0.596
C	3.481	15.305	53.274	0.227	0.161	12.326	7.49	1.986	0.013	1.114
AVERAGE	3.104	15.300	47.493	0.203	0.119	11.589	7.55	1.411	0.010	0.855
Std Dev	0.533	0.008	8.176	0.035	0.059	1.043	0.08	0.813	0.004	0.366

OVERVIEW	2.5 mM Pi	5 mM Pi	10 mM Pi	20 mM Pi	30 mM Pi
290					
500					
1000					

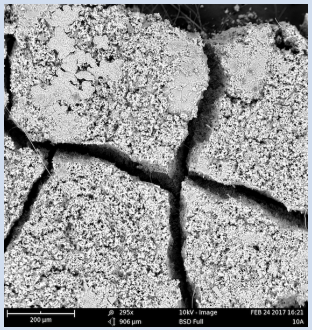
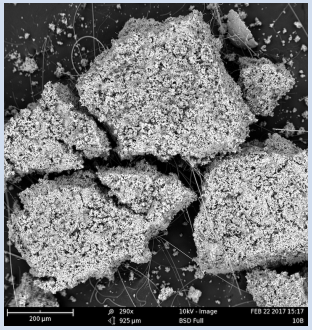
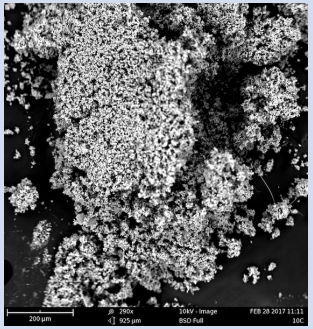
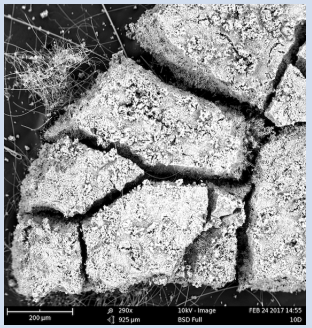
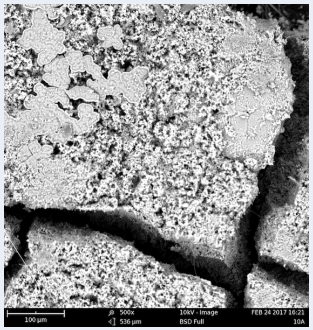
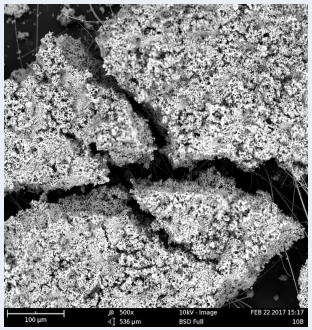
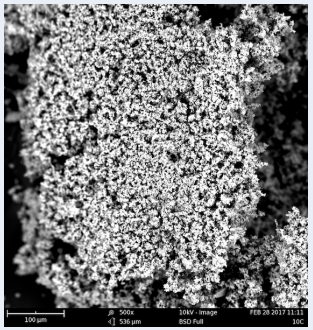
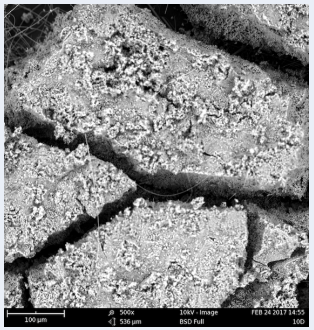
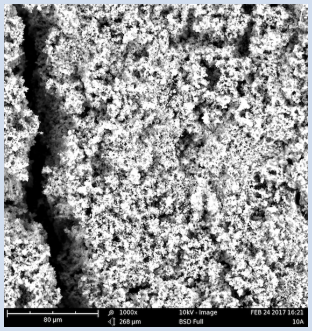
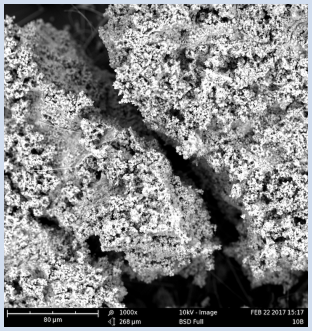
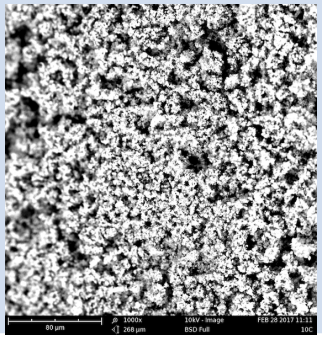
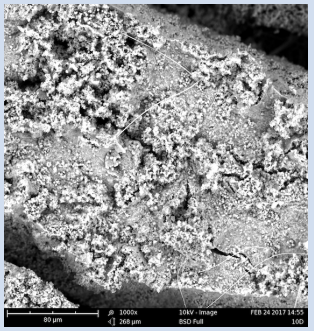
C12

2.5 mM Pi	A	B	C	n/a
x290				
x500				
x1000				

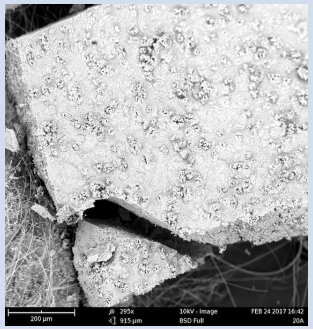
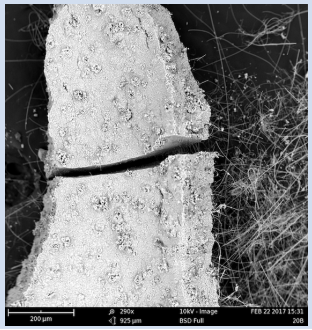
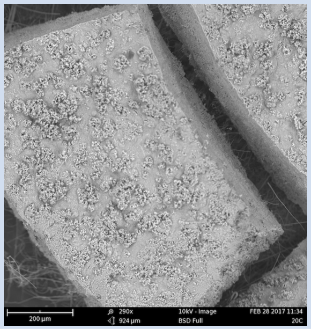
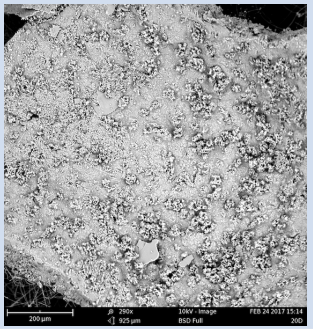
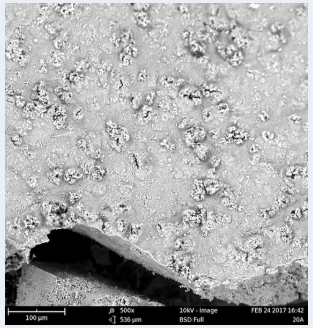
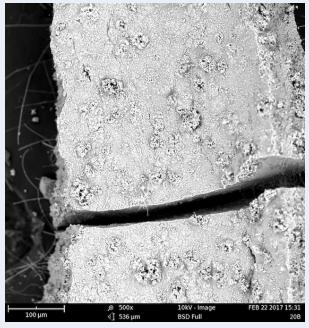
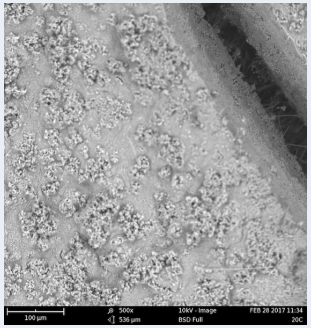
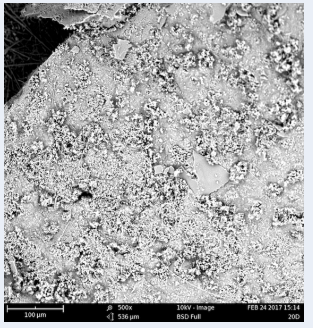
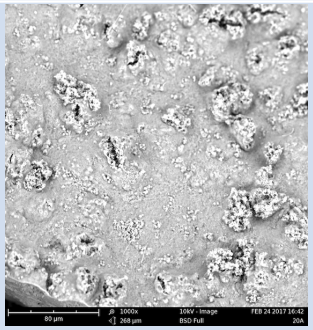
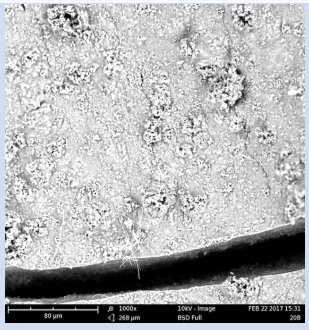
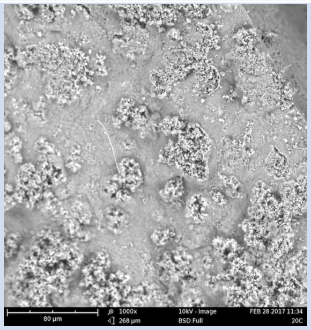
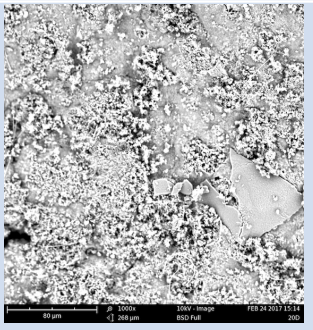
C13

5 mM Pi	A	B	C	D
x290	Insufficient precipitate			
x500	Insufficient precipitate			
x1000				

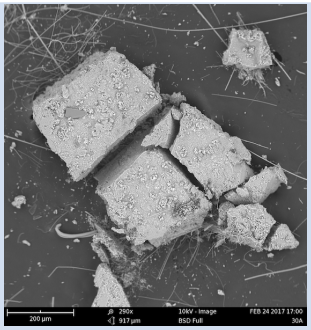
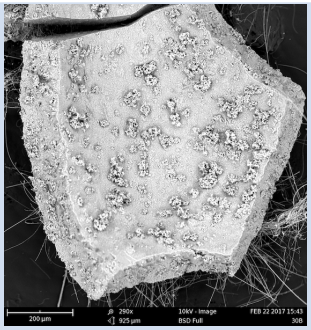
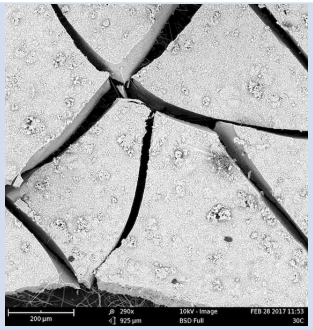
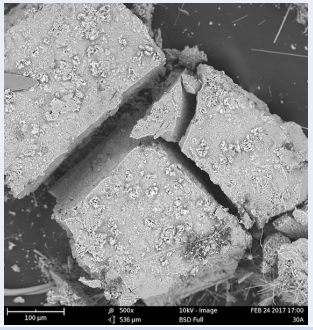
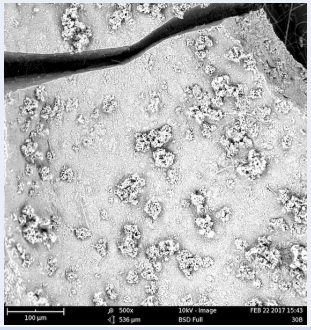
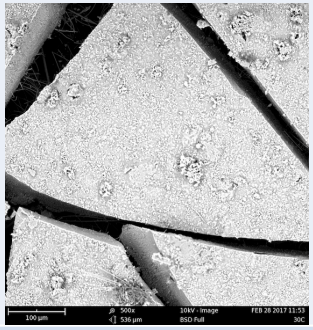
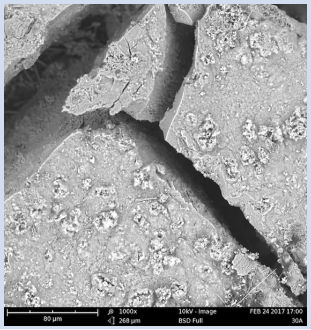
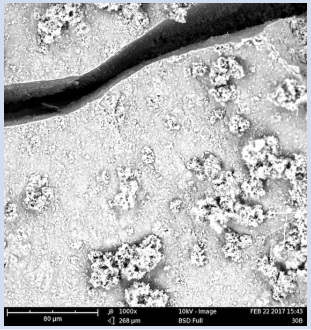
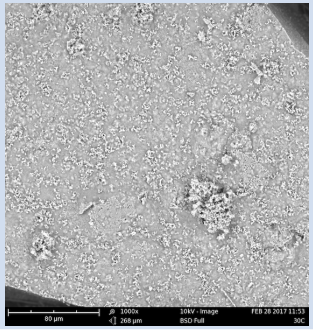
C14

