MODIFICATION OF HYDROXYAPATITE (HAP) WITH 1-HYDROXYETHANE-1, 1-DIPHOSPHONIC ACID (HEDP) FOR THE SELECTIVE SORPTION OF METAL IONS FROM WATER

by

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Abstract

MODIFICATION OF HYDROXYAPATITE (HAP) WITH 1-HYDROXYETHANE-1, 1-DIPHOSPHONIC ACID (HEDP) FOR THE SELECTIVE SORPTION OF METAL IONS FROM WATER

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Adviser: Professor Spiro D. Alexandratos

The United States Center for Disease Control and Prevention (CDC) has linked several diseases to water pollution. Metal ions such as lead, cadmium and copper are among the biggest contributors to water pollution and can leach into water from corroded plumbing, battery and paint discharges, glass and electronic production wastes and natural deposits. Toxic amounts of these metals have been shown to cause kidney failure, liver damage, developmental delay and several forms of cancer. The effect of groundwater pollution on disease has created a dire need to safely remove toxic metal ions from groundwater systems. The application of organophosphate-modified hydroxyapatite (mHAP) for water remediation is presented in this study. Hydroxyapatite (HAP) was modified with complexant 1-hydroxyethane 1, 1-diphosphonic acid (HEDP) and its effect on metal ion affinity and selectivity was determined. HAP was synthesized from calcium hydroxide and phosphoric acid, calcined at 700^{o}C and modified by a post-functionalization method with HEDP. The influence of time and temperature on the extent of modification was investigated. An increasing concentration of HEDP (0.01 to 0.50 M) resulted in more modification. Both untreated and HEDP-treated HAP were characterized using Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive x-ray spectroscopy (EDS), ICP-OES and specific surface area (SSA) measurements. Ca/P ratios, acid capacities and phosphorus elemental analyses provide information about the effect of modification on mHAP composition, surface characteristics and interactions. A high reaction temperature during modification produced new, distinct phosphate bands (993cm^{-1}, 1082cm^{-1}, 1144cm^{-1}) indicating the presence of HEDP. This was independent of reaction time. HAP modified at both high temperature and long reaction time had the highest HEDP loading and revealed the sharpest XRD peaks. The emergence of new HAP-HEDP strands was observed in SEM images for treated samples while EDS and ICP showed high phosphorus contents in these strands. HAP modified at high temperature for the long reaction also had a high acid capacity and more organic phosphorus than the controls, resulting from the presence of additional P-OH groups in HEDP. Selectivity for Pb(II) (90%) and Cd(II) (80%) over Zn(II) (25%), Ni(II) (18%) and Cu(II) (0%) from 10^{-4} N nitrate solutions was high for this sample compared to the metal ion sorption of unmodified HAP and HAP modified for the short reaction time at low temperature. The newly synthesized mHAP was not only selective for Pb(II) and Cd(II) but had unique chemical properties that were different from HAP-HEDP salts prepared by alternative pre-functionalization methods and different from Ca-HEDP salts.

Aims of the Dissertation

HAP will be synthesized, calcined at 700^{o}C and post-functionalized with 1-hydroxy-ethylidene-1, 1-diphosphonic acid (HEDP). The goal is to modify HAP to increase its metal ion selectivity.

Specific Aims

Aim 1: Establish parameters for producing mHAP samples.

Aim 2: Successfully incorporate HEDP into HAP.

Aim 3: Characterize the chemical and physical properties of mHAP.

Aim 4: Assess the metal ion affinity and selectivity of mHAP.

Acknowledgements

Many years ago, I never imagined that I would ever have the potential to become a successful scientist and obtain a Ph.D. It was certainly not the career of choice for any of the teenage girls I grew up with in Brooklyn. Today, I can proudly say that I have succeeded beyond my own expectations.

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My very first encounter with research occurred when I was in high school, in an animal behavior lab under the supervision of Dr. Mimi Halpern at the State University of New York Downstate Medical Hospital. I am grateful to Dr. Halpern for stirring me in the right direction at such a young age.

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Dedication

To my grandmother, Ruby Didier (recently deceased) who has been one of the strongest female icons in my life; I dedicate this professional achievement to you. A mother of 5, grandmother to 8 and great-grandmother to 4, she instilled a strong sense of discipline, hard work, patience and faith in us all. Without these fundamental life lessons, my incessant drive for success and the ultimate completion of my doctoral dissertation could not be fulfilled. Thank you grandma. I love you and may you rest in peace.

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CHAPTER 1. Water Remediation: Chemistry, Policy and Environmental Perspectives

1.1 Introduction

Water is an essential part of living organisms. The human body alone is comprised of ~60% water therefore continuous access to clean water is crucial for life preservation. Toxic metals, wastes, bacteria, parasites and infectious agents can leach into ground or surface water and produce long term effects on human health, causing problems like intestinal, kidney and bladder diseases as well as blood and skin-related conditions.[1,2] Efforts to develop efficient water remediation strategies are therefore mandatory.

The primary approach to water remediation involves chemical analyses to identify pollutants, assess toxicity and provide chemical treatment. The problem with polluted water systems lies not only in their toxicity but also in limitations to find safe, environmentally friendly, energy-efficient and economically sound ways of removing these pollutants, to generate clean water without producing waste by-products. Advancements in water remediation efforts are also limited by sociopolitical factors which control clean water standards.

The definition of clean water is primarily determined by environmental perspectives which vary throughout different geographical regions. This prevents the practice of clean water distribution from developing into a regulated global standard. It also causes variation in the quality of water. In spite of U.S. waste regulatory laws and current evidence by the U.S. CDC linking over 150 diseases to water pollution,[3] water continues to be polluted today by textile factories, chemical industries and power plants. This becomes worse in countries with little to no water safety regulators or environmental enforcement. Water treatment is not always practical for societies with limited resources, since these methods can be very costly. This chapter briefly reviews the current methods used to make water safe with respect to factors like accessibility, economy and environmental impact. It also suggests the use of a cheap, safe and selective hydroxyapatite (HAP) polymer, which can be used to remove toxic metals from water.

1.2 Factors affecting water access

Although water occupies over 10^{18} cubic meters of the earth, only 3% is freshwater while the remaining 97% is salt water.[4,5] Organisms rely on freshwater for essential life processes as it is one of the most important resources on earth.[6] On average, the humans consume 7% of their body weight in water, which can range from 100 to 200 oz per day.[7] Like many valuable natural resources however, the freshwater supply only remains available if it is not exploited.

In order to preserve water, nature utilizes a hydrologic cycle, which is a dynamic process that sustains water through evaporation, transpiration, condensation, transportation and precipitation. It works as a natural system to recycle water and enables it to be continuously regenerated. There are several factors which interrupt these natural processes and in some cases diminish them. Some of these include anthropogenic activities like pollution and the overproduction of greenhouse gases. Industrial, agricultural, and domestic activities such as deforestation, urbanization, resource exploitation, reservoir depletion and human population growth have all limited the access to clean water and consequently increased water demands globally.[8,9,10] Additionally, only 8% of freshwater supplied globally is allocated to domestic use while the remaining 22% is used in industry and 70% in agriculture.[11,12]

In the environment, especially in societies with limited access to clean water and water remediation technology, natural water bodies become the primary water source. Species relying on this source are negatively affected by water misuse and pollution causing potential declines in the biodiversity of freshwater habitats.[13] Both surface water and groundwater can be used for domestic purposes however, since groundwater is not directly exposed to all forms of environmental pollution, it is frequently assumed to be cleaner. Improper waste disposal however can cause groundwater pollution which has become an increasing concern in under-developed countries.[6]

Although natural bodies are an affordable water source for many populations this is not always a feasible option especially to those living in urban or inland locations. Additionally, some populations may not have the technology or resources to pump freshwater into their homes from distant water bodies. The concept of bottling water for redistribution and sale is therefore an adaptive measure. The problem with this practice is that it does not come without additional environmental pollution; plastic waste bottles are a result. A study by the Forestry and National Resource group at Purdue University revealed that people using bottled water believed it was safer and tasted better than tap water and preferred to continue to use it despite the increased plastic waste concern. They argued that recycling could reduce this environmental impact.[14]

Modern technology has been implemented to purify water for domestic use as well as for agricultural and specialized industrial applications. The kind of treatment administered depends on the intended use. Water for human consumption will typically be treated for bacteria and microorganisms but may still have high levels of calcium or magnesium. On the contrary, industrial applications can operate with microorganism-containing water but not scale causing chemicals.

One of the most commonly used wastewater treatment methods is ion-exchange. This method uses a solid ion-exchanger which sequesters metal ions from the polluted water. It is a relatively simple process and usually only requires a pH pretreatment to create an environment with a high enough pH to allow the metal ions to load onto the exchanger, but low enough to prevent metal hydroxide precipitation.[15] Mechanisms for ion-exchange depend on the type of exchanger used, treatment parameters and chemical properties of the metal ions in the water. The advantage of ion-exchangers over other treatment methods is attributed to the fact that they can be regenerated after metal loading by acid or salt conditioning. This changes the exchanger back to its initial state.[4,15]

1.3 Pollutants

Water pollutants can range from a variety of substances that include trace elements, heavy metals, organically-bound metals, radionuclides, inorganic pollutants, asbestos, algal nutrients, acids and bases, excess salts, trace organic pollutants, polychlorinated biphenyls, fertilizers and pesticides, detergents, petroleum, sewage, human and animal wastes, pathogens, chemical carcinogens, sediments, odorants and dyes. These have adverse effects on humans and aquatic organisms and have forced environmentalists to seek more efficient ways of reducing them. Techniques extrapolated from the hydrologic cycle such as thermal treatment and distillation (evaporation and precipitation) as well extraction, adsorption and ion-exchange have been used.[4]

1.3.1 Metals and ionic species

Some of the most pervasive pollutants in water are metals and ionic species. Metal pollutants can be classified as heavy or trace metals. Trace elements are normally found in natural water bodies. Heavy transition metals exist naturally at low levels in the environment, with metals like mercury, lead and cadmium can be toxic. Arsenic, beryllium, boron, chromium, copper, fluorine, iodine, manganese, molybdenum, selenium and zinc are other metal pollutants found in natural water.[4]

These species are present in ground, tap and spring water. In Toyama Prefecture, Japan, ionic species (Ca^{2+}, K^{+}, Si^{4+}, Mg^{2+}, Na^{+}, SO_4^{2-}, HCO_3^{-}, NO_3^{-} and Cl^{-}); trace metals (As(V), Cd(II), Cr(II), Co(II), Cu(II), Fe(II), Pb(II), Mn(II), Mo(II), Ni(II), V(II), Zn(II), Hg(II)); and several organic species were identified by ion chromatography (IC), inductively coupled plasma atomic emission spectroscopy (ICP-AES) and headspace gas chromatography mass spectrometry (GC-MS) in water. [16] Although their levels were reported to be below World Health Organization (WHO) standards, it is clear that the water, even after treatment, was not pollutant-free.

Of the heavy metal and metalloid water pollutants, mercury and arsenic are two of the most toxic. Mercury comes from minerals of continental rocks and anionic arsenic is found in the Earth's crust and can be produced as a mining by-product or as a by-product of fossil fuel combustion. These pollutants are extremely difficult to treat since they are not easily identified. Ion-exchange (IE) techniques have proven to be successful at removing arsenates as well as nitrates, fluorides, perchlorates, chromates, phosphates and thiocyanates from polluted water.[12] The removal of these pollutants requires extreme urgency since they can easily be ingested from natural water sources and cause health-related problems.[4]

1.3.2 Non-metal species

Non-metal water pollutants like pathogens, pharmaceuticals, hormones and turbidity are also problematic. They too have increased awareness to organizations such as the WHO and the United States Environmental Protection Agency (EPA) to implement better methods for controlling water pollution.

The pathogenic species, *Cryptosporidium*, has caused morbid diarrhea in about 0.15% of the population in China drinking the contaminated water.[17] Taiwan suffers from water turbidity resulting from excessive rainfall that causes landslides, soil erosion and debris translocation. This increases the level of toxic organics and particulates present in water.[18] Suspended particles in water can enter the body orally and through the lungs or skin. According to a study in Ohio, household showers and humidifiers transfer particles in water to the skin and also create crystallized mineral particles after the water evaporates. These particles contribute to indoor air particulate levels and can often be respiratory irritants.[19]

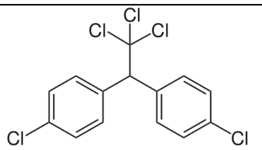
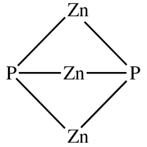
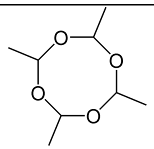
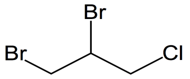
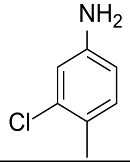
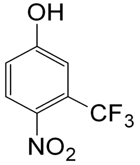
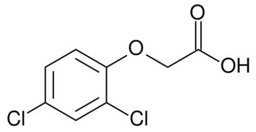
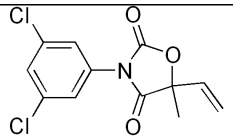
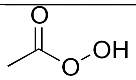
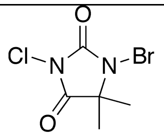
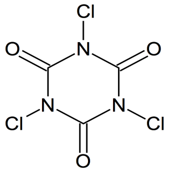
Pharmaceuticals and hormones are another class of non-metal water pollutants which can enter water supplies from processing plant wastes or household wastes. Painkillers, antibiotics, psychotropic drugs, and beta-blockers have been found in water supplies.[20]

The agricultural industry has played a major role in contributing to groundwater pollution by using pesticides (Table 1). After being sprayed, these pesticides not only poison the targeted species but they settle into water bodies or combine with agricultural drainage where they are easily accessible to human contact and cause sickness.[4]

The toxins produced by pesticides are dangerous to the species they target as well as to humans, at certain doses. For example, 2,4-Dichlorophenoxyacetic acid (2,4-D) is an herbicide which was used during the Vietnam war to kill enemy crops and reduce protective forest canopies. The herbicide was later linked to cancer and nerve damage in humans. The chemicals within pesticides can also react with water to produce secondary toxins that have adverse affects on human health. Zinc phosphide is a rodenticide that produces phosphine and zinc hydroxide by after reacting with water according to the following reaction:

$$Zn_3P_2\,(s) + 6\,H_2O\,(l) \rightarrow 2\,PH_3\,(g) + 3\,Zn(OH)_2\,(s) \qquad (1.1)$$

Table 1.1 List of pesticides, chemical structures and target species

Pesticide (targeted species)	Chemical structure and name
Insecticide (invertebrates)	 dichlorodiphenyltrichloroethane ($C_{14}H_9Cl_5$)
Rodenticide (vertebrates)	 Zinc Phosphide (Zn_3P_2)
Molluscicide (snails and slugs)	 Metaldehyde $(CH_3CHO)_4$)
Nematicide (microscopic roundworms)	 1,2-Dibromo-3-chloropropane ($C_3H_5Br_2Cl$)
Avicide (birds)	 3-chloro-4-methylaniline (C_7H_8ClN)
Piscicide (fish)	 3-trifluoromethyl-4-nitrophenol ($C_7H_4F_3NO_3$)
Herbicide (plants)	 2,4-Dichlorophenoxyacetic acid-2,4-D ($C_8H_6Cl_2O_3$)
Fungicide (fungi)	 Vinclozolin ($C_{12}H_9Cl_2NO_3$)
Bactericide (bacteria)	 Peracetic acid ($C_2H_4O_3$)
Slimicide (slime-causing organisms)	 1-Bromo-3-chloro-5, 5 dimethylhydantoin ($C_5H_6BrClN_2O_2$)
Algicide (algae)	 Trichloroisocyanuric acid ($C_3Cl_3N_3O_3$)

The dense phosphine gas produced can combine with air and spontaneously ignite. Phosphorus pentoxide forms as a product of phosphine combustion and is a severe lung irritant.[21,22]

Organic pollutants can also be generated from domestic sources. These include human bodily wastes, household products, garbage, cooking fuels, disinfectants, soaps and detergents. If these wastes are improperly treated, they end up in groundwater and on ocean beds where they react with dissolved chemicals to form residues.[4]

1.4 Water remediation

Although environmental species and minerals can facilitate the removal of wastes naturally from water, in processes like photosynthesis, nitrogen fixation, dissolution-precipitation, acid-base reactions, oxidation-reduction and ion-exchange, they are not ideal for treating large amounts of wastewater.[4] These chemical reactions are very important for sustaining an ecosystem with clean water and can serve as a model for manmade water treatment applications that function to remove toxins from water and remain nontoxic in the environment.

Ion-exchange is one of the most effective water remediation methods reported. It works by exchanging cationic, anionic or amphoteric groups. The following reaction illustrates the process of cation exchange:

$$A^+X^- + B^+\,(aq) \rightarrow B^+X^- + A^+\,(aq)^6 \qquad (1.2)$$

where A^+X^- is the ion-exchanger and B^+ is the ionic species of interest present in water. The ion B^+ is exchanged with ion A^+ and trapped on the exchanger for disposal or concentration.

The use of ion-exchangers for water treatment has led to treatment technologies that are capable of removing toxic metals like lead, mercury, cadmium, zinc, uranium, plutonium, and americium from water. The commercial Diphonix Resin®, shown in Figure 1.1, is one of the most well-known ion-exchange resins developed.[23] The resin has a polymeric support functionalized with diphosphonic, sulphonic and carboxylic acid groups used for the sorption of Cu(II), Zn(II), Co(II) and Pb(II) and the retention of actinides. The diphosphonic acid ligands increase selectivity and the removal of metal ions and the hydrophilic sulphonic acid functional groups increase metal ion accessibility to improve the exchange kinetics of Diphonix Resin®.

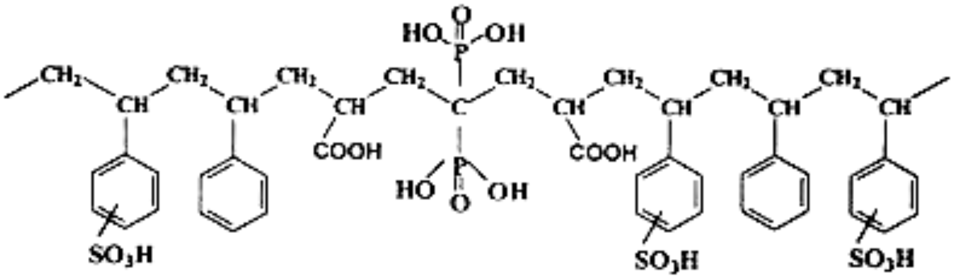


Fig 1.1 Diphonix Resin®[23]

The inorganic polymer HAP, which also has excellent ion exchange abilities, has been investigated for water remediation purposes as well. It can be functionalized with ion-selective ligands which may enhance its metal ion selectivity. Following metal ion sequestration, the salt retains it non-toxic properties. Hydroxyapatite has been reported to valorize or add value to heavy-metal polluted soils where it can be safely integrated into the soil matrix.[24]

1.4.1 Treatment options

Commercial ion-exchange technology is effective in treating large amounts of metal ion polluted water however it can only be used in areas where accessibility is not limited by its costs, local policies and its limited ability to be reused. Homemade water filtration systems have been developed as a result of these limitations. In India, an affordable corn maize powder, *Zea mays,* was modified with dimethylamine and thioglycolic acid to produce two modified materials which removed arsenic from water.[25] The need to address arsenic polluted water is a concern primarily in areas like India and Bangladesh where life-threatening cases have been reported because of limited treatment technology.

Some areas with limited access to clean water have resorted to using defective household water treatment systems (HWTS). In southern African communities, silver-impregnated porous pots (SIPP) filters produced water with little turbidity (0.7-1.0 NTU) and a decreasing coliform bacteria population, compared to other HWTS devices like the biosand filter-standard (BSF-S), biosand filter-zeolite (BSF-Z), bucket filter (BF) and the ceramic candle filter (CCF).[26] This technique reduced turbidity and bacterial substrates in order to limit the survival rate of microbiomes and their subsequent advancement into larger water bodies. It did not however eliminate all strains of bacteria from water.[27]

In Texas, residents used rooftop rainwater harvesting systems in their households as a means of obtaining clean water. Although the idea is promising, the practice is subject to harmful outcomes if it is done improperly or by using defective materials.[28] The mean amount of copper detected after filtration from this system was five times higher compared to pre-filtered water samples. Additionally, the maximum amount of arsenic measured was found in a post-filtered sample, even though the post-filtration mean was lower.

Water treatment criteria vary according to the wastewater composition and the application for which it will be used. Water used for showering, boilers, recharge aquifers and recreational water activities are very well treated, however water used for applications like industrial quenching often only require mild treatment conditions. Solid wastes can be removed using sedimentation and filtration however more precise methods are required to treat biological and chemical wastes. These include biological treatment for organic species; phosphate lime precipitation for algae; denitrification for nitrogen, and sulfide precipitation or reverse osmosis for heavy metals, cations and anions. Coagulation devices, foam flotation, electrolysis and activated sludge are also used,[12] as well as disinfection methods such as chlorination, ozonation and hydrogen peroxide oxidation.[4] Many of these methods are expensive, non-selective and can generate secondary wastes following treatment. This reiterates the need to develop cheap, selective and environmentally safe water remediation technology.

The increasing global demand for clean water has created a fine line between safe and unsafe water, as less concern is given to analyzing the water source and more towards meeting demands. Many societies have resorted to using processed wastewater which contains various degrees of pollution. One example is the use of dirty river water exposed to sewage. Although this kind of water has normally been used for non-drinking purposes, its use in agricultural and industrial process can still be dangerous to human health.[4]

The affordable, inorganic and insoluble HAP polymer is a strong candidate for water remediation applications. Additionally, with the emergence of functionalized polymers like the Diphonix Resin® selectivity can now be achieved through HAP modification[29] using ligand modifiers to enhance its ion-exchange properties. HAP has been shown to effectively remove copper[30], nickel[31], and palladium[32] from aqueous effluents. Furthermore, it can function as a recyclable material without additional steps to remove toxins. HAP therefore shows promise as a suitable inorganic polymer that can be functionalized to remove heavy metals from groundwater. Furthermore, it fulfills the requirements of safety and low production cost.

1.4.2 Drawbacks

Current methods to clean wastewater can produce secondary pollutants that are detrimental to human health. Water disinfectants for example, produce by-products resulting from reactions between the disinfectant and organic wastes in the water.

Chlorine, bromine and ozone disinfectants form trihalomethanes (THMs) from interactions with organic matter found in industrial (fossil fuel by-products) and human (excretion, hair, skin particles) wastes (Figure 1.2). Some of the most common THMs include chloroform ($CHCl_3$), bromoform ($CHBr_3$), dichlorobromomethane ($CHCl_2Br$) and dibromochloromethane ($CHClBr_2$). Toxic aldehydes are also formed by ozonation.[33]

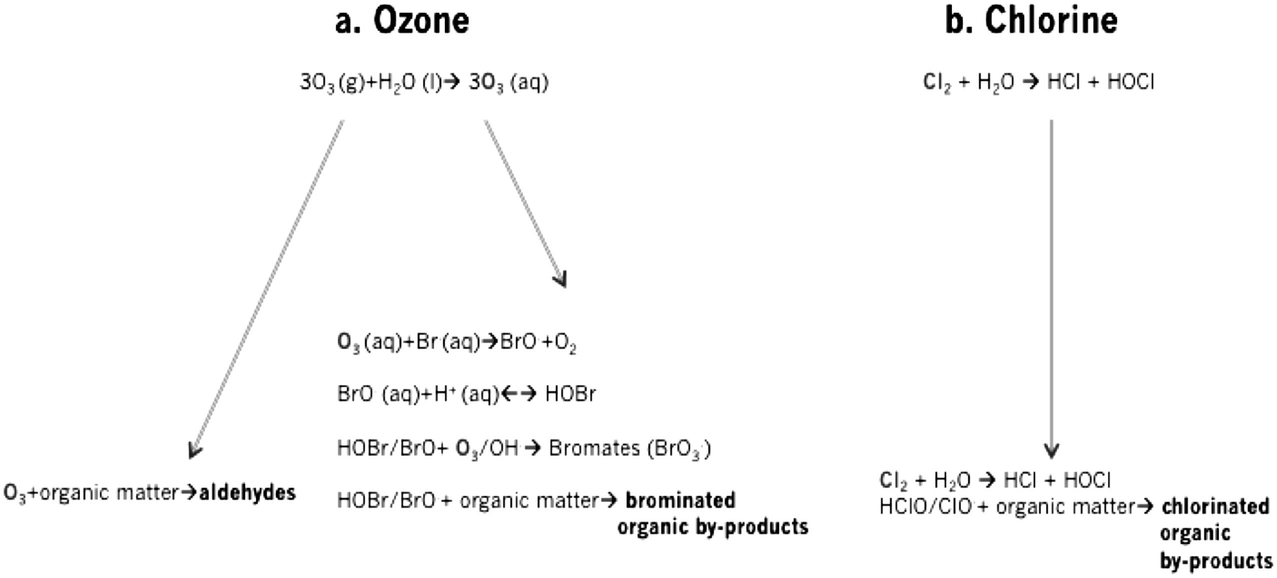


Fig 1.2 Harmful aldehydes and THMs from water treated with (a) ozone, bromine and (b) chlorine

THMs may enter the body by inhaling particles from water that has been nebulized or vaporized by showerheads. They can also enter through the skin and mouth. Swimmers are considered especially susceptible to THMs since they spend considerably more time in chlorinated pools.[34,35,36] THMs have also been linked to epidemiological studies showing reduced adolescent serum testosterone levels consistent with increasing swimming time.[33,37] Additionally, cancer[38,39,40] and premature birthing[41] can result from exposure.

Although the health effects of these by-products have raised concerns, the WHO reported risks to cause fewer illnesses or deaths than those caused by pathogenic pollutants.[42,43] It is apparent however that improved water treatment methods are needed. The long term effects of current water remediation applications have not been thoroughly evaluated therefore efforts to produce safer methods are necessary. Although HAP functions as an ion-exchange polymer, the idea of using this non-toxic polymer for environmental applications moves in a direction towards produce safer water remediation applications.

1.4.3 Regulation and policy

One of the biggest problems with addressing the clean water crisis on a global scale is scattered authority and determining practical methods for enforcing policy. In China, the Ministry of Housing, Agriculture, Land and Resources as well as the Environmental Protection and State Meteorological Administration are all separate groups which oversee water supply and water pollution.[44] This makes it difficult to come to a general consensus as to how wastewater will be treated effectively as well as which funds get allocated to the matter.

Global water policies are also threatened by large-scale contamination, terrorism, overconsumption, catastrophic events like flooding and droughts, and interruptions in the hydrologic cycle by climate changes.[45] As a result, the WHO and the U.S. Hazard Analysis and

Critical Control Point (HACCP) groups have come together to monitor water quality and risk assessment globally.[46] Specific countries have also instilled their own regulatory groups and policies especially pertaining to drinking water. The U.S. EPA Safe Drinking Water Act (SDWA),[47] the Australian Drinking Water Guidelines (ADWG),[46] the European Drinking Water Directive (98/83/EB),[48] the Canadian Federal Provincial-Territorial Committee on Drinking Water (CDW),[49] and the Lithuanian Hygienic Norm (HN24:2003) have all been developed.[48] In South America, where regions have adopted U.S. and Canadian drinking water standards, scientists who obtained conflicting data using the two different standards eventually turned to the global WHO standards.[50]

In India, water treatment plants Selep and VIP Complex were sampled for the total fecal coliform count and it was found to be lower than amounts reaching consumers. Although levels were below the standards set by the Bureau of Indian Standard specifications, variations were said to be due to improper water handling.[51] In an effort to unify water monitoring programs, the WHO and UNICEF have implemented a 2015 Millennium Development Goal (MDG) to classify treated water as "improved" or "unimproved."[52,53]

Not only will clean water scarcity increase poverty and the use of dirty water, but it may also lead to economic and political conflict causing violence between regions. To prevent circumstances from escalating to these levels, Levy and Sidel. suggest strict standards to aid in:

> "(1) reducing use of water, such as by decreasing wasteful uses and increasing efficient uses; (2) increasing availability of clean water, such as by reducing industrial pollution and sewage contamination of water, improving sewage and wastewater treatment, and improving watershed management; (3) establishing and maintaining new groundwater wells; (4) designing and implementing improved methods of desalinization; and (5) expanding use of greywater (wastewater from domestic activities that can be recycled for some uses), as has been done extensively in Singapore and Israel."[54]

Segregated authority resulting from disparities among local or international clean water regulating groups requires a system of unified laws, as well as frequent colloquia and mediation incentives.[54]

1.5 Conclusion

Clean water accessibility is a growing concern for nations under rapid economic, industrial and population growth and for regions with limited financial, technological or geographical resources. Clean water supplies are essential for preserving and sustaining a healthy life, however the issue is not simply resolved by the use of expensive technologies to treat the tainted water. In addition, some materials can only provide single functionality: to trap or remove toxins. The use of dual-purpose materials like HAP is a promising material for treating water pollution since it both removes metal ions and can be valorized. Furthermore, current water disinfectants produce THMs and household water treatment systems leach chemicals from defective materials. These secondary pollutants have been linked to several health problems and suggest a need for safer methods to be implemented.

A combined effort for the continuous monitoring of water quality and an international water quality standard need to be strictly enforced in order to see substantial progress. Additionally, the materials used for water remediation need to be good enough such that political discord pertaining to any financial and environmental concerns can be put to rest. The development of such materials requires a chemical, step-wise approach where synthesis, characterization, modification and model wastewater interactions can be obtained leading to information for their application.

CHAPTER 2. Modification of Inorganic Polymers with Ion-Selective Ligands

2.1 Introduction

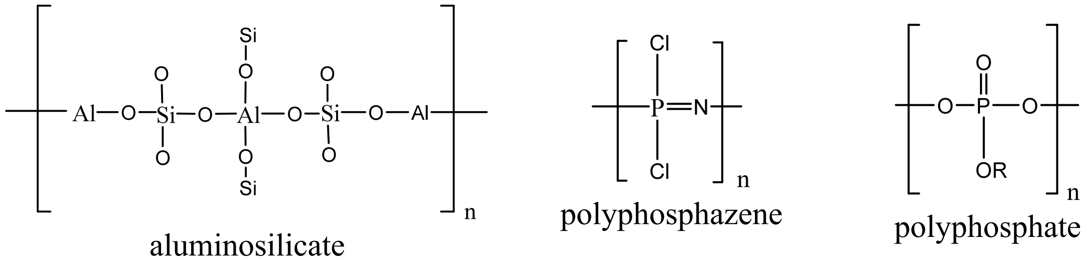
Inorganic polymers consist of a large group of compounds containing purely inorganic, organometallic or hybrid organic-inorganic subunits. These polymers are becoming increasingly popular in materials sciences as demands for functional materials to develop new, specialized applications increases.[55,56] Inorganic polymer applications span from nanoparticle fabrication to complex electronic and biomedical materials.[57] The growing interest in these polymers results from their ability to be chemically modified by altering elements in their backbones and side-chains.[55,56] Specially designed materials have a high potential of retaining unique properties.

The use of inorganic polymers offers many advantages over organic polymers. They are more stable under extreme thermal conditions and have increased chemical resistivity and mechanical strength.[58] Organic polymers, on the other hand, become brittle at low temperatures, and when exposed to extreme heat, can undergo oxidative degradation.[55] When exposed to flames, organic polymers may combust and they are highly sensitive to some of the solvents and fluids used in industry.[55,59] Inorganic polymers are less prone to temperature-induced quality reduction, degradation caused by wear and tear, and do not normally release toxic fumes into the environment after combustion.[58,59]

On a commercial scale, inorganic polymers can be synthesized and functionalized without the use of expensive raw materials, solvents and equipment and normally do not require the extreme conditions traditionally used for preparing similar organic materials.[58] These polymers can be synthesized from more than 40 elements which combine in different ways to produce a large number of unique polymers with distinct profiles.[56,60,61] Silicon is the most common element for inorganic polymer synthesis since it ranks second to oxygen in geological element abundance. It is also part of the Group 14 elements, giving it similar valence properties to carbon. Although most organic polymers contain carbon, it is only the seventeenth most abundant element in the earth's crust.[59,62] A move towards inorganic material use will decrease the consumption of limited resources and simultaneously reduce the addition of organic pollutants into the environment which are typically generated during organic polymer synthesis or produced as result of organic matter degradation. Furthermore, some inorganic materials can function as sorbents for toxic metal ions, radioactive materials and organic wastes through ion exchange processes.[63,64] This makes them ideal candidates for environmental applications.

Inorganic polymers function as sequestration materials for radioactive wastes and metal toxins, and as energy and material storage units. Additionally, fireproof buildings and vehicles can be prepared using surface coatings made from these polymers. Heavy metal ion exchange materials, bacteriocidal materials for water purification and photo degrading materials used to treat environmental pollutants have also been made from inorganic polymers. This is because of new developments that have improved the synthesis of these materials.[63,65]

Purely inorganic polymers can be silicon-based like aluminosilicates, or non-silicon containing, like polyphosphazenes and polyphosphates (Figure 2.1).[62] Polyphosphazene however can also be grouped as a hybrid organic-inorganic materials where chloro groups are substituted.



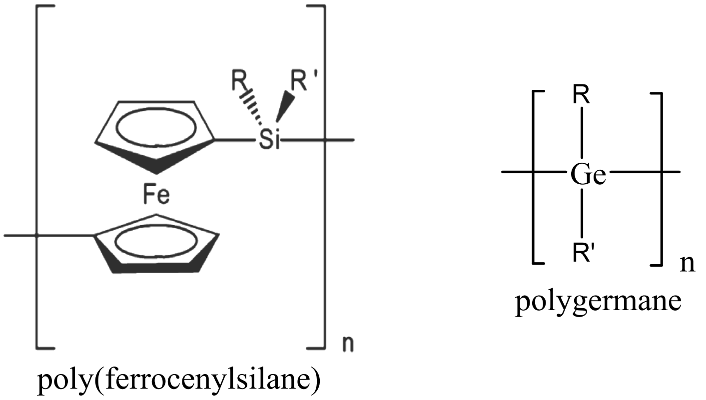
aluminosilicate

polyphosphazene

polyphosphate

Figure 2.1 Purely inorganic polymers: aluminosilicate, polyphosphazene and polyphosphate

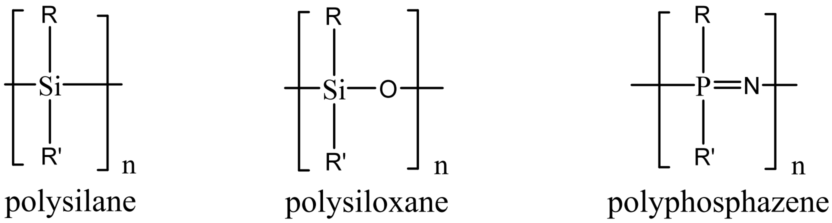
The second kind of inorganic polymers, organometallic polymers, are normally conductive or magnetic. Poly(ferrocenylsilane)s for example, shown in Figure 2.2, are organometallic ceramics with magnetic properties.[66,67]



poly(ferrocenylsilane) polygermane polystannane

Figure 2.2 Organometallic polymers: poly(ferrocenylsilane), polygermane and polystannane

Inorganic-organic hybrids are the last group of inorganic polymers and can be synthesized from polysilane ($(R_2Si)n$), polysiloxanes ($(R_2SiO)n$) and organo-substituted polyphosphazenes ($(R_2PN)n$) (Figure 2.3).[68,69] Creating unique and distinct materials from inorganic polymers opens up an array of possibilities for specially functioning materials.[62]



polysilane polysiloxane polyphosphazene

Figure 2.3 Organic-inorganic hybrid polymers: polysilane, polysiloxane, polyphosphazene

The methods for preparing inorganic polymers are very similar to those used in organic polymer synthesis. One such method, ring-opening polymerization, involves thermal treatment of inorganic rings or catalysis by transition metal complexes. Polymerization is frequently accompanied by the loss of a hydrogen, water, silyl ether, silyl chloride, sodium chloride or lithium iodide. [62,66]

Although a large number of inorganic polymers have already been established, the list continues to expand as more inorganic polymers bearing distinct and unexpected properties, superior to organic polymers, emerge.[69,70]

2.2 Classes of Inorganic Polymers

Of the three groups, the hybrid polymers are the biggest consisting of all copolymers containing combinations of organic, inorganic and organometallic subunits. These copolymers can assemble by polycondensation, grafting, heat polymerization and a variety of surface functionalization reactions.[71,72,73,74,75]

A unique group of naturally occurring inorganic polymers includes diamond (C), quartz (SiO_2), olivine $(Mg,Fe)_2SiO_4$, potassium feldspar ($KAlSi_3O_8$), corundum (Al_2O_3), magnetite (Fe_3O_4), calcite ($CaCO_3$), dolomite ($CaCO_3 \bullet MgCO_3$), pyrite (FeS_2), galena (PbS), gypsum ($CaSO_4 \bullet 2H_2O$), halite (NaCl) and fluorite (CaF_2). Specific details regarding many of these polymers are excluded from this review due to their limited modification potential.

2.2.1 Pure Inorganic Polymers

Purely inorganic polymers have no organic component.[4] These materials have proven to be an invaluable alternative to the traditional organic polymers due to their unique chemical and mechanical properties.

2.2.1.1 Silicon-containing materials

Silicon, because of its relative abundance, is used to synthesize many inorganic materials, from small desiccant beads to high performance materials used in many applications. Silica gel is an amorphous silicon dioxide made of siloxane groups (Si-O-Si) in the bulk and silanol groups (Si-OH) on the surface. The Si-OH groups are sites for chemical modification. The silicon family extends to aluminosilicates and silicon nitrides.

Aluminosilicates are inorganic polymers with AlO_4 and SiO_4 subunits. [76,77,78,79] They are hard at room temperature compared to other alkali-activated clays that require special thermal treatment.[80] Aluminosilicates are synthesized from metakaolinite; one of the most abundant sources of both alumina and silica, and can also be made from ground granulated blast furnace slag[81] or flyash.[82]

One of the most common aluminosilicate polymers is the zeolite. They belong to the family of molecular sieves and have the ability to ion-exchange, adsorb, dehydrate or rehydrate and catalyze. This makes them a very popular material for several applications.[83] They are especially beneficial to environmental applications, since they can improve cation-exchange in soils and increase water sorption capacities.[84] Some of their uses include cement aggregation, acid gas drying, selective catalytic activities, petrochemical processes, oxygen from air separations, ammonia removal from water, heavy metal cation removal from water and wastewater, radionuclide removal from nuclear wastes and detergent building.[83] They can also be found in everyday products such as athletic footwear, hatcheries, barns and refrigerators, functioning as deodorizing agents. A great deal of work is being done to improve their function as sensors, membranes, optoelectronics, electrorheological fluids and functional nanomaterials.[85]

Another group of aluminosilicates is the polysialate. Polysialates are eco-friendly materials made without the emission of CO_2 and can be made from recycled mineral wastes. They are stable at temperatures up to1400 °C and therefore are ideal for heat-resistant materials. Their physical and mechanical properties are altered easily by varying the Si/Al ratio.[84,86,87]

Silicon nitrides are very hard and mechanically stable polymers. They resist wear and tear, can provide electrical insulation and sustain temperatures up to 1800 °C. They are popular materials for engines. Although their mechanical properties make them ideal materials for numerous applications, their preparation can be quite energy consuming, requiring a reaction temperature exceeding 1300 °C and the use of large amounts of inert gases.[59] This limits the number of applications they can be used for.

2.2.1.2 Non-silicon-containing materials

Silicon-containing materials make up a large portion of the purely inorganic polymer family, however, there are several inorganic networks that do not contain silicon and are made of aluminum, boron, nitrogen, sulfur and phosphorus. Some materials formed from these elements include aluminum metal, boron and phosphorus nitrides; some polyphosphazenes; and polyphosphates such as apatites.[59,62]

Aluminum and boron nitrides are ceramic polymers that are stable at temperatures close to 2700 °C. They provide both high electrical insulation and good thermal conductivity. Phosphorus nitrides (P_3N_5) on the other hand cannot sustain high temperatures and sublime easily from the pyrolysis of polyphosphazenes.[59]

Polyphosphazenes are one of the largest groups of inorganic polymers sharing similar structural features with polysiloxanes. They contain two alternating atoms (phosphorus and nitrogen vs. silicon and oxygen) in their backbone, with only one carrying a side group. The phosphorus has two inorganic, organometallic or organic “R” side-groups. This allows them to be a part of any of the three groups of inorganic polymers.[59,88]

The most common polyphosphazenes are poly(heterophosphazene)s such as $(Cl_2NP)_n$ (Figure 2.1) and sulfur-containing poly(thiophosphazene)s such as $[(NPCl_2)_2(NSCl)]_n$ and $[(NPCl_2)_2(NS(O)Cl)]_n$. These polymers are able to attach organic side groups to their phosphorus backbones and are often grouped as organic-inorganic hybrid polymers. Pentachloro-cyclothiophosphazene ($N_3P_2SCI_5$) polymers contain purely inorganic species.[62]

Phosphorus is commonly found in non-silicon inorganic polymers because it has the unique ability to form a wide range of polymers and to undergo a variety of allotropic structural changes especially under high pressure and temperature. As polymerization of elemental phosphorus occurs, it changes color from red, to violet, to black. Phosphorus-containing polymers are rather complex and may be structurally similar to graphite. Although it is difficult to fully characterize them all, data suggests that no heavy, long chain polymers of elemental phosphorus currently exist therefore many phosphorus-containing polymers exist in combination with other elements.

Phosphorus has a remarkable ability to retard flames, facilitate metal adhesion and improve metal ion binding. It is therefore an excellent inorganic material for applications involving flame retardation, ion-exchange and adhesion. Phosphorus compounds and polyphosphates can be easily made by the reaction of phosphoric acids or salts in controlled basic conditions. They can be incorporated into polymer networks by a reaction of phosphorus trichloride, oxygen and the polymer of choice. Polyolefins, acrylics, polyester resins, epoxies and proteins all contain polymers of phosphorus.[59]

Polyphosphates are largely insoluble polymers that are structurally similar to silicates and belong to the family of inorganic phosphorus-containing polymers. Their tetrahedral PO_4 groups are linked together through oxygen atoms. Polyphosphates may exist as salts, acids and organic-inorganic hybrids found in biological components such as adenosine mono phosphate (AMP), adenosine diphosphate (ADP) and adenosine triphosphate (ATP), and the nucleic acids guanosine triphosphate (GTP), cytidine triphosphate (CTP) and uridine triphosphate (UTP). They are the main components of bones and teeth and are therefore biocompatible and non-toxic. Large phosphorus polymers result from combinations of linear oligomers or cross-linked chains and from cyclic structures tightly bound to cations. Since these materials are strong chelating agents, they are often used in water treatment processes.[59] Apatites are one such example existing mainly as hydroxyapatite, fluorapatite or chlorapatite. Traditionally, they have been used as fertilizers providing nutritional phosphates, however there is a growing interest in the use of apatites in water treatment processes because of their remarkable metal ion chelating tendencies. Furthermore, they can serve as a potential storage for nuclear wastes.[89]

When phosphorus combines with elements like sulfur, oligomers of P_4S_3, P_4S_5, P_4S_7, and P_4S_{10} form.[90,91] The substitution of phosphorus polymers with sulfur to yield compounds like poly(thiophosphazene) occurs by ring-opening polymerization of heterocyclic compounds.

Phosphorus polymers are also known to exist as hybrid organic-inorganic polymers since their side-groups are readily modified. The idea of modifying polyphosphate polymers to generate highly selective or functional materials is of key interest in water remediation chemistry and engineering because they have strong chelating properties and are cheap to modify.

2.2.2 Organometallic polymers

Organometallic polymers combine elements found in traditional organic polymers (C, N, S, P, O, etc.) with more than 44 metals. The metals improve the electronic, optical and magnetic properties of the polymers and add variety to polymer functionality with each oxidation state.[92] Organometallic polymers are strikingly different from purely inorganic polymers. Their bulk consists of an organic and a transition metal component. Together, these components form a variety of polymeric chelates which are ideal for making dyes or pigments, especially in the advanced field of dye-sensitized solar cell technology. Metalloporphyrins are another organometallic polymer with unique electronic and optical properties. These properties can be altered both by varying the type of substituents attached and the kinds of metal ions placed inside the units.[55]

The term organometallic has been extended to groups of nonmetal-containing polymers that are conductive or display other kinds metal-like characteristics. Some sulfur nitrides, polyphosphazenes, boron nitrides and polyphosphinates fall into this category.[92]

Metals are incorporated into a polymer through addition, condensation and coordination reactions.[92] Metal oxides, hydrous oxides and metal ferrocyanides all belong to the family of organometallic polymers. The thermochromatic, photoconductive and semiconductive properties of Group 14 polysilanes, are extended to inorganic polymers containing metals of the same group. These include the polygermanes and polystannanes (Figure 2.2).

Iron-containing organometallic polymers have received considerable attention because of their ability to be used as a fuel additive, replacing tetraethyllead. They are also used as pharmaceutical agents[93] and in carbon nanotube catalysts.[94,95] Ferrocene is thermally and electrochemically robust and incorporating ferrocene into polymer networks may create new polymers and materials with similar properties.

Another group that combines metals with organic polymer moieties are the polyynes which are rigid-rod organometallic polymers. They are prepared by polymerization reactions involving acetylene functional groups.[62] Polyynes are the starting materials of fullerenes, soot and carbon dust, and are the components of thousands of plants, fungi, and microorganisms. Their structures serve as a model for understanding and treating diseases and tumors, as they can provide vital information needed to synthesize antibiotics, anticancer, or anti-viral treatments.[96]

2.2.3 Organic-inorganic hybrid polymers

Polysilanes have an unusual ability to be thermochromic, radiation sensitive and contain nonlinear optical properties,[62] and polysiloxanes and polyphosphazenes are known for their flexibility. Polysiloxanes are made of silicon atoms containing two side groups and oxygen atoms with no side groups, alternating in their backbones.[62,76,97,98] They can be hydrophobic, have low viscosity and high thermal stability[98] like poly(dimethylsiloxane). They are also excellent materials for high-temperature insulation, anti-foam applications, bio-transplants, drug-delivery systems and elastomers.[99]

Hybrid polyphosphazenes are prepared by a two step reaction involving the synthesis of poly(dichlorophosphazene) followed by a nucleophilic attachment of the “R” group. The side groups determine the flexibility, solubility, hydrophobicity, conductivity and bioactivity of these materials.

Although purely inorganic polymers have been used to develop unique materials with superior properties to their organic counterparts, a great deal of work is being done to produce inorganic-organic hybrid polymers. These copolymers have the superior mechanical properties of their inorganic precursors and the essential organic functional groups that will help to specify their application.[100] These hybrids, often referred to as copolymers, retain enhanced mechanical, chemical, electrochemical, optical, and magnetic properties such as improved conductivity, hardness, durability and thermal resistance.

Organic-inorganic systems are perhaps the largest group of inorganic polymers, being comprised of any material having both organic and inorganic (or metallic) moieties. Organometallic polymers can therefore be placed into this category as well. Organic-inorganic systems essentially refer to any inorganic polymer modification involving the addition or incorporation of ligands to inorganic networks.[88,101]

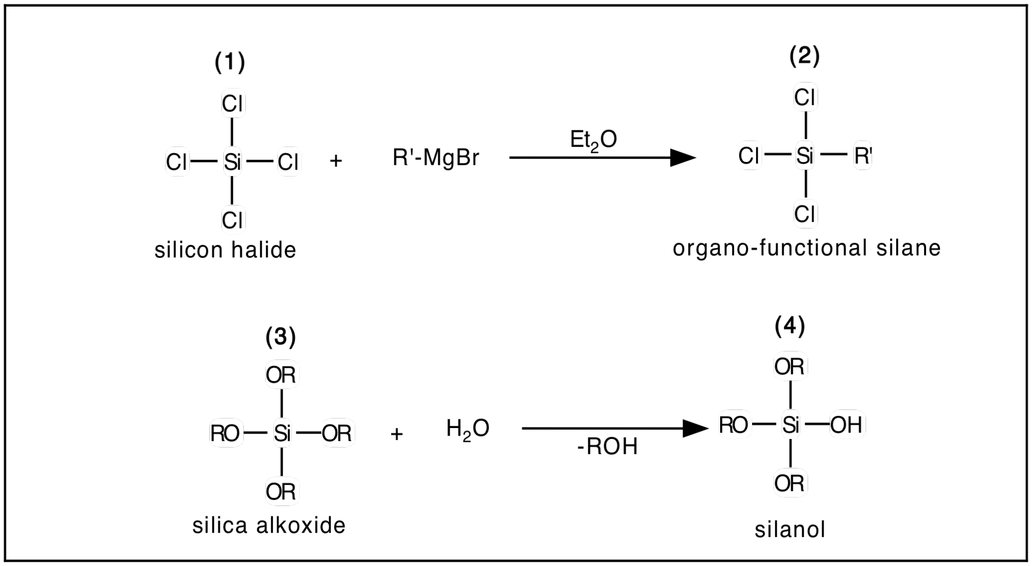
Copolymer networks are synthesized by numerous methods. The most common process, a sol-gel reaction, makes it possible to insert morphological and physical modifications to the polymer structure on a molecular level.[102,103,104,105,106] This process also facilitates incorporation of organic oligomers into the inorganic matrices.[107] Hybrid materials have different dimensions of cross-linking within the sol-gel networks, where inorganic and polymer phases come into contact. A reactive organic phase ordinarily serves as the template for extending the organic network and also for reacting with the inorganic moieties.[6] Alternate preparation of hybrid materials include copolymerization of alkoxide and organic monomer species,[108] in situ alkoxide condensation throughout an organic matrix,[105,106,109] surface binding of one phase to the other by physical or chemical bonds and a physical insertion of either the inorganic monomers into the organic matrix or organic oligomers into the inorganic network.[88,110] Solvent impregnating techniques are also used.[111]

The preparation of hybrid polymers requires more delicate conditions than those used to prepare purely inorganic polymers. Hybrid polymers cannot be synthesized under high temperature conditions since this destroys the chemical integrity of the organic phase. Ideally, sol-gel preparation fulfills this mild chemistry requirement.[101,112,113] Sol-gel precursors include aqueous metal salts, metal alkoxide solutions or mixed organic and inorganic phases as shown in Figure 2.4.[108,114] Alternative copolymerization techniques can be used to react the inorganic phases with organic monomers, or to introduce alkoxide precursors into swollen polymers to form the hybrid.[110] The introduction of an organic species into an inorganic network is easily accomplished by polycondensation during the colloidal formation step. A covalently bonded organo-substituted silico-ester is formed by the reaction of inorganic alkoxides with organic oligomers (Figure 2.4).[105,106,109,112,115]

The formation of hybrid polymers by hydrogen bond interactions between the sol-gel silanol intermediates and the basic groups in organic polymers is also reported.[107,109,116] Common hybrid materials include heteropolyacids and polybasic salts.

Of the three classes of inorganic polymers, it is clear that the organic-inorganic hybrid polymers allow the most diversity. As a result, a great deal of work is being done to modify inorganic polymers and produce new functional materials. Nanotechnology has benefitted from inorganic polymer modification since the sol-gel reactions allow molecular level dispersion of the two phases. As a result, nano-sized materials can be blended with high homogeneity compared to traditional composite modifications.[109] This kind of technological advancement may lead to state-of-the-art improvements in the biological and pharmaceutical industries where applications for capturing, storing and converting light energy as well as robotics and electrical devices are being developed. Furthermore, it will also benefit environmental applications.

A. Precursor formation



B. Polymerization/Polycondensation

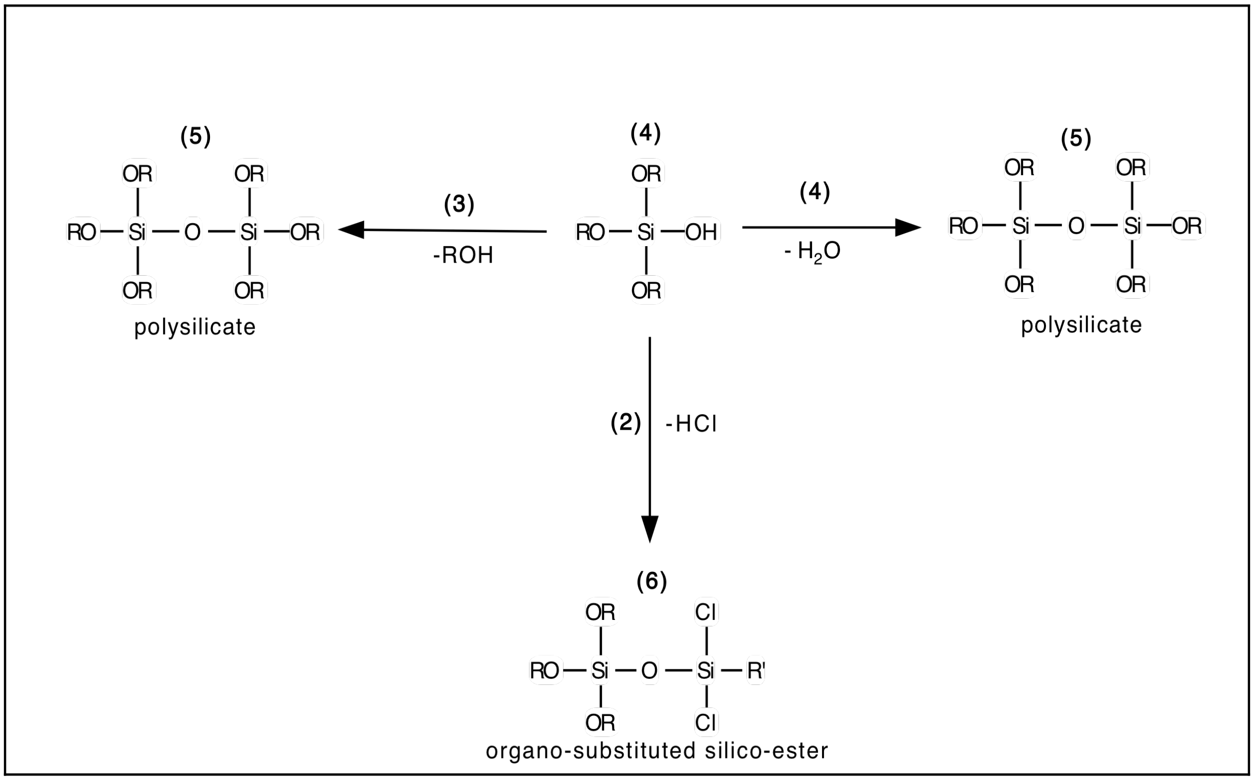


Figure 2.4 Scheme for organo-substituted silico-ester formation

2.3 Modifying inorganic polymers

The development of unique, multifunctional polymers is accompanied by some level of modification. Modified inorganic polymers are selective, more functional and do not require the use of complex syntheses and excessive solvents. They are especially important to environmental applications like wastewater treatment since they can be tailored to selectively separate the toxic components without adding to carbon emissions. Factors affecting modification typically include availability of the precursors, cost, efficiency, ease of modification and environmental impact.

Hybrid materials are comprised of different proportions of precursors.[116] This increases the number of available combinations of copolymers that can be produced. Although copolymers made with inorganic and organic subunits are conventionally referred to as hybrids, some are also macro-scale composites. The difference between the two lies in their synthesis and the dimensions of their dispersion.[109]

In addition to sol-gel reactions, inorganic-organic materials can be prepared by poly-condensation and surface grafting polymerization. The method of preparation typically depends upon the starting materials used, as well as the desired size, strength and properties of the final product.

Polysilanes like poly(phenylsilane) ($H(PhHSi)_nH$) are modified by free-radical-assisted hydrosilylation (Figure 2.5). Substitution of 70-90% is possible with this kind of reaction using a cyclohexanone substrate. Different kinds of functionalized polysilanes can be subsequently modified by attaching tetraphenylporphyrin groups to their backbone which facilitates charge transfer between the silicon network and the side-chains of the porphyrin.[62]

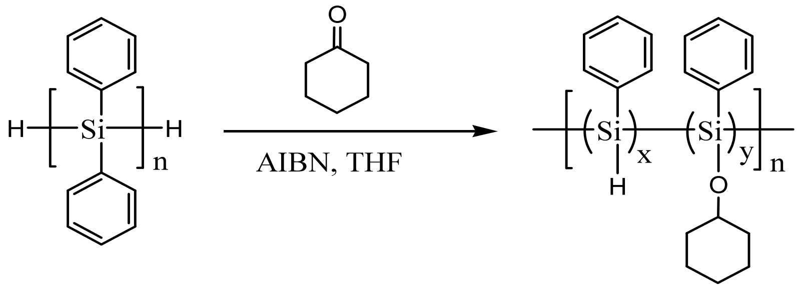


Figure 2.5 Free-radical-assisted hydrosilylation of poly(phenylsilane)[62]

Modified inorganic materials can also be crystalline coordination polymers showing large variations in their levels of bonded interactions. The strengths of these chemical interactions from weakest to strongest are: van der Waals forces, H-bonding, coordination bonding, ionic bonding and covalent bonding. Modified polymers with weak interactions are Class I hybrid materials and those with strong interactions are Class II hybrid materials.[117]

2.3.1 Applications of modified inorganic polymers

Inorganic polymers have been used for several applications including surface coatings,[100] membranes for gas separation,[102,118] electronic displays and bio-medicine,[119,120,121] for enhancing metal oxides[122] in photovoltaic devices[123] and in environmental applications.[58,79] The use of hybrid materials as surface coatings is ideal for making materials with specific optical, electronic or abrasion resistant properties. Organically modified ceramics are most commonly used for this purpose.[100] They can be prepared by first condensing the inorganic network, then proceeding with organic cross-linking. Modified surface coatings were prepared from silicone polymers having phenyl substituents. The new coatings remained stable at higher temperatures than organic surface coatings alone. Inorganic surface coatings are commonly used in cements and dental composites.

Since many inorganic polymers are solvent or fire-resistant and can provide insulation against heat, electricity or sound they are often used in specialized electrical, chemical, nuclear and civil engineering applications. Furthermore, new advancements through modification have made it possible to produce fire-retardant fabrics, specialized drug delivery technology, hydrogels, membranes and optical materials.[59,124] Hybrid materials are also used as fuels which combine beryllium, boron, magnesium or aluminum with organic radicals to produce heteropolymers.[124]

Most modified inorganic fibers are silicate or alumina based and are used in the glass-fiber industry. Silicone rubber is a modified silicone with several methyl groups (Figure 2.6).[125] These rubbers are chemically inert and can often withstand high temperatures compared to their organic congeners. They are often used in automotive applications, household and cooking appliances, apparel and footwear and medical devices.[62]

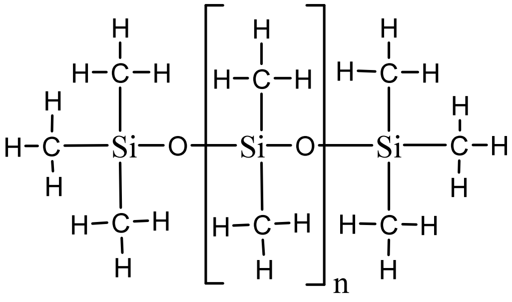


Figure 2.6 Natural silicone rubber[125]

Hybrid nanomaterials are prepared by physically or chemically binding the two phases which allows the new material to retain their original structural and mechanical properties. Asymmetric silica/polystyrene nanoparticles were prepared in this way. Silica particles were first surface modified with n-octadecyltrimethoxysilane then dispersed into an oil phase containing styrene and hexadecane. Subsequent addition of the water phase containing surfactant sodium dodecyl sulfate (SDS) and sodium bicarbonate dissolved in deionized water was performed. The miniemulsion polymerization reaction was allowed to proceed with a potassium persulfate as initiator. The resulting hybrid material had an asymmetrical morphology which could be altered by adjusting the ratio of styrene to silica. These materials have significant potential in complex media stabilization applications, electronic displays, and bio- medicine.[121]

Modified inorganic polymers are also used to enhance the light-harvesting and charge-collecting properties of photovoltaic devices. These properties determine how much light is transformed into useful power, referred to as the power conversion efficiency (PCE). Hybrid photovoltaic devices were prepared by immersing ZnO nanorods in a ruthenium-based complex, coumarin, indoline or squaraine dyes each containing a 1:1 (by volume) ratio of acetonitrile and tert-butyl alcohol.[123] The dyes formed covalent bonds between their carboxylic or carboxylate groups and the ZnO surface. They also participated in H-bonding interactions between the -OH groups of ZnO and the dye's carboxylic acid groups. Squaraine modified nanorods had the best PCE (1.02%) of all dyes used, which is a 0.14% increase over standard high performing CdSe-sensitized ZnO nanorods.[126]

Membrane gas separations by hybrid polymers have potential advantages over organic polymeric membranes because of their molecular-sieving characteristics and their ability to withstand high temperatures.[118] Membrane composites were successfully prepared from a silane-polyimide surface reaction. A series of silanes, (tetramethoxysilane (TMOS), methyltrimethoxysilane (MTMOS), and phenyltrimethoxysilane (PTMOS)) were modified with a polyimide made from 4,4'-hexafluoroisopropylidenediphthalic anhydride (6FDA), 4-4'-hexa fluoroisopropylidene dianiline (6FpDA) and 3,5-diaminobenzoic acid (DABA). This produced the silica immobilized 6FDA-6FpDA-DABA polyimide dianhydride membranes. Modification occurred via sol-gel reactions, combining the solution polyimides with the appropriate silicon alkoxides. The morphology of the hybrid polymer was highly dependant on the type and concentration of methoxysilane alkoxide used as well as the amount of cross-linking occurring. TMOS polymers showed a higher degree of modification and increased reactivity compared to MTMOS and PTMOS hybrids, which were mostly uncondensed.[102]

In a separate study, methoxysilanes were used for the modification of silicate films, to improve the rate of ion-exchange on glassy carbon electrodes. The modified materials were prepared by coupled hydrolysis-copolymerization reaction where 3-aminopropyltriethoxysilane was functionalized with PTMOS, MTMOS, TMOS or isobutyltrimethoxysilane (BTMOS). The voltammetric response was measured after surface modified electrodes were placed in hydrogen phthalate (KHP) buffer solutions of potassium ferricyanide ($Fe(CN)_6^{3-}$) or ruthenium hexaammine ($Ru(NH_3)_6^{3+}$). There was an increase in Faraday current for films contacting the iron solution, however this was not seen with films placed in solutions containing ruthenium.[64]

2.3.2 Ion-selective ligands

The enhanced ion-selectivity of organically modified inorganic polymers has expanded their role as materials for environmental applications. Modified silica gel surfaces have been found to selectively trap metal ions even when only trace amounts of the metal are present. This is important in industrial wastewater treatment processes and also for the extractive concentration of metals like uranium.[63]

A majority of what is known about ion selective ligands comes from organic polymer research.[127] Polymer-bound ligands selectively complex or exchange metal ions from solutions.

They have been used as chelating ion-exchange materials; to treat metal poisoning; to make antibiotic or imaging metal complexants; for hydrometallurgy applications; and in some metal binding detergents.[128]

Ion-selective ligands are very specific in function and understanding the mechanism by which they work will help to determine how they bind metal ions. It will also help to explain processes like biological cation transport, protein binding and siderophores. These ligands have functional groups which can donate electrons needed to specifically bind the metal ion.

Ligands play a major role in biological functions. The most important of these include enzyme-substrate binding where a substrate molecule or protein within the cell binds specific peptides, neurotransmitters, hormones, drugs, toxins or other ligands to trigger a physiochemical response. The substrates may bind through non-covalent interactions, such as hydrogen bonding and Van der Waals forces. Since ligand selectivity is influenced by many secondary factors, their affinities for ions and molecules can vary. These factors include molecule or ion concentration levels and memory imprints left in ligands that had been previously exposed to these species. Pharmaceutical drugs that are normally not selective for particular substrates, may bind if they are administered in high doses. Drug-to-substrate binding is also influenced by the structure of the substrate receptor. Hence, isolation of the receptor can provide vital information for developing new agonist or antagonist ligands. Ion selectivity is also determined by the nature of the ions used, where characteristics like coordination geometry, charge, size and oxidation state, come into play.

During chelation therapy metal ions are selectively removed from the body. A person with an excess of iron (β-thalessemia), can be treated with ligands like desferoxamine, which specifically bind Fe(III) to form stronger complexes than with Fe(II). Similarly, copper overload in individuals with Wilson's disease is treated with chelating agents which target the Cu(II). The electron donating atoms of ligands can form strong bonds with many transition and heavy metals however selectivity is not always easy in the presence of non-toxic ions like calcium or magnesium. Ethylenediaminetetraacetate (EDTA), for example is administered as a calcium salt during chelation therapy to account for the unintentional loss of bone calcium by EDTA complexation.[129]

Metal ions may exist in a hydrated state or as a complex with inorganic anions or organic ligands. Polydentate metal ion complexes form readily in the presence of chelating agents and are more stable than unidentate complexes since the complex is stabilized by the increased number of chelating sites.

In the environment, a number of naturally occurring chelating agents exist. These include many humic and proteins in water and soil. Naturally occurring ligands contain carboxylate, heterocyclic nitrogen, phenoxide, aliphatic aromatic amino and phosphate chelating groups. Common synthetic ligands include sodium tripolyphosphate, EDTA, sodium nitrilotriacetate (NTA), and sodium citrate.[4]

In separation science, ion-selectivity can be measured by a distribution coefficient and a selectivity coefficient. The distribution coefficient is a ratio of the concentration of ions within the solution and those bounded by the ligand, at equilibrium.[130] The selectivity coefficient describes the at-equilibrium separation of two ions by a matrix.[131]

Ion-selective ligands are being developed as chemical sensors[132] and can be a powerful tool for targeting trace toxins in the environment. Selection of ion exchange ligands for inorganic polymer modification has primarily been based on the chemical and physical properties of both polymers and ligands, the efficiency and stability of the polymer-to-ligand complex and the application of the modified material. Ion-selective ligands form complexes with metals and can also ion-exchange. The fate of these ligand-ion complexes include disposal, purification for metal preconcentration and participation in important life processes involving hemoglobin or chlorophyll production. During ion exchange, ions of the solution and ions from the ligand (e.g. H^+) move between the stationary ligand and mobile solution.[6] Modification of inorganic polymers with ion exchange ligands increases the capacity, applicability, and selectivity of the polymer. These polymer-bound ligands can be limited in application due to their radiation and thermal sensitivities. This sensitivity is less pronounced when the polymers are inorganic. Additional limitations can be seen in highly acidic or basic environments and by any instability within the inorganic polymer-to-ligand bond. Inorganic hybrid materials are predicted to offer dual properties from the thermally stable inorganic polymers and the selective organic moeities.[6,133]

2.3.2.1 Modification with ion-selective ligands

Traditionally, the selective removal of toxic metal ions from aqueous solutions has been accomplished by solvent- and solid-phase extractions;[134,135] however, polymer immobilized ligands can also be used for this purpose. Examples include: the selective removal of sodium, Pb(II) and Cu(II) with silica-immobilized calixarenes;[136] the removal of As(V) from aqueous solution using surface ion-imprinted amine-functionalized silica gel;[137] and a solid-phase extraction of Cd(II) from aqueous solution using ion-imprinted organic-inorganic silica-based hybrids.[138,139] These imprinted polymers have the potential to be selective for uranyl ions as well.[140]

Hybrid silica materials functionalized with polyamines are ideal for attaching ion selective ligands since the amine groups are sites for additional modification. These polymers are particularly selective for Ni(II) and Cu(II).[141] Cu(II) can also strongly coordinate to ligands immobilized on photoluminescent porous silicon.[142] Silica-immobilized ligands are popular among the hybrid organic-inorganic materials for selective metal ion sorption. A thiol-substituted aniline ligand was immobilized on silica for selective removal of palladium in the presence of other heavy metal ions.[143] Non-silica inorganic polymer like polyphosphazene, have also been modified with ligands for the selective removal of metal ions.[144] The processes by which ligands attach to polymers include acid/base surface functionalization,[141] graft polymerization,[142] refluxing[143] and azobisisobutyronitrile (AIBN) initiated copolymerization.[144]

The modification of silica gel surfaces by calixarene has been shown to produce hybrid polymers which preferentially bind to sodium,[145,146,147] Pb(II) and Cu(II),[148] and cesium and potassium.[149] Calixarenes can be easily made, and are also directly modified at their phenolic oxygens or aromatic carbons. These hybrid materials have been used in a variety of applications that include radionuclide complexing agents, electrodes, phase-transfer agents and catalysts.[136]

One of the most effective ways of synthesizing hybrid polymers for the selective sorption of metal ions is by a process known as ion-imprinting functionalization. The method copolymerizes functional and cross-linking monomers with the imprinting metal ion. Imprinted metal ions and functional monomers form an initial complex which later becomes polymerized, and can carry different degrees of cross-linking. After polymerization occurs, the imprinted metal ion is removed with strong acid, leaving behind a memory of the binding site, which will facilitate selectivity for the same metal ion. Ion-imprinting has been used to successfully modify organic polymers[150] and this process has been adopted for inorganic polymer modification as well. Polysilanes and silica gel were modified by the ion-impinting method for the removal of arsenic (V),[137] cadmium (II),[138,139] uranyl ions,[140] zirconium (VI),[151] nickel (II)[152] and iron (III)[153] from aqueous effluents.