10 mM Pi	A	B	C	D
x290				
x500				
x1000				

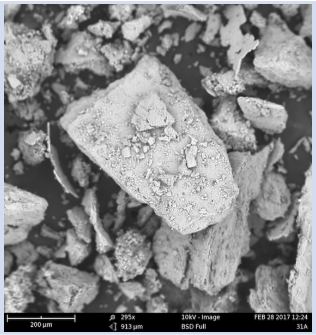
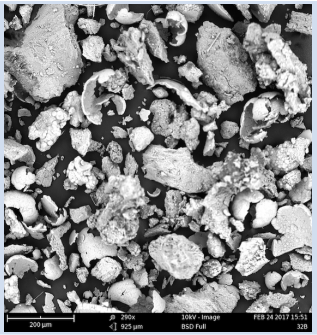
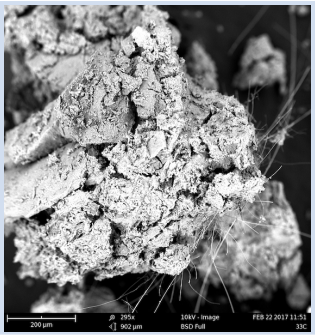
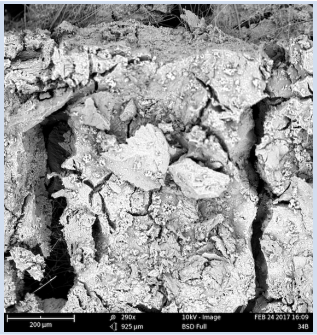
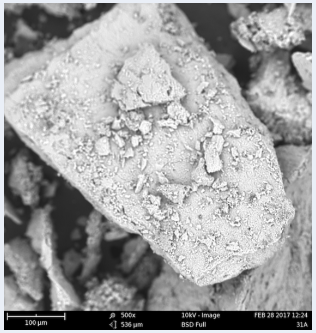
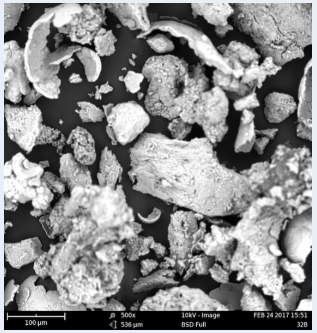
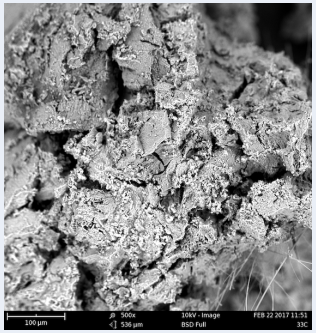
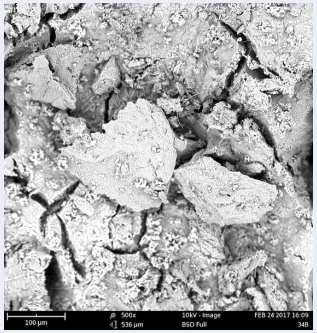
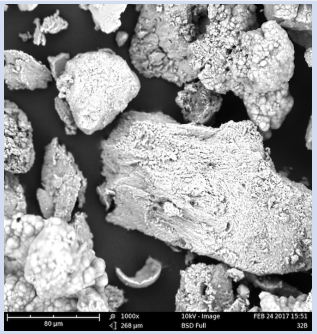
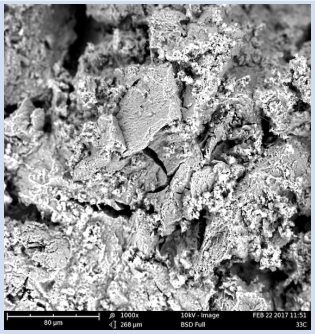
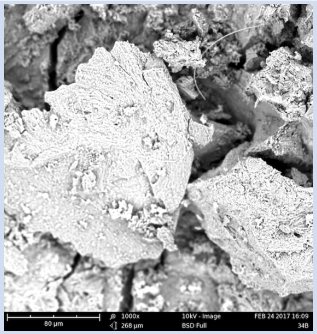
C15

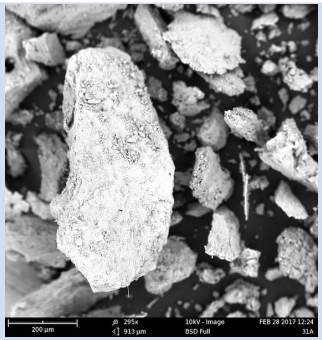
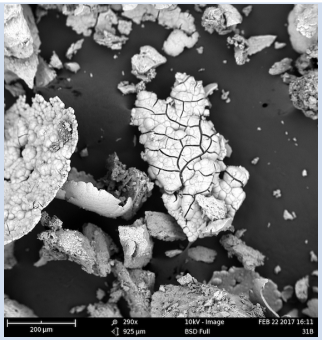
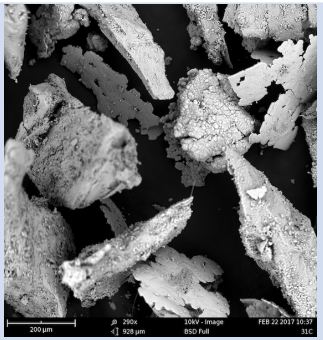
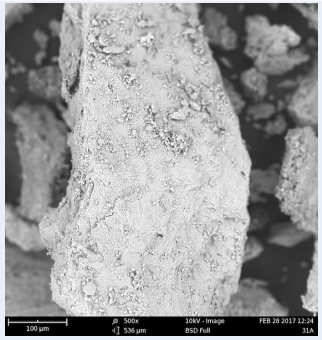
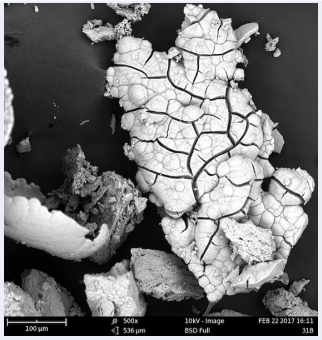
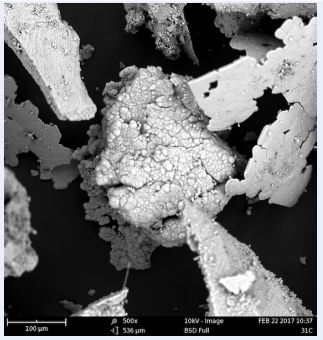
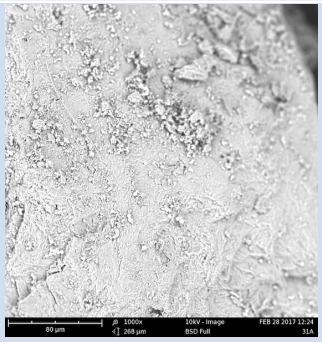
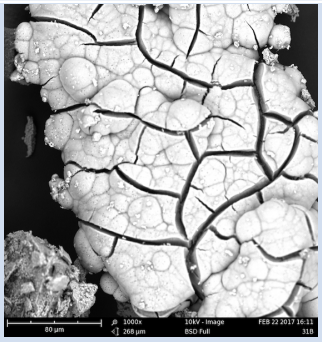
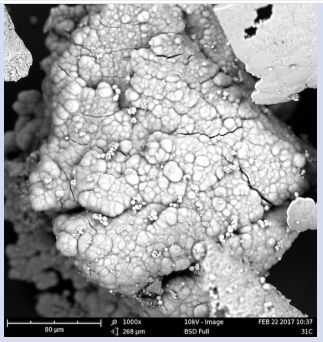
20 mM Pi	A	B	C	D
x290				
x500				
x1000				

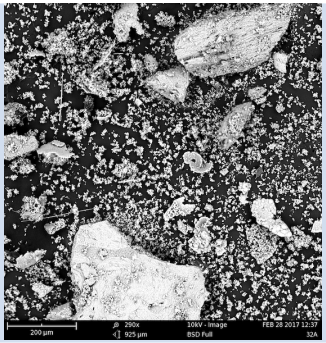
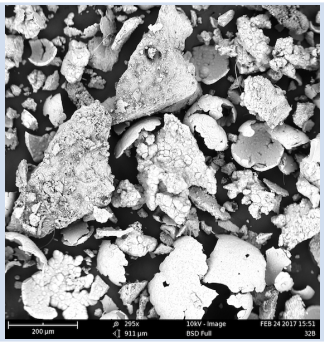
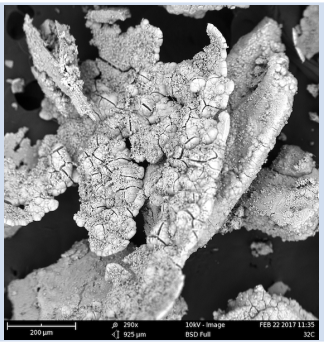
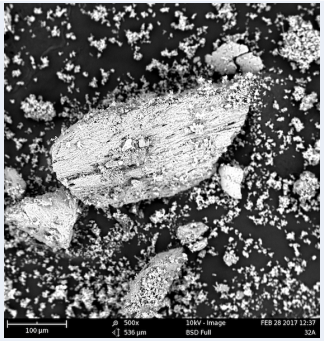
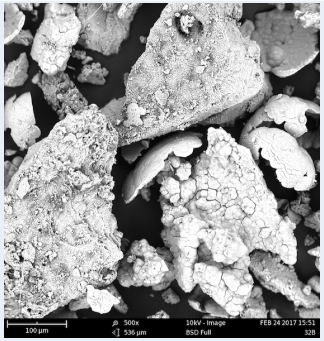
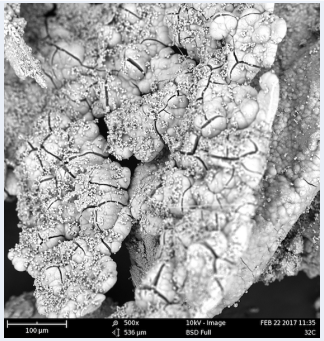
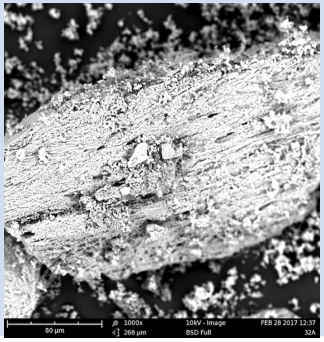
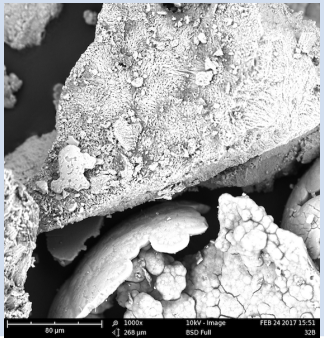
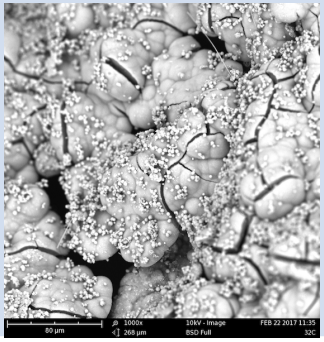
C16