One example of an ion-imprinted polymer network is the ruthenium (III)-thiosemicarbazide (TSd) and ruthenium (III)-acetaldehyde thiosemicarbazone (AcTSn) complex. These were made using a copolymerization method: the functional monomer methacrylic acid and crosslinking agent ethylene glycol dimethacrylate were combined with a 2,2-azobisisobutyronitrile initiator. Ru(III) complexes were eluted using thiourea (TU) and HCl solutions. Ru(III) separation was measured in the presence of interfering matrixes such as acids (HNO_3 CH_3COOH, $HClO_4$ and HCl); transition metals Co(II), Ni(II), Fe(III), Ag(I) and Pb(II); and platinum group metals Ru(III), Pd(II) and Pt(IV). The Ru-TSd imprinted polymers shown in Figure 2.7 had better separation efficiency that the Ru-AcTSn imprinted polymers.[150]

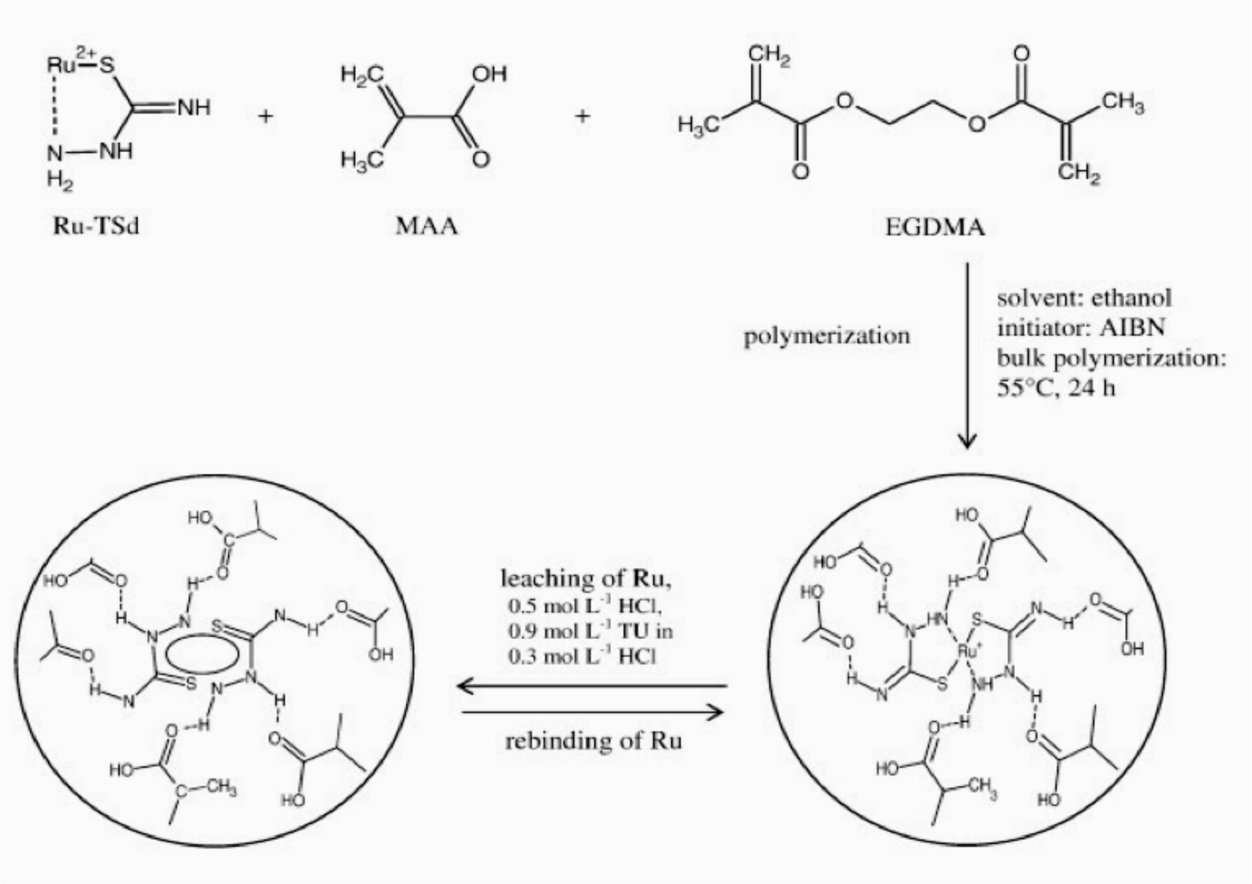


Figure 2.7 Ion-imprinted method for Ru(III)-Tsd polymer. Reprinted from Zambrzycka, E.; Roszko, D.; Leśniewska, B.; Wilczewska, A.Z.; Godlewska-Żyłkiewicz, B. *Spectrochim. Acta Part B: Atom. Spectrosc.* **2011**, *66*, 7, 508-516, with permission from Elsevier.

Ion-imprinted inorganic polymers were made by similar methods. Arsenic(V) was selectively removed by a surface-ion-imprinted amino-functionalized silica gel sorbent. The silica gel was modified with functional monomer 3-(2-aminoethylamino)propyltrimethoxysilane, then combined with As(V) and epichlorohydrin as the cross-linking agent. The As-imprinted sorbent was more selective for As(V) over phosphate, Cd(II), Cu(II), Pb(II), and Ni(II) since the ligand groups on the sorbent remained in a specific orientation for coordination to the As(V) only. Strong coordination of the 3-(2-aminoethylamino)-propyltrimethoxysilane ligand to other metal ions was negligible in comparison to As(V), emphasizing the high specificity of the ion imprinting technique.[137]

A cadmium-imprinted silica gel was prepared with 3-mercaptopropyltrimethoxysilane (MPS), stirred and heated in a solution of $CdCl_2$, H_2O and methanol. After the Cd(II) and MPS complex was formed, the solution was added to methanesulfonic acid-activated silica gel and allowed to co-condense. The functionalized sorbent was filtered, conditioned to remove the imprinted Cd(II) and MPS, then assessed for its selective separation and preconcentration of Cd(II) ions. The ion-imprinted silica gel was highly selective for Cd(II) in the presence of Hg(II), Cu(II), and Pb(II) and among alkali metal and alkali earth metal ions. This was because of the thiol-functional group's affinity for soft acids. Additionally, the cadmium ions had a precise fit inside the Cd(II)-imprinted cavity compared to other divalent metal ions of similar charge and size because the ligands on the sorbent retained a specific geometry to limit coordination to Cd(II) ions.[138]

Another cadmium-imprinted silica gel was prepared with and cetyltrimethylammonium bromide (CTMAB) by the step-wise self-hydrolysis, self-condensation, and co-condensation of a solution mixture containing the functional (3-(2-aminoethyl-amino)-propyltrimethoxysilane), the cadmium ion solution and cross-linking agent (tetraethoxysilicate) precursors. This was done in an alkaline media and followed with alcohol and acid conditioning to remove the imprinted species.[139]

The Cd-functionalized sorbent was contacted with a solution containing Cd(II) and Zn(II) ions and showed a significantly higher selectivity for Cd(II). Zn(II) ions were expected to have a strong coordination to the diamine ligands based on the metal-diamine complex stabilities (Cu(II) > Ni(II) > Co(II) > Zn(II) > Cd(II) > Pb(II)), this however was not detected. The imprinted-silica gel could not coordinate well with the smaller ionic radius of Zn(II) even though Zn(II) had a similar charge to Cd(II) and the same coordination configuration.[139]

Imprinting modification can be used to prepare silica gels that selectively bind uranyl ions. Aminopropyl silica gel was used as the support for the azo-initiator, followed by metal ion imprinting by graft polymerization. The azo initiator 4,4′-azobis(4-cyanopentanoic acid chloride) (ACPC) was added to the silica surface in the presence of pyridine to facilitate its reaction with the amino groups. Surface grafting was then carried out in an agitated solution of the initiator-modified silica, uranyl nitrate hexahydrate and cross-linking monomers. The uranyl ions were removed with concentrated hydrochloric acid. Imprinted polymers had a higher affinity for uranyl ions compared to Fe(III) and Th(IV). The sorbent was also used in preconcentration studies where more than 97% of uranyl ions were recovered from spiked tap water, Caspian Sea water and ore leach liquor.[140]

Some silica gels are modified initially to make them more reactive for subsequent modification with ion-selective ligands. Silica polyamine composites (SPC) was modified with polyallylamine (PAA) and polyethyleneimine (PEI), and subsequently functionalized with chloroacetate and nitriloacetic acid (NTA) anhydride.[141] SPCs are silica gels covalently bound to water soluble polyamines. They are ideal for modification with metal selective chelating groups because their amine groups are sites for additional modification. SPC immobilized acetates were prepared by adding the SPC to sodium chloroacetate and water under precise temperature and pressure conditions. The pH was then adjusted with NaOH and after completion, the reaction mixture was filtered and conditioned. Modification with NTA anhydride was achieved by mixing the SPC with NTA anhydride in the presence of an acetic acid/ethanol solution. The reaction was heated and allowed to proceed to completion, then conditioned accordingly. Other ligands which have been reported to successfully modify SPCs include picolylamine, 7-amino-methyl-8-hydroxyquinoline, amino-methyl-phosphonate, amino-acetate, and ethylenediamine tetraacetic acid functional groups.[154]

PAA-modified SPCs had a higher degree of modification with the acetate groups than the SPCs made with PEI. The SPC-PAA-acetate polymer was selective for Cu(II) only, compared to other divalent metal ions studied, between pH 1 and 3. The SPC-PEI-acetate polymer however, was selective for Cu^{2+} only at pH 1, and at pH 2 and 3, showed Ni^{2+} selectivity. Both the SPC-PAA-NTA and the SPC-PEI-NTA polymers had the following selectivity profiles: Cu(II) > Ni(II) > Zn(II), Co(II) and Ga(III) > Fe(III)> Eu(III) > Al(III). These results were compared to EDTA immobilized SPCs, and were reported to have an overall higher metal ion capacity for Ni(II), Zn(II) and Co(II), even though the affinity series for EDTA and NTA were identical.[141]

As a general rule, chelating ligands containing strong donor atoms can be used to prepare ion-selective polymers. Nitrogen and oxygen donor ligands with terminal alkene and alkyne groups were used to modify hydride-terminated, photoluminescent porous silicon surfaces.[142] Ligand attachment was achieved by hydrosilylation using white light and Lewis acid at room temperature and pressure.[155] A 100 W desk lamp was used to radiate the silicon wafer and facilitate hydrosilylation of the ligands sitting on top. Irradiation with white light causes the formation of a silyl radical or cation with subsequent reaction with the vinyl momomer (Figure 2.8).[156]

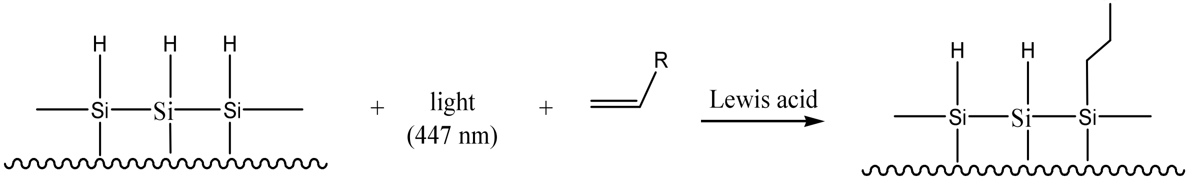


Figure 2.8 Hydrosilylation reaction with a vinyl monomer[156]

The photoluminescent surface was identified by its bright orange color seen under UV light and the presence of a Si-H stretch (2100 cm^{-1}) and bend (665 cm^{-1}) in attenuated total reflectance (ATR) IR spectra. The absence of a C=C or C≡C stretch from the ligands in the ATR spectrum was indicative of surface hydrosilylation.[142] The new silicon-immobilized ligands were contacted in aqueous solutions of Ni(II), Cu(II), Z (II), and Pb(II) and were seen to selectively complex Cu(II) over the other metal ions. The selective sorption of copper can be useful for decontaminanting natural and wastewaters. Immobilized ligands had a low affinity for Pb(II) since not many ligands were N donors and lead(II) is known to strongly coordinate to N-donors species. Similarly, zinc(II) and nickel(II) showed low affinities for the immobilized ligands.[142]

Silica gel was also modified with five different silane ligands: (1) [(2-(triethoxysilyl)-ethyl)thio]benzene (S-Ph)); (2) 2-[(2-(triethoxyasilyl)ethyl)thio]anlline (2-SNH_2); (3) 3-[(2-(Tri-ethoxysilyl)ethyl)thio]aniline (3-SNH_2); (4) 4-[(2-(Triethoxysilyl)ethyl)thio]aniline (4-SNH_2); and (5) 2-[(2-(Triethoxysilyl)ethyl)thio]-N-(diphenylphosphino)-aniline (2-$SNHPPh_2$) to produce the silica-immobilized ligands, SIL-S-Ph, SIL-2-SNH_2, SIL-3-SNH_2, SIL-4-SNH_2 and SIL-S_4, respectively. The modified silica was prepared by adding dry toluene and the designated silane ligand to dried silica gel, under argon gas. After reflux, the reaction was allowed to cool, then followed with appropriate conditioning.[143]

The SIL-ligand polymers were used to complex palladium(II). Palladium(II) complexes were characterized both during their separation from solutions containing Rh(III), Ir(III), and base metals as well as from preconcentration studies of Pd(II) in dilute aqueous solutions.[143]

Results showed that the Pd(II) capacity of SIL-S-Ph was half that of SIL-2-SNH_2, and SIL-2-SNH_2 ligands had relatively high affinities for Pd(II), Au(III), Ag(I), Pt(I1), Pt(IV), Os(IV) and Ru(III)). The SIL-3-SNH_2 and SIL-4-SNH_2 isomers also had higher capacities for

Pd(I1) than SIL-S-Ph but had no significant advantage over SIL-2-SNH_2. The SIL-S4 ligands has the highest Pd(II) capacity.[143]

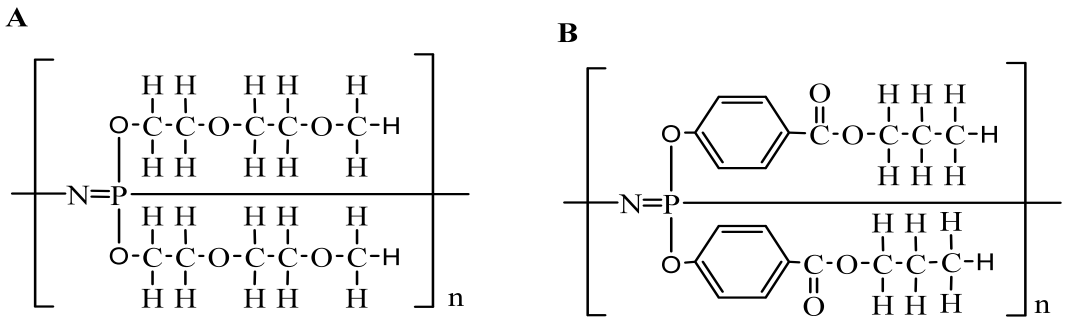


Figure 2.9 Chemical structures of (a) poly-[bis(2-(2-methoxy-ethoxy)ethoxy)-phosphazene] and (b) poly[bis(propyloxy-benzoate) phosphazene][144]

Another group of inorganic polymers that have been modified with ion-selective ligands are the polyphosphazenes. Two polyphosphazenes polymers, poly-[bis(2-(2-methoxy-ethoxy)ethoxy)-phosphazene], $[NP(OCH_2CH_2OCH_2CH_2OCH_3)_2]_n$ and poly[bis(propyloxy-benzoate) phosphazene], $[NP(OC_6H_4COOPr)_2]_n$ shown in Figure 2.9, were used to synthesize interpenetrating polymer networks(IPNs) with four different polymers: (1) poly(acrylic acid), (2) poly(vinylsulfonic acid sodium salt), (3) poly[bis(undecenyl phosphate)], and (4) poly[(*p*-methyliminodiacetoxy)styrene]. Contrary to the previous hybrid polymers described, this kind of modification uses an organo-substituted polyphosphazene instead of the purely inorganic or silica polymer. Ligands increased the number of coordination sites for metal ions and metal ion specificity since each ligand had separately shown favorable complexation for these metal ions.[144]

To synthesize the IPN, polyphosphazene matrices were cross-linked by ^{60}Co γ-radiation exposure then placed in a vinylsulfonic acid monomer sodium salt solution with an AIBN initiator and ethylene glycol dimethacrylate cross-linker. After swelling, the monomer was able to polymerize inside the polyphosphazene matrix. The IPN was extracted from the matrix with water, for each ethoxy-based IPN, or with THF for each benzoate-based IPN. Seven IPNs were prepared using different combinations of each polyphosphazene polymer and organic ligand. IPN polymers were contacted with mercury(II)nitrate, magnesium(II)nitrate, calcium chloride, zinc sulfate, silver nitrate, iron(II) chloride, and copper(II) chloride to determine their metal ion complexation capacities.[144]

Results showed that each IPN had a different kind of complexation with the metal ions studied. There were no similarities in the complexation strengths observed or in the amount of sodium ion and solvent-induced replacements. Each of the three ethoxy-based IPNs had strong complexations with at least three different cations (Hg^{2+}, Ca^{2+}, Cu^{2+}). Benzoate-based IPNs also had different complexation affinities with cationic species. Control experiments showed that without interpenetrating polymers the ethoxy polyphosphazenes complexed iron, and the benzoate polyphosphazene complexed silver.[144] This revealed that ligands were not responsible for iron and silver complexation, respectively.

Of all the ion-selective modification techniques described, ion-imprinting appears to be the best approach since it creates a hybrid polymer that specifically binds the metal ion of interest. The disadvantage of this method however is that it can only be used with polymers and resins that are not sensitive to acid-catalyzed hydrolysis since the imprinted ions have to be removed with acid.

2.3.2.2 Environmental remediation and the future

The versatility of hybrid (modified) inorganic polymers offers considerable potential for environmental applications. As increasing levels of organic wastes, radionuclides, fluorides, pesticides and toxic heavy metals enter the environment, they seep into water sources and can easily become dangerous.[6,157] Although some wastewater pollutants are easily removed with filtration and sedimentation, heavy metal pollutants cannot be treated by these methods. As a result, new materials are being developed for water remediation applications specifically in the area of metal ion sequestration. These materials function by metal ion exchange, coordination and complexation mechanisms which are all grouped as one collective metal ion sorption process.

The efficient separation of hazardous metal ions from water requires the use of materials with enhanced ion sorption properties where both ion exchange and ligand selectivity are employed. Hydroxyapatite is an ideal metal ion sorption material because it not only has ion-exchange capabilities but it can also be functionalized easily with metal chelating ligands.

The future of engineered hybrid materials lies in the production of functionalized nanomaterials. These materials will have increased specificity because of their high surface area and as a result they will work more efficiently. Additionally, they may be a cheap alternative for environmental remediation applications since macro-scale materials require more raw material and energy for processing.

2.4 Conclusion

It is clear that the modification of inorganic polymers with ion selective ligands enhances their metal-ion sorption properties. Inorganic polymers offer many advantages over traditional polymers due to their enhanced physical, chemical and mechanical properties and their limited output of pollutants. They function as double environmental remediators by also participating in toxic heavy metal removal from water. Ligand selection is based on the type of material to be functionalized, the distribution coefficients and selectivity factors of separation, and the complexation constants of metal-ligand complexes. Also important is the specific application to which the modified organic-inorganic sorbent will be applied, as well as ligand availability, ease of modification and ligand-sorbent stability during sorption.

CHAPTER 3. Phosphate Chemistry: Hydroxypatites and Bisphosphonates

3.1 Hydroxyapatite

Hydroxyapatite, $Ca_5(PO_4)_3OH$, gets its name from the hydroxy groups within its chemical structure. Apatites can also have chloro and fluoro groups producing the chlorapatite $(Ca_5PO_4)_3Cl$, and the fluorapatite $(Ca_5PO_4)_3F$, respectively. Apatites are inorganic polymers and the most abundant sources of phosphorus on Earth. They are extremely important because phosphorus is an essential element for living things. Hydroxyapatite (HAP) has a similar structure to the calcium phosphate in bones and teeth, and has therefore been used in applications to make artificial bone and dental implants.[158,159] The biocompatibility of HAP has also made it an important material for drug delivery vehicles[160] and environmental applications.[161]

Mineral apatites undergo a series of dissolution and ion exchange reactions within soil and as a result they make excellent materials for soil remediation and wastewater treatment applications. Calcium can be exchanged for alkaline earth metals like Sr^{2+} or Mg^{2+} and for divalent metal ions like Cu(II), Cd(II), Pb(II) and Zn(II). Phosphate can be substituted with anions like SO_4^{2-}, AsO_4^{3-}, VO_4^{3-}, CO_3^{2-}, SiO_4^{4-} and hydrogen phosphates ($H_2PO_4^-$ and HPO_4^{2-}).[162] HAP has specifically been used for waste stabilization, to treat contaminated soils and for heavy metal adsorption.[163,164,165,166,167] Additionally, it has been used for making gas sensors[168] and in heterogeneous catalysis.[169]

The ability of HAP to function in these applications is primarily based on its surface chemical properties. Hydroxyl groups on HAP surfaces make them reactive species and allow functionalization so that they can easily adapt to biomedical applications. The reactivity of HAP is influenced by its particle size, specific surface area (SSA) and the modifiers added during or after synthesis. During synthesis, HAP undergoes several transformations where different calcium phosphate phases of varying Ca/P ratios form. A final stoichiometric and crystalline HAP salt is considered to be thermodynamically stable and although this is the form suggested for biomedical applications, it is not important for environmental applications. Instead, these applications are more concerned with reducing production costs and the overall efficiency of metal ion sorption.[161]

3.1.1 Synthesis, Stoichiometry and Structure

HAP can be synthesized by reacting aqueous solutions of calcium such as CaO, $CaCl_2$, $Ca(NO_3)_2$ or $Ca(OH)_2$, with phosphate solutions such as $KH_2PO_4^-$, H_3PO_4, Na_3PO_4, $(NH_4)_3PO_4$) in a wet method synthesis.[161,170,171] Studies have also reported the synthesis of HAP by adding the calcium species to a combination of organophosphate and soluble phosphate in order to increase the specific surface area and porosity of HAP.[172] The organic species were decomposed between 500 °C and 800 °C to produce the stoichiometric hydroxyapatite. Alternate methods of synthesis include sol−gel,[173] microwave-assisted[174] and hydrothermal[175] synthesis or by using organic modifiers and templates[29,176] to control size and morphology. A spray-drying synthesis can also be used for morphological control. [177,178]

HAP was synthesized using an acid-base reaction method, similar to one developed by Verwilghen et al.[161] They combined 77.18 g of $Ca(OH)_2$ with 2.5 L of deionized water and 40 mL of 85% phosphoric acid over a period of 15 minutes. The rate of H_3PO_4 addition was slow enough to prevent acidification of the solution but high enough to completely dissolve the $Ca(OH)_2$. The use of $Ca(OH)_2$ and H_3PO_4 precursors eliminates by-products like nitrates from forming within the HAP crystal. The pH and temperature of the reaction also have a strong influence on the forming particle shape and size.

Although Verwilghen's procedure was adopted for the present study, a few, modifications were made. Reactants were reduced by a factor of 20 so that less $Ca(OH)_2$ (3.859 g) and 85% H_3PO_4 (2 ml) would be used. A 140 ml volume of dH_2O was used instead of the 125 ml equivalence from the original procedure, to ensure complete dissolution of the $Ca(OH)_2$. H_3PO_4 was added to the $Ca(OH)_2$ while continuously stirring over a period of 10 minutes at a rate of 0.2 ml per minute. After 4 h, the pH was checked and adjusted with dilute H_3PO_4 or KOH, to the 8-8.2 range where HAP is known to form. The addition of K^+ was found to have no significant effect on the HAP crystal structure and the adsorption or the exchange of Ca^{2+} for K^+ can therefore be ignored.[179] The 8-8.2 pH range was well above the pH at which the presence of hydrogen phosphates occur therefore more deprotonated phosphate (eq. 3.1, 3.2, 3.3) was expected to be incorporated into the HAP.[180] At this pH $Ca(OH)_2$ was also expected to dissolve completely. After 48 h the reaction was stopped and the mixture was filtered and air dried for 24 h, then dried in a vacuum oven at 60 °C for 8 h.

$$H_3PO_4 \rightleftharpoons H_2PO_4^- + H^+ \quad (pKa_1 = 2.16) \qquad (3.1)$$

$$H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+ \quad (pKa_2 = 7.21) \qquad (3.2)$$

$$HPO_4^{2-} \rightleftharpoons PO_4^{3-} + H^+ \quad (pKa_3 = 12.32) \qquad (3.3)$$

Ion clustering during the initial mixing of precursors precedes the formation of HAP. This is followed by an intermediate nucleation stage where different phases of amorphous calcium phosphate begin to form. The basic reaction between calcium hydroxide and phosphoric acid forms tricalcium phosphate (TCP), $Ca_3(PO_4)_2$, which is usually most abundant phase seen after precipitation (eq. 3.4). HAP forms after enough $Ca(OH)_2$ is taken up into the forming salt.[180]

$$3\ Ca(OH)_2 + 2\ H_3PO_4 \rightleftharpoons Ca_3(PO_4)_2 + 6\ H_2O \qquad (3.4)$$

The ability to form stoichiometric HAP over the other phases of calcium phosphate requires both the use specific amounts of precursors during synthesis and calcination at high temperatures. Stoichiometric HAP forms according to the reaction presented in equation 3.5. Calcium phosphates undergo several conformational changes until the thermodynamically stable and crystalline salt has formed. This process is accelerated by high drying temperatures which calcine the amorphous salt into a crystalline state. Thermodynamically stable HAP is both stoichiometric and crystalline.

$$10\ Ca(OH)_2 + 6\ H_3PO_4 \rightleftharpoons Ca_{10}(PO_4)_6(OH)_2 + 18\ H_2O \qquad (3.5)$$

The Ca/P ratio of $Ca_{10}(PO_4)_6(OH)_2$ is 1.67. Water is the only by-product formed by this reaction (eq. 3.5) and can be easily vaporized at high temperature. HAP synthesis with different precursors (eq. 3.6, 3.7 and 3.8) form additional species which cannot be easily removed.

$$10\ CaCl_2 + 6\ Na_3PO_4 + 2\ NaOH \rightleftharpoons Ca_{10}(PO_4)_6(OH)_2 + \mathbf{20\ NaCl} \qquad (3.6)$$

$$10\ Ca(NO_3)_2 + 6\ K_2HPO_4 + 8\ KOH \rightleftharpoons Ca_{10}(PO_4)_6(OH)_2 + 2\mathbf{0\ KNO_3} + 6\ H_2O \qquad (3.7)$$

$$10\ Ca(NO_3)_2 + 6\ (NH_4)_2HPO_4 + 8\ NH_4OH \rightleftharpoons Ca_{10}(PO_4)_6(OH)_2 + \mathbf{20\ NH_4NO_3} + 6\ H_2O \qquad (3.8)$$

Ca/P ratios are useful for characterizing the different kinds of calcium phosphates present (Table 3.1). For example, calcium phosphate dibasic dihydrate (DCPD), dicalcium phosphate anhydrous (DCPA) and calcium pyrophosphate (CCP) have Ca/P ratios of 1, whereas octacalcium phosphate (OCP) has a 1.33 ratio. The 1.5 and 1.67 ratios were reported for TCP and HAP, respectively. Ca/P ratios that go beyond 1.67 to a ratio of 2 form what is known as tetracalcium phosphate (TTCP).

Table 3.1 Types of calcium phosphate with different Ca/P ratios

Calcium phosphate	**Chemical formula**	**Ca/P ratio**
calcium phosphate dibasic dihydrate (DCPD)	$Ca(HPO_4){\bullet}2H_2O$	1
dicalcium phosphate anhydrous (DCPA)	$CaHPO_4$	1
calcium pyrophosphate (CCP)	$Ca_2P_2O_7$	1
octacalcium phosphate (OCP)	$Ca_8H_2(PO_4)_6{\bullet}5H_2O$	1.33
tricalcium phosphate (TCP)	$Ca_3(PO_4)_2$	1.5
Hydroxyapatite (HAP)	$Ca_{10}(PO_4)_6(OH)_2$	1.67
tetracalcium phosphate (TTCP)	$Ca_4(PO_4)_2O$	2

HAP is often accompanied by a mixture of different phases (e.g. TCP) and the Ca/P ratio therefore varies between 1.5-2.0.[181] When this happens, the salt is represented by the general formula: $Ca_{(10-x)}(HPO_4)_x(PO_4)_{(6-x)}(OH)_{(2-x)}$,[162] where salts below a 1.67 ratio are called calcium deficient HAP. When x = 1, HAP will have a chemical formula of $Ca_9HPO_4(PO_4)_5OH$, which has a Ca/P of 1.5,[182] and when x = 2, $Ca_8(HPO_4)_2(PO_4)_4$ (or OCP) with a Ca/ P of 1.33 forms.[183]

Different phases of HAP were studied as a function of calcination temperature.[180] XRD data revealed that a significant amount of HAP was present, over TCP, at calcination temperatures exceeding 700 ^{o}C therefore this temperature was chosen for calcination of all HAP salts throughout this dissertation. HAP also became very dense and began to shrink at temperatures approaching 780 ^{o}C where significantly lower specific surface areas (SSA) were observed.[184]

The structure of HAP is described as a hexagonal lattice (Figure 3.1). Calcium and phosphate atoms occupy 3.1 atom/nm^2 and 5.1 atom/nm^2 respectively,[24] and variations in the surface –OH groups is heavily dependent upon the calcination temperature.

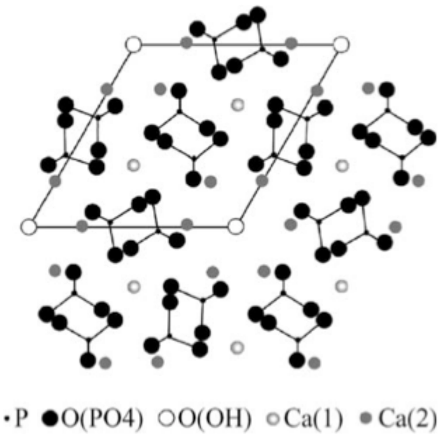


Figure 3.1 The crystal structure of hydroxyapatite with a hexagonal arrangement of hydroxyl groups. Reprinted from Nzihou, A.; Sharrock, P. *Waste Biomass. Valor*. **2010**, 1, 163-174, with kind permission from Springer Science and Business Media.

3.1.2 Solubility and Stability

Although thermodynamically stable HAP is relatively insoluble, acidic pH conditions can cause dissolution and increase the concentration of calcium solution. In Figure 3.2 the low solubility of HAP relative to other calcium phosphates, based on the solution pH, is shown.[185]

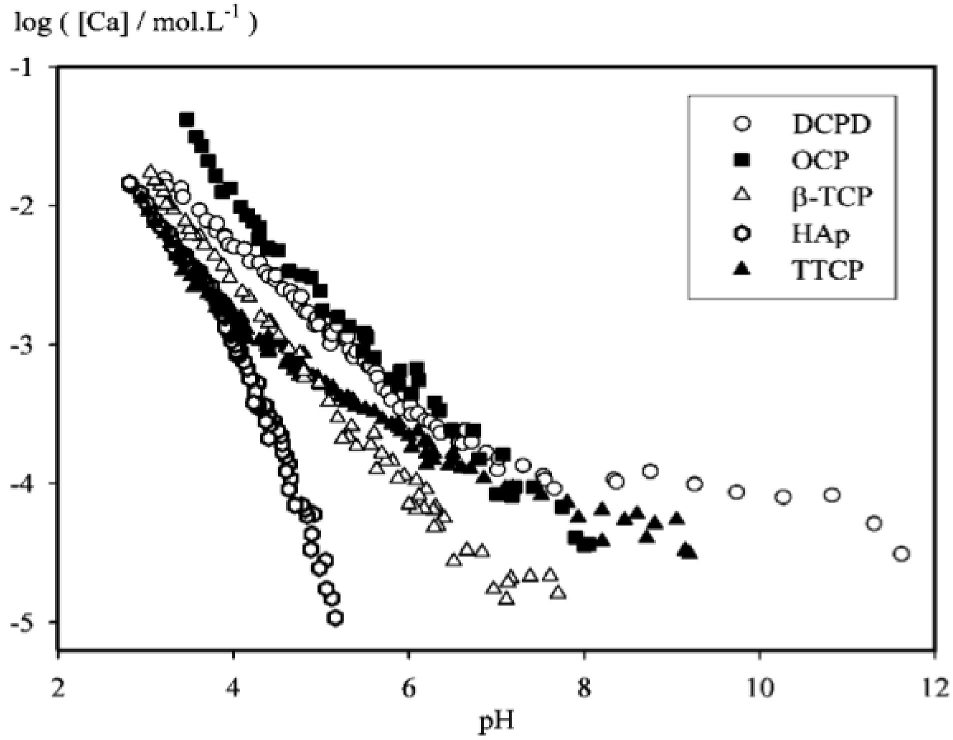


Figure 3.2 Solubility isotherm for different kinds of calcium phosphate (DCPD, OCP, ß-TCP, HAP and TTCP). Reprinted with permission from Pan, H.-B.; Darvell, B. W. *Crystal Growth Design* **2009,** *9*, 2, *639-645.* Copyright 2009 American Chemical Society.