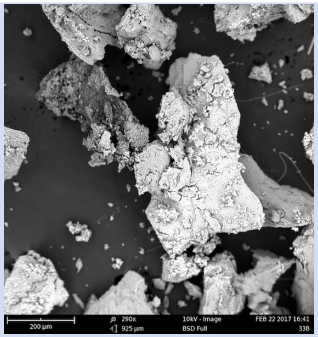
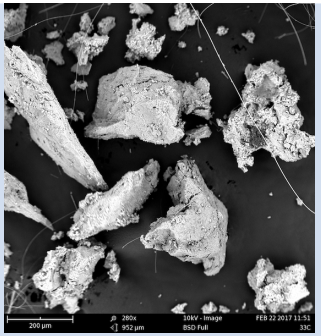
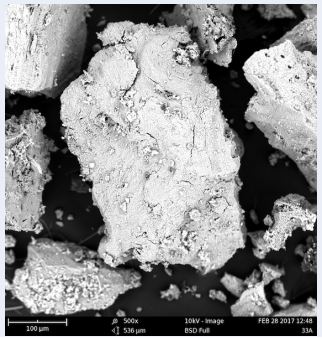
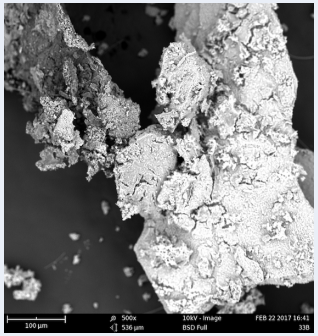
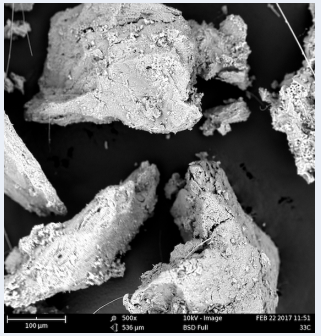
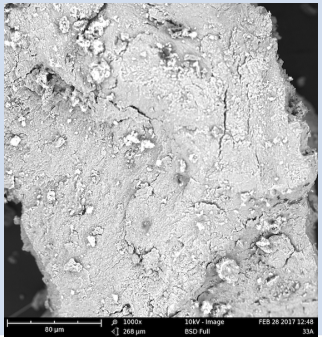
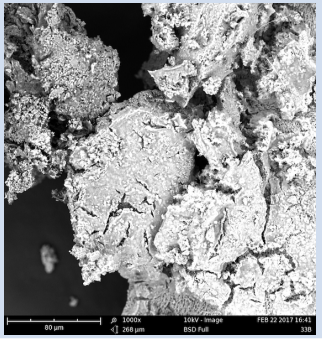
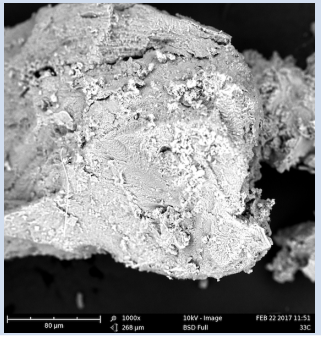
30 mM Pi	A	B	C	n/a
x290				
x500				
x1000				

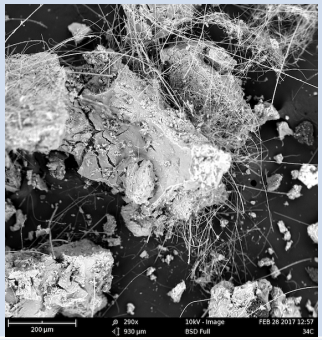
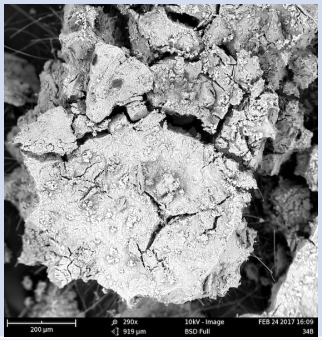
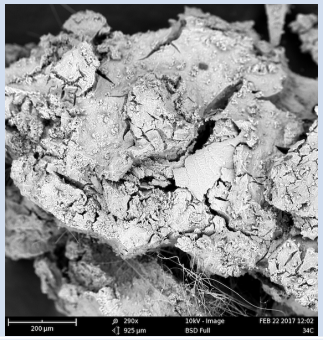
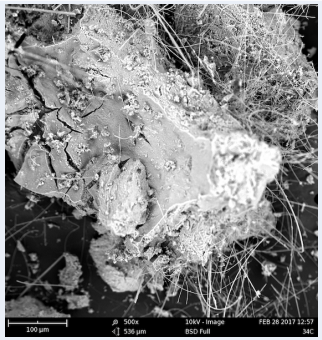
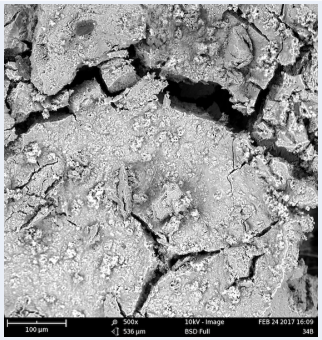
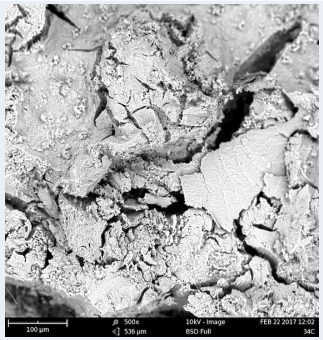
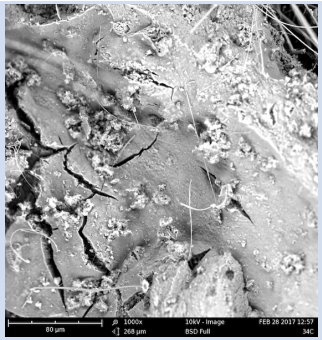
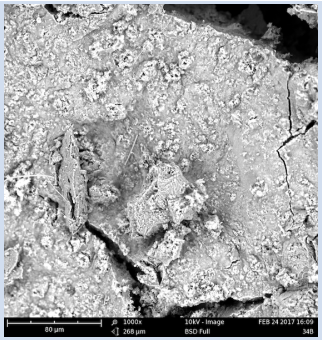
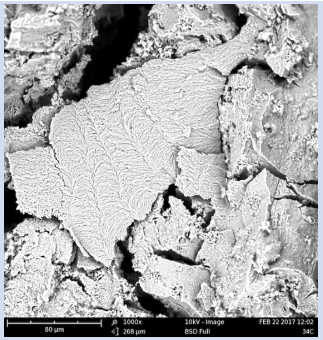
C17

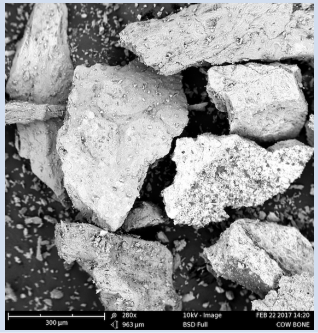
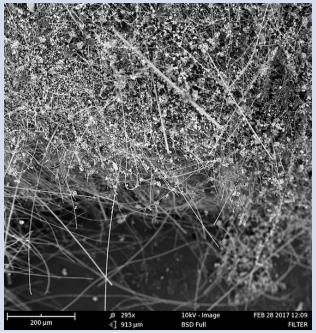
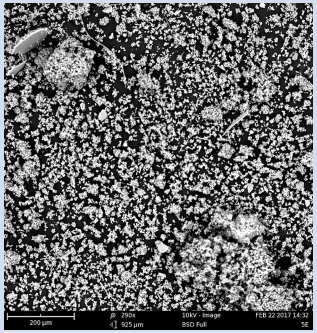
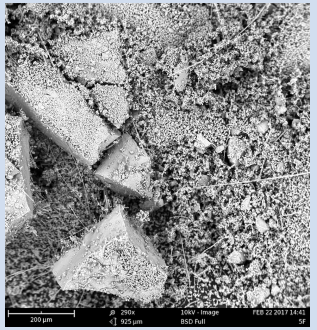
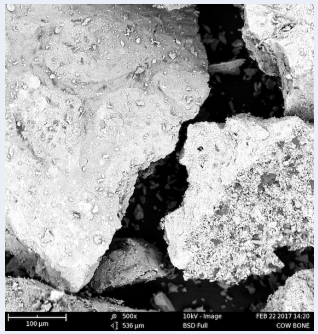
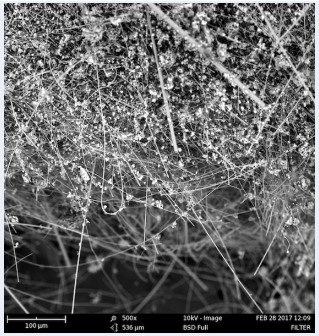
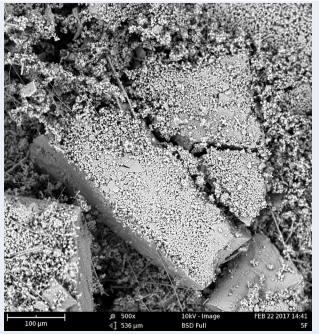
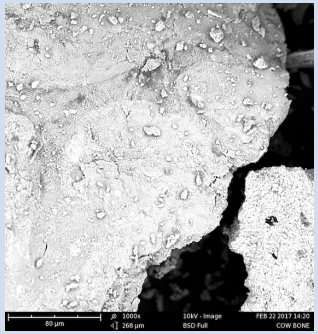
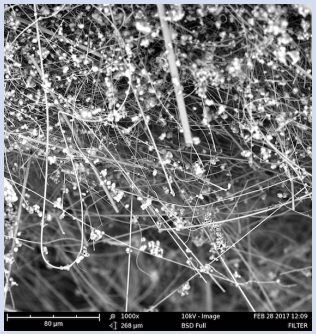
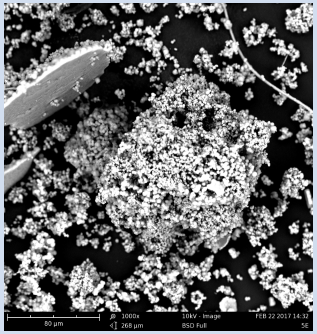
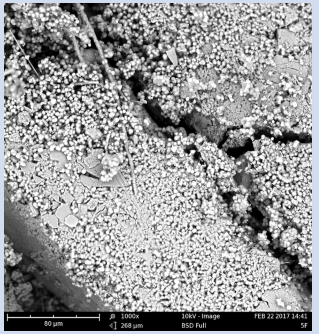
SUMMARY	31	32	33	34
X290				
X500				
X1000 C18				

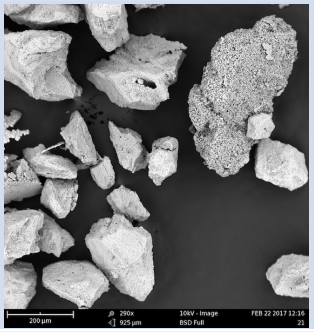
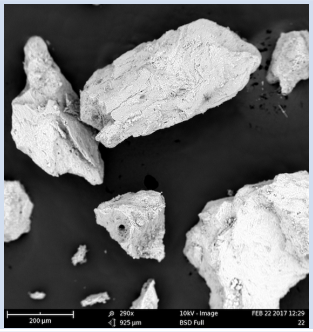
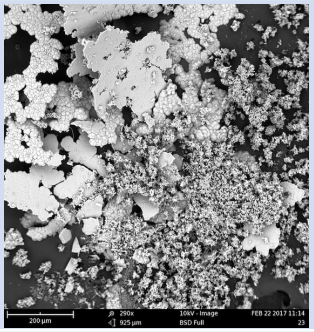
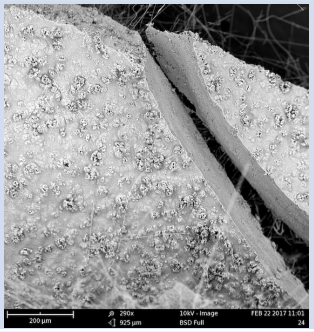
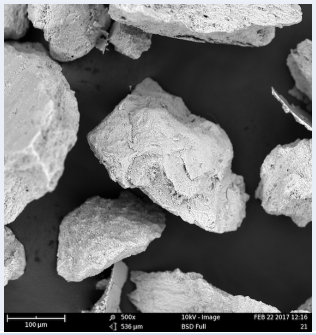
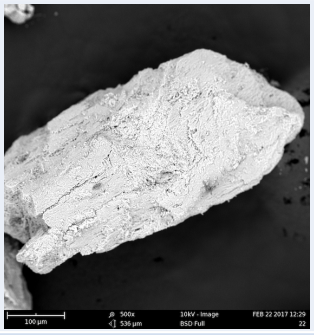
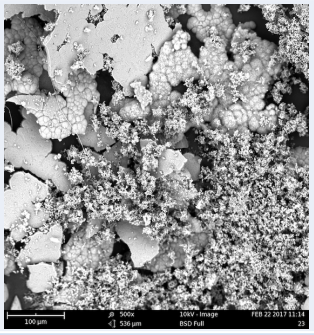
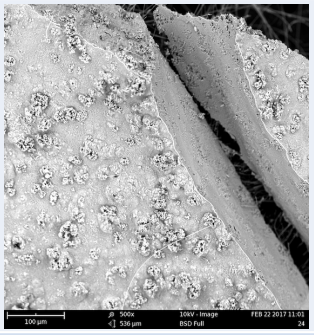
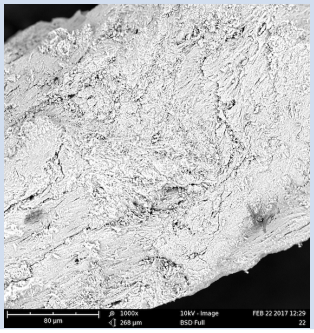
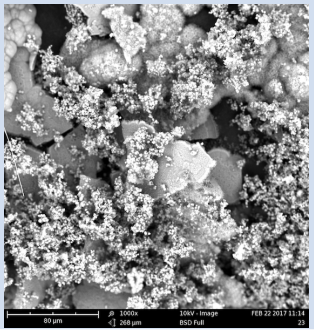
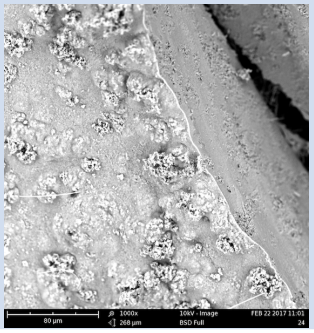
31	5 mM Pi 2 g seed / L	A	B	C
	X290			
	X500			
C19	X1000			

32	5 mM Pi 0.5 g seed / L	A	B	C
	X290			
	X500			
C20	X1000			

33	30 mM Pi 2 g seed / L	A	B	C
	X290			
	X500			
C21	X1000			

34	30 mM Pi 0.5 g seed / L	A	B	C
	X290			
	X500			
C22	X1000			

OTHER	COW BONE	FILTER (5E)	5E	5F
X290				
X500				
X1000				
C23				

OTHER	21 6 mM Pi, 1 g seed / L	22 27 mM Pi, 1 g seed / L	23 (seed in 5E) 6 mM Pi, no seed	24 (seed in 5F) 27 mM Pi, no seed
X290				
X500				
X1000				
C24				

Annex D

Competitions and Conferences

Over the course of preparing this thesis, I had the enriching opportunity to participate in a number of conferences and competitions. The application or presentation prepared for each is attached as an appendix, as well the results of the competition.

These events, including the results, are as follow:

Appendix D1:
Canadian Science Policy Conference, 8-10 November 2016.
Recognized by the Hon Kirsty Duncan (Science Minister) as a runner-up for the Science Policy Excellence Award (Youth), for policy entitled *"Rethinking Phosphorus: Contaminant or Commodity? Securing Food for Our Future."*

Appendix D2:
Canadian Nutrient Platform inaugural teleconference, 21 March 2017.
Invited to present introduction to set the stage for the talk for participants (note: scheduled changed last minute, planned talk not delivered.)

Appendix D3:
Ma These en 180 secondes / Three Minute Thesis, 22 March 2017.
Participated in competition, delivering the presentation in French titled *"Attention aux excès: le phosphore."*

Appendix D4:
University of Ottawa Design Day, 29 March 2017. Organized the lab group's participation in competition, presenting "*Renewable phosphorus fertilizer."*
The lab group won top prize both in our assigned category, as well as the overall top prize for design out of the 100 groups participating.

Appendix D5:
University of Ottawa 10th Engineering and Computer Science Graduate Research Poster Competition, 30 March 2017. Participated in Chemical and Biological Engineering Peer Award competition.
Earned 1st Place for the Women In Science and Engineering Awards, for presentation entitled *"Closing the phosphorus loop: Our future's food security – Precipitation of carbonate apatite from municipal wastewater."*

ANNEX D - Appendix D1

Canadian Science Policy Conference 2016

Science Policy Excellence Award - Youth

Title of Policy Proposal

Rethinking Phosphorus: Contaminant or Commodity? Securing Food for Our Future.

Biography

Jessica studied Chemistry at Simon Fraser University from 2001-2003, and she completed her Bachelor's Degree in Chemical Engineering from the Royal Military College of Canada in 2007.

She returned to school in September 2015 and is working on a Master's of Applied Science in Chemical Engineering, with a specialization in Science, Society and Policy.

Inspiration

I came upon this topic through a chance encounter, when Dr. Sidney Omelon invited me to work on a short crystallization project. Specifically, I investigated how to recycle phosphorus from municipal wastewater streams in a form that would be suitable for agriculture use.

Over the course of my readings and experiments, I learned that Canada is one of the largest importers of phosphorus for fertilizer production. The resource required for phosphorus fertilizer production is in a specific form known as phosphate rock (Koven, 2016). It is not widely known that there is a finite global phosphate rock reserve (USGS, 2015). My fascination grew at the mismatch between the information available in scientific journals, and the popular awareness of the topic. I also realized that regardless of how successful I was in crystallizing a suitable phosphate product, the issues surrounding the global phosphorus economy were larger than what science alone could resolve.

This compelled me to enroll in the Collaborative Master's program in Chemical Engineering with a specialization in Science, Society and Policy. As a student of this program, in addition to my engineering research, I am studying the social and geopolitical forces and systems that bring such topics into the public consciousness. Understanding what tools and actions are available to enable a country to understand and take action on a forecasted problem *before* it becomes a crisis is critical regardless of one's field of interest. In my case, I hope that this multidisciplinary approach will help to define the problem and shape a Canadian-specific strategy to mitigate the upcoming global phosphate rock limitation that will ultimately impact our food availability and cost.

Need for Action

Phosphorus is essential to life as we know it on Earth; it is forms the backbone of our DNA, and is a key constituent in the molecules that undergo cellular respiration in our bodies (Jahnke, 2000). It is present in or added to soil as a fertilizer, absorbed from the soil by plants, and ingested by humans and animals from crops. Unfortunately, it is also known to be harmful to waterways when present in high concentrations, causing blooms of algae which destroy fish and plant life. Significant progress has been made over the last 30 years to reduce the phosphorus load in waterways. These efforts continue today (ECCC, 2013), most recently with the joint announcement by the Environmental Protection Agency and ECCC of a binational target to reduce the amount of phosphorus entering Lake Erie by 40% (GoC, 2016).

Less well known, however, is that as a non-renewable resource and non-replaceable element, there is a finite amount of useful phosphorus – extracted from mineral deposits in a form known as phosphate rock - available for fertilizer production. By some estimates, there remains as little as 100 years' worth of phosphate rock reserves (Cordell, 2011). More importantly, however, the much-disputed territory of Western Sahara (controlled by Morocco) holds approximately two thirds of the world's reserve (USGS, 2015), and Canada is the single largest importer of phosphate rock from this area (Koven, 2016). Canada has no viable phosphate rock mines or reserves, and thus is extremely reliant on Morocco for this resource (FAO, 2016). The political climate in Western Sahara is delicate, and with very few other producers of phosphate rock exporting their goods, Canada is in a difficult moral position (FAO, 2016; Koven, 2016).

It is clear that while the harmful effects of excess "phosphorus as contaminant" are generally well understood, there is still a need to pay attention to where this phosphorus originated and to fully appreciate its value as it passes through Canada's food and waste systems.

The European Union and Australia have made positive advances with respect to identifying the need to recycle phosphorus. They continue to improve their understanding of their respective phosphorus cycles – from extraction, to processing, agricultural or industrial use, disposal, and finally recapturing – and enable the multidisciplinary research required to improve identify and implement possible solutions (Cordell, 2011; Metson, 2016; SCU, 2013; Withers, 2015).

Canada is falling behind other countries' advances in phosphorus recycling technologies, as we are still largely of the "phosphorus as contaminant" mindset. We need to evolve in order to mobilize the academic, industrial, and political resources required to harness our own phosphorus cycles, improve the security of our phosphorus fertilizer, and therefore our food security.

Proposed Action

A national strategy is required in order to foster cooperation and knowledge sharing between academic institutions, as well as industry and various levels of government. Phosphorus recycling solutions must be economically viable and energy efficient. The expertise of civil and chemical engineers, geochemists, farmers, economists, and policy specialists, to name just a few, is required to fully understand the flow of phosphorus within Canada's agricultural and municipal systems and how to encourage recycling.

This strategy must speak to all levels of government. Wastewater treatment occurs at the municipal level, while agricultural and environmental concerns are the domain of both provincial and federal governments and Ottawa. ECCC regulations speak to phosphorus levels permitted in waterways, yet do not recommend guidelines for how the captured phosphorus should be recycled or disposed of, or consider phosphorus retention approaches that could support agricultural needs.

This problem is unique in that the technical solution will differ from region to region, depending on local farming and industry practices, as well as municipal waste treatment procedures. For instance, wastewater from sewage is known to be rich in phosphorus, and every municipality has a treatment plant and/or plan in order to reduce the phosphorus load in the treated water that returns to the local environment. However, chemical properties of the wastewater stream can differ significantly between municipalities, due to local water conditions, nearby industry, freeze / thaw cycles, and the chemicals used to treat their municipal wastewater. This means that the protocol used to capture phosphorus in one municipality may not be effective at another. A strong network to share information and expertise is thus needed to help account for all of these variables.

We cannot wait until the demand for phosphate rock increases to the point that recycling it into agricultural fertilizer becomes a desperate option. Canada has time to connect technical and policy experts under a national strategy in order to research and implement technology in a deliberate manner. There's no time like the present to take action to avoid the undesirable effects of the impending phosphate rock shortage.