The surface charges on HAP which control reactivity, are also influenced by the acidity and basicity of the solution environment. An acidic pH causes the surface to be positively charged and basic conditions make them negative.[24] A considerably low pH will also dissolve the HAP completely into its respective calcium cations and hydrogen phosphate anions. At basic pH, the salt remains stable.[162] At pH 7 and under standard environmental conditions, negative and positive surface charges on HAP are equal, therefore this pH defines the point of zero charge.[24]

The solubility of HAP is largely influenced by the chemical properties of its surface layer with little influence coming from the bulk phase.[162] The solubility product ($\log K_{sp}$) for HAP was found to vary with its Ca/P ratio. HAP with a Ca/P of 1.67 was reported to have a $\log K_{sp}$ between -56[186] and -59[187] while TCP with a Ca/P ratio of 1.5 had a $\log K_{sp}$ of -29 and DCDP with a Ca/P ratio of 1 had a $\log K_{sp}$ of -7.[188]

3.1.3 Chemical Reactivity

The chemical reactivity of HAP is not only influenced by the pH of the surrounding solution but also by its thermodynamic stability or degree of crystallinity. Its SSA and the number of surface –OH groups, as well as any functional groups added to the surface (e.g. ligands) may also affect reactivity. Additionally, in the presence of solutions containing different ionic species, HAP can undergo several ion exchange reactions.

When high temperature is used to achieve thermodynamic stability, the SSA decreases and particle density increases. As a result, larger particle agglomerates form (Figure 3.3). This lowered SSA significantly reduces the potential surface reactions to occur.

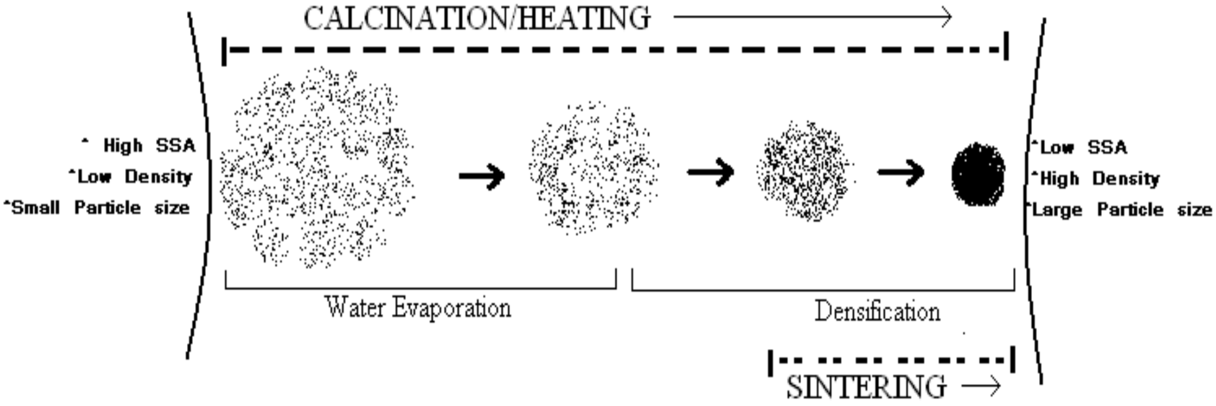
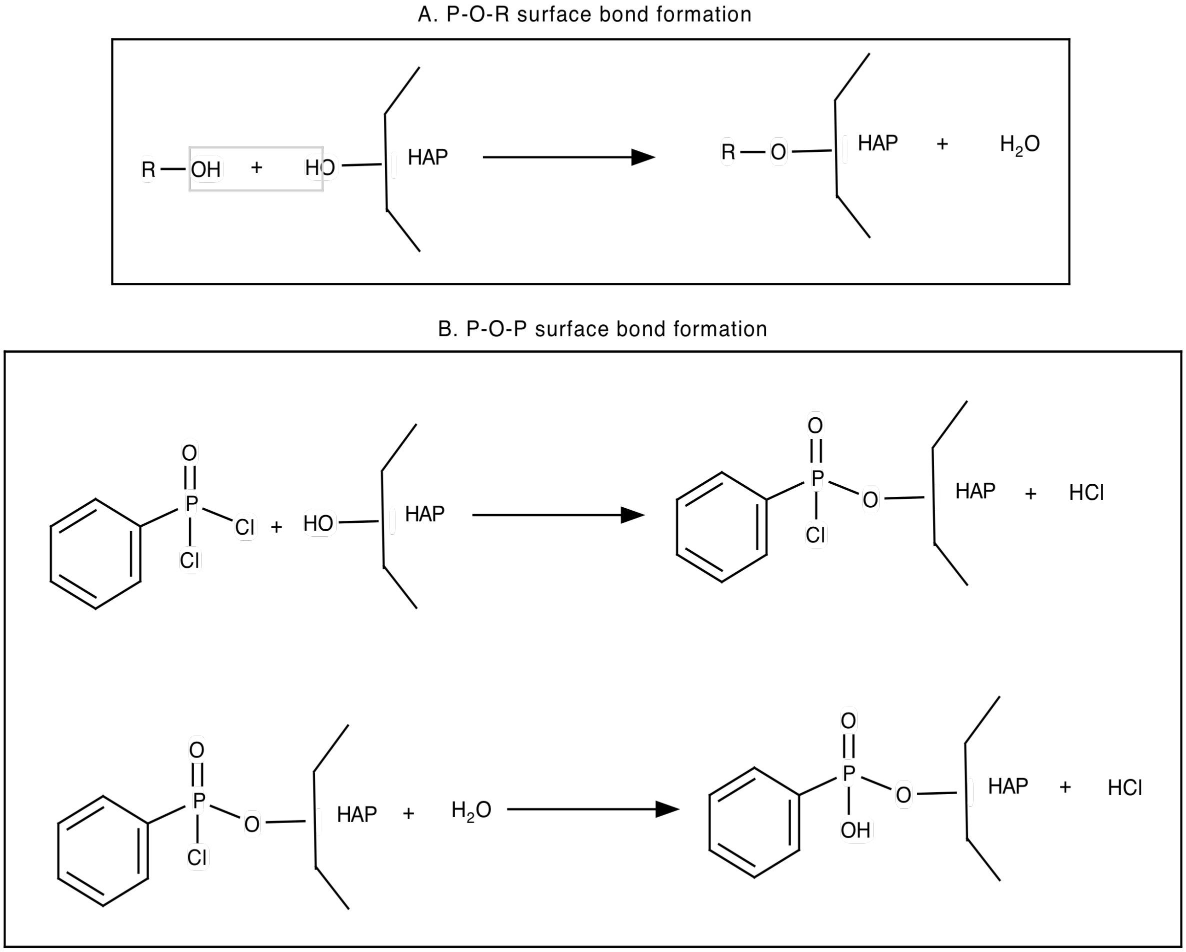


Figure 3.3 Calcination and sintering of HAP particles with increasing temperature causing a decrease in SSA, increase in particle density to produce large particle sizes.

To define the chemical properties of HAP surfaces, a Constant Capacitance Model (CCM) -Surface Complexation Model (SCM) was developed by Charlet et al.[189] The model revealed that four different species were present on the HAP surface: (1) -POH, (2) -PO$^-$, (3) -CaOH, and (4) -CaOH$_2^+$. The pKa of –POH was reported to be 6.6 and -CaOH$_2^+$, 9.7. Surface reactions will therefore occur more favorably with the –POH groups at close to neutral pH.

HAP surfaces can be easily modified through reactions between the surface hydroxy groups. A phosphoesterification reaction creates P-O-R bonds and a similar mechanism is suggested for P-O-P surface bonds (Figure 3.4).[72,190]


A. P-O-R surface bond formation

B. P-O-P surface bond formation

Figure 3.4 Scheme of HAP surface reactions

A majority of the reactions occurring with HAP have been shown to occur on the surface leaving the bulk phase unchanged, however when ions get incorporated inside the apatite, lattice parameters may be affected.

A. Ca^{2+}/ H^+ Ion exchange

$$Ca_{10}(PO_4)_6(OH)_{2\,(s)} + M(NO_3)_{2\,(aq)} \rightleftharpoons MCa_9(PO_4)_6(OH)_{2\,(s)} + Ca(NO_3)_{2\,(aq)}$$

$$Ca_{10}(PO_4)_6(OH)_{2\,(s)} + M(NO_3)_{2\,(aq)} \rightleftharpoons Ca_{10}(PO_4)_6(O_2M)_{(s)} + H(NO_3)_{(aq)}$$

B. P-OH Coordination

$$Ca_{10}(PO_4)_6(OH)_{2\,(s)} + M(NO_3)_{2\,(aq)} \rightleftharpoons Ca_{10}(PO_4)_6(OH)_2\text{---}M_{\,(s)} + NO^-_{3\,(aq)}$$

C. Dissolution/precipitation

$$Ca_{10}(PO_4)_6(OH)_{2\,(s)} \rightleftharpoons (Ca_9(PO_4)_6(OH)_2)^{2-}_{(aq)} + Ca^{2+}_{(aq)}$$

$$Ca^{2+}_{(aq)\,)}+(Ca_9(PO_4)_6(OH)_2)^{2-}_{(s)} + M^{2+}_{(aq)}+ 2NO^-_{3\,(aq)} \rightleftharpoons MCa_9(PO_4)_6(OH)_{2\,(s)} + Ca(NO_3)_{2\,(aq)}$$

Figure 3.5 Scheme for HAP ion exchange, coordination and dissolution/precipitation reactions

Due to the remarkable ability of HAP to substitute different divalent or trivalent metal ions and anionic species, it has taken a leading role in metal ion sequestration processes.[24] The proposed mechanisms for metal ion sorption include ion exchange, coordination and dissolution/precipitation and are shown in Figure 3.5.

3.1.4 Characterization

HAP characterization is typically carried out using Fourier transform infrared spectroscopy (FT-IR), x-ray diffraction (XRD), scanning electron microscopy (SEM), Brenner Emmett Teller (BET) for SSA analyses and phosphorus nuclear magnetic resonance (^{31}P-NMR) spectroscopy.

FT-IR spectra of HAP (Figure 3.6) show bands for –OH, H_2O, HPO_4^{2-}, PO_4^{3-} and CO_3^{2-} bands. A P-O deformation band is seen at 570 cm^{-1} and 610 cm^{-1}.[191] Between 628 cm^{-1} and 635 cm^{-1}, another band for O-H bending and deformation appears. HPO_4^{2-} bands for in plane and out of plane stretching appear between 720 cm^{-1} and 760 cm^{-1},[192] and at 876 cm^{-1}.[193] Several bands for PO_4^{3-} appear at 937 cm^{-1}, 950 cm^{-1}, 1014 cm^{-1}, 1040 cm^{-1} and 1090 cm^{-1}.[192] CO_3^{2-} bands are seen between 1400-1550 cm^{-1}. Bands from 3100 cm^{-1} to 3500 cm^{-1} were assigned to absorbed molecular water. Between 3570 cm^{-1} and 3670 cm^{-1} a sharp band is typically seen for vibration of the non H-bonded -OH.[192]

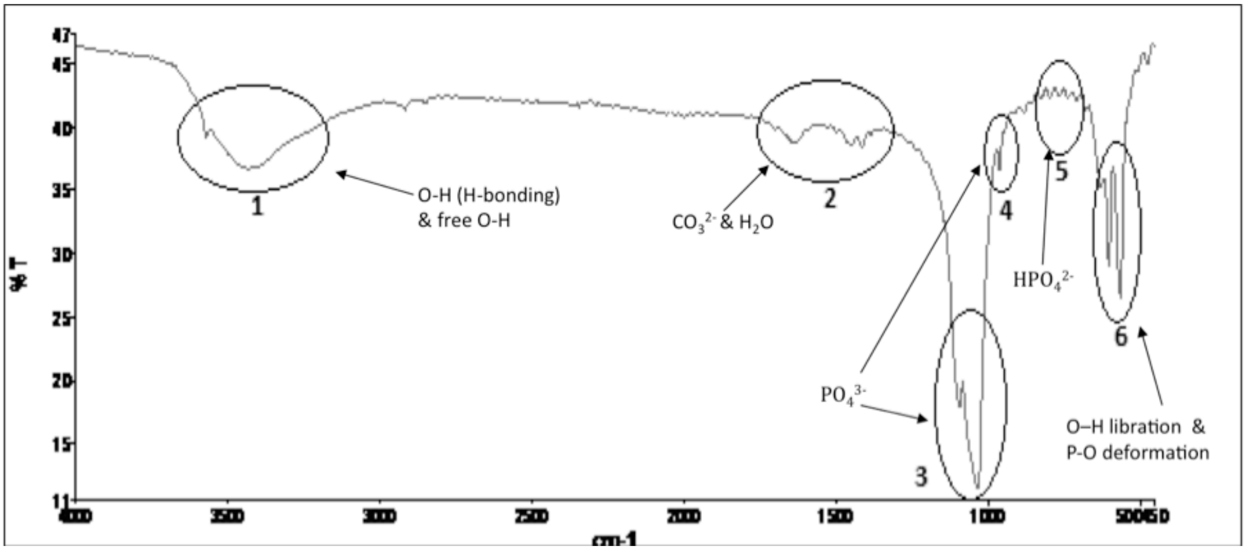


Figure 3.6 FT-IR of HAP showing the absorbance bands for –OH, H_2O, HPO_4^{2-}, PO_4^{3-} and CO_3^{2-} groups.

The SEM of HAP can vary depending on the calcination temperature used during drying.[194] High temperature drying produces structures that are spherical and at low temperature they are more cylindrically shaped. XRD peaks (2θ) for HAP appear at 25.9, 31.8, 32.2, 32.9, 34, 39.8, 46.7, 49.5, 50.5 and 53.2.[184] HAP has a ^{31}P-NMR isotropic chemical shift occurring at 2.8 ppm.[195] SSA measurements for HAP are primarily based on its drying temperature. For example, HAP dried at 105 °C has an SSA of 124 m^2/g[161] however as the drying temperature increases to 700 °C the SSA decreases to about 40 m^2/g. At 850 °C, the SSA decreases drastically and SSA measurements can be seen to approach 2 m^2/g for the fully sintered state.[181]

3.2 Bisphosphonates

Unlike HAP, bisphosphonates are organic phosphate compounds which contain two phosphonate groups attached to a central carbon atom. Each bisphosphonate has a unique structure determined by its R1 and R2 groups (Table 3.2). Bisphosphonate structures are responsible for their function and binding affinity.[196]

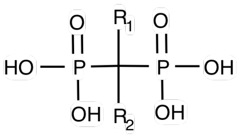
Biomedical applications have explored the use of bisphosphonates to treat bone disorders like Paget's disease and osteoporosis because bisphosphonates have a high affinity for bone and are reported to reduce bone resorption.[197] The mechanism for reducing resorption is not fully understood, however adsorption to the bone mineral is said to play a major role.[198] The affinity of bisphosphonates to bind bone is attributed to their P-C-P backbone. Single phosphonates are found to have a significantly lower affinities to calcium phosphate.[198]

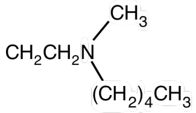
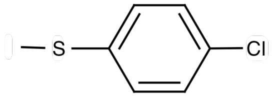
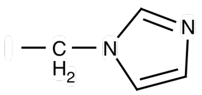
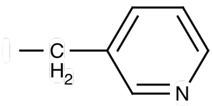
An ATR-FT-IR study of one of the simplest bisphosphonates etidronate, in the form 1-hydroxyethane-1,1-diphosphonic acid (HEDP) revealed bands appearing at 968 cm^{-1}, 1077 cm^{-1} and 1099 cm^{-1} assigned to PO_3^{2-}. Additional bands at 1142 cm^{-1} were contributed by HPO_3^{-} and a 1351 cm^{-1} band by the –OH group of the central carbon. A 1644 cm^{-1} band resulted from dissolved carbonate.[199]

In addition to reducing bone loss, bisphosphonates can also immobilize divalent metal ions[200] and uranium ions[201] from aqueous effluents. The affinity of the free HEDP ligands for different metal ions is as follows: Fe(II) > Cu(II) >>Zn(II) > Cd(II) > Ni(II) >>Ca(II). These were determined from experimental calculations where complexation constants were obtained.[200] The HEDP metal ion affinity however may vary when comparing free ligands to bound ligands.

Table 3.2 Bisphosphonate structures

Generic structure



Name	R_1	R_2
Etidronate	OH	CH_3
Clodronate	Cl	Cl
Pamidronate	O	$CH_2CH_2NH_2$
Ibandronate	OH	 $CH_2CH_2N(CH_3)(CH_2)_4CH_3$
Alendronate	OH	$CH_2CH_2CH_2NH_2$
Tiludronate	H	
Zoledronate	OH	
Risedronate	OH	

3.3 Hydroxyapatites and Bisphosphonates

The ability for HAP to immobilize heavy metals can be enhanced by introducing them into composite materials[24] or by modifying them with functional ligands.[176] The high affinity of bisphosphonates for calcium phosphate[192] and their metal ion chelating properties make them ideal modifiers for HAP adsorbents.

Binding of six bisphosphonates to bone was measured using clodronate, etidronate, risedronate, ibandronate, alendronate, and zoledronate.[198] Although the binding affinity of each bisphosphonate varied, all were found to have significantly high affinities for HAP compared to other species (>10 x) known to influence HAP crystal growth.

At a pH of 7.4, HAP surfaces were sufficiently negative (zeta potential= -4.2mV) to enable surface reactions with the bisphosphonates to occur.[200] A similar pH was used during the modification of HAP with HEDP, discussed in Chapter 6.

3.4 Conclusion

HAP modified with bisphosphonates has the potential to be selective for metal ions. The precise mechanism by which modification and the retention of heavy metals occurs is not fully understood. Detailed procedures are being investigated to determine the extent of HAP modification as well as the new metal ion affinity. Sequestered metal ions become immobilized on HAP and resist leaching after being calcined.[184] HAP does not require disposal following metal ion sequestration and studies have suggested combining HAP with cements to build infrastructure in a process known as valorization. Bisphosphonate-modified HAP is expected to not only remove metal ions from water but also to be transformed back to unmodified HAP upon calcination, since organophosphates decompose at high temperatures.

CHAPTER 4. Design and synthesis of hydroxyapatite with organic modifiers for application to environmental remediation

4.1 Introduction

Composites of HAP and organic compounds have been prepared for biomedical applications. These same composites may be applicable to environmental remediation. The organic compounds used for modification include organic acids, calcium chelating agents, proteins, compounds capable of ring-opening polymerization, and hydrophobic silicon-containing molecules. The methods for modification that have been studied are co-precipitation and post-HAP particle formation. It is proposed that modified HAP (mHAP) could have enhanced metal ion selectivities.

Hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, is an inorganic, insoluble salt.[202] It belongs to a family of calcium phosphates and is one of the most stable crystal structures of the calcium phosphates.[203] This inorganic salt has a similar chemical composition to that of human bones and teeth,[204] and may consequently serve as a useful coating for human implantations and dental affixtures.[205] The goal is to review the syntheses of HAP modified for biological applications and use that as a starting point for the preparation of mHAPs for application to environmental remediation.

4.1.1 HAP synthesis

HAP synthesis can be manipulated so that characteristics like strength, size and affinity are controlled.[206,207,208] HAP is typically synthesized from a calcium precursor (calcium nitrate, calcium hydroxide, calcium alkoxide, calcium chloride, calcium carbonate, etc.) and a soluble phosphate (phosphoric acid, sodium hydrogen phosphate, ammonium phosphate, etc.). There have been various attempts to control the composite yield, growth efficiency and particle properties of HAP, thus giving rise to a diverse group of parameters which can affect the HAP growth process.

Parameters such as temperature, pH, reaction time and precursors may be adjusted so that the ratio of Ca/P varies between 1.5 and 1.67.[203,209,210, 211, 212, 213] The temperature and drying time of the precipitate may be equally important. Some methods used in drying HAP are autoclaving,[214] freeze drying[215] and thermal treatment under ambient conditions.[216, 217, 218, 219]

The surface of HAP can be modified with chelants that can bind to Ca^{2+}, -OH and -POH. Organic substrates bound to the HAP surface include carboxylic acids, phenolates and carboxylates,[220, 221] isocyanates,[71,222, 223,] sulfonic acids and sulfonates.[224, 225, 226]

4.1.2 *Enhancing the properties of HAP*

Novel pathways of modifying HAP have been proposed, both in terms of shuffling the steps in the synthesis and also broadening the array of modifiers used. Although researchers have attempted both surface modification and modification within the bulk phase of HAP, there is no confirmation as to which modifier or method is best.

Modified HAP may be used in two ways: the biological principle behind modification is that by coating a porous metal prosthetic with mHAP, the newly formed bone may bind physicochemically to the mHAP surface, increasing bone adhesion strength and rate of binding. Without mHAP or HAP coatings, patients run a risk of experiencing pain due to micromotion of the cement-less prosthesis.[158] In the future, mHAP may consist of metal modifiers which could facilitate better implant mechanical properties. For environmental applications, the nature of the modifier may be able to produce mHAP selective for specific metal ions.

Organic polymers have been modified with HAP in order to increase the rate of metal ion sorption. A composite hydrogel of HAP and crosslinked polyacrylamide was prepared and found to sorb Pb^{2+} from aqueous solutions.[227] The function of the polyacrylamide was to increase accessibility of the lead ions to the HAP. This was more effective than coating the HAP onto a polyurethane foam.[228] Along the same lines, HAP was blended with a solution of poly(vinyl alcohol) and applied onto poly(vinyl alcohol) or polyurethane foams in order to obtain HAP on a macroporous matrix The porosity of the foam was an important variable in affecting the time to equilibrium in the sorption of Cd^{2+} from aqueous solutions.

The optimum method of modifying HAP with small-molecule modifiers is not fully understood and is still being studied. A list of modifiers which bind best and most efficiently has not yet been established. The use of organic compounds as modifiers is an important pathway for modifying HAP.

4.2 Organically modified HAP

Modification may be grouped into two categories; pre-functionalization and post-functionalization. Pre-functionalization describes the modification of HAP while it is still in an aqueous suspension, whereas post-functionalization refers to a modification performed after HAP particles have been precipitated and dried. HAP modified via both pre- and post-particle formation can give rise to surface-modified HAP; a post-functional modification of the bulk phase has yet to be confirmed.

4.2.1 Pre-funtionalization

Pre-functionalization is accomplished during the co-precipitation of calcium and phosphate ions in a simultaneous addition of a known concentration of modifier, before or after pH adjustment of the calcium phosphate mix. The point of addition of a modifier, relative to the time of pH adjustment, may affect the binding affinity of the modifier to HAP.

4.2.1.1 Co-precipitation

During co-precipitation, the calcium precursor may be added first to the phosphate precursor followed by the addition of modifier, or the calcium precursor can be mixed with the modifier first, before contacting the phosphate. In the first case, even though the modifier is added after the precursors have been mixed, modification is still considered pre-functional because calcium phosphate has not yet fully formed.

Most of the organic compounds added to HAP during synthesis are commonly used as chelating agents. These include citrates,[205] glycine,[229] and EDTA.[230] Chelating agents are normally removed thermally from HAP in the final stages of synthesis, leaving only pure HAP particles. At this point, they are no longer considered modifiers but they are important for controlling mineral growth and can provide useful information about similar kinds of organic molecules which may be used for modification and applied to environmental remediation.

4.2.1.1.1 Surface and bulk phase modification

Modified HAP synthesized by co-precipitation may give rise to surface modified HAP or HAP modified in the bulk phase. The difference between the two is governed by the parameters set for synthesis.[205]

Surface-modified HAP using cetylphosphate (CP) was prepared by mixing an aqueous solution of $CaCl_2$ with Na_2HPO_4 and NaOH, then adding an emulsified chloroform solution of cetylphosphate. The resulting CP-mHAP has a hydrophobic surface and a decrease in particle diameter.[231] This modification also increased the surface adsorption for organic compounds such as sodium *p*-dodecylbenzenesulfonate (SDBS) because of an interaction between the alkyl chains of SDBS and the CP-modified HAP surface.[231]

Derivatives of precursors are sometimes used during HAP modification. One example is the use alkyl phosphates[232] in place of inorganic phosphates such as phosphoric acid. Alternatively, adding calcium chelants such as citrate to an aqueous solution of calcium chloride may be used to control particle size and crystallinity.[205]

There have been studies showing the effect of HAP modification with collagen on the elasticity of the composite.[215] Collagen-modified HAP, used to fill holes in rat bones, allowed bone regeneration to occur within the mHAP pores. This mHAP was reported to be very flexible and have a rubber-like elasticity.

The desire to use organic modifiers in HAP synthesis has not only been for the purpose of producing a modified HAP composite, but also as a means of controlling the carbon content and pore size of the precipitated HAP.[229] Glycine has been used as a template for HAP synthesis, after which the HAP-glycine pair was heated at temperatures exceeding 600° C in order to decompose the glycine and produce carbon-free, porous HAP.

4.2.2 Post-functionalization

Post-functionalization is typically achieved by contacting the HAP particles with a given modifier for several hours so as to ensure maximum adsorption on the HAP surface. Some of the most common ways by which HAP has been post-functionalized are by surface modification procedures which include ring opening surface and grafting polymerization, ultrasonic irradiation and heat polymerization.

4.2.2.1 Surface modification

The surface of HAP can be modified by post-functionalization so as to preserve the HAP crystal. Post-functionalization may be a better way to modify HAP as compared to pre-functionalization because once molecules enter the bulk phase, they interfere with the standard HAP crystal structure and may give rise to a product which is not quite HAP.[71]

An esterification reaction on the surface of hydroxyapatite is one of the ways in which the HAP surface has been modified. This was done by contacting the HAP in dodecyl alcohol (DA) at 115°C and 190°C, for long periods of time.[72] Results showed that the HAP surface was successfully modified by dodecyl groups since C–H vibrational modes for dodecyl alcohol remained at 2962, 2930, and 2860 cm^{-1}. After undergoing a thermogravimetric analysis, DA-HAP had a greater mass loss once heated (about 4.8%) as compared to the control HAP (2.5-3.2 %).[72] This confirmed that the HAP was modified.

Monohexyl phosphate (HP) and monodecyl phosphate (DP) are two other compounds used to modify the surface of HAP. In this case, HAP was contacted with HP and DP in acetone at 25°C. The morphology of the HAP particles remained the same after modification. Two alkyl groups per nm^2 were bound to the surface of HAP. Once the alkyl groups were thermally removed at 300°C, the HP- and DP- treated HAP had more P-OH groups on the surface as well as a higher negative electrophoretic mobility compared to the HAP which had not been treated. Furthermore, the unmodified HAP adsorbed much more H_2O and CO_2 than the modified salt.[233]

Pyrophosphoric acid (PPA, $H_4P_2O_7$), is another phosphate which can be used for the surface modification of HAP. This is accomplished by contacting the HAP with PPA in acetone. The higher the PPA concentration used in the contact, the greater the number of PO_4 groups in the resulting HAP, leading to a decreased Ca/P ratio, from 1.62 to 1.35.[234]

The surface of HAP is not only modified by the attachment of novel compounds, but also by increasing the surface charges so as to increase the surface wettability and surface energy.[230] When an induced surface charge is applied to HAP, it produces a type of mHAP with an unchanged volume. Experiments show that the wettability and polarity change allows for the adsorption of inorganic ions $Ca^{2+,}$ Cl^-, Na^+ and HCO_3^- and cell-adhesive proteins such as fibronectin and vitronectin. Furthermore, the induced charge and subsequent binding of ions and proteins can change the rate of mineralization, and cell adhesion and proliferation on the newly polarized HAP surface.[230]

4.2.2.1.1 Ring opening surface and grafting polymerization

L-lactide (LLA) has been used in a surface grafted ring-opening polymerization on the surface of hydroxyapatite nanoparticles. This was done through a chemical linkage, by attaching the LLA directly to the HAP surface. These HAP nanoparticles after polymerization had the same dimensions and conformation before and after reaction.[73]

Another compound used in surface grafting is phenylphosphonic dichloride ($PhP(O)Cl_2$).[190] Hydroxyapatite and fluoroapatite (FAP) were used as starting materials in this modification and contacted with different concentrations of $PhP(O)Cl_2$. The HAP exposed to more of the dichloride had a carbon composition of 3.82% and that contacted with a lower concentration had a carbon composition of 2.23%. In addition, the surface concentration or grafting density of the phosphate was 5.63 molecule/ nm^2 for the HAP with less phosphonate and 9.92 molecules/nm^2 for the HAP from the higher concentration. A monolayer would typically contain about 4.3 molecules/nm^2. This suggests the presence of polyphosphonates on the surface of HAP.[190]

Vinyl phosphonic acid (VPA)[235] has been graft polymerized onto the surface of hydroxyapatite nanocrystals. This was done by first degassing the HAP, exposing it to a potassium persulfate / sodium metabisulfite solution, then contacting it with VPA at room temperature for 3h.

Results from these studies suggest that a surface modification of HAP will only occur at the HAP nanosurfaces because once the crystal phase is altered, the mHAP no longer has characteristics inherent to HAP.[71] It is therefore necessary to verify that modification is occurring on HAP surfaces and that HAP-specific crystalline properties are maintained.

4.2.2.1.2 Ultrasonic irradiation

Ultrasonic irradiation was used to treat nanocrystalline hydroxyapatite prepared by a precipitation method using calcium nitrate, ammonium phosphate and urea. The amount of needle-like HAP crystals formed using ultrasonic irradiation increased as temperature and time increased. Urea was also used to help produce HAP nanoparticles.[236]

An intensive ultrasonic field was used in another study to break down particles in order to coat them with a poly(D,L-lactide-co-glycolide) (PLGA) polymer. The apatite was mixed with a polymer solution containing 2% PLGA in acetone, followed by dropwise addition of ethanol to enhance precipitation in the ultrasonic field.[75]

4.2.2.1.3 Heat polymerization

Heat polymerization refers to surface modification in which HAP is contacted with a modifier under high heat or reflux temperatures. One example is the synthesis of poly(methyl methacrylate) (PMMA) / HAP complexes wherein the aim is to determine whether incorporating HAP into the PMMA matrix improves the osteoblast response in comparison to unmodified PMMA. HAP was placed in a solution of PMMA/MMA, mixed thoroughly and allowed to sit overnight. Polymerization began once the temperature was raised to 37°C over a period of several days. In the last step, the sample was placed in a 100°C oven for 24 h for complete polymerization and removal of unpolymerized monomers.[237] Results showed that polymer-modified HAP have different properties; this should be explored for environmental remediation.

HAP was modified with poly ε-caprolactone (PCL) by refluxing in dry toluene, removing the toluene, and adding caprolactone with stannous octoate ($Sn(Oct)_2$) at 25°C under nitrogen. The reaction was kept at 130 °C for 25 h. Grafting PCL onto the surface of HAP enhanced the spreading of HAP nanoparticles in the PCL solution. It also enhanced biocompatibility, as was evident in protein adhesion and cell experiments.[238]

4.3 Parameters affecting modification efficiency

There are numerous parameters that affect the morphology of mHAP. In synthesizing PLGA/ HAP composites, parameters include the intensity of the applied ultrasonic field, weight % ratio of polymeric and ceramic parts, temperature of the medium, pH, surfactant type, and the order of synthesis steps.[75] Additionally, modifier size as well as its polarity and hydrophobicity may equally affect mHAP morphology and conformation.

4.3.1 Temperature: synthesis and drying

The temperature at which mHAP is synthesized depends on the precursors used in the reaction and on the morphology desired for the final particles. The drying temperature is dependent upon the decomposition temperature of the modifier used. At calcination temperatures ranging from 700-900 °C, HAP is the thermodynamic product.[184] The problem with calcining mHAP at such high temperatures is that in doing so, the organic modifiers will decompose leaving only HAP. As a result, modifying HAP requires that drying temperatures not exceed the decomposition temperature of the modifier.