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ANNEX D - Appendix D2

Inaugural Canadian Nutrient Platform Teleconference

Good morning. I'm Jess. It is a real privilege to be speaking with you today – I've admired from afar the work of many experts on the line, so thank you! This is a very exciting initiative to be part of.

I am currently a Master's student in Chemical Engineering at uOttawa, and my thesis research – which is what led me to you – involves recycling phosphorus from wastewater. I am also specializing in Science, Society and Policy, and the research of that aspect of my thesis is how I connected with Barbara – trying to follow the phosphorus breadcrumbs to understand not only who in Canada is involved, but why, as well as what *has been* done, and what *could be* done.

So over the next 5 minutes, I will define the contours of Canada's phosphorus network and policy environment.

[Next slide]

This is a massively complex and nuanced problem, and no one in their right mind would really try to fix all of it. So it's both fascinating and critically important to recognize that not everyone who has a stake in this problem needs to care or even agree on all of its components.

However, if these various efforts can be coordinate, a lot more progress across all fronts could be made.

[Next slide]

On this next slide I have a table outlining the simplified stages of phosphorus extraction, processing, and disposal along the top, with the different categories of stakeholders along the left side. (If you move the text box you can look at my first estimate of mapping 'who is where' which would certainly benefit from input by those around the table here, but that is a more in-depth discussion for another time.)

[Next slide]

The outline for a deeper analysis is on this next slide – I have removed my own initial assessment as I suspect this would lead to a lively debate which should probably happen in person over refreshments. The take-away here, though, is that from the initial problem definition, the three main motivations can be distilled, and it will be important to consider when CNP wants to reside, and how to frame message to the various interested parties, and in fact which parties we want to engage with.

[Next slide]

Changing gears on the next slide to policy – we are very fortunate to have the functional ESPP as an example, but must be mindful to understand differences that would affect how their policies and approaches may or may not work for Canada.

Factors such as our vast geography and dispersed population mean that we have different pressures for fresh water and waste management, as well as how these are perceived by the public. Furthermore, we are more fortunate than our EU counterparts in that the regulations here in Canada are more open to recycling municipal waste. Specifically, the CCME explicitly recognizes that the reuse of biosolids from waste is a valuable source of nutrients, and the CFIA's guidelines regarding the use of materials as fertilizer focus more on the sterility standards that are required, than the initial source of the material.

It is also important to know that ECCC's current efforts are largely focused on Lake Erie, and finding effective means to reduce the phosphorus load into that watershed. Ideally, the initiatives applied here should translate to other lake systems, however it will be important that the instruments selected reward 'recycle' options more than 'recover & remove' options, or else this is a missed opportunity.

The final consideration I will bring up today is the industry side, and the balance of phosphate rock, as well as potash, around the world. Canada's PR reserves are negligible, however we hold the largest potash share in the world. In addition to this, the world's largest fertilizer company, Agrium-PotashCorps, is a Canadian company. It is also the largest customer of the world's largest phosphate rock producer (PhosBoucraa – in Morocco, which controls the largest PR reserves in the globe in Western Sahara). So – an interesting dynamic there to be aware of. In the short term, there is no risk that efforts at recycling phosphorus will compete with this global market. But at some time in the future this dynamic will change, especially as the the cost of extracting and shipping raw material increases, while recycling options become more widespread and accessible.

[Next slide]

In summary, first, it is of critical importance to consider not only *who* is engaged, but *how*, by examining each stakeholder's motivation and role within the larger phosphorus cycle. And second, care must be taken to tailor policy recommendations to suit regional dynamics for them to have any lasting effect.

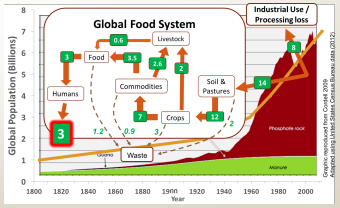
Thank you!

Canadian Nutrient Platform
Background
March 21st 2017

Jessica Z. Ross
B.Eng (Chemical Engineering), Royal Military College of Canada, 2007
MASc Candidate (Chemical Engineering: Specialization in Science, Society and Policy)
University of Ottawa, Phosphorus Lab

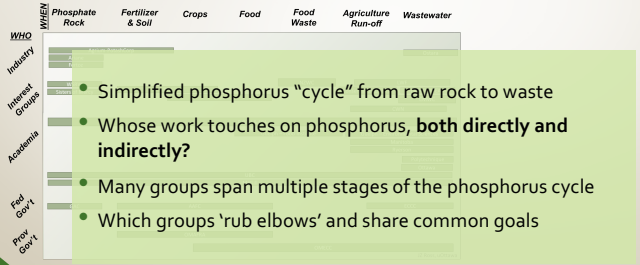
What is the "Phosphorus Problem"

- Imbalance between the extraction of a *non-renewable resource*, of which 72% is controlled by a *single country*, while at the same time allowing *run-off* to damage important waterways, and still *wasting* about one third of the food produced for the world's 7 billion+ inhabitants.



….A broken and unsustainable cycle

Stakeholder Analysis
Who Cares – When?

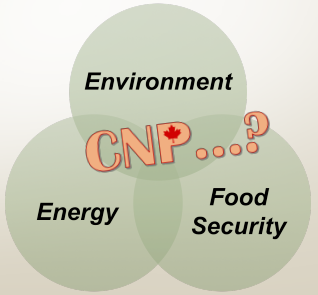


- Simplified phosphorus "cycle" from raw rock to waste
- Whose work touches on phosphorus, **both directly and indirectly?**
- Many groups span multiple stages of the phosphorus cycle
- Which groups 'rub elbows' and share common goals

Stakeholder Analysis
Who Cares – Why?

AAFC = Agriculture and Agri-Food Canada
CAPI = Canadian Agri-Food Policy Institute
CCME = Council of Canadian Ministers of the Environment
CMWC = Canadian Municipal Wastewater Consortium
CWN = Canada Water Network
CWWA = Canadian Water and Wastewater Association
ECCC = Environment and Climate Change Canada
ESPP = European Sustainable Phosphorus Platform
GAC = Global Affairs Canada (aka Foreign Affairs)
IPNI = International Plant Nutrition Institute
LWF = Lake Winnipeg Foundation
NZWC = National Zero Waste Council
OMAFRA = Ont Ministry of Agriculture, Food and Rural Affairs
OMECC = Ont Ministry of Environment and Climate Change
P-RCN = Phosphorus Research Coordination Network
SoM: Sisters of Mercy
SPA = Sustainable Phosphorus Alliance
WEAO = Water Environment Association of Ont
WSRW = Western Sahara Resource Watch

….. WHO ELSE?



Canada and the EU
Policy Diffusion

- Cannot assume a policy that worked elsewhere will work here… built in Canada option
- Consider:
  - Canada's vast and varied geography
  - Plentiful water, ~7% of world's renewable fresh water
  - CCME recognizes removing phosphorus from wastewater in way that allows 'beneficial re-use' is ideal
  - USEPA & ECCC bi-national plan to reduce phosphorus load on Lake Erie
  - Global agriculture giant Agrium-PotashCorp is Canadian (#1 for K, #2 for N); OCP's largest customer
  - Canada holds world's largest potash reserves (~30%), only 0.1% of phosphorus reserves
  - Three potential mines in Canada: Fertoz in BC, Arnaud and Arianne in Qc

Summary

- Scope and key stakeholders are part of today's discussion
  - *Who do we want to engage in building a national/regional collaborative*
- Policy and implementation must be tailored to each region

- References
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ANNEX D – APPENDIX D3

MA THESE EN 3 MINUTES (MT3)

Vous avez probablement entendu parler des algues bleues, qui nuisent aux lacs et aux rivières – dont le plus fameux était le lac Érié en 2015, quand la prolifération d'algues était visible de l'espace – et vous vous souvenez peut-être aussi des algues dans le canal a la fin d'été.

Moi aussi je les ai vues, et j'étais curieuse – qu'est-ce qui a causé ces algues ? J'ai vite appris que c'était le phosphore. Spécifiquement, le phosphore des écoulements agricoles.
Depuis les années 60, le phosphore est ajouté aux engrais en grande quantité pour augmenter la productivité de l'industrie agricole. Sans l'ajoute de phosphore à la terre, on ne pourrait pas faire pousser assez de nourriture pour même la moitié de nos 7 milliards d'humains.
Donc – évidemment, le phosphore est une ressource à protéger, alors je me suis demandée : d'où ça vient ?

La réponse m'a surprise. Le phosphore ajouté à nos engrais vient de roche phosphatée, qui est une ressource non-renouvelable qui se forme pendant des millions d'années à partir des corps des petits organismes aquatiques.

Pour compliquer encore plus la situation, trois quarts des réserves de roche phosphatée sont contrôlés par un seul pays – le Maroc.
De cette façon, nous pouvons peut-être le comparer à l'huile. Et comme l'huile, il va arriver un jour qu'on n'en aura plus.

Alors – d'un côté, nous avons une ressource essentielle à la vie, et non-renouvelable. Et de l'autre côté, nous avons des excès de phosphore qui nuisent à nos lacs.

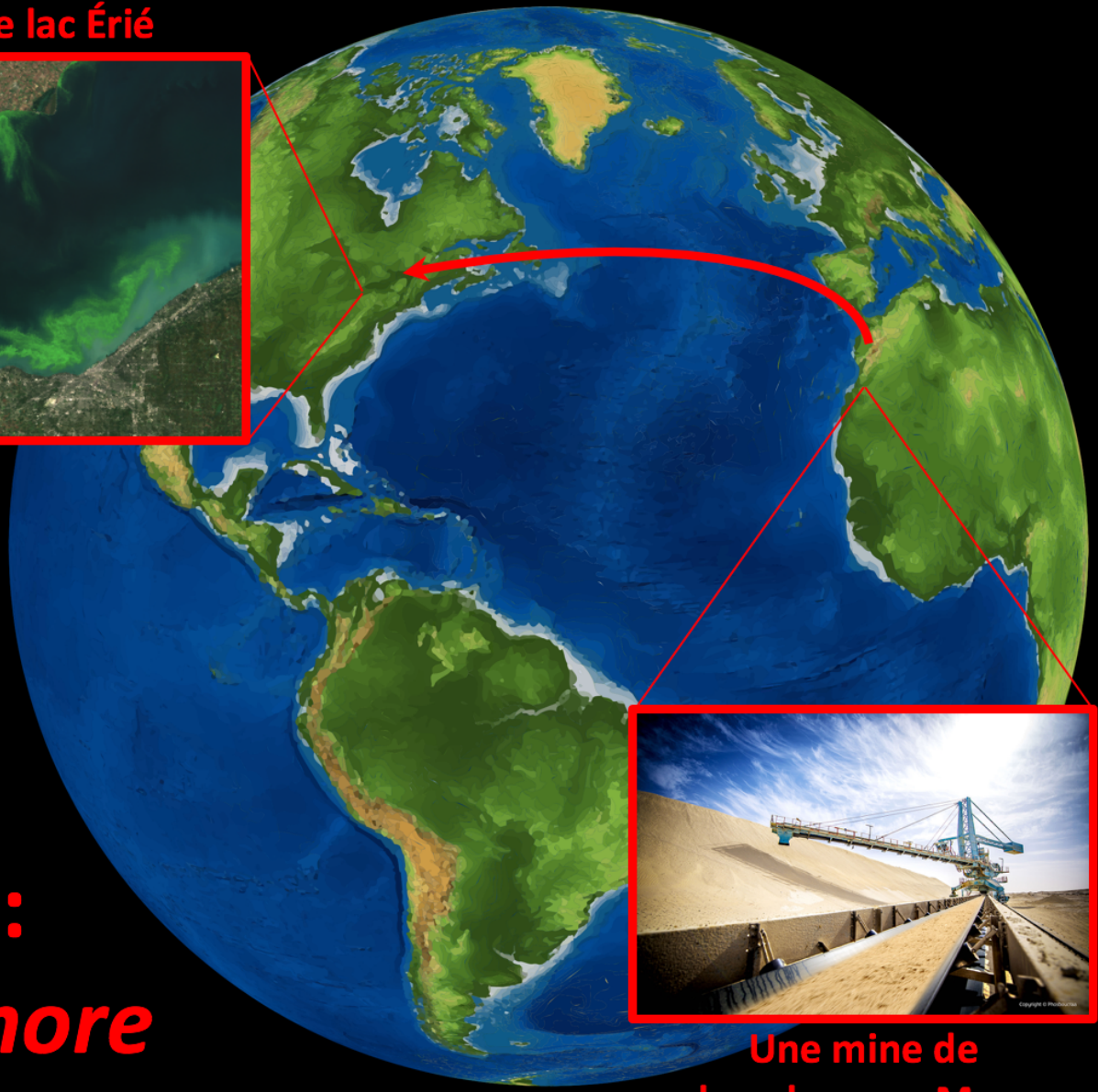
C'est un problème pour une ingénieure !

Mes recherches portent sur une façon de recycler le phosphore des eaux usées, afin de créer un engrais renouvelable ici au Canada. Notre équipe a déjà trouvé que le carbonate de calcium réagit avec le phosphore, et que le produit de cristallisation ressemble beaucoup à la roche phosphatée. Encore mieux, le Canada est riche en calcaire, qui est une source naturelle et peu chère de carbonate de calcium.

Nous sommes en train de construire un réacteur dans notre laboratoire pour tester notre processus, et nous envisageons de commencer des essais très bientôt comme… probablement cet après-midi.

Le phosphore est une ressource précieuse qu'il faut gérer. Afin de protéger l'environnement, et d'assurer la sécurité alimentaire pour nos enfants, il faut absolument trouver un moyen de recycler le phosphore, et je suis convaincue que nous avons pris les premiers pas sur le bon chemin.

Des algues dans le lac Érié



Attention aux excès: *Le phosphore*

Une mine de phosphore au Maroc

ANNEX D – APPENDIX D4

DESIGN DAY

Brief Description:
Our lab is exploring methods to extract and recycle phosphorus from municipal wastewater, in a form that could be used to make fertilizer.

What problem are you solving:
Canada uses over 1,400,000 metric tonnes of phosphorus fertilizer every year, all of which is imported from other countries. At the same time, phosphorus entering waterways causes significant damage to aquatic ecosystems every year, particularly apparent in the toxic algae blooms in Lake Erie and Lake Winnipeg. By developing a process that recycles this essential nutrient, we will be able to help solve this two-fold problem, i.e. assist in reducing phosphorus-induced eutrophication, as well as producing Canadian-sourced phosphorus for fertilizer which in turn improves our food security.

How are you solving it:
Our process uses calcium carbonate (which can be sourced from limestone) to react with phosphorus in wastewater streams to produce a calcium phosphate that resembles the phosphate rock used to produce chemical fertilizer.

What solutions currently exist:
One of the most successful technologies to recycle phosphorus is the Ostara process, which uses magnesium chloride to react with phosphorus in wastewater streams. However, this process is not compatible with all wastewater treatment plants, and magnesium chloride is not economically available everywhere. Our goal is to scale up our process and close that gap.

Do you have a prototype, what are its dimensions:
Our current prototype uses a series of peristaltic pumps and reaction vessels (500 - 2000mL) to mix a synthetic phosphorus wastewater stream with a calcium carbonate stream. After allowing sufficient contact time with the seed material in the main reaction vessel, the resulting slurry is separated for recycle back through the system. All components can fit on a 3' X 4' mobile cart, although we require access to power to plug in the pumps.

DESIGN DAY PITCH

[JESS] Our design tackles a looming global problem – food security. The world's population has doubled in the last 50 years to 7 billion people, who depend on fertilizer to provide the essential nutrients nitrogen, phosphorus, and potassium to our crops. This is because modern intensive agriculture techniques strip the soil of these elements very quickly.

[LU] Canada is rich in potash – which is rich in potassium – but we have a phosphorus problem. Every year, millions of tons of phosphorus are imported for use in fertilizer. The extraction and transportation of this raw material is very energy intensive, and while Canada has no *raw* phosphorus mineral deposits, there is another option…

[JESS] Our process recycles two important waste products – carbon dioxide, and sewage – by reacting them with an abundant mineral in Canada – limestone. Our resulting product chemically resembles the raw material used to create phosphorus fertilizer.

[LU] Even better, this additional processing step could be incorporated into existing sewage treatment plants, and has the potential to be adapted to other waste streams such as septic tanks and manure.

[JESS] Right now the vast majority of phosphorus waste ends up in landfills in a chemical form that cannot be used as fertilizer. Our process captures the phosphorus in a form that could be used for plant food. By closing this phosphorus cycle, we also contribute to food security for Canada, and the world.

ANNEX D – APPENDIX D5

GRADUATE POSTER COMPETITION

Abstract – CHG Graduate Poster Composition

JZ Ross, L Gao, EE Anthony, D Sutarwala, O Meouch, H Mamo, Dr S Omelon

Closing the phosphorus loop: Our future's food security
Precipitation of carbonated apatite from municipal wastewater

The world's 7 billion inhabitants depend on chemical fertilizers to meet the growing demand for food. The phosphorus used in fertilizer is sourced from ancient sedimentary deposits of Phosphate Rock (PR), largely in the form of carbonated calcium phosphate, called carbonated apatite. PR is non-renewable and Canada's reserves are extremely limited; in fact, all 1,400,000 tonnes of phosphorus products used annually is imported. At the same time, excess use of phosphorus leads to run-off, causing significant damage to watersheds. This project investigates a novel method to recycle phosphorus from municipal wastewater in a form that will enable its reuse as a fertilizer, thus contributing to a solution for both of these issues.
A series of inorganic phosphate (PO_4^-, or P_i) solutions was prepared to simulate the concentrations found in Ottawa's municipal wastewater, between 2.5-30 mM P_i. These solutions were mixed with saturated $CaCO_3$ solutions, while monitoring pH, $[Ca^{2+}]$ and $[P_i]$. Batch tests successfully reduced the $[P_i]$ and $[Ca^{2+}]$, and a precipitate formed. The precipitation products were characterized using Scanning Electron Microscopy (SEM), Raman spectroscopy (488 nm), X-Ray Diffraction (XRD), and These these techniques confirmed the presence of both P_i and CO_3 in a bone-like apatite. Although other technologies are being explored to recycle phosphorus from wastewater streams, this is the first indication that it is possible to precipitate a carbonate apatite using relatively cost-effective $CaCO_3$.

GRAD POSTER COMPETITION DAY

Introduction & Motivation

This time last year, I was an M.Eng student working on a little one-semester project to learn about crystallization and precipitation, and to try to find the supersaturation limit when mixing calcium and phosphorus.

But the more I learned about the motivation behind the "little project" and the more I struggled with the actual hands on chemistry of it, the more I realized that this was more than a one-semester project – it was a thesis. So last summer I made the switch to do a thesis, which was particularly terrifying because I had yet to find any meaningful results and it really could have been a disaster. But I am really proud and happy today to say that not only have I been able to find meaningful results, but that we have also taken the first steps toward putting these results to practical use.

So – what is this problem? In the really big picture, it is food security. In the last 50 years, the world's population has more than doubled to over 7 billion people, due in large part to the use of chemical fertilizers and intensified agriculture to grow enough food to feed us all.

But what I didn't realize until I started working on this project is the the phosphorus used to make these fertilizers is not renewable – so this is a critical, through long-term problem to address.

In the short term, there are also acute effects to the use of this phosphorus. If you step back a bit, you might be able to see better that these lovely greens and blues in the poster's background are not accidental – this is an image of a massive algae bloom in Lake Erie in 2015, so large that it was visible from space. This increased use of phosphorus in the soils leads to increased run-off and thus phosphorus load on our waterways.

So this project has a dual short and long-term motivation.

My specific project narrows the focus to just one waste phosphorus stream, municipal wastewater, although in essence the chemistry should work the same way for other waste streams as well.

The objectives were first of all to determine if was actually possible to precipitate phosphorus from a waste stream using a low cost calcium carbonate – which can be sourced from limestone which is literally dirt cheap. Next, assuming it worked, identify the range of concentrations that would work. Thirdly, analyze the species that were made to figure out whether the product could actually have value as a substitute for the non-renewable raw material for phosphorus fertilizer, aka Phosphate Rock, or if we had simply found another way to remove phosphorus from waste streams, but made an amorphous solid. And finally, assess what effect – if any – the presence of a seed material had an effect on the crystallization process.

CLOSING THE PHOSPHORUS LOOP: OUR FUTURE'S FOOD SECURITY

Precipitation of carbonate apatite from municipal wastewater

JZ Ross, L Gao, EE Anthony, D Sutarwala, O Meouch, H Mamo, Dr S Omelon

Department of Chemical and Biological Engineering, University of Ottawa, Ottawa, Ontario

Motivation

Canada uses over 1,400,000 metric tonnes of phosphorus fertilizer every year (1), all of which is imported from other countries. At the same time, phosphorus entering waterways causes significant damage to aquatic ecosystems every year, particularly apparent in the toxic algae blooms in Lake Erie and Lake Winnipeg. By developing a process that recycles this essential nutrient, we will be able to help solve this two-fold problem:

1) assist in reducing phosphorus-induced eutrophication in the *short* term, as well as 2) producing a Canadian-sourced phosphorus for fertilizer which in turn improves our food security in the *long* term.

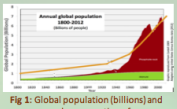


Fig 1: Global population (billions) and annual consumption of phosphate rock (million metric tonnes per year) (2,3).

*"We may be able to substitute nuclear power for coal, and plastics for wood, and yeast for meat, and friendliness for isolation – but **for phosphorus there is neither substitute nor replacement**."*

- Isaac Asimov, 1974

Objectives

1. Determine if it is **possible** to precipitate calcium phosphate solids from a synthetic wastewater solution using calcium carbonate via batch test;
2. Identify acceptable range of **concentrations**;
3. Confirm phosphate **speciation** and K_{sp} of precipitation products;
4. Verify what effect, if any, caused by the presence of a **seed** material.

Methods

A. PREPARATION

Synthetic solutions:

- Preliminary measurements found available $[P_i]$ in municipal wastewater process stream to be between 20 – 50 mM.
- Na_2HPO_4 was used to prepare a series of solutions at 2.5, 5, 10, 20, and 30 mM P_i.
- The saturated $CaCO_3$ solution was prepared by dissolving calcite in tap water and treating with CO_2 (g) to achieve a $[Ca^{2+}]$ between 4-6 mM. Tap water was used due to its relatively high initial $[Ca^{2+}]$ and $[CO_3^{2-}]$. $[Ca^{2+}]$ varied due to the solution's interaction with CO_2 in air.

B. SET-UP

Batch test:

- Equal volumes of synthetic P_i solution and saturated $CaCO_3$ solution were mixed.
- Aliquots were withdrawn every 24 hours over a period of 5 days.
- The pH was monitored and was allowed to drift as reaction proceeded.
- The solution was vacuum filtered to collect precipitate, which was dried overnight in a vacuum oven at 40°C and 5 mm Hg.