4.3.2 Modifier size and structure

The chemical structure of organic modifiers affects HAP particle size.[239] After modifying HAP with Tween 20, there appeared to be small-sized HAP particles. This was caused by steric hindrance from the dendriform structure of Tween 20 as well as strongly coordinated Tween 20 on the HAP surface.[240]

PEG 600 had the opposite effect when it was used to modify HAP. There were longer HAP nanorods seen when PEG 600 was used as a modifier than when prepared in the blank experiment. The increased length may be due to the flexibility of the PEG 600, a linear molecule with many ether bonds. As the temperature increases, the flexibility of the PEG molecules in an aqueous solution also increases and hence the PEG molecules should cause a lengthening axis orientation of HAP.[240]

4.3.3 Effect of pH

Depending on the solution pH, mHAP may undergo a phase transformation and turn into pure HAP. At a pH less than or equal to 8.0, the diffraction peaks of calcium phenylphosphate (CaPP) become weaker and completely disappear at pH 7.0. The appearance and intensity of peaks associated with HAP increase as the pH of the solution decreases.[209]

4.3.4 Modifier polarity and hydrophobicity

HAP modified with cetylphosphate revealed that the higher the initial concentration of CP in a chloroform solution, and the higher the surface concentration of CP on HAP, the greater the contact angle of water.[231] This means that water droplets had difficulty spreading on the particle and would minimize their contact with the surface of the CP-modified HAP due to the hydrophobic tails of the CP on the CP-HAP surface. Modifying HAP with CP thus makes the crystal more hydrophobic. CP also decreases the mean diameter of the particles compared to unmodified HAP. The specific surface area, however, increased as the CP concentration increased. Sodium dodecylbenzenesulfonate (SDBS) adsorbed onto CP-HAP due to a hydrophobic interaction of the alkyl chains.[231]

4.3.5 HAP precursors

The calcium and phosphate precursors used to synthesize HAP may have an effect on the final mHAP produced. HAP synthesized with calcium hydroxide has hydroxyl groups on the surface which are capable of forming hydrogen bonds to organic modifiers.[241,242] On the other hand, mHAP synthesized with calcium carbonate will produce a pure calcium phosphate after decarboxylation at high temperatures. The precursors may also affect the Ca/P ratio.

For environmental applications, calcium precursors derived from waste materials are the most practical source.

4.4 Conclusion

The use of modified HAP for biomedical applications has been of great interest and much of the research attempting this modification can provide useful insight into the field of environmental remediation. Research from our laboratory is focusing on the synthesis of pre- and post-functionalized HAP modified with phenylphosphonic acid and a series of amino acids. The resulting affinity for a series of metal ions is being determined. The results will be presented in due course.

CHAPTER 5. Distinguishing between organic and inorganic phosphates in hydroxyapatite

5.1 Introduction

The simplicity and precision of the vanadate-molybdate method has made it a useful tool for measuring the total amount of phosphorus in phosphate compounds. It can be important, however, to distinguish between organic and inorganic phosphate in modified (hybrid) phosphate polymers and this method does not distinguish between the two. A method was thus developed to determine the amount of organic phosphate in hydroxyapatite (HAP) modified with 1-hydroxyethane-1,1-diphosphonic acid (HEDP) relative to its inorganic phosphorus content.

Determination of the phosphorus content in phosphate-containing compounds has been extensively evaluated by spectrophotometric methods.[243,244] Although the phosphorus capacities of orthophosphates, condensed phosphates, and phosphates bound to organic polymers can be measured using a vanadate-molybdate reagent,[245,246,247] the method is not capable of distinguishing between organic and inorganic phosphates because the procedure requires strong acid ($HClO_4$ or H_2SO_4) digestion and peroxodisulfate ($S_2O_8^{2-}$) oxidation to convert all phosphates into the orthophosphate form. This method also cleaves stable P-C bonds in organophosphates to produce orthophosphates and organic fragments (Figure 5.1).

Orthophosphates react with the ammonium salts of vanadate ($H_2VO_4^-$) and molybdate (MoO_4^{2-}) to produce a yellow phosphovanadomolybdate complex. The intensity of this yellow color is proportional to the concentration of phosphate and is analyzed photometrically at 470 nm.[248]

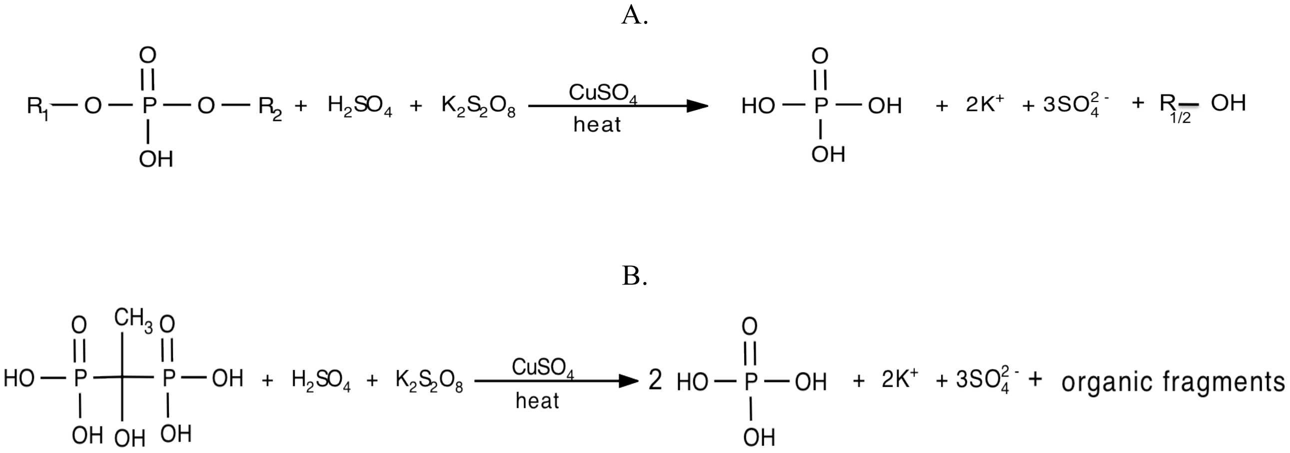


Figure 5.1. Oxidation of organophosphates (A) with cleavage of P-C bonds (B)

This method is useful for determining the total phosphorus content of pure organic and inorganic phosphates, but quantifying the separate phosphorus capacities is problematic for materials containing both types of phosphates. The amount of phosphorus contributed by each type is difficult to evaluate since all phosphates are converted to the orthophosphate. Since distinguishing the organic from the inorganic phosphates became important in our research, a method to distinguish between the two kinds of phosphate was developed.

5.2 Total phosphorus capacity

Precise measurements of the total phosphorus capacity of polystyrene-bound tris(hydroxymethyl)aminomethane (Tris) resins modified with diethylchlorophosphate (DECP)[249] were obtained using the vanadate-molybdate method:[248] digestion of the modified resin (20 mg) in concentrated sulfuric acid (10 mL) was accelerated by the addition of a 3.19 mg copper sulfate catalyst and increased temperature. Mixing the digested sample with 10 mL of the ammonium vanadate-molybdate reagent resulted in formation of an intense yellow complex that was measured at 470 nm using a Milton Roy Spectronic 21D.

The accuracy of the phosphorus capacities was supported by their agreement with the acid and nitrogen capacities. Therefore the total phosphorus capacity can be accurately determined using this method to analyze phosphonate-modified polymers.

5.3 Inorganic phosphorus capacity

Unlike organophosphates, inorganic phosphates can dissociate into their respective ions and orthophosphates in the presence of dilute acid. Oxidizing agents, catalysts and heat are not required for this process. The dissociation of hydroxyapatite with HCl is shown eq. 5.1. This produces calcium chloride, water and protonated orthophosphates.

$$Ca_{10}(PO_4)_6(OH)_2 + 20\ HCl \rightleftharpoons 6\ H_3PO_4 + 10\ Ca^{2+} + 20\ Cl^- + 2\ H_2O \qquad (5.1)$$

To determine the inorganic phosphorus capacity, 20 mg of the polymer was added to 10 ml of 1N HCl and stirred for 3 h. Five drops of 0.1% phenolphthalein indicator solution were added and the pH was adjusted with dilute NaOH until the solution turned slightly pink. At the equivalence point, a few drops of 0.1 N HCl were added to turn the solution back to clear. The dilute HCl was added drop-wise to remove any cloudiness while keeping the solution neutral. The solution was diluted to 100 ml with de-ionized water and a 25 ml aliquot was transferred to a 50 ml volumetric flask along with 10 ml of the ammonium vanadate-molybdate reagent. It was filled to the mark with de-ionized water and allowed at least 15 min to develop. The yellow color intensity was measured at 470 nm on a Milton Roy Spectronic 21D. Calibration standards were generated with K_2HPO_4 solutions and the absorbance was plotted against mg P. The concentration of P in the unknown solutions was calculated using the Beer-Lambert equation.

5.4 Organic phosphorus capacity

The organic phosphorus (%) in HAP modified with HEDP was determined by difference from the total phosphorus and inorganic phosphorus capacities (eq. 5.2.)

$$\% P_{org} = (P_T - P_{inorg}) / P_T \times 100 \tag{5.2}$$

where P_T is the total phosphorus capacity, P_{inorg} is the inorganic phosphorus capacity and P_{org} is the organic phosphorus capacity.

5.5 Phosphorus capacity of HEDP-modified HAP

HAP modification was achieved by stirring a 2.0 g sample of HAP with 100 ml of 0.5 M HEDP at 20°C. Six reaction times were used (17 h, 28 h, 56 h, 84 h, 112 h and 140 h) to determine the effect of reaction time on the extent of modification. The phosphorus capacities for all HEDP-modified HAPs are reported in Table 5.1.

Table 5.1 Phosphorus capacity of HEDP-modified HAP

Sample	**Modification Time**	**P_T (mequiv/g)**	**P_{inorg} (mequiv/g)**	**P_{org} (%)**
A	17 h	4.72	4.68	0.7
B	28 h	4.78	4.41	7.8
C	56 h	4.92	3.84	22.0
D	84 h	5.85	3.80	35.0
E	112 h	5.15	2.64	48.7
F	140 h	4.98	2.54	49.0

5.6 Discussion

Digestion of modified HAP with H_2SO_4 gave, as expected, a higher phosphorus capacity than digestion using HCl. As modification times increased, HEDP-modified HAP had a larger organic phosphorus capacity, which was indicative of a greater degree of modification. Results show that the organic phosphorus capacity of HEDP-modified HAP can be determined by a combination of the P_T and the P_{inorg} vanadate-molybdate procedures. The effect on the selective removal of metal ions from water in the environment is currently being investigated.

CHAPTER 6. The modification of hydroxyapatite with an ion-selective complexant: Binding of 1-hydroxyethane-1,1-diphosphonic acid (HEDP) to hydroxyapatite

6.1 Introduction

Hydroxyapatite (HAP) has a chemical composition similar to bones and teeth.[250,251,252] It is synthesized by combining calcium hydroxide or other calcium precursors with soluble phosphates.[161,184,253] Temperature and pH conditions for HAP synthesis are adjusted so that characteristics like mechanical strength as well as particle and pore size can be controlled.[208,254,255,256]

During synthesis and drying, the calcium phosphate goes through intermediate, amorphous stages until the thermodynamically stable and crystalline phase of HAP is formed.[257] Thermodynamically stable HAP has a Ca/P ratio of 1.67 and is typically obtained from combining precursors in the appropriate stoichiometric proportions as well as drying the calcium phosphate at high temperature.[205,258,259] Reaction time and precursor concentration may also be adjusted to vary the final Ca/P ratio between 1.5 and 1.67.[209,211,212,257,260,261] After the calcium phosphate has precipitated, the drying temperature and duration can be adjusted to influence the final structure and degree of crystallinity. Methods for drying HAP include autoclaving,[214] freeze drying[262] or thermal treatment.[219,263,264]

HAP may have an important role in environmental applications due to its metal ion sequestering capabilities.[161,163,166] Its advantage over other ion exchange resins is that it is inexpensive and can be valorized by combining with cement to build infrastructure after sequestering metal ions.[265,266] Additionally, it is stable at neutral pH and is therefore an excellent candidate for groundwater treatment.[24] Some of the biggest groundwater polluters are metal ions such as copper, cadmium, lead, mercury and arsenic.[267] The increasing effect of groundwater pollution on disease has created a dire need to safely remove these toxic metal ions from groundwater without having to redeposit the wastes into remote disposal sites.

HAP can undergo several interactions with metal ions in order to facilitate their removal from aqueous solutions. Ion exchange,[268,269,270,271,272] surface complexation,[272,273,274] dissolution of HAP and precipitation of metal phosphate,[272,275] as well as substitution of the heavy metals for the Ca^{2+} in HAP[272,276] are all possible mechanisms for metal ion removal.

HAP has been immobilized onto organic polymer matrices to increase the metal ion sorption capacity compared to organic polymers not containing HAP.[29] A mixed hydrogel of HAP crosslinked with polyacrylamide was found to have a high Pb^{2+} sorption capacity in comparison with the polyacrylamide in the absence of HAP.[227] In a similar study, HAP was coated onto polyurethane foam and found to increase lead sorption as well.[228]

HAP has been combined with poly(vinyl alcohol) to produce a cryogel which when immobilized onto poly(vinyl alcohol) and polyurethane foams create a macroporous matrix.[277] HAP-organic hybrids have also been synthesized by combining the calcium precursors with organic phosphates in the initial batch experiments for a co-precipitation of the HAP-organophosphate.[198,205,209] The organophosphate was later decomposed during the calcination process to produce an apatite with high SSA and porosity.

The present study aims to modify HAP by incorporating organophosphates into the already prepared HAP crystals to enhance its metal ion selectivity. To distinguish between HAP modification by the co-precipitation method and modification of the already precipitated HAP particles, the terms pre-functionalization and post-functionalization will be assigned respectively.

Using organic compounds for modifiers is an important pathway for functionalizing HAP since these compounds introduce metal ion selectivity. This study uses the 1-hydroxyethane 1,1-

diphosphonic acid (HEDP) which belongs to a group of bisphosphonates known to bind HAP with high affinity[198,278,279] and to also possess metal ion sequestering capabilities.[200,280,281] mHAP salts may have applications as selective materials in wastewater treatment.

6.1.1 Proposed mechanism

A 3 step phospho-esterification reaction was proposed for HAP modification with HEDP (Figure 6.1) based on surface reactions for HAP with similar organic modifiers shown in figure 3.4. In the first step, surface –OH groups on HAP bind to the electrophilic P of the organophosphate modifier. In step 2, P–O^- removes H from new the P-O-P bridge formed between HAP and HEDP by proton transfer. The phosphoryl oxygen forms by elimination to produce mHAP and water in the final step. Reaction conditions such as temperature and time may influence the number of reactions occurring between each phosphonic acid group and HAP.

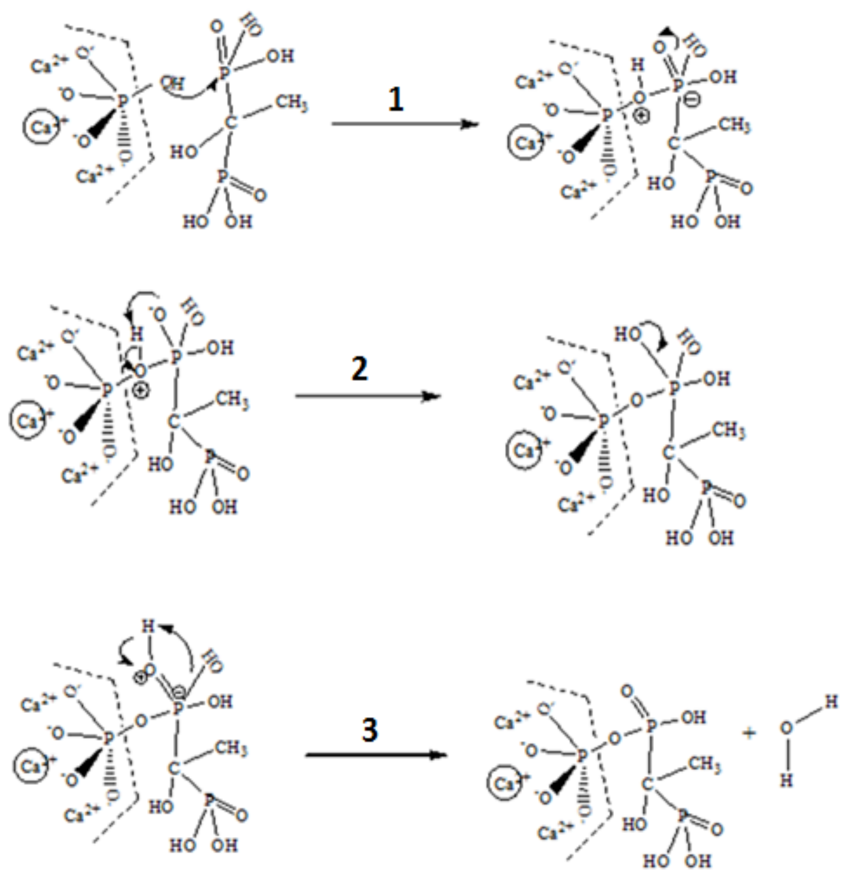


Figure 6.1 Proposed phospho-esterification mechanism by (1) addition, (2) proton transfer and (3) elimiation reactions for HAP-HEDP modification based on similar reported mechanisms.[72,190]

6.2 Materials and methods

6.2.1 HAP preparation

HAP was synthesized by the wet method using calcium hydroxide and phosphoric acid in a 1.78 Ca:P molar ratio from a previously established procedure.[282] In a typical experiment, 3.86 g of $Ca(OH)_2$ were combined with 140 ml dH_2O and 2 ml of H_3PO_4 and the reaction was allowed to proceed for 48 h while maintaining a constant pH of 8.0-8.2, with dilute H_3PO_4 or KOH solutions. The salt was dried at ambient temperature and pressure followed by vacuum oven drying at 60 ^{o}C. Calcination was carried out at 700 ^{o}C for 3 h, to obtain HAP with a Ca/P ratio of 1.52. This was followed by treatment with the HEDP.

6.2.2 mHAP preparation

All mHAP salts were prepared by suspending HAP calcined to 700 ^{o}C, in HEDP solutions of different concentrations (0.01 M-0.50 M). In a typical experiment, 2.0 g HAP was combined with 100 ml of the desired concentration of HEDP and the reaction was left to proceed at 20 ^{o}C or 80 ^{o}C for 4 h, 168 h or 720 h. The pH of the HEDP solution was previously adjusted to 7.6 to prevent dissolution of the HAP. HAP-modifier suspensions were filtered, washed three times with de-ionized water and dried at ambient temperature for 48 h before analysis. During modification, HEDP concentration, reaction temperature and reaction time were adjusted to produce different mHAP samples presented in Table 6.1.

To account for other solvation effects, control experiments consisting of HAP in de-ionized water under similar modification times and temperatures were carried out. Results for the control sample prepared for 168 h and 80 ^{o}C (cHAP) are reported. Stoichiometric HAP (sHAP1) with a Ca/P ratio of 1.67 was purchased from Sigma Aldrich. This HAP was also modified with HEDP for 168 h and at 80 ^{o}C (sHAP2) in order to determine whether the use of non-stoichiometiric HAP had an affect on modification efficiency.

Table 6.1 HAP and salt identification

Type of HAP	HEDP concentration (mol•L^{-1})	Reaction temperature (^{o}C)	Reaction time (h)
HAP	0	-----	------
mHAP1	0.01	80	168
mHAP2	0.05	80	168
mHAP3	0.1	80	168
mHAP4	0.2	80	168
mHAP5A	0.5	80	168
mHAP5B	0.5	80	4
mHAP5C	0.5	80	720
mHAP6A	0.5	20	168
mHAP6B	0.5	20	4
mHAP6C	0.5	20	720
sHAP1	0	-----	------
sHAP2	0.5	80	168
cHAP	0	80	168
Ca-HEDP	0	80	168

6.2.3 Preparing Ca-HEDP salt

In order to understand the chemical properties of HEDP modified HAP, a Ca-HEDP salt was prepared. The salt was synthesized using the 168 h/ 80 ^{o}C condition (Table 6.1) since this was later determined to be the condition providing the most HEDP modification. Chemical differences between the salts were evaluated using FT-IR and XRD analyses.

Since mHAP preparation used about 20 mmoles of calcium (2.0 g HAP) and 100 ml 0.5 M HEDP, the Ca-HEDP was prepared using an equivalent number of moles of calcium (1.47 g of $Ca(OH)_2$) added to 100 ml of 0.5 M HEDP.

6.2.4 Characterization

6.2.4.1 Instrumental analysis

FT-IR spectra were generated by a Perkin Elmer Spectrum 65 FT-IR Spectrometer. The PANalytical X'Pert Pro X-ray powder diffraction system was used to obtain XRD patterns. SEM images and EDS were obtained from a Zeiss Supra 55 VP field emission SEM at City College of the City University of New York. SSA measurements were made using a Micromeritics Tristar 3000 Surface area and porosity analyzer. ICP-OES analyses were carried out on acid digested HAP and mHAP samples as well as on metal ion solutions on a Perkin Elmer Optima 7000 DV ICP-OES (optical emission spectroscopy). The ^{31}P-NMR spectra for a select group of mHAP salts were also obtained.

6.2.4.2 Effect of pH

HAP and mHAP samples were suspended in dilute solutions of NaOH to determine their surface acid capacities. Each suspension consisting of 0.25 g HAP or mHAP, 50 ml NaOH and 2.5 g NaCl was allowed to reach equilibrium for 17 h. The mixture was then filtered and the NaOH filtrate was titrated with 0.10 N HCl to determine the amount of unreacted NaOH. Modification was characterized as a function of increasing acid capacity which resulted from the incorporation of diphosphonic acid.

In a separate study, 20 ml of a 0.10 N KNO_3 solution was used to equilibrate 0.10 g HAP and the mHAP5A salt for 1 h and 24 h at varying solution pH (2-8). The pH of each solution was adjusted with KOH or HNO_3 to obtain the desired range. The effect of pH on salt stability and solubility was determined by measuring the concentration of calcium released into solution.

6.2.4.3 Elemental analysis

Samples were digested in acid in order to determine their organic and inorganic phosphorus capacities. The organic phosphorus capacity was measured by dissolving 20 mg of HAP or mHAP in 10 ml of hot concentrated sulfuric acid in the presence of a copper sulfate catalyst and a potassium persulfate oxidizing agent. For inorganic phosphate measurements, a 0.1 N HCl solution was used in the absence of the catalyst and oxidizing agent. All digested samples were neutralized, combined with a vanadate-molybdate reagent to produce the yellow colored vanadomolydbophosphoric acid and analyzed by using a Spec 21 instrument. The phosphorus (% P) contributed by HEDP was calculated using the following relation:

$$(P_T - P_{inorg})/P_T \times 100 \qquad (6.1)$$

where P_T is the total phosphorus capacity and P_{inorg} is the inorganic phosphorus capacity. This method is explained in more detail in chapter 5.

EDS measurements were used to determine the calcium and phosphorus elemental quantities and compared against ICP measurements of acid-digested samples. These were used to generate Ca/P ratios.

6.2.4.4 Metal ion sorption

Metal ion sorption capacities were measured for HAP and selected mHAP samples. The salts (0.10 g) were combined with individual nitrate solutions of Cu^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} prepared with dH_2O and having an initial concentration of 10^{-4} N. In a different experiment, 10^{-4} N divalent metal ion solutions were prepared using 1 N $Ca(NO_3)_2$ to determine the influence of competing, non-toxic ions on heavy metal ion sorption. HAP and mHAP were contacted at ambient temperature (20±2 °C) for 5 h followed by centrifugation and micro-syringe filtration (0.45 μm pore). HAP-free metal ion solutions were analyzed by ICP for determination of the % metal ion sorption.

6.3 Results

6.3.1 FT-IR

In the initial concentration study, HAP was modified with 0.01 M, 0.05 M, 0.10 M, 0.20 M and 0.50 M HEDP for 168 h at 80 °C (Table 6.1). As the concentration of HEDP increased, there was a gradual split in the FT-IR phosphate band appearing between 1083 cm^{-1} and 1144 cm^{-1} as well as the emergence of a new band at 993 cm$^{-`1}$. The intensity of the bands at 943 cm^{-1}, 879 cm^{-1} and 825 cm^{-1} also increased with increasing HEDP concentration. Additionally, the free –OH band (3572 cm^{-1}) disappeared while a new band for intermolecular H-bonds appeared at 3204 cm^{-1} (Figure 6.2). Modification was most pronounced for the 0.50 M concentration (mHAP5A) and hence this concentration was used for all subsequent modifications.

Low temperature (20 °C) and high temperature (80 °C) conditions were combined with reaction times 4 h, 168 h and 720 h, generating 6 different mHAP samples (mHAP5A-C and mHAP6A-C) listed in Table 1. All samples modified at 80 °C or for the long reaction times (168 h and 720 h) showed the phosphate band split (Figures 6.3 and 6.4). The mHAP6B sample modified for 4 h at 20 °C showed no phosphate band split and had a spectrum resembling the untreated HAP in Figure 6.2. In Figure 6.5, the FT-IR spectrum of cHAP was identical to HAP and sHAP1. When sHAP1 was modified with HEDP for 168 h at 80 °C, the new sHAP2 had a similar FT-IR spectrum to mHAP5A, but with a slightly broader phosphate peak at 1083 cm^{-1} (Figure 6.5).

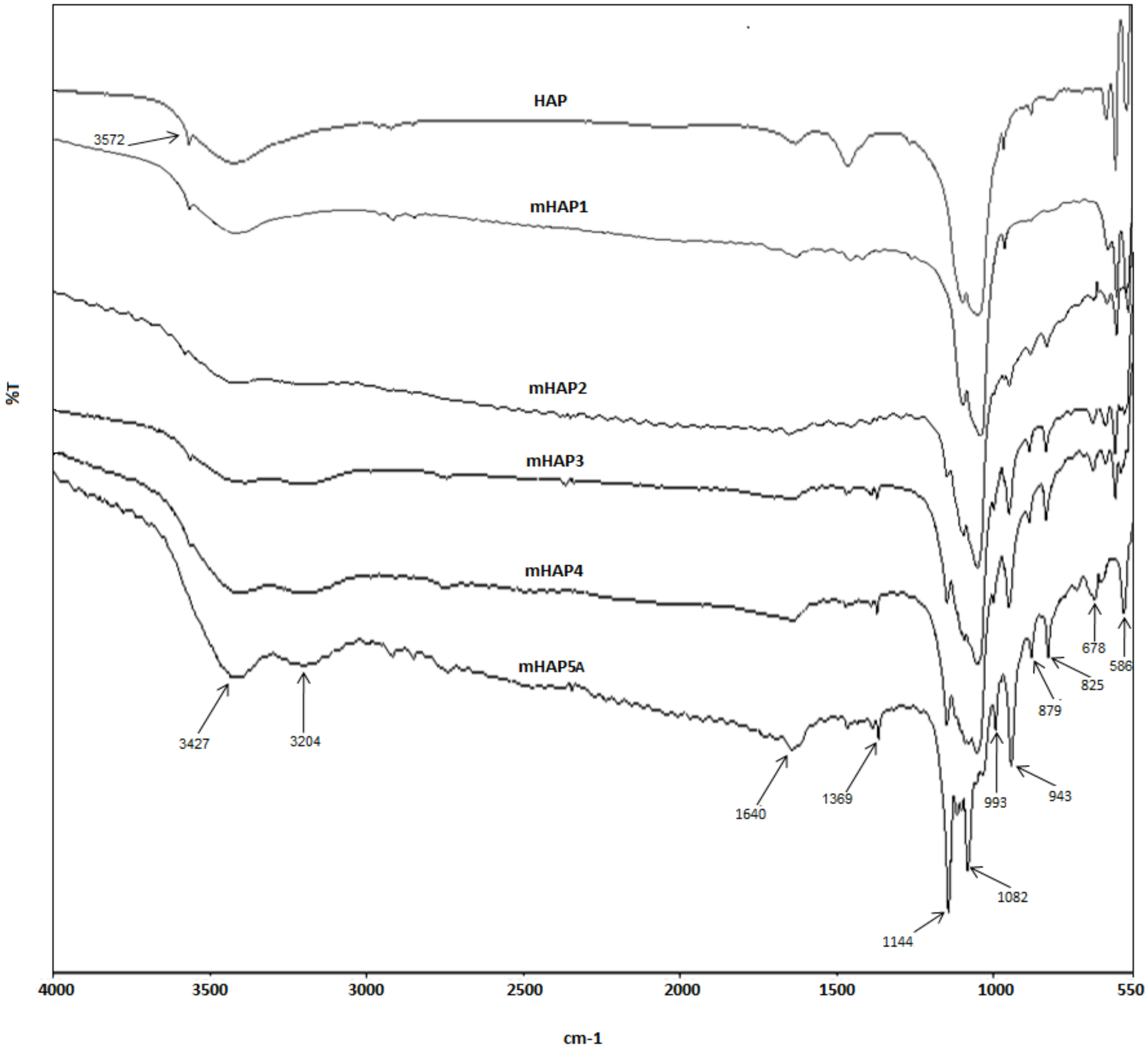


Figure 6.2 FT-IR spectra of HAP, and HAP modified at 80 °C for 168 h using 0.010 M (mHAP1), 0.050 M (mHAP2), 0.10 M (mHAP3), 0.20 M (mHAP4) and 0.50 M (mHAP5A) HEDP.

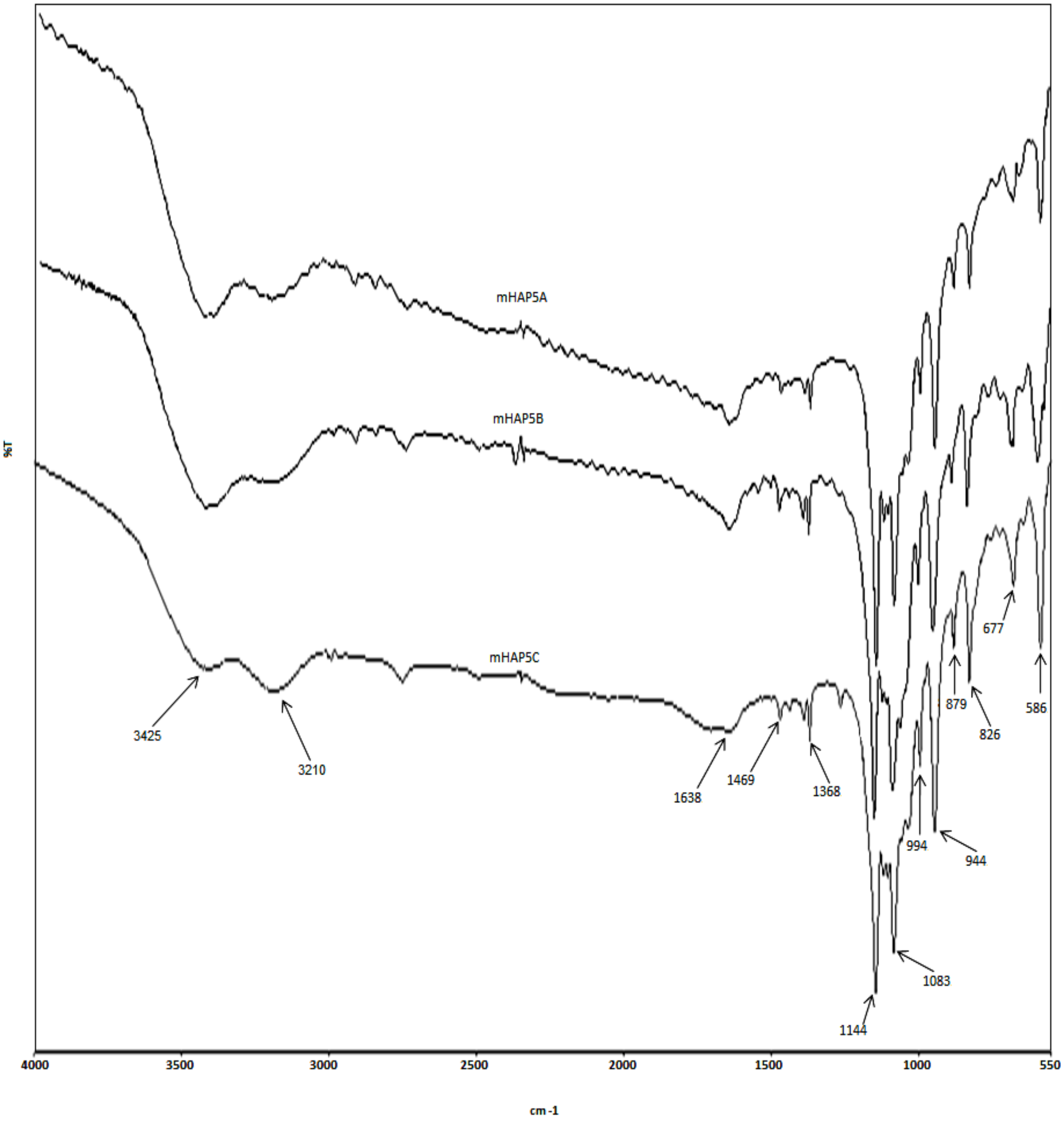


Figure 6.3 FT-IR spectra of HAP modified with 0.50 M HEDP at 80 ^{o}C, for 168 h (mHAP5A), 4 h (mHAP5B) and 720 h (mHAP5C).