C. CHARACTERIZATION

Colorimetry:

- The $[P_i]$ and $[Ca^{2+}]$ of the sample aliquots was measured using colorimetry.
- The absorbance of the reaction solutions was compared with the absorbance of standard solutions of Ca^{2+} and P_i to determine their corresponding concentrations (9,10,11).

Microscopy:

- Precipitate was inspected visually using SEM at magnifications of 290x, 500x, and 1000x.

Spectroscopy:

- The solid products were examined and analyzed using Raman spectroscopy to identify what form of phosphate was present.

Conclusions

1. **This series of experiments demonstrated that it is in fact possible to precipitate P_i when mixed with a saturated $CaCO_3$ solution.**
2. **$[P_i]$ between 5-30 mM definitively interacts with $[Ca^{2+}]$ of 4-6 mM to form a precipitate.**
3. **The phosphorus was present in its inorganic form, the (PO_4^{3-}) ion, and carbonate substitutions were also detected. This means that *a carbonate apatite was indeed precipitated, which is the form required to produce fertilizer.***
4. **The precipitate formed proved itself to be effective as a seed material to further the reaction. This will increase the reaction's efficiency, and will be an important consideration in the reactor's design.**

Future Work

REACTOR: The Lab Group is in the process of testing a reactor prototype to evaluate a suitable residence time and reagent flow rates.

GENUINE WASTE: Bench scale tests are currently underway to test the feasibility of applying this method to liquid waste generously provided by the City of Ottawa's wastewater treatment plant.

ECONOMIC ASSESSMENT: Comparison of this novel method with existing methods of recovering P from waste streams.

CHARACTERIZATION: Additional precipitate is being prepared to better in order to control for additional parameters (residence time, pH, temperature, filtering and drying conditions), and thus improve characterization of the final product (solubility, CO_3^{2-} content.)

Results & Discussion

1. **POSSIBLE!** The Ca^{2+} and P_i ions precipitated out of solution, as confirmed both by a decrease in their respective concentrations and the presence of a solid in the reaction vessel. The ratio of Ca / P that came out of solution varied between 0.85 – 1.53 ± 0.28.

2. **CONCENTRATIONS, pH & MICROSCOPY:** The solids formed upon mixing 5 mM Ca^{2+} with 5-30 mM P_i are shown below, magnified 290x using SEM. Insufficient product was collected below this concentration, although both $[Ca^{2+}]$ and $[P_i]$ still decreased. The pH was allowed to drift throughout the reaction, and generally a slight increase in pH was observed over time, and with increasing initial $[P_i]$.

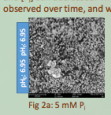


Fig 2a: 5 mM P_i

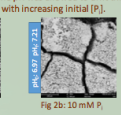


Fig 2b: 10 mM P_i

Fig 2c: 20 mM P_i

Fig 2d: 30 mM P_i

3.a) Ksp: As defined below, the Ksp was approximated by Ca x P. This was calculated both at the start of the reaction to assess the precipitation reaction's driving force, and again after 5 days. The differences in the initial $[P_i]$ and minor fluctuations in the starting $[Ca^{2+}]$ led to very different initial Ca x P. However, in all cases the Ca x P value approached an average of 1.71 ± 0.26 (mMol/L)² at eqm.

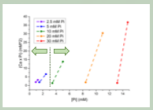


Fig 3a: Ca x P versus $[P_i]$, metastable limit

Of note is that at and below 5 mM P_i, the solid formed primarily on the reactor walls, or heterogeneously. Above 5 mM P_i, solid formed homogeneously within the solution. Often, spontaneous homogeneous nucleation above the critical supersaturation zone is avoided due as these products tend to be very fine and thus not desirable. However, ***the inverse of this expected relationship was observed*** throughout this series of experiments as is evident in Figs 2a-d; lower supersaturations yielded fine, crumbly solids, while higher supersaturations gave rise to apparently more crystalline solids.

3.b) SPECIATION: Raman shifts (488nm) were used to determine to identify P_i peaks in the solids, and confirm that it precipitated as (PO_4^{3-}) vice (HPO_4^{2-}). The presence of (CO_3^{2-}) substitutions was also verified using this method. The products were compared against a standard hydroxyapatite (HAP) as well as a biological CAp (emu bone).

Table 1: Raman shifts

Shift (cm^{-1})	Assignment	Description (8,11)
430	$v_2PO_4^{3-}$	Strong band
450	$v_2PO_4^{3-}$	Shoulder on 430 cm^{-1}
584-590	$v_4PO_4^{3-}$	Multiple partially resolved components
959-962	$v_1PO_4^{3-}$	Mature bone mineral, characteristic of carbonate apatite
1017-1048	$v_3PO_4^{3-}$	Stretching mode
1070	$v_1CO_3^{2-}$	B-type carbonate band (i.e. substitute for PO_4^{3-})

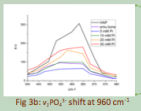


Fig 3b: $v_1PO_4^{3-}$ shift at 960 cm^{-1}

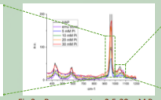


Fig 3c: Raman spectra, 2.5-30 mM P_i

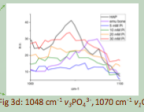


Fig 3d: 1048 cm^{-1} $v_3PO_4^{3-}$, 1070 cm^{-1} $v_1CO_3^{2-}$

4. SEED: Two different seed materials were tested, bone powder (biological CAp) and the precipitation product of the previous reaction (synthetic CAp). In both seeded cases, the final Ca x P was lowe than without the presence of the seed to provide a reaction surface. This is a valuable finding as it means that the ***spontaneous product can be recycled through the reactor to harvest a greater amount of P_i.*** The final Ca x P of the reaction seeded with a product of precipitation was 0.24 $(mMol/L)^2$ at equilibrium compared to the unseeded Ca x P value of 1.71 $(mMol/L)^2$.

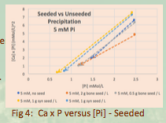


Fig 4: Ca x P versus [PI] - Seeded

Definitions

Apatite: A geological mineral that easily accepts many different substitutions due to its hexagonal geometry. In this project, apatite always means a calcium phosphate mineral.

Phosphate Rock (PR), or phosphorite: A sedimentary deposit of biological carbonate apatite, formed over tens of thousands of years. For a deposit to be economically feasible for processing into fertilizer, it must contain over 9% P_i (4).

Inorganic phosphate (P_i): the soluble phosphate ion (PO_4^{3-}) that is available to plants within soil.

Carbonate Apatite (CAp): Apatite in which some (PO_4^{3-}) ions have been substituted by (CO_3^{2-}) ions, thus increasing its solubility (5). This bio-mineral is commonly found in bone.

Ca x P: Due to the presence of substitutions within the lattice, CAp dissolves incongruently. As such, it has no agreed upon K_{sp}. In order to compensate for this, researchers use the approximation of $[Ca^{2+}]$ X $[P_i]$, or "Ca x P" to compare relative solubility of biological apatites (6,7), such as bone and PR.

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Background image: NASA Earth Observatory, Lake Erie Toxic Algal Bloom, July 28 2015, URL accessed 11 Mar 2017: http://earthobservatory.nasa.gov/IOTD/view.php?id=86327&eocnvimage&eocnvrelated_image

Acknowledgements

This project would not have been possible without the many invigorating talks with my lab-mates, most usually accompanied by something sweet, hot, and caffeinated. The fine gentlemen in the Machine Shop and Engineering IT were also instrumental in finding and building the materials that we needed – thank you Franco, Gerard, James, and Chris! And of course, Dr Omelon's energy and wisdom kept me on track, and helped to make sense of weird and wonderful chemistry of phosphates.

ANNEX E
Statistical Analysis

Calculated molar Ca/P ratio in product based on change in [Ca^{2+}] and [P_i]

ANOVAOneWay (7/17/2017 22:09:38)

Descriptive Statistics

	N Analysis	N Missing	Mean	Standard Deviation	SE of Mean
1	4	0	1.835	0.85955	0.42978
2	4	0	1.47	0.22964	0.11482
3	4	0	1.455	0.42977	0.21488
4	4	0	1.08	0.19149	0.09574
5	3	0	1.47667	0.18448	0.10651

One Way ANOVA

Overall ANOVA

	DF	Sum of Squares	Mean Square	F Value	Prob>F
Model	4	1.1413	0.28533	1.28572	0.32235
Error	14	3.10687	0.22192		
Total	18	4.24817			

Null Hypothesis: The means of all levels are equal.
Alternative Hypothesis: The means of one or more levels are different.
At the 0.05 level, the population means are not significantly different.

Fit Statistics

R-Square	Coeff Var	Root MSE	Data Mean
0.26866	0.32208	0.47108	1.46263

Means Comparisons

Bonferroni Test

	MeanDiff	SEM	t Value	Prob	Alpha	Sig	LCL	UCL
2 1	-0.365	0.33311	-1.09575	1	0.05	0	-1.47281	0.74281
3 1	-0.38	0.33311	-1.14078	1	0.05	0	-1.48781	0.72781
3 2	-0.015	0.33311	-0.04503	1	0.05	0	-1.12281	1.09281
4 1	-0.755	0.33311	-2.26655	0.39792	0.05	0	-1.86281	0.35281
4 2	-0.39	0.33311	-1.1708	1	0.05	0	-1.49781	0.71781
4 3	-0.375	0.33311	-1.12577	1	0.05	0	-1.48281	0.73281
5 1	-0.35833	0.3598	-0.99594	1	0.05	0	-1.5549	0.83824
5 2	0.00667	0.3598	0.01853	1	0.05	0	-1.1899	1.20324
5 3	0.02167	0.3598	0.06022	1	0.05	0	-1.1749	1.21824
5 4	0.39667	0.3598	1.10248	1	0.05	0	-0.7999	1.59324

Tukey Test

	MeanDiff	SEM	q Value	Prob	Alpha	Sig	LCL	UCL
2 1	-0.365	0.33311	1.54962	0.8059	0.05	0	-1.40294	0.67294
3 1	-0.38	0.33311	1.6133	0.78297	0.05	0	-1.41794	0.65794
3 2	-0.015	0.33311	0.06368	1	0.05	0	-1.05294	1.02294
4 1	-0.755	0.33311	3.20538	0.21261	0.05	0	-1.79294	0.28294
4 2	-0.39	0.33311	1.65576	0.76718	0.05	0	-1.42794	0.64794
4 3	-0.375	0.33311	1.59208	0.79072	0.05	0	-1.41294	0.66294
5 1	-0.35833	0.3598	1.40847	0.85287	0.05	0	-1.47943	0.76277
5 2	0.00667	0.3598	0.0262	1	0.05	0	-1.11443	1.12777
5 3	0.02167	0.3598	0.08516	1	0.05	0	-1.09943	1.14277
5 4	0.39667	0.3598	1.55914	0.80253	0.05	0	-0.72443	1.51777

Sig equals 1 indicates that the difference of the means is significant at the 0.05 level.
Sig equals 0 indicates that the difference of the means is not significant at the 0.05 level.

Carbonate content of products (unseeded, or seeded with precipitate)

ANOVAOneWay (7/17/2017 15:43:41)

Descriptive Statistics

	N Analysis	N Missing	Mean	Standard Deviation	SE of Mean
1	3	0	1.95667	0.08145	0.04702
2	4	0	1.21	0.43305	0.21653
3	4	0	1.1325	0.13623	0.06811
4	3	0	1.10333	0.03786	0.02186
--	0	7	--	--	--

One Way ANOVA

Overall ANOVA

	DF	Sum of Squares	Mean Square	F Value	Prob>F
Model	4	1.54554	0.38639	5.48144	0.01621
Error	9	0.63441	0.07049		
Total	13	2.17995			

Null Hypothesis: The means of all levels are equal.
Alternative Hypothesis: The means of one or more levels are different.
At the 0.05 level, the population means are significantly different.

Fit Statistics

R-Square	Coeff Var	Root MSE	Data Mean
0.70898	0.20038	0.2655	1.325

Means Comparisons

Bonferroni Test

	MeanDiff	SEM	t Value	Prob	Alpha	Sig	LCL	UCL
2 1	-0.74667	0.20278	-3.68218	0.05058	0.05	1	--	--
3 1	-0.82417	0.20278	-4.06437	0.02823	0.05	1	--	--
3 2	-0.0775	0.18774	-0.41281	1	0.05	1	--	--
4 1	-0.85333	0.21678	-3.93642	0.03425	0.05	1	--	--
4 2	-0.10667	0.20278	-0.52603	1	0.05	1	--	--
4 3	-0.02917	0.20278	-0.14384	1	0.05	1	--	--
-- 1	-1.95667	--	1.5849E300	0	0.05	1	--	--
-- 2	-1.21	--	9.801E299	0	0.05	1	--	--
-- 3	-1.1325	--	9.17325E299	0	0.05	1	--	--
-- 4	-1.10333	--	8.937E299	0	0.05	1	--	--

Tukey Test

	MeanDiff	SEM	q Value	Prob	Alpha	Sig	LCL	UCL
2 1	-0.74667	0.20278	5.20739	0.03138	0.05	1	--	--
3 1	-0.82417	0.20278	5.74789	0.01811	0.05	1	--	--
3 2	-0.0775	0.18774	0.58381	0.99282	0.05	1	--	--
4 1	-0.85333	0.21678	5.56694	0.02174	0.05	1	--	--
4 2	-0.10667	0.20278	0.74391	0.98231	0.05	1	--	--
4 3	-0.02917	0.20278	0.20341	0.99988	0.05	1	--	--
-- 1	-1.95667	--	2.24139E300	0	0.05	1	--	--
-- 2	-1.21	--	1.38607E300	0	0.05	1	--	--
-- 3	-1.1325	--	1.29729E300	0	0.05	1	--	--
-- 4	-1.10333	--	1.26388E300	0	0.05	1	--	--

Sig equals 1 indicates that the difference of the means is significant at the 0.05 level.
Sig equals 0 indicates that the difference of the means is not significant at the 0.05 level.

Solubility of product: [P_i]

ANOVAOneWay (7/17/2017 11:41:50)

Descriptive Statistics

	N Analysis	N Missing	Mean	Standard Deviation	SE of Mean
1	3	0	0.15947	0.02485	0.01435
2	4	0	0.22683	0.03537	0.01768
3	4	0	0.50745	0.11664	0.05832
4	3	0	0.44947	0.08621	0.04977
5	4	0	0.22163	0.00726	0.00363

One Way ANOVA

Overall ANOVA

	DF	Sum of Squares	Mean Square	F Value	Prob>F
Model	4	0.34091	0.08523	18.21581	3.05392E-5
Error	13	0.06082	0.00468		
Total	17	0.40174			

Null Hypothesis: The means of all levels are equal.
Alternative Hypothesis: The means of one or more levels are different.
At the 0.05 level, the population means are significantly different.

Fit Statistics

	R-Square	Coeff Var	Root MSE	Data Mean
	0.8486	0.2179	0.0684	0.31391

Means Comparisons

Bonferroni Test

	MeanDiff	SEM	t Value	Prob	Alpha	Sig	LCL	UCL
2 1	0.06736	0.05224	1.28934	1	0.05	0	-0.10883	0.24355
3 1	0.34798	0.05224	6.6609	1.56161E-4	0.05	1	0.1718	0.52417
3 2	0.28062	0.04837	5.80196	6.15527E-4	0.05	1	0.11751	0.44374
4 1	0.29	0.05585	5.1925	0.00173	0.05	1	0.10165	0.47835
4 2	0.22264	0.05224	4.26168	0.00927	0.05	1	0.04645	0.39883
4 3	-0.05798	0.05224	-1.10988	1	0.05	0	-0.23417	0.1182
5 1	0.06217	0.05224	1.18993	1	0.05	0	-0.11402	0.23835
5 2	-0.00519	0.04837	-0.10737	1	0.05	0	-0.16831	0.15792
5 3	-0.28582	0.04837	-5.90932	5.15657E-4	0.05	1	-0.44894	-0.1227
5 4	-0.22783	0.05224	-4.36108	0.00771	0.05	1	-0.40402	-0.05165

Tukey Test

	MeanDiff	SEM	q Value	Prob	Alpha	Sig	LCL	UCL
2 1	0.06736	0.05224	1.8234	0.70193	0.05	0	-0.09714	0.23185
3 1	0.34798	0.05224	9.41994	1.27091E-4	0.05	1	0.18349	0.51248
3 2	0.28062	0.04837	8.2052	4.90293E-4	0.05	1	0.12833	0.43292
4 1	0.29	0.05585	7.34331	0.00135	0.05	1	0.11415	0.46585
4 2	0.22264	0.05224	6.02693	0.00684	0.05	1	0.05815	0.38714
4 3	-0.05798	0.05224	1.56961	0.79865	0.05	0	-0.22248	0.10651
5 1	0.06217	0.05224	1.68282	0.75693	0.05	0	-0.10233	0.22666
5 2	-0.00519	0.04837	0.15184	0.99997	0.05	0	-0.15749	0.1471
5 3	-0.28582	0.04837	8.35704	4.122E-4	0.05	1	-0.43811	-0.13353
5 4	-0.22783	0.05224	6.1675	0.00573	0.05	1	-0.39233	-0.06334

Sig equals 1 indicates that the difference of the means is significant at the 0.05 level.
Sig equals 0 indicates that the difference of the means is not significant at the 0.05 level.

Solubility of product – $[Ca^{2+}]$

ANOVAOneWay (7/17/2017 11:39:06)

Descriptive Statistics

	N Analysis	N Missing	Mean	Standard Deviation	SE of Mean
1	3	0	0.163	0.016	0.00924
2	4	0	0.18013	0.03261	0.01631
3	4	0	0.18088	0.02078	0.01039
4	3	0	0.16927	0.05763	0.03327
5	4	0	0.2144	0.01311	0.00655

One Way ANOVA

Overall ANOVA

	DF	Sum of Squares	Mean Square	F Value	Prob>F
Model	4	0.00576	0.00144	1.53977	0.24837
Error	13	0.01216	9.35058E-4		
Total	17	0.01791			

Null Hypothesis: The means of all levels are equal.
Alternative Hypothesis: The means of one or more levels are different.
At the 0.05 level, the population means are not significantly different.

Fit Statistics

	R-Square	Coeff Var	Root MSE	Data Mean
	0.32147	0.16687	0.03058	0.18324

Means Comparisons

Bonferroni Test

	MeanDiff	SEM	t Value	Prob	Alpha	Sig	LCL	UCL
2 1	0.01713	0.02335	0.73325	1	0.05	0	-0.06164	0.09589
3 1	0.01788	0.02335	0.76536	1	0.05	0	-0.06089	0.09664
3 2	7.5E-4	0.02162	0.03469	1	0.05	0	-0.07217	0.07367
4 1	0.00627	0.02497	0.25099	1	0.05	0	-0.07794	0.09047
4 2	-0.01086	0.02335	-0.46493	1	0.05	0	-0.08962	0.06791
4 3	-0.01161	0.02335	-0.49704	1	0.05	0	-0.09037	0.06716
5 1	0.0514	0.02335	2.20072	0.46436	0.05	0	-0.02737	0.13016
5 2	0.03427	0.02162	1.58504	1	0.05	0	-0.03865	0.10719
5 3	0.03352	0.02162	1.55036	1	0.05	0	-0.0394	0.10644
5 4	0.04513	0.02335	1.93239	0.75397	0.05	0	-0.03363	0.12389

Sig equals 1 indicates that the difference of the means is significant at the 0.05 level.
Sig equals 0 indicates that the difference of the means is not significant at the 0.05 level.

Solubility of product – Ca x P

ANOVAOneWay (7/17/2017 11:45:16)

Descriptive Statistics

	N Analysis	N Missing	Mean	Standard Deviation	SE of Mean
1	3	0	0.02613	0.006	0.00346
2	4	0	0.0417	0.0135	0.00675
3	4	0	0.0904	0.01551	0.00776
4	3	0	0.0746	0.02091	0.01207
5	4	0	0.04755	0.00393	0.00197

One Way ANOVA

Overall ANOVA

	DF	Sum of Squares	Mean Square	F Value	Prob>F
Model	4	0.00954	0.00239	13.7172	1.35207E-4
Error	13	0.00226	1.73903E-4		
Total	17	0.0118			

Null Hypothesis: The means of all levels are equal.
Alternative Hypothesis: The means of one or more levels are different.
At the 0.05 level, the population means are significantly different.

Fit Statistics

	R-Square	Coeff Var	Root MSE	Data Mean
	0.80845	0.23253	0.01319	0.05671

Means Comparisons

Bonferroni Test

	MeanDiff	SEM	t Value	Prob	Alpha	Sig	LCL	UCL
2 1	0.01557	0.01007	1.54555	1	0.05	0	-0.0184	0.04953
3 1	0.06427	0.01007	6.38078	2.41538E-4	0.05	1	0.0303	0.09823
3 2	0.0487	0.00932	5.22265	0.00164	0.05	1	0.01725	0.08015
4 1	0.04847	0.01077	4.50127	0.00596	0.05	1	0.01215	0.08478
4 2	0.0329	0.01007	3.26651	0.0613	0.05	0	-0.00107	0.06687
4 3	-0.0158	0.01007	-1.56872	1	0.05	0	-0.04977	0.01817
5 1	0.02142	0.01007	2.12638	0.532	0.05	0	-0.01255	0.05538
5 2	0.00585	0.00932	0.62736	1	0.05	0	-0.0256	0.0373
5 3	-0.04285	0.00932	-4.59529	0.00502	0.05	1	-0.0743	-0.0114
5 4	-0.02705	0.01007	-2.68569	0.18697	0.05	0	-0.06102	0.00692

Tukey Test

	MeanDiff	SEM	q Value	Prob	Alpha	Sig	LCL	UCL
2 1	0.01557	0.01007	2.18574	0.55354	0.05	0	-0.01615	0.04728
3 1	0.06427	0.01007	9.02379	1.95415E-4	0.05	1	0.03255	0.09598
3 2	0.0487	0.00932	7.38594	0.00128	0.05	1	0.01934	0.07806
4 1	0.04847	0.01077	6.36576	0.00447	0.05	1	0.01456	0.08237
4 2	0.0329	0.01007	4.61954	0.0406	0.05	1	0.00119	0.06461
4 3	-0.0158	0.01007	2.2185	0.54022	0.05	0	-0.04751	0.01591
5 1	0.02142	0.01007	3.00715	0.26642	0.05	0	-0.0103	0.05313
5 2	0.00585	0.00932	0.88722	0.96789	0.05	0	-0.02351	0.03521
5 3	-0.04285	0.00932	6.49872	0.00379	0.05	1	-0.07221	-0.01349
5 4	-0.02705	0.01007	3.79814	0.11083	0.05	0	-0.05876	0.00466

Sig equals 1 indicates that the difference of the means is significant at the 0.05 level.
Sig equals 0 indicates that the difference of the means is not significant at the 0.05 level.