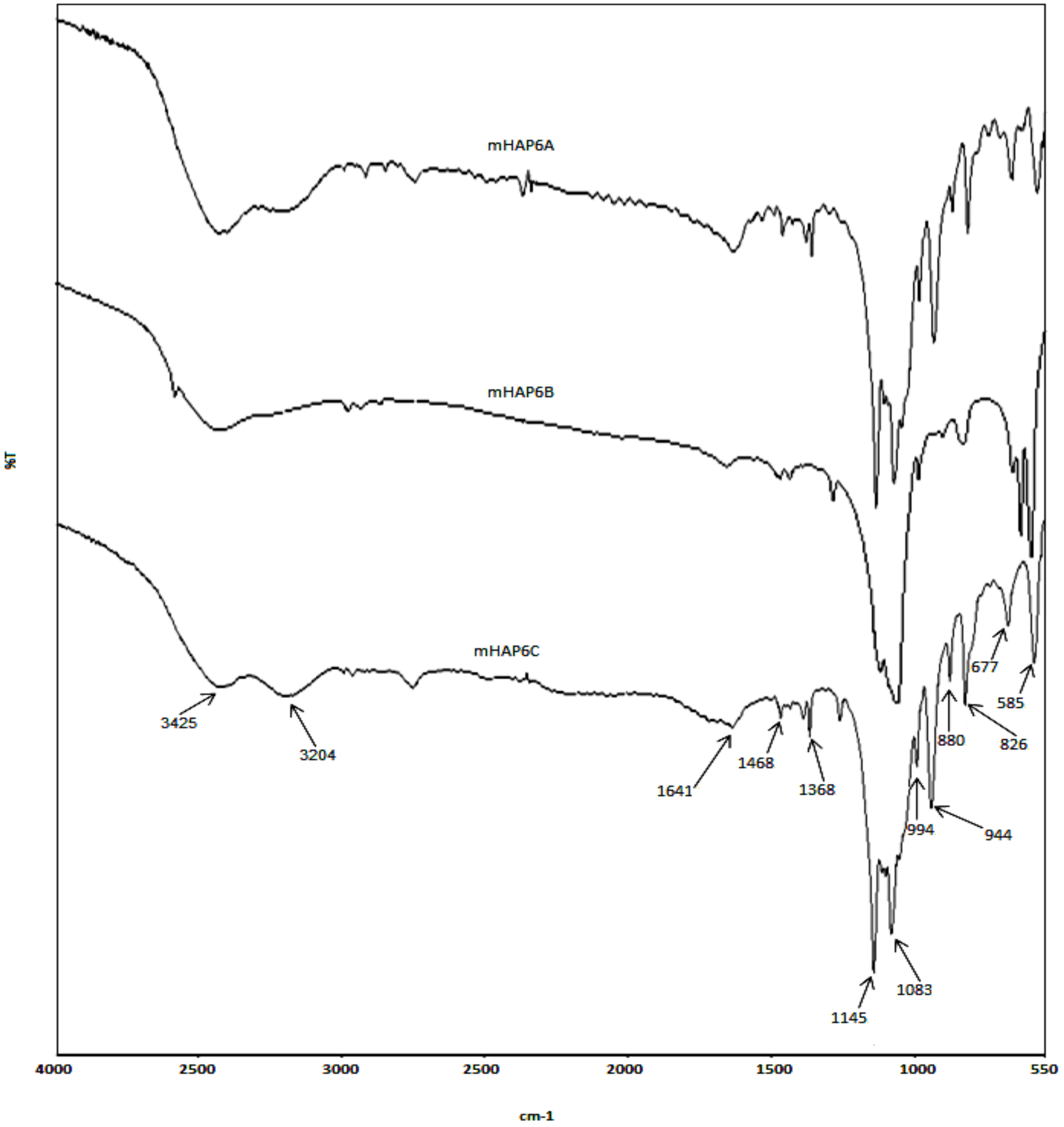


Figure 6.4 FT-IR spectra HAP modified with 0.50 M HEDP at 20 ^{o}C, for 168 h (mHAP6A), 4 h (mHAP6B) and 720 h (mHAP6C).

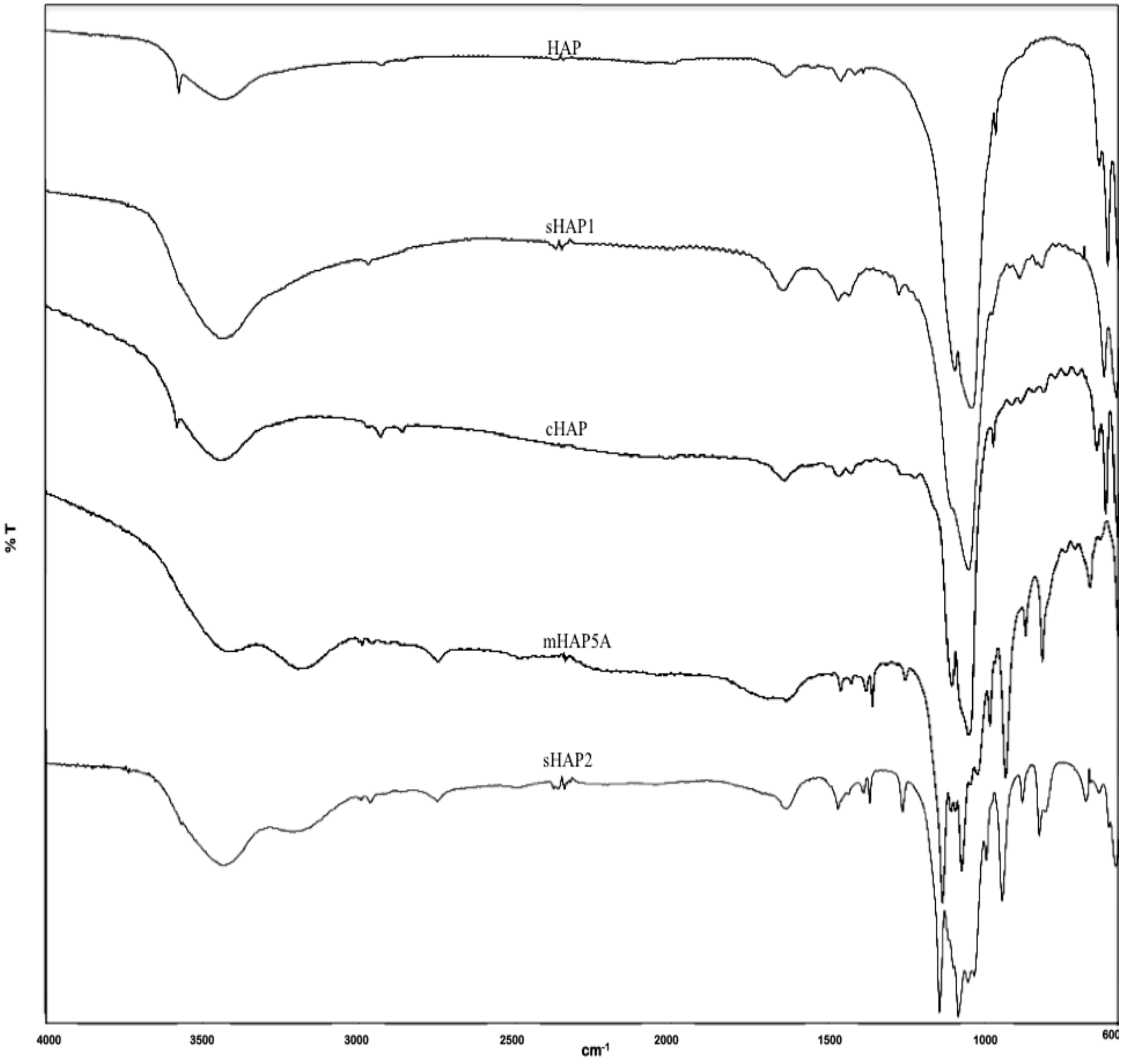


Figure 6.5 FT-IR of HAP, stoichiometric HAP (sHAP1), HAP contacted in dH_2O for 168 h at 80 ^{o}C (cHAP), HAP modified with 0.5 M HEDP for 168 h at 80 ^{o}C (mHAP5A) and stoichiometric HAP modified with 0.5 M HEDP for 168 h at 80 ^{o}C (sHAP2).

6.3.2 XRD

All samples modified at 80 ^{o}C showed a new diffraction pattern when compared to unmodified HAP (Figure 6.6). Increasing the reaction time to 168 h (mHAP5A) and 720 h (mHAP5C) at this temperature produced sharper diffraction peaks indicating more crystallinity. There was no significant difference in the diffraction patterns of the 168 h and 720 h samples.

At low temperature, new diffraction patterns were only seen in samples mHAP6A and mHAP6C modified for longer reaction times (≥168 h) (Figure 6.7). The XRD pattern of the 4 h sample at this temperature (mHAP6B) was the same as unmodified HAP. Samples modified for 168 h (mHAP6A) and 720 h (mHAP6C) had an XRD pattern similar to mHAP5B in Figure 6.6. Results indicate that crystallinity favored high temperature and long reaction time.

There was no difference when comparing the XRD patterns of samples modified for the two long reaction times (168 h and 720 h) within each temperature bracket. The diffraction pattern of mHAP5A was similar to mHAP5C (Figure 6.6) and mHAP6A resembled mHAP6C (Figure 6.7). Subsequent analyses for the long reaction time condition was limited to the mHAP5A and mHAP6A conditions only in order to reduce the wait for generating new modified samples.

The XRD of cHAP revealed that in the absence of HEDP, no modification of the HAP crystal occurred even when the HAP was exposed to the high temperature (80 ^{o}C) and length agitation (168 h) (Figure 6.8). Additionally, the sHAP1 sample had a similar diffraction pattern to both the HAP and cHAP samples but was more crystalline than. This crystallinity did not seem to affect modification efficiency since the XRD pattern of sHAP2 had identical peaks to that obtained for mHAP5A. The only difference seen was in the extent of crystallinity. Results show that the same modification can occur at the 168 h, 80 ^{o}C condition regardless of the initial Ca/P ratio.

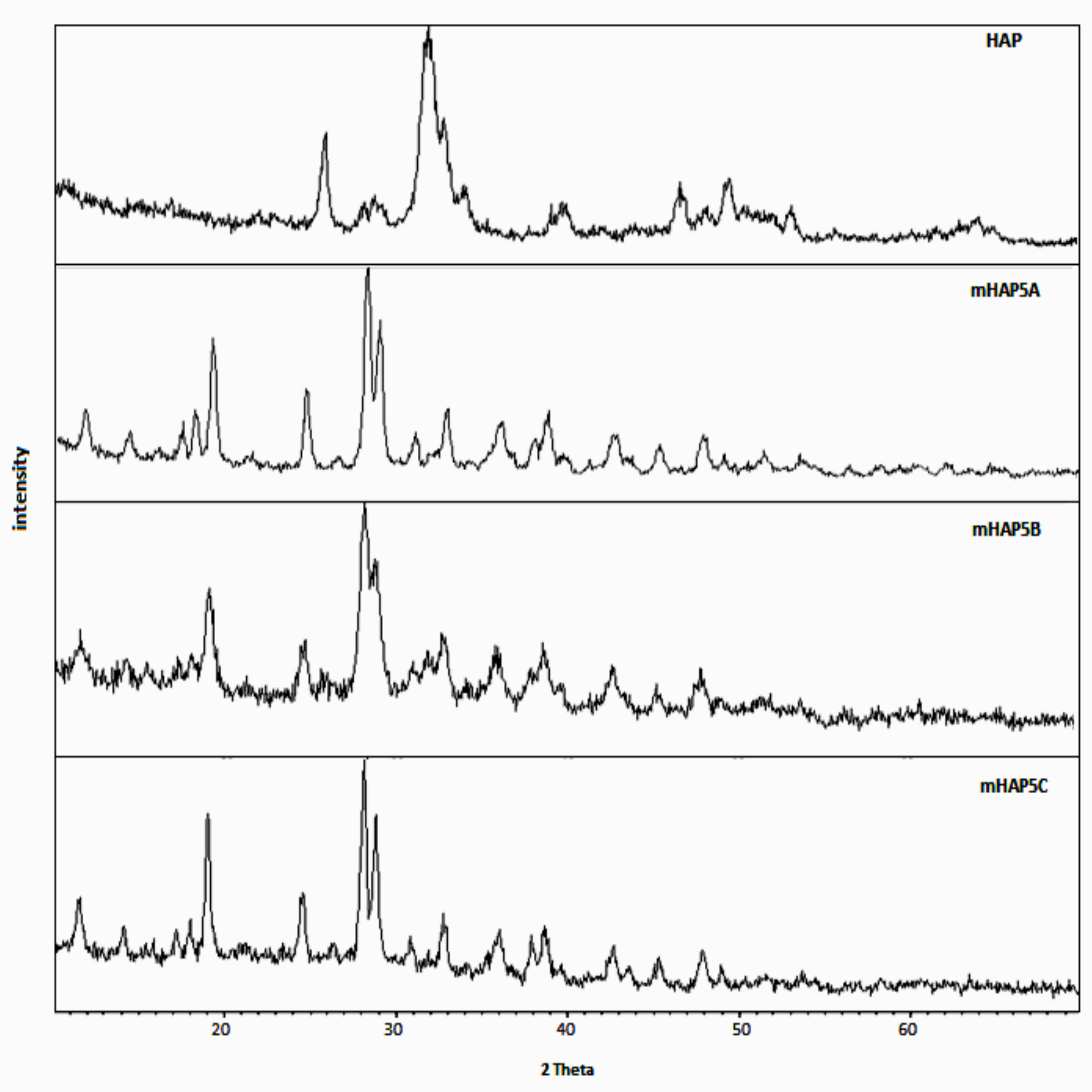


Figure 6.6 XRD patterns of HAP and HAP modified with 0.50 M HEDP at 80 ^{o}C for 168 h (mHAP5A), 4 h (mHAP5B) and 720 h (mHAP5C).

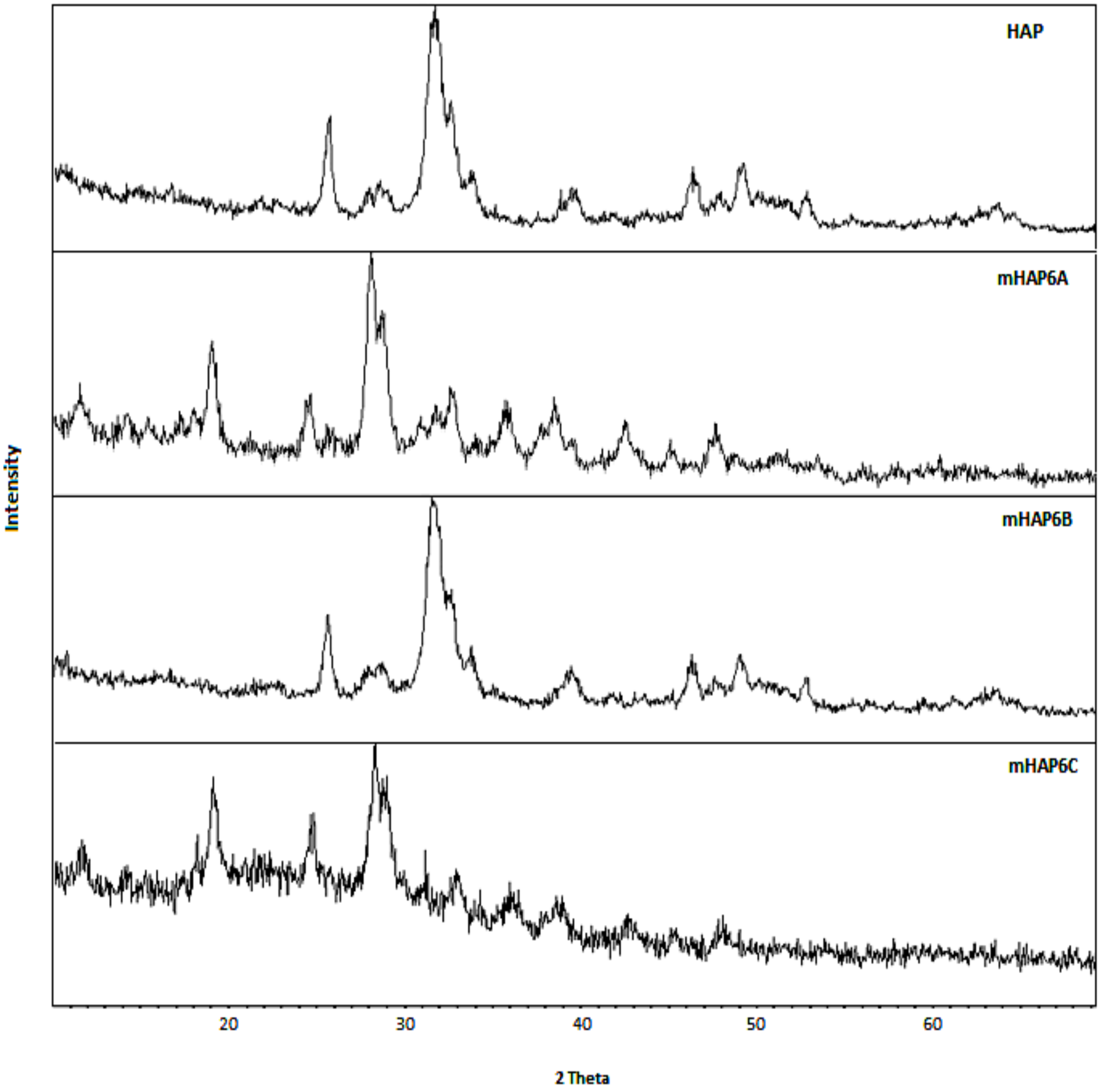


Figure 6.7 XRD patterns of HAP and HAP modified with 0.50 M HEDP at 20 °C, for 168 h (mHAP6A), 4 h (mHAP6B) and 720 h (mHAP6C).

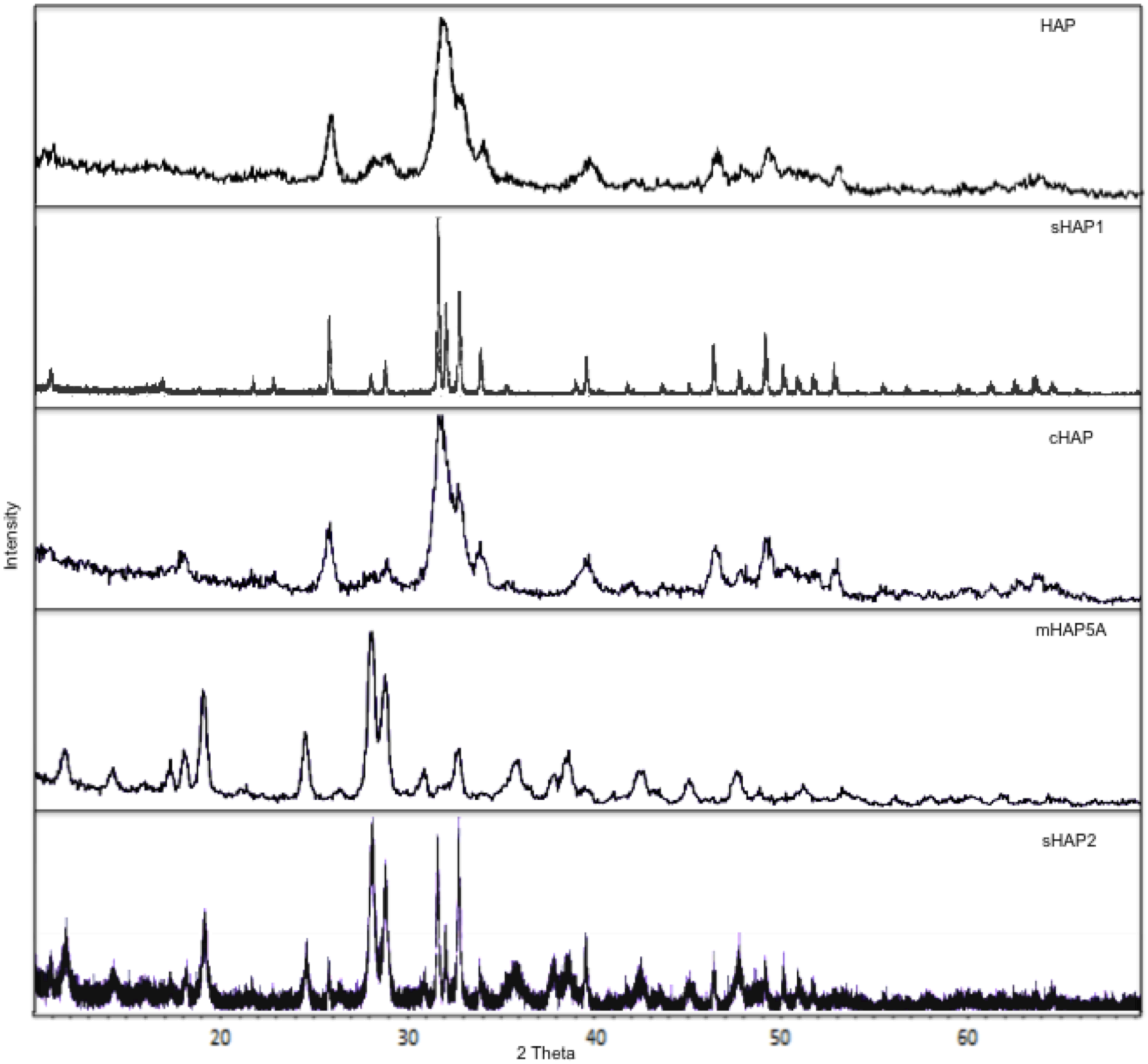


Figure 6.8 XRD of HAP, stoichiometric HAP (sHAP1), HAP contacted in dH_2O for 168 h at 80 ^oC (cHAP), HAP modified with 0.5 M HEDP for 168 h at 80 ^oC (mHAP5A) and stoichiometric HAP modified with 0.5 M HEDP for 168 h at 80 ^oC (sHAP2).

6.3.3 SEM

SEM results were consistent with the FT-IR spectra and the XRD patterns but revealed the appearance of new strands in modified samples. All three analyses supported the notion of an increasing salt transformation resulting from the higher temperature and longer reaction time. The strands were very pronounced and most homogenously distributed for the mHAP5A and mHAP5B samples, both modified at 80°C (Figure 6.9).

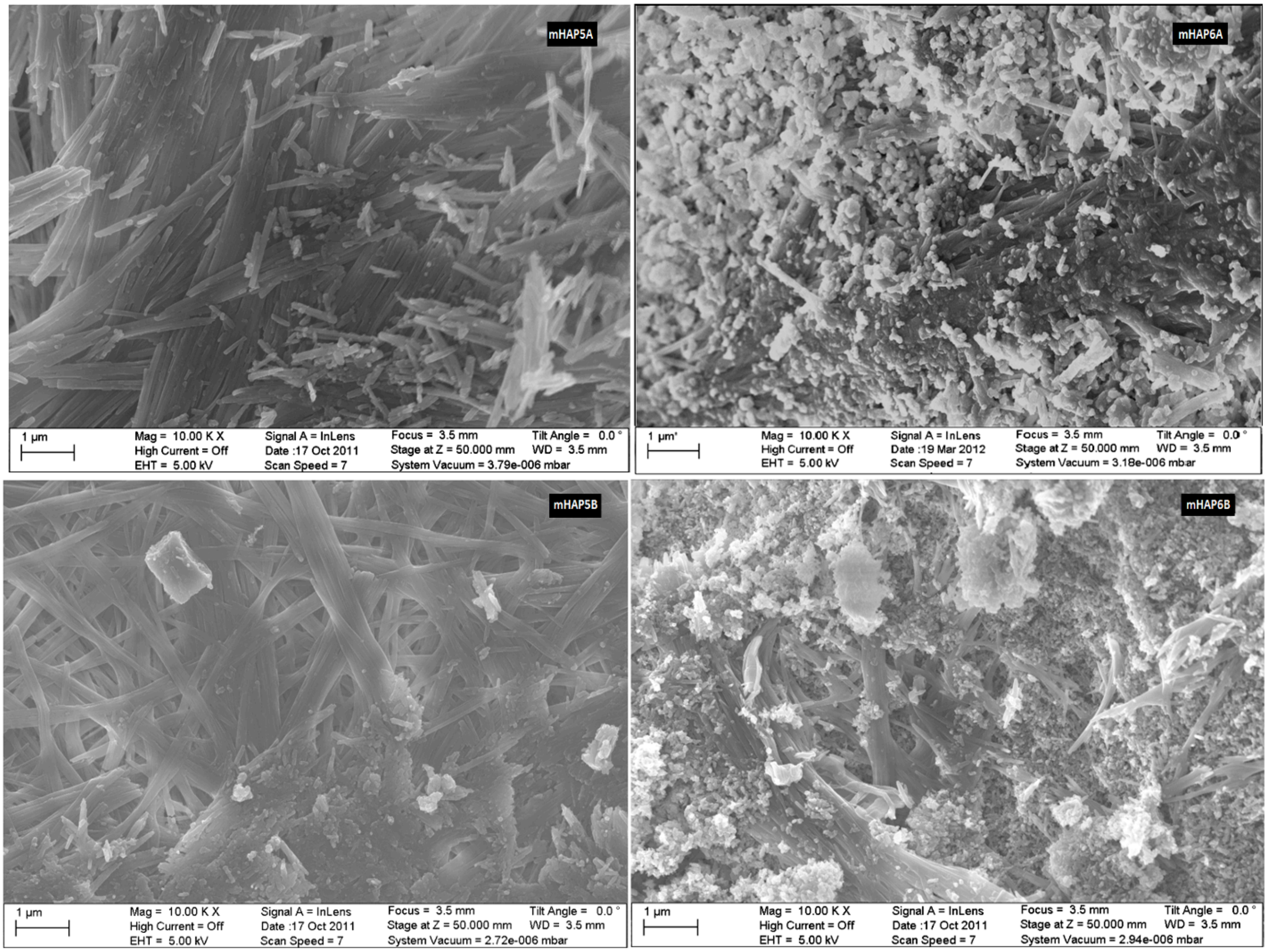


Figure 6.9 SEM of HAP modified with 0.5 M HEDP at 80 °C, for 168 h (mHAP5A), 4 h (mHAP5B) and at 20 °C for 168 h (mHAP6A) and 4 h (mHAP6B).

At low temperature, the SEM revealed a micro-bead structure consistent with the SEM of HAP.[283] There was also a trace appearance of strands within both low temperature samples (mHAP6A and mHAP6B) suggesting that the incorporation of the new modified phase may be present in low amounts.

The new phase is confirmed by XRDs and FT-IR spectra for all modified samples except mHAP6B which appeared to be chemically identical to unmodified HAP. SEM images however reveal the presence of the new phase within this sample.

6.3.4 Specific surface area (SSA)

Samples modified at high temperature (mHAP5A-B) had a low SSA compared to both the untreated HAP and the samples modified at low temperature (mHAP6A-B) (Table 6.2). The disappearance of micro-bead structures in the SEMs of high temperature mHAP samples and an emergence of continuous strands may account for the SSA decrease.

Table 6.2 Specific surface areas for HAP and mHAP

Type of HAP	**SSA (m^2/g)**
HAP	61.9
mHAP5A	56.8
mHAP5B	57.9
mHAP6A	74.6
mHAP6B	74.6

6.3.5 Effect of pH

6.3.5.1 Acid capacity

The acid capacities of HAP, mHAP and cHAP listed in Table 6.3 indicate that temperature, reaction time and the presence of HEDP, affect modification efficiency. The higher the reaction temperature (mHAP5A and mHAP5B), the higher the acid capacity. Similarly, longer reactions (mHAP5A and mHAP6A) had a higher acid capacity compared to samples modified for shorter reaction times (mHAP5B and mHAP6B). In the absence of HEDP, the control HAP sample (cHAP) contacting water for 168 h at 80 °C showed no difference in its acid capacity compared to the unmodified HAP. This suggests a correlation between HEDP modification and acid capacity.

Table 6.3 Acid capacities of HAP and mHAP

Type of HAP	**Acid capacity** (mequiv/g)
HAP	0.98
cHAP	0.99
mHAP5A	3.89
mHAP5B	3.14
mHAP6A	3.62
mHAP6B	1.55

Acid capacities can be used to predict the potential of HAP surfaces to react with HEDP. Acid sites on HAP can bind to HEDP in a 1:1 or 2:1 ratio. This is show in Figure 6.10.

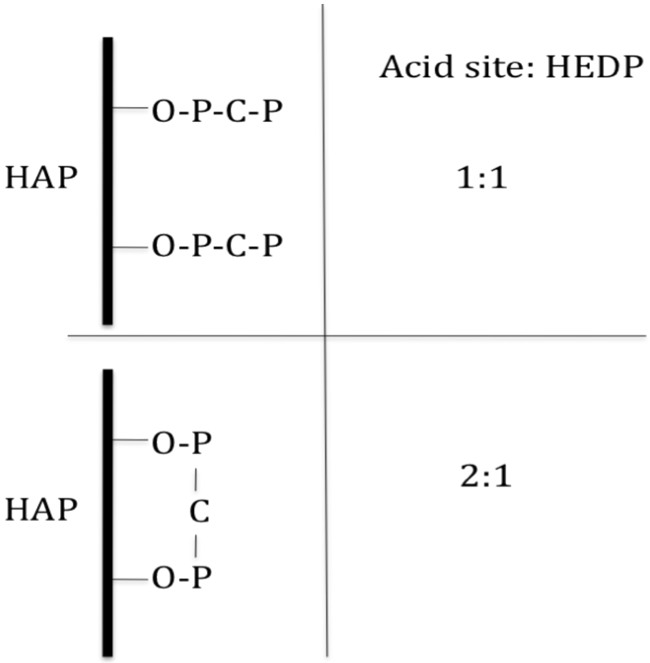


Figure 6.10 Theoretical HEDP-HAP surface reaction

Structures bound by the 1:1 ratio will theoretically have three times the number of available acid sites as unmodified HAP. These acid sites come from unbound POH groups in HEDP. The theoretical acid capacity of this new structure will therefore be 2.94 mequiv/g (0.98 mequiv/g times 3).

A 2:1 ratio is also possible when two acid sites bind to one HEDP ligand producing fewer bound ligands (Figure 6.10). For this ratio each P on HEDP loses one acid site after binding at one HAP acid site. The new acid capacity will therefore be the same as the unmodified HAP (0.98 mequiv/g). For acid capacities between 0.98 mequiv/g and 2.94 mequiv/g, modification of HAP is predicted to occur on the surface, however for acid capacities greater than 2.94 mequiv/g an additional modification mechanism is suggested since this exceeds the maximum surface capacity.

When modification assumes a 1:1 ratio, the 0.98 mequiv/g acid capacity in HAP suggests that the amount of HEDP able to bind the surface of HAP is 0.98 mmoles/g. For the 2:1 ratio, only 0.46 mmole/g of HEDP will bind. This means that the wt % of HEDP in mHAP can be between 10.1 % (0.46 mmole/g) for the 2:1 ratio and 20.2 % (0.98 mmole/g) for the 1:1 ratio where the maximum amount of HEDP that can modify the entire surface of HAP is 20.2 wt %. If the wt % of HEDP in mHAP exceeds 20.2 % this would suggest something more than a surface modification.

6.3.5.2 Solubility and salt stability

When HAP and mHAP5A were placed in 0.1 N KNO_3 solutions, the effect of pH on salt stability was observed. mHAP5A was chosen to represent HAP having the most homogeneous modification compared to the untreated HAP. These experiments showed that the chemical reactivity of the salts was also very different.

At pH 2, both HAP and mHAP5A samples dissolved and released high levels of calcium (1.6 mmol- 2.1 mmol) per gram of sample (Figures 6.11 and 6.12). This was the highest amount of Ca^{2+} released for all pH and time conditions studied in both salts. Both salts released similarly lower amounts of Ca^{2+} at pH 4 which remained low at pH 6.

When the salts were placed in solutions at pH 8, they behaved differently from one another. HAP, which has been shown to remain stable at high pH,[162] released low amounts of calcium at pH 8, as expected. This result is similar to trends shown in Figure 3.2 from Chapter 3 which confirms the 1.5 Ca/P ratio of our HAP, since its dissolution is similar to TCP. At the same pH, mHAP5A released almost as much Ca^{2+} as it did at pH 2. This can be explained by two possible mechanisms, both of which result from excess the KOH added to raise the pH.

In the first mechanism, high concentrations of K^+ force ion exchange interactions with Ca^{2+} to occur, causing Ca^{2+} to be dissociated into solution. Although the complexation constant for potassium-HEDP complexes is significantly lower (log K=1.8)[280] than for the calcium-HEDP complex (log K=6.4)[280], these values only represent equilibrium measurements that assume equal concentrations of both ions (K^+ and Ca^{2+}). At very high concentrations of K^+ relative to concentrations of Ca^{2+} however, the potassium-HEDP complex will form more favorably and cause Ca^{2+} to be released into solution.

For the second mechanism high concentrations of –OH destabilize mHAP and Ca^{2+} is eluted from the HEDP ligand into solution. This suggests that mHAP5A is chemically different from HAP and that a unique calcium-HEDP complex for the mHAP5A salt may be forming.

Both mechanisms may be used to explain the increased Ca^{2+} concentration for the solution contacting mHAP5A at pH 8.

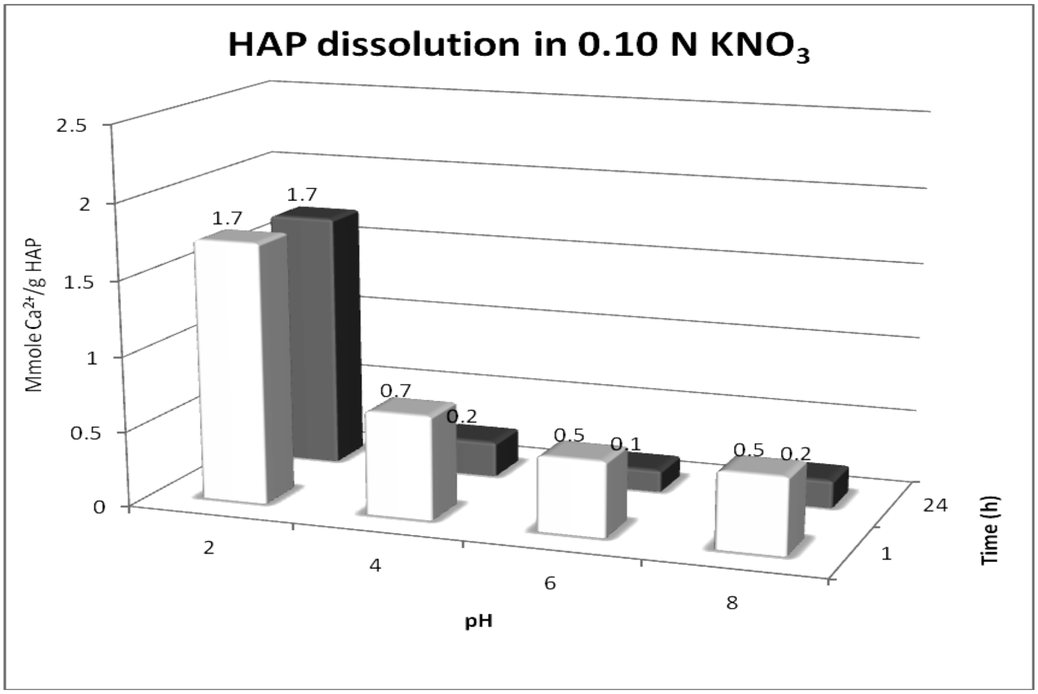


Figure 6.11 Calcium release for HAP in solutions of KNO_3 at pH 2, 4, 6 and 8

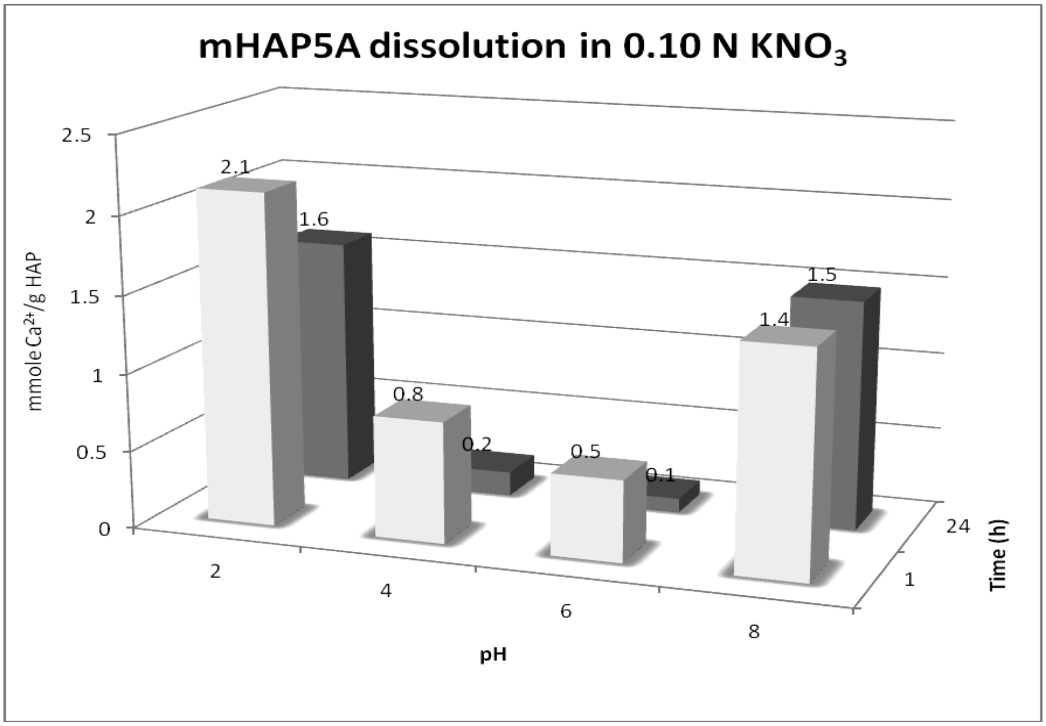


Figure 6.12 Calcium release for mHAP5A in solutions of KNO_3 at pH 2, 4, 6 and 8

6.3.6 Phosphorus analysis

6.3.6.1 Phosphorus elemental

The phosphorus capacity was measured using a 0.10 N HCl solution as well as a concentrated H_2SO_4. The weaker HCl digested only inorganic phosphates while concentrated H_2SO_4 digested both the inorganic and organic phosphates. This allowed for a calculation of % organic phosphate.

As reaction time increased the amount of organic phosphate relative to inorganic phosphate increased for mHAP5A and mHAP6A (Table 6.4). Short reactions (mHAP5B and mHAP6B) had more inorganic phosphate compared to longer reactions. The increase in % P_{org} was found to be time dependent and less influenced by temperature since similar trends were seen at high temperature for mHAP5A and mHAP5B (high vs. low % P_{org}) and low temperature for mHAP6A and mHAP6B (high vs. low % P_{org}).

Table 6.4 Phosphorus elemental analysis of HAP and mHAP

HAP	**P$_T$** (mequiv/g)	**P$_{inorg}$** (mequiv/g)	**P$_{org}$** (%)
HAP	5.23	5.21	0.3
mHAP5A	5.97	0	100
mHAP5B	5.63	2.47	56.8
mHAP6A	5.34	0.28	94.8
mHAP6B	5.26	4.70	10.6

The % P$_{org}$ calculated in Table 6.4 describes the amount of organic P relative to the total P in each sample. It does not reflect the wt % of P relative to all other atoms in the compound. Table 6.5 shows the wt % of P$_{org}$ and the wt % of HEDP for mHAP5A, mHAP5B, mHAP6A and mHAP6B in mHAP samples. These calculations are consistent with FT-IR spectra (Figures 6.3 and 6.4) which reveal new bands for mHAP5A, mHAP5B and mHAP6A only, but not for mHAP6B. A 5.7 wt % of HEDP is at the detection limit of the FT-IR.

Table 6.5 Phosphorus wt % in mHAP

HAP	**P$_{org}$** (mequiv/g)	**P$_{org}$ in mHAP** (g/g)	**P$_{org}$ in mHAP** (% wt)	**HEDP in mHAP** (% wt)
mHAP5A	5.97	0.185	18.5	61.4
mHAP5B	3.16	0.098	9.8	32.6
mHAP6A	5.06	0.157	15.7	52.1
mHAP6B	0.56	0.017	1.7	5.7

P-elemental results suggest that for samples mHAP5A, mHAP5B and mHAP6A the modification mechanism is more than a surface phenomenon. This is consistent with acid capacity results where acid capacities for mHAP5A, mHAP5B and mHAP6A are greater than the maximum allowable capacity following surface modification (2.94 mequiv/g). Acid capacity results also predicted that for an HEDP wt % greater than 20.2 %, modification occured beyond the surface. This is seen in samples mHAP5A, mHAP5B and mHAP6A but not with mHAP6B since there is so much HEDP present (Table 6.5). The 100 % P_{org} is therefore possible for HAP modified in the bulk phase and 10.6 % P_{org} is reasonable for surface modified HAP.

Acid capacity results can be used to predict phosphorus capacities of functional ligands. In HEDP, there are two acid sites for every P atom. The highest acid capacity measured among mHAP samples was for mHAP5A which gives a theoretical P-capacity of 1.95 mequiv/g (3.89 mequiv/g divided by 2). The experimental P-capacity however is 5.97 mequiv/g which means that there are more P atoms than there are acid sites. Theoretically, there should be 11.94 mequiv/g acid sites based on the measure P-capacity.

This suggests a polymerization amongst phosphonate ligands, forming a P-C-P-O-P-C-P network where the number of P atoms no longer corresponds to the number of acid sites. The mHAP6B sample was the only sample to have a theoretical P-capacity (0.78 mequiv/g) based on its acid capacity, that was close to its experimental P-capacity (0.56 mequiv/g). Comparisons between theoretical and experimental calculations for other mHAP samples are challenging since modification was predicted to occur within the bulk phase. It is therefore unclear whether surface acid capacities are contributed by inorganic or organic P.

6.3.6.2 ^{31}P-NMR

^{31}P-NMR spectra were obtained for mHAP, mHAP6B, mHAP5B, mHAP6A and mHAP5A (Figure 6.13). A peak at 3 ppm represented the inorganic P from HAP. As reaction time and modification temperature increased, this peak decreased and a new peak at 19 ppm emerged. The new peak resulted from the HEDP. The sample modified for 4 h at 20 °C (mHAP6B) had a ^{31}P-NMR that was almost identical to unmodified HAP indicating little to no HEDP present. The sample modified for the longest time (168 h) and at the highest temperature (80 °C), (mHAP5A), only had a peak corresponding to HEDP. All other sample appeared to have mixed phases. These results were consistent with P elemental results.

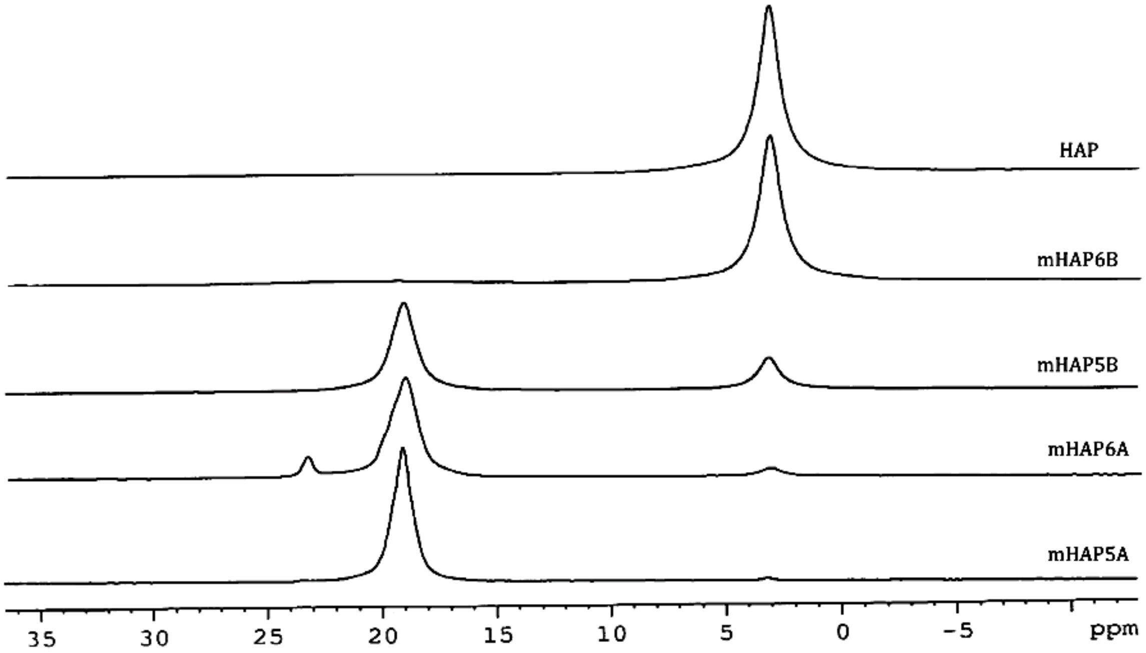


Figure 6.13 ^{31}P-NMR of unmodified HAP, HAP modified with 0.5 M HEDP at 20 °C for 4 h (mHAP6B), 80 °C for 4 h (mHAP5B), 20 °C for 168 h (mHAP6A) and 80 °C for 168 h (mHAP5A).

6.3.7 mHAP thermogravimetric analysis

HAP and mHAP samples were heated to 1000 ^oC in order to determine the mass (%) loss resulting from the incorporated HEDP. Thermogravimetric peaks appeared between 400 ^oC and 700 ^oC. The unmodified HAP and mHAP6B (4 h / 20 ^oC) samples had a mass loss of 5.6 % and 5.8 %, respectively (table 6.6). When the reaction time was increased (168 h/ 20 ^oC), for sample mHAP6A, the mass loss increased to 20.7 %, however when the temperature increased (4 h / 80 ^oC) for sample mHAP5B, the mass loss only increased to 12.3 %. This suggests that the longer reaction time allows more HEDP incorporation into the HAP compared to the increased temperature. This is consistent with the P-elemental results, where mHAP6A had 52.1 % HEDP compared to mHAP5B which had 32.6 % HEDP. The mHAP5A sample modified for 168 h / 80 ^oC however, had a mass loss of 14.8 % which is not consistent with P-elemental results (table 6.6).

Table 6.6 Thermogravimetric analysis for HAP and mHAP

Type of HAP	TGA weight loss (%)
HAP	5.6
mHAP5A	14.8
mHAP5B	12.3
mHAP6A	20.7
mHAP6B	5.8

6.3.8 Comparing mHAP to other HEDP salts

The mHAP5A sample appeared to have a unique chemical identity compared to all other mHAP samples prepared and the highest amount of HEDP. In order to better characterize this salt, similar HEDP salts were synthesized using different methods.

HAP was previously modified by a co-precipitation reaction where HEDP was combined with the calcium and phosphate precursors to produce pre-functionalized HAP-HEDP. Specific details regarding this modification procedure can be found in Appendix B. The precipitated HAP-HEDP salts were dried at 60 ^{o}C and at 400 ^{o}C. FT-IR spectra for both samples (Figure B.18) resembled unmodified HAP. The sample dried at 400 ^{o}C had a smaller –OH band due to greater water loss. These spectra showed that mHAP5A is uniquely different from pre-functionalized HAP-HEDP. Furthermore, copper(II) sorption experiments for the pre-functionalized salts revealed that high temperature drying of HEDP-modified HAP significantly reduceed its sorption capacity (Figure B.19). This was because the organophosphate decomposed at high temperature and suggests that synthesis of mHAP that is both thermodynamically stable and organically modified, is best obtained by a post-functionalization method.

6.3.8.1 mHAP and calcium-HEDP

Calcium-HEDP salts were synthesized using a similar method to the one used to make mHAP5A. FT-IR spectra in Figure 6.14 revealed that the Ca-HEDP salt was very different from mHAP5A and more closely resembled the unmodified HAP. Phosphate bands contributed by the HEDP appeared at 944 cm^{-1} for Ca-HEDP, mHAP5A and the HEDP. Comparable bands were also seen at 880 cm^{-1} and 826 cm^{-1}.

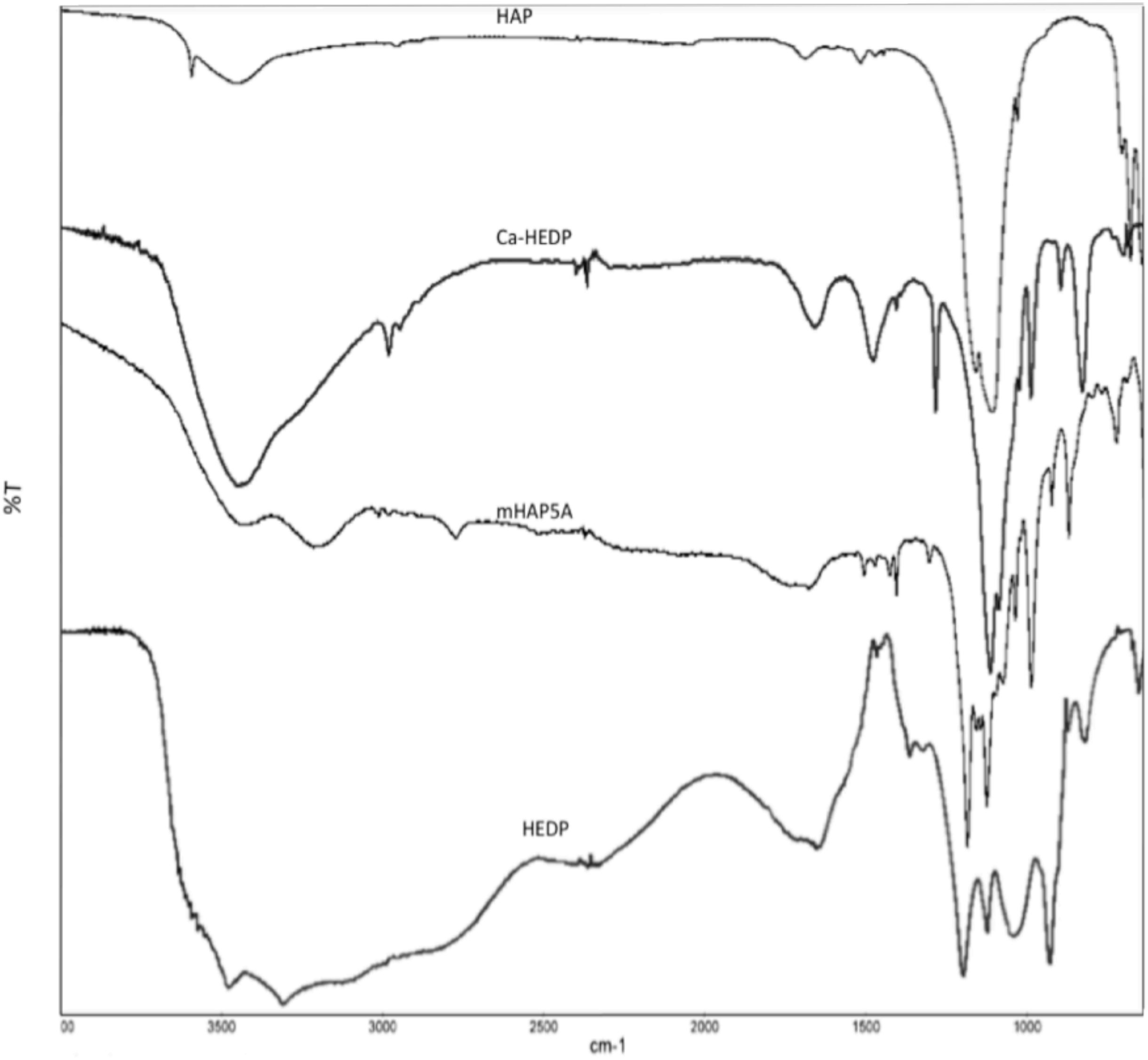


Figure 6.14 FT-IR of HAP, a calcium salt of HEDP (Ca-HEDP), HAP modified with 0.5 M HEDP for 168 h at 80 °C (mHAP5A) and HEDP alone.

In a similar study, Ca-HEDP salts with different Ca/HEDP ratios were prepared.[284] XRD patterns reveal 4 distinct peaks at 7, 12, 16 and 17 degrees in the Ca-HEDP salt prepared with a 1:1 Ca/HEDP ratio. As the ratio of Ca to HEDP increased, the XRDs showed a more amorphous structure forming. A comparison between Figures 6.15 and 6.6 indicate the mHAP5A is not the same as a Ca-HEDP salt.

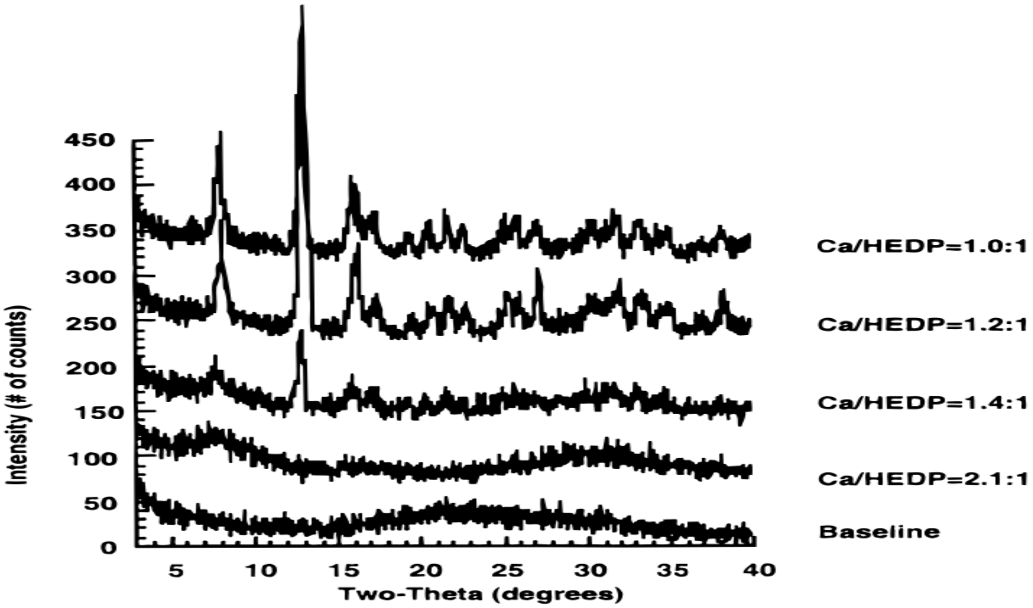


Figure 6.15 XRD of calcium-HEDP salts of different Ca/HEDP ratios.[284] Reprinted with permission from Browning, F.H.; Fogler, H.S. *Langmuir* **1996,** *12,* 5231-5238. Copyright 1996 American Chemical Societv.

6.3.9 EDS and ICP

EDS showed a decrease in the Ca/P ratio with increasing reaction time. Additionally, the Ca/P ratio decreased with increasing reaction temperature. Results from the ICP were consistent with EDS measurements. A decreased Ca/P ratio was associated with a higher P content corresponding to HEDP incorporation into the HAP (Table 6.7).

Table 6.7 Analysis of calcium to phosphorus ratio

Sample	**Ca/P ratio (EDS)**	**Ca/P ratio (ICP)**
HAP-700	1.51	1.52
mHAP5A	0.50	0.55
mHAP5B	0.56	0.58
mHAP6A	0.54	0.59
mHAP6B	1.45	1.21

6.3.10 Metal ion studies

Samples modified for 4 h at 20 ^{o}C (mHAP6B), 4 h at 80 ^{o}C (mHAP5B), 168 h at 20 ^{o}C (mHAP6A) and 168 h at 80 ^{o}C (mHAP5A) were individually contacted in lead (II) nitrate solutions to determine their sorption capacities. The sorption of Pb^{2+} for mHAP6B was the highest among all samples and Pb^{2+} sorption decreased for the mHAP5B and mHAP6A samples. At the 168 h at 80 ^{o}C condition however, Pb^{2+} sorption increased (Figure 6.16) suggesting that there may be a similarity between the mHAP6B and mHAP5A mechanism of Pb^{2+} sorption. Metal ion sorption studies for mHAP6B and mHAP5A were therefore carried out using four new divalent metals (Cu^{2+}, Ni^{2+}, Zn^{2+} and Cd^{2+}) to determine whether they showed similar behaviors (Figure 6.17).

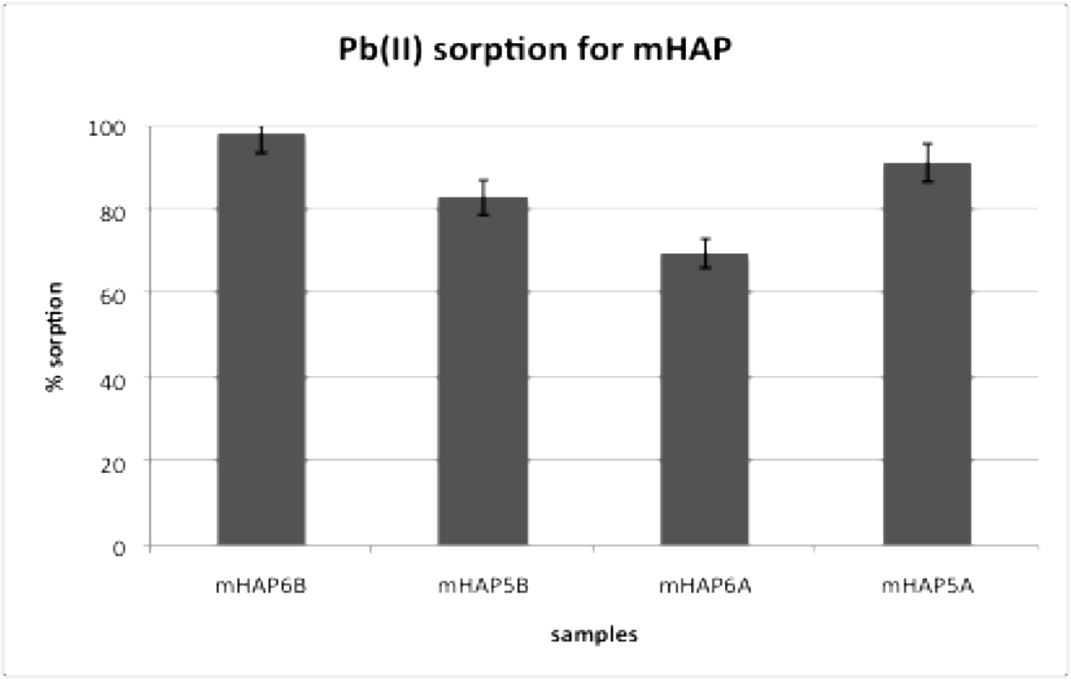


Figure 6.16 Pb(II) ion sorption for HAP modified with 0.5 M HEDP for 4 h at 20 ^{o}C (mHAP6B), 4 h at 80 ^{o}C (mHAP5B), 168 h at 20 ^{o}C (mHAP6A) and 168 h at 80 ^{o}C (mHAP5A).

Unmodified HAP removed all metal ions from solution with high efficiency (>85%) (Figure 6.17) and showed no selectivity among metal ions. mHAP6B also had a high affinity for metal ions and showed no selectivity. mHAP5A however removed high levels of Cd^{2+} (82%) and Pb^{2+} (90%) from solution but less than 25% of all other metal ions studied. No Cu^{2+} was removed by mHAP5A and control samples containing the metal solutions only (not shown) had no loss of metal ion (<3%).

Results revealed that mHAP5A may have a unique selectivity towards Pb^{2+} and Cd^{2+}. Selectivity of mHAP5A was tested in a solution containing high concentrations of calcium (1 N), where the presence of calcium was expected to simulate a non-toxic, aqueous environment. Sorption for Pb^{2+} was still high (~89%), however Cd^{2+} decreased (16%). The unmodified HAP also showed a decreased metal ion sorption in high calcium conditions but only for Ni^{2+}, Zn^{2+}, and Cd^{2+}. It still however remained relatively unselective.

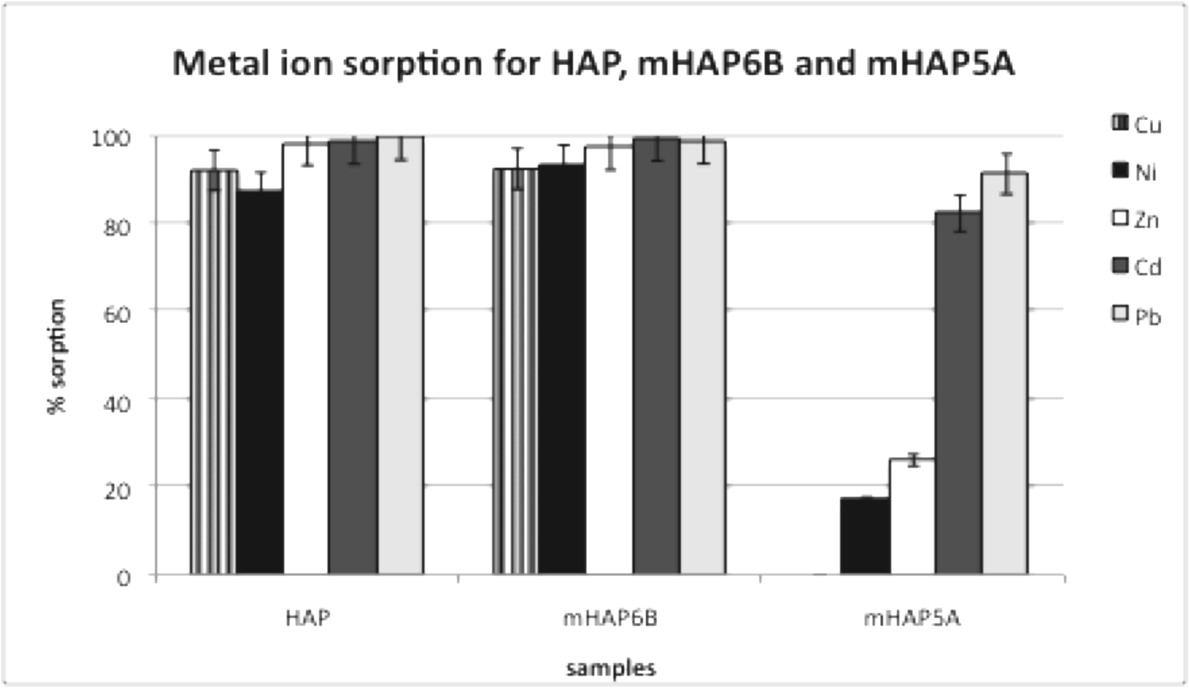


Figure 6.17 Metal ion sorption for HAP, mHAP6B and mHAP5A in nitrate solutions of Cu(II), Ni(II), Zn(II), Cd(II) and Pb(II)

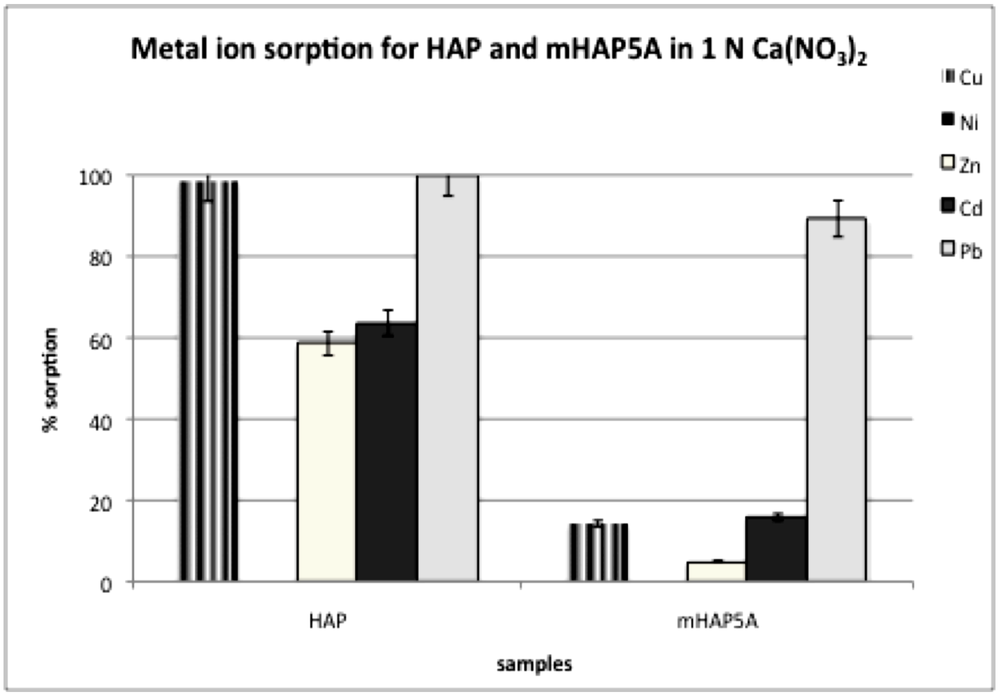


Figure 6.18 Metal ion sorption for HAP and mHAP5A in nitrate solutions of Cu(II), Ni(II), Zn(II), Cd(II) and Pb(II) made using 1 N $Ca(NO_3)_2$

6.4 Discussion

6.4.1 Reaction time and temperature

This study investigated the modification of HAP with HEDP influenced by three distinct variables: HEDP concentration, reaction time and reaction temperature. As HEDP concentration increased, the appearance of new phosphate bands emerged in FT-IR spectra. A high reaction temperature produced new, distinct phosphate bands (994 cm^{-1}, 1083 cm^{-1}, 1144 cm^{-1}) indicating the presence of HEDP. This was seen in all high temperature modifications for short and long reaction times (Figure 6.3) and also in low temperature samples only for the long reaction (Figure 6.4). FT-IR spectra of all high temperature reactions were identical to one another however, the same pattern was not observed for low temperature samples. The short reaction sample at low temperature (HAP6B) had no change in its FT-IR spectrum relative to untreated HAP however, SEM images revealed HAP-HEDP strands still present in that sample. The amount of HEDP incorporated may be too low (<5.7 wt %) to be detected in the FT-IR.

6.4.2 Instrumental and elemental analyses

P elemental results also confirmed the presence of HEDP in mHAP6B, however analysis by ^{31}P-NMR showed a similar result to the FT-IR, where the spectrum of mHAP6B was the same as unmodified HAP. The disappearance of the free –OH band (3572 cm^{-1}) in FT-IR spectra, initially present in unmodified HAP, and the emergence of a 3204cm^{-1} intermolecular H-bond stretch in modified samples suggests that –OH groups in HAP may be reacting with HEDP to produce a modified HAP.

SEM images revealed a clear distinction between HAP micro-beads and HEDP modified strands. These HAP-HEDP strands had a higher phosphorus content (low Ca/P ratio) than samples containing more micro-beads, based on EDS analysis. Additionally, the acid capacities of samples mHAP5B, mHAP6A and mHAP5A were significantly higher than unmodified HAP indicating the incorporation of HEDP. Acid capacity results also showed that the mechanism of modification for these samples may be occurring within the bulk phase. These results were complimented by SSA data which showed a lower SSA for samples with more HEDP-HAP strands (mHAP5A and mHAP5B) and higher a SSA for samples with more micro-beads (mHAP6A and mHAP6B).

New diffraction patterns and sharp XRD peaks indicate an increase in the crystallinity of the salt upon modification for the long reaction time at high temperature. It also suggests the presence of a new phase for the modified salt. Samples modified under the other conditions did not have the same extent of crystallinity. Both XRD and FT-IR data confirmed that mHAP5A, containing only the organic phosphonate, was similar to modified stoichiometric HAP (sHAP2) but chemically different from HAP modified with HEDP by pre-functionalization and calcium-HEDP salts prepared from soluble calcium.

Modified HAP behaved chemically different from unmodified HAP during pH equilibration and metal ion sorption studies. At pH 8, mHAP5A released high levels of Ca^{2+} compared to HAP, indicating that the salt was unstable at high pH. mHAP5A also selectively removed Cd^{2+} and Pb^{2+} from nitrate solutions with an overall high efficiency compared to sorption of other divalent metal ions studied. The mHAP6B sample did not show selectivity among metal ions. In concentrated calcium solutions, mHAP5A retained its selectivity for Pb^{2+} but its affinity for Cd^{2+} decreased.

6.5 Conclusion

Modification of HAP with 0.5 M HEDP produced a new compound with properties that were different from the initial HAP. The degree of transformation of HAP to the newly crystalline mHAP depended on the three conditions (concentration, time and temperature) used during modification. XRD and phosphorus elemental results suggest a new phase being formed for samples containing more HEDP. The implications of a new phase are confirmed by ^{31}P-NMR data. mHAP with the highest amount of HEDP had greater metal ion selectivity compared to the selectivity of mHAP with lower levels of HEDP and the unmodified HAP.

The newly synthesized HEDP salt (mHAP5A) is significantly different from pre-functionalized HAP-HEDP therefore this method is a good way to prepare the highly selective organic-inorganic polymer. Hybrid organic-inorganic HAP polymers have been converted back to pure phase HAP in previous studies by high temperature calcination, therefore following metal ion sorption, the HEDP can be decomposed, leaving the heavy metal immobilized within the HAP. High calcination temperatures also prevent the toxic metals from leaching out of the HAP and allow HAP to be used in other environmental applications.

CHAPTER 7. The future of mHAP

7.1 Current findings

This dissertation discusses specific experimental conditions which can be used to control the amount of HEDP incorporated into the inorganic polymer HAP. Experiments show that HEDP incorporation can occur on the surface as well as in the bulk phase. Bulk phase incorporation can be further classified as a partial bulk phase modification; where a fraction of the inorganic phosphates are replaced by organic phosphates, or a full bulk phase modification where all of the inorganic phosphates are replaced with organic phosphates. This is shown in Chapter 6, where HAP is modified with the organophosphate HEDP and the extent of modification is influenced by HEDP concentration, modification temperature and modification time.

A phosphorus elemental analysis was developed to distinguish the organic from inorganic phosphorus in hybrid mHAP polymers (Chapter 5) and used to quantify the extent of HAP modification with HEDP. The higher the organic phosphorus capacity, the more HEDP incorporated into HAP. There was a significant increase in the amount of HEDP measured in the mHAP5A sample (61.4 % wt.) prepared at high temperature and long reaction time (80 ^{o}C / 168 h) compared to the HEDP found in the mHAP6B sample (5.7 % wt.) prepared at low temperature and for the short reaction time (20 ^{o}C / 4 h). Two additional samples (mHAP6A and mHAP5B) were prepared using a low temperature / long time condition (20 ^{o}C / 168 h) and a high temperature / short time condition (80 ^{o}C / 4 h), respectively. HEDP levels for these two samples were 52.1 % and 32.6 % respectively and the higher amount of HEDP appeared to result from the long reaction time. Results from these P-elementals were compared to instrumental analyses in order to determine whether there were any correlations. The instruments used for these analyses were FT-IR, XRD, SEM, BET, ^{31}P-NMR, TGA and ICP-OES. Additional elemental analyses consisted of solution-based experiments involving acid digestions and metal ion solutions.

FT-IR studies revealed distinct, new bands in mHAP samples containing high amounts of HEDP, which resulted from the HEDP presence. XRD patterns of mHAP samples with higher amounts of HEDP were different and more crystalline than unmodified HAP and HAP containing low amounts of HEDP. This suggested the presence of a new phase forming as a result of the modification reaction. SEM, BET and ^{31}P-NMR showed similar results to the FT-IR, where higher amounts of HEDP revealed new phase characteristics of the mHAP salts. For HAP samples with higher amounts of HEDP, the SEM images revealed rod-like strands. BET analyses showed a temperature-dependant SSA change, where samples modified at the low temperature had a high SSA and those modified at the high temperature had a low SSA. The new phase was confirmed by ^{31}P-NMR data which showed the gradual disappearance of the inorganic phosphate peak and the emergence of the organic phosphate peak contributed by the HEDP.

Results suggest that a new compound was formed after HAP was fully modified with HEDP. This compound was chemically different from the unmodified HAP, the HEDP and the salts of HEDP prepared from $Ca(OH)_2$ and HEDP. The new compound, although not yet identified, is proposed to be an organic salt containing Ca^{2+}, HAP and HEDP species. Several phosphate peaks have been identified by FT-IR, XRD and ^{31}P-NMR within this compound however the exact compound has not yet been determined. The identification of unknown crystals by powder diffraction can be difficult particularly when there is no evidence of it ever existing previously. Minor similarities observed between known compounds and unknowns do not always confirm their identity, but can simply suggest the possibility of some unexplained relationship or coincidence.

7.2 Future work

This work has not only initiated a new research direction into inorganic polymers within the group but has also established a collaboration with Ecole des Mines and Université de Toulouse in France. There is a great deal of work that remains however, which will continue in an attempt to increase the metal ion selectivity of HAP using the HEDP modifier. The following additional experiments are therefore suggested.

Experiments can be divided into two phases; HAP modification and metal ion sorption. A mechanism for the modification of HAP using HEDP can be explored by taking a closer look at modification conditions which include concentration, temperature and time. All of the initial HEDP concentrations used for modification Chapter 6 (0.01 M – 0.5 M) should be reexamined under all time and temperature conditions. Previously, only the 0.5 M HEDP concentration was studied in depth. Additionally, modification temperatures should include smaller increments of 10 ^{o}C to account for occurrences taking place in between 20 ^{o}C and 80 ^{o}C. This will help to determine the temperature at which inorganic phosphates in mHAP become fully organic. Similarly, modification times should include smaller increments (every 4 h) to detect when small changes are occurring with the salt as well.

High temperature and long reaction time both have an effect on HEDP incorporation, and the combined effect appears to be most pronounced. At high modification temperature and for long modification times, surface modification is exceeded and HEDP is believed to penetrate the HAP crystal. This produces an insoluble calcium-HAP-HEDP salt, which is chemically different from the $Ca(OH)_2$ derived HEDP salt. One experiment which has been suggested to determine the stability of this salt, is to suspend the salt in de-ionized water and measure the amount of calcium, phosphorus or HEDP released. DSC-TGA analyses can also be used to determine the % mass loss of each mHAP sample prepared and at what decomposition temperature this occurs.

A series of control experiments should be carried out to determine whether the diphosphonic acid is capable of modifying another inorganic polymer (i.e. silica or alumina). This will allow comparisons to be made between the mHAP and the inorganic polymer + HEDP. Controls may also aid in defining the surface vs. bulk phase mechanism of modification. ^{31}P-NMR data should be compared to ^{13}C-NMR and ^{1}H-NMR data in order to develop structural information about the newly formed mHAP.

In the second phase of experiments, metal ion sorption studies will not only determine the sorption capacity of mHAP but possibly help to explain the modification mechanism. Kinetic and Langmuir isotherms should be obtained to determine the precise amount of each metal ion removed per gram HAP or mHAP. Calculations can then be made to determine how the amount of HEDP incorporated corresponds to the amount of metal ion uptake. Knowing the metal ion sorption capacity of each salt will be useful for enhancing selectivity and assessing its potential environmental application.

Following metal ion sorption, metal ion solutions should be measured for released calcium and phosphorus ions. The solid mHAP + metal should then be equilibrated in dH_2O and the metal ion, calcium and phosphorus concentrations of that dH_2O should be measured as well. Comparing the amount of metal removed from solution to any of the ions released from mHAP will help to determine a mechanism for metal ion sorption. It will also provide information about the stability of the bound metal ions and modifier.

Since HEDP is reported to have a high affinity for several metal ions, the mHAP is predicted to bind metal ions through the HEDP ligand. In order to test this theory, a mass spectrometry study is suggested for HEDP + metal ion mixtures to determine the different complexes that HEDP forms with metal ions. A pure sample of HEDP should be analyzed first in order to determine which peaks are unique to HEDP. Following this, the mixed samples of HEDP+M^{++} can analyzed and peaks should appear at the combined mass of the HEDP (~206 g/mole) and M^{++} (lead for example, MW ~207g/mole). This would give a 413 m/z peak.

The primary aim of this study was to develop an mHAP compound that would selectively remove metal ions from water and showed potential for safe environmental application. This goal has been successful in part; a unique mHAP salt was developed which was highly selective for lead. The identity of this salt however has yet to be determined. Although the polymer's mode of environmental applications has not yet been designed beads, cartridges, discs and columns are suggested.

Appendix A

Abbreviations

Abbreviation	**Meaning**
ACPC	4,4′-azobis(4-cyanopentanoic acid chloride)
ADP	Adenosine diphosphate
ADWD	Australian Drinking Water Guidelines
AES	Atomic emission spectroscopy
AIBN	Azobisisobutyronitrile
AMP	Adenosine mono phosphate
ATP	Adenosine triphosphate
ATR	Attenuated total reflectance
BET	Brenner Emmett Teller
BSF-S	biosand filter-standard
BSF-Z	biosand filter-zeolite
BTMOS	isobutyltrimethoxysilane
CCF	ceramic candle filter
CDW	Committee on Drinking Water

CP	cetylphosphate
CTMAB	cetyltrimethylammonium bromide
CTP	cytidine triphosphate
DA	dodecyl alcohol
DABA	3,5-diaminobenzoic acid
DECP	diethylchlorophosphate
dH_2O	De-ionized water
DP	monodecyl phosphate
DSC-TGA	Differential Scanning- Thermo Gravimetric Analysis
EDS	Energy Dispersive x-ray Spectroscopy
EDTA	Ethylenediaminetetraacetic acid
EGDMA	ethylene glycol dimethacrylate
EPA	Environmental Protection Agency
FAP	Fluoroapatite
FT-IR	Fourier Transform Infrared
GC-MS	Gas Chromatography- Mass Spectroscopy
GTP	Guanosine triphosphate

HACCP	Hazard Analysis and Critical Control Point
HAP	Hydroxyapatite
HEDP	1-hydroxyethane 1, 1-diphosphonic acid
HP	Monohexyl phosphate
HWTS	Household Water Treatment Systems
IC	Ion chromatography
ICP	Inductively Coupled Plasma
IE	Ion Exchange
IPN	interpenetrating polymer networks
LLA	L-lactide
MAA	methacrylic acid
MALDI MS	Matrix-assisted laser ionization Mass Spectroscopy
MDG	Millennium Development Goal
mHAP	Modified Hydroxyapatite
MTMOS	Methyltrimethoxysilane
NTA	nitriloacetic acid
OES	Optical emission spectroscopy

PAA	Polyallylamine
PCE	Power conversion efficiency
PCL	ε-caprolactone
PEG	Polyethylene glycol
PEI	Polyethyleneimine
P_{inorg}	Inorganic phosphorus capacity
PLGA	poly(D,L-lactide-co-glycolide)
PMMA	poly(methyl methacrylate
^{31}P-NMR	phosphorus nuclear magnetic resonance
P_{org}	Organic phosphorus capacity
PPA	Pyrophosphoric acid
P_T	Total phosphorus capacity
PTMOS	Phenyltrimethoxysilane
Ru-Tsd	Ruthenium (III)-thiosemicarbazide
SDBS	sodium dodecylbenzenesulfonate
SDWA	Safe Drinking Water Act
SEM	Scanning Electron Microscopy

SIPPS	Silver-impregnated porous pots
SPC	Silica polyamine composites
SSA	Specific Surface Area
TCP	tricalcium phosphate
THF	Tetrahydrofuran
THM	Trihalomethane
TMOS	Tetramethoxysilane
Tris	Tris(hydroxymethyl)aminomethane
TU	Thiourea
UNICEF	United Nations International Children's Emergency Fund
UTP	uridine triphosphate
VPA	Vinyl phosphonic acid
WHO	World Health Organization
XRD	X-ray Powder Diffraction

Appendix B

Alternative HAP modification

Preliminary experiments were conducted to determine which modifiers were best suited for HAP modification and the kind of HAP to be used. Pre-functionalization, where modifiers were added to the calcium and phosphate precursors during HAP synthesis, as well as post-functionalization, where modifiers contacted the precipitated HAP particles, were used.

Three kinds of HAP were used during these preliminary studies: HAP dried at 60 ^{o}C (HAP-60), HAP dried at 400 ^{o}C (HAP-400) and HAP dried at 700 ^{o}C (HAP-700). Pre-functionalized HAP was dried either at 60 ^{o}C or both at 60 and 400 ^{o}C. Post-functionalized HAP was dried before the modifier was added, at 400 ^{o}C or 700 ^{o}C. Following post-functionalization, drying occurred at RT. HAP-400 was initially taken to be thermodynamically stable however in subsequent post-functionalization experiments HAP-700 was used. The use of a thermo-dynamically stable form of HAP (HAP-700) is essential for obtaining reproducible results.

Six modifiers were used during preliminary experiments. These include L-alanine and ß-alanine (pre-functionalization), EDTA (pre-functionalization), phenylphosphonic acid (pre- and post-functionalization), HEDP (pre-functionalization) and alendronic acid (post-functionalization).

FT-IR spectra and N-elemental results of HAP+L-alanine showed significant incorporation of the alanine but this sample did not have a significant dye and uranium sorption over the unmodified HAP. HAP+EDTA revealed new FT-IR bands which were indicative of EDTA incorporation however no sorption studies were carried out on this sample. Pre-functionalized HAP+PPoA showed no new FT-IR bands however, post-functionalized HAP+PPoA revealed new bands. Successful modification using the post-functionalization method for phosphonic acid was therefore confirmed. Pre-functionalized HAP+HEDP removed 100% Cu(II) from solution, only for samples dried at 60 ^{o}C. Samples dried at 400 ^{o}C had low sorption. Preliminary experiments determined that HEDP was a suitable modifier for enhancing metal ion sorption since it was the only modifier found to remove 100% of the metal ions tested. The second post-functionalization study (HAP+alendronic acid) did not show new FT-IR bands compared to post-functionalized HAP+PPoA. Post-functionalization of HAP with HEDP was later attempted. Results are presented in chapter 6.

B.1. L-Alanine and ß-Alanine

A. Structure and Properties

L-alanine

ß -alanine

Molecular weight: 9.09g/mol
Molecular formula: $C_3H_7NO_2$

Figure B.1 Structures of L-alanine and ß –alanine

B. Pre- functionalization

- i. Add 7.762 g $Ca(OH)_2$ to 10 g of L-alanine or ß-alanine
- ii. Pour 280 ml dH_2O while stirring
- iii. Add 4 ml of 85% H_3PO_4 over 10 minutes (1 minute in between each)
- iv. Adjust pH to 8.2 with base
- v. Stir for 48 h
- vi. Decant
- vii. Dry for 24 h in a vacuum oven at 60 ^{o}C
- viii. Take FT-IR
- ix. Prepare HAP in the same manner without alanine as a control

C. Amaranth Red Dye and Uranyl nitrate sorption

- i. Measure 10 ml of uranyl nitrate (10^{-4} M) or amaranth dye (2.28ppm)
- ii. Add 0.01grams of HAP/mHAP in a plastic vial
- iii. Stir for 5 h
- iv. Take the final pH
- v. Filter and centrifuge to remove all particle matter
- vi. Analyze dye filtrate with Spec 21 at 520 nm and use ICP for uranium solutions

D. Characterization

i. FT-IR

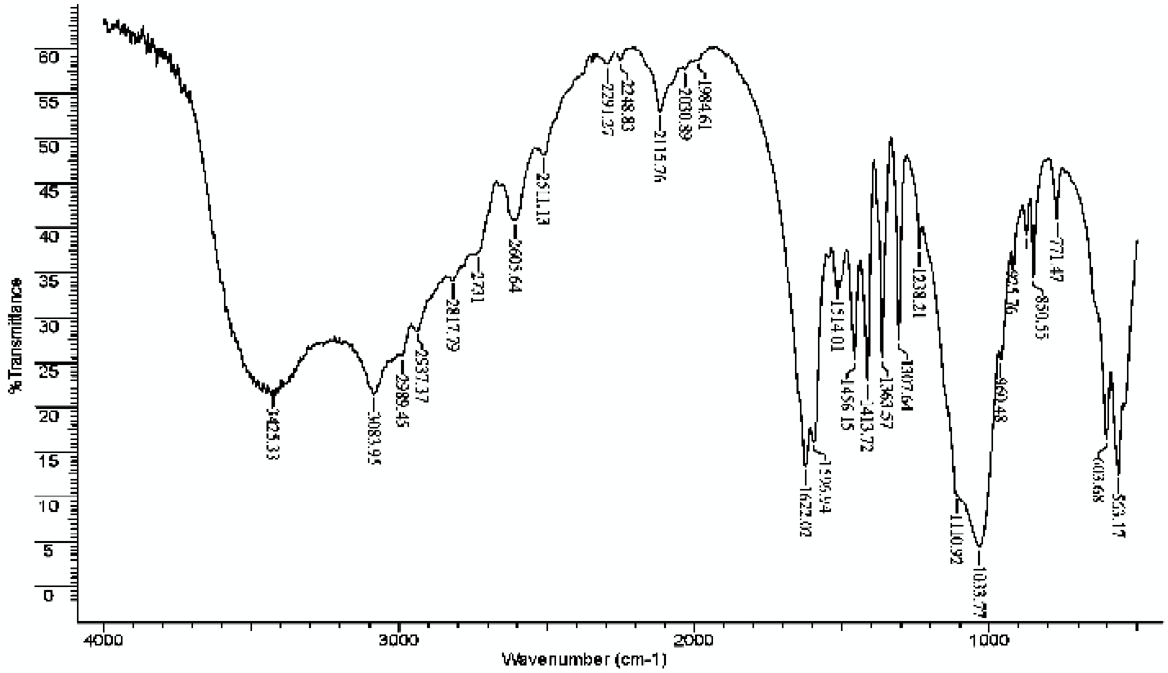


Figure B.2 FT-IR of pre-functionalized HAP + L- alanine

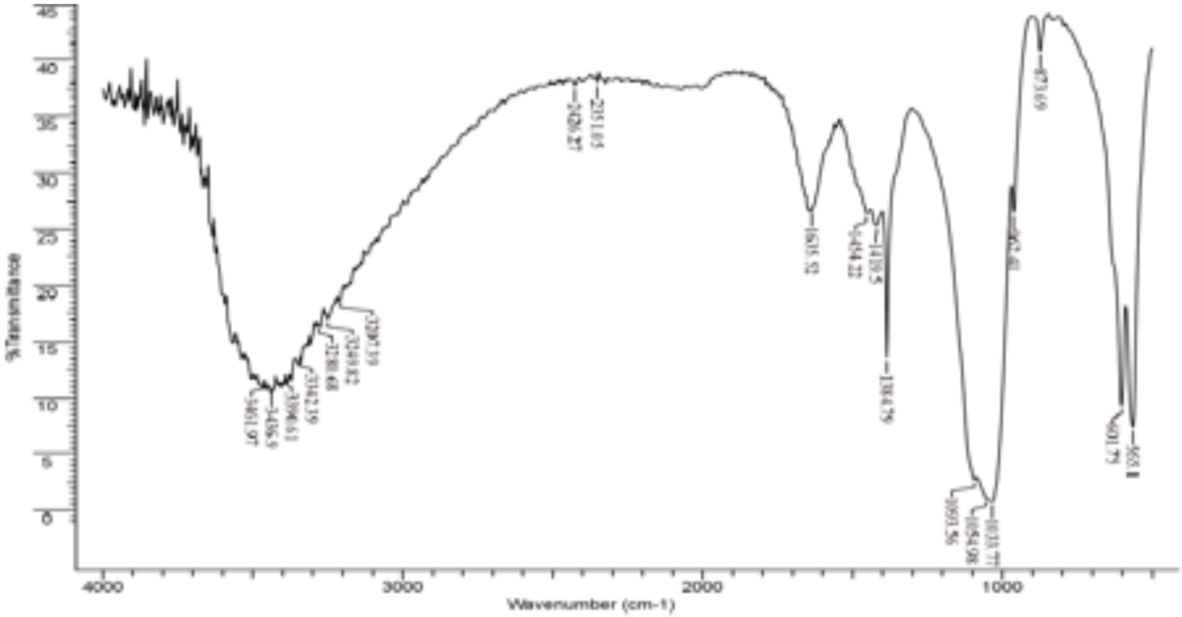


Figure B.3 FT-IR pre-functionalized HAP + ß-alanine

ii. Sorption studies

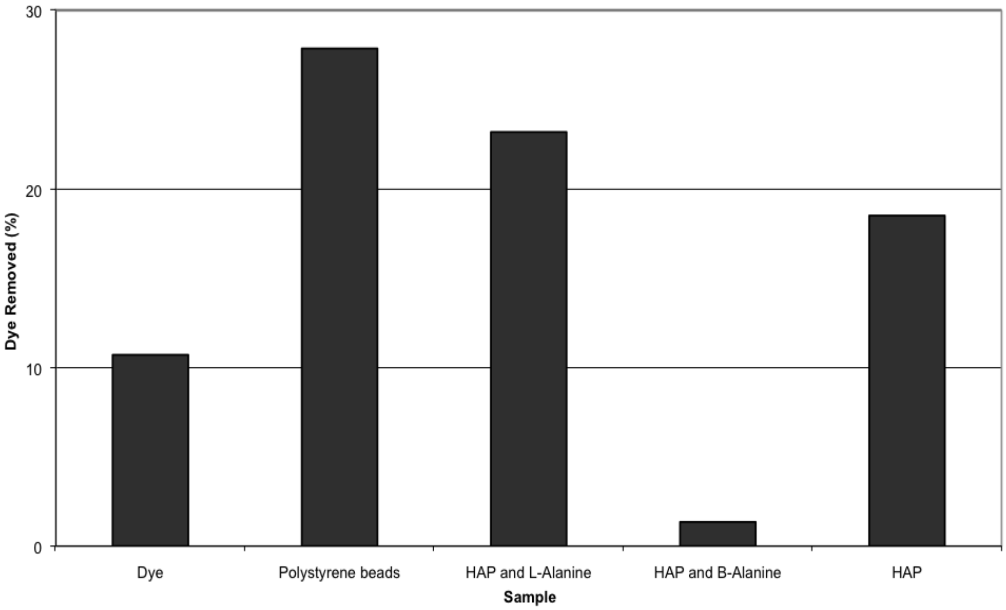


Figure B.4 Amaranth Red dye sorption for HAP+alanine (L and ß)

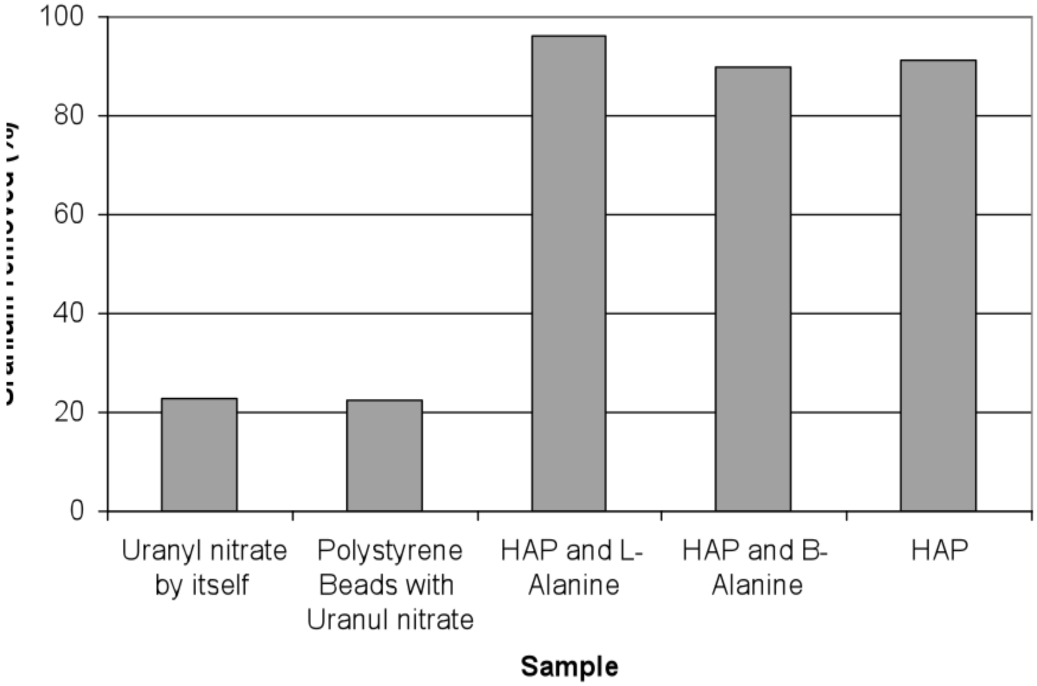


Figure B.5 Uranium sorption for HAP+ alanine (L and ß)

iii. Nitrogen elemental of unmodified HAP, L-alanine and HAP + L-alanine

a. Measure 0.2 g of dry HAP, L-alanine and HAP+L-alanine
b. Add each portion to a different 500 ml 3-necked round bottom flask
c. Add 0.25 g $CuSO_4$ and 10.0g K_2SO_4 to each
d. Add 25 ml concentrated H_2SO_4
e. Heat 8 h then dilute to 100 ml with dH_2O
f. Add 150 ml 6 N NaOH and collect distillated liquid into 50 ml 0.1 N HCl
g. Titrate a diluted amount with 0.1N NaOH and calculate the N-capacity

Table B.1 Nitrogen capacity HAP + L-alanine

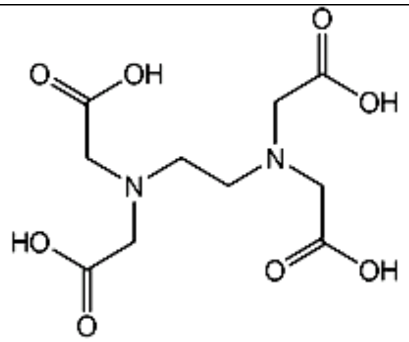
Sample	**Nitrogen capacity** (theoretical) (mequiv / g)	**Nitrogen capacity** (experimental) (mequiv / g)
HAP	0	0.33
L-alanine	11.23	10.80
HAP + L alanine	5.48	3.24

E. Conclusion

FT-IR spectra showed a higher degree of incorporation of L-alanine into HAP than ß-alanine. In the dye sorption studies, HAP+L-alanine removed considerably more dye than HAP+ß-alanine. In uranium sorption experiments, HAP+L-alanine also performed slightly more uranium than HAP+ß-alanine. Unmodified HAP, polystyrene beads and blank solutions were used as controls in both sorption studies. Although modification was intended to enhance sorption, the removal of dye and uranium by alanine-modified HAP was not significantly higher than unmodified HAP samples. L-alanine was determined to be a better modifier and subsequent N-elemental analyses were performed. Experimental and theoretical N-capacity calculations revealed the accuracy of the technique and also indicated that a significant amount of L-alanine was incorporated into HAP (3.24 mequiv/g).

B.2 Ethylenediaminetetraacetic acid (EDTA)

A. Structure and Properties



Molecular weight: 292.25g/mol
Molecular formula:
$(HOCOCH_2)_2N(CH_2)N(HOCOCH_2)_2$

Figure B.6 Structure of EDTA

B. Pre-functionalization

i. Add 3.881 g $Ca(OH)_2$ to 16.4 g (0.056 moles) EDTA
ii. Pour in 140 ml dH_2O while stirring
iii. Add 2 ml of 85% H_3PO_4 over 5 minutes
iv. Adjust pH to 8.2 with base
v. Stir for 48 h
vi. Decant
vii. Dry for 24 h in 110 ^oC oven
viii. Dry for 3 h in 400 ^oC oven
ix. Run FT-IR
x. Prepare HAP in the same manner without EDTA as a control

C. Characterization

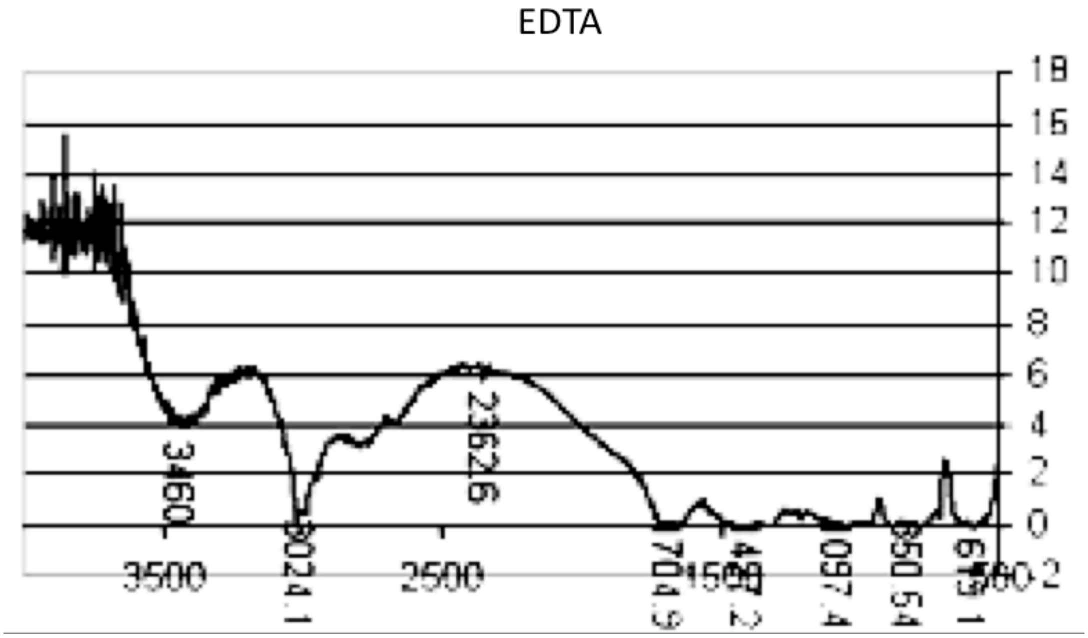


Figure B.7 FT-IR of EDTA

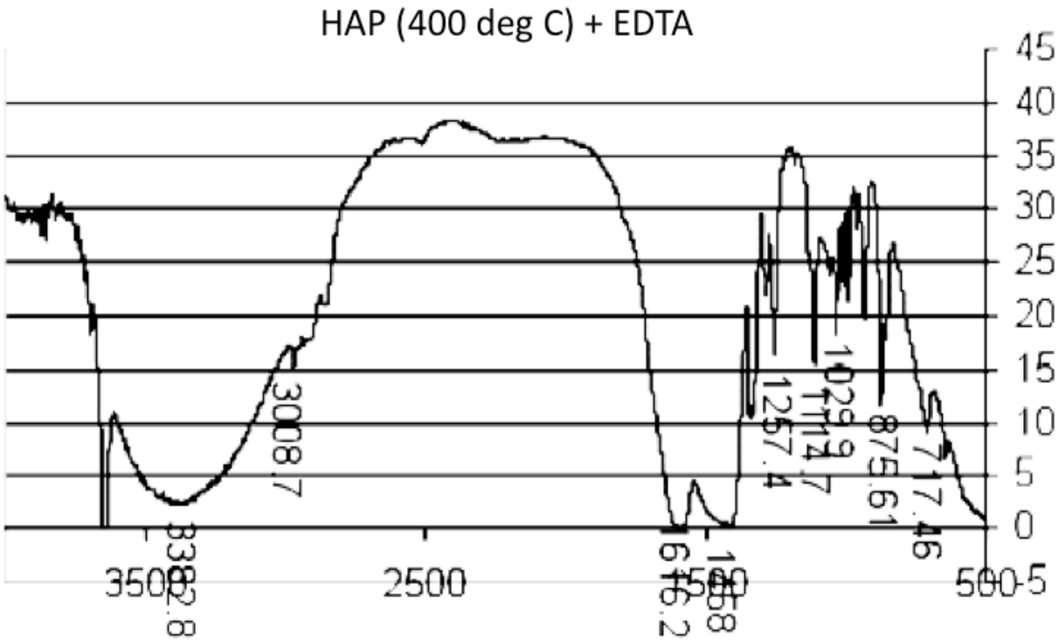


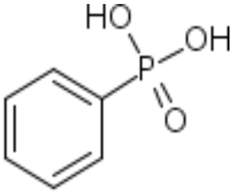
Figure B.8 FT-IR of pre-functionalized HAP + EDTA dried at 400 ^{o}C

D. Conclusion

The FT-IR spectrum of EDTA was obtained however bands appeared to be extremely broad and difficult to be clearly identified. FT-IR bands of HAP pre-functionalized with EDTA revealed several new bands compared to the unmodified HAP dried at 400 ^{o}C (Figure B.13). It was later discovered that HAP-400 was not thermodynamically stable enough to generate reproducible results and that experiments needed to be repeated with HAP+EDTA dried at 700 ^{o}C. These experiments were not carried out because EDTA was expected to fully decompose from the high temperature. Metal ion and dye sorption experiments were not conducted with the HAP+EDTA samples.

B.3 Phenylphosphonic acid (PPoA)

A. Structure and Properties



Molecular weight: 158.09g/mol
Molecular formula: $C_6H_5P(O)(OH)_2$

Figure B.9 Structure of phenylphosphonic acid

B. Pre-functionalization

- i. Crush 3 portions of 3.859 g $Ca(OH)_2$
- ii. Add 140 ml dH_2O
- iii. Add specified amount of modifier to each, corresponding to the amount of $Ca(OH)_2$ added, using the ratio in part iv:
  - a. 0.025 mole PPoA
  - b. 0.075 mole PPoA
  - c. 0.15 mole PPoA
- iv. Add H_3PO_4 in the following manner (at ~0.2 ml per min) and stir:

$$\frac{1.783 \text{ moles } Ca(OH)_2}{1 \text{ mole } H_3PO_4 - x \text{ moles PPoA}}$$

- v. After 4 h, adjust the pH to 8.0-8.2 if not at that pH already
- vi. Check the pH after 17 and 24 h and adjust the pH to 8-8.2 if necessary
- vii. Check the pH after 48 h and turn off stirrer
- viii. Filter using ashless filter paper
- ix. Vacuum oven dry for 8 h at 60 ^{o}C
- x. Wash in the soxhlet for 24 h and vacuum oven dry for 3 h at 60 ^{o}C
- xi. Obtain FT-IR
- xii. Prepare HAP in the same manner without PPoA as a control

C. Post-functionalization

i. Prepare a 1:2 mass ratio of HAP-400 to PPoA:

a. add 0.5 g HAP-400 to 0.06326 M PPoA (aq)

iii. Reflux for 7 days

iv. Wash and recover crystals

v. Air dry 48 h

vi. Prepare a control where HAP-400 is also refluxed without PPoA

D. Characterization

i. Pre-functionalization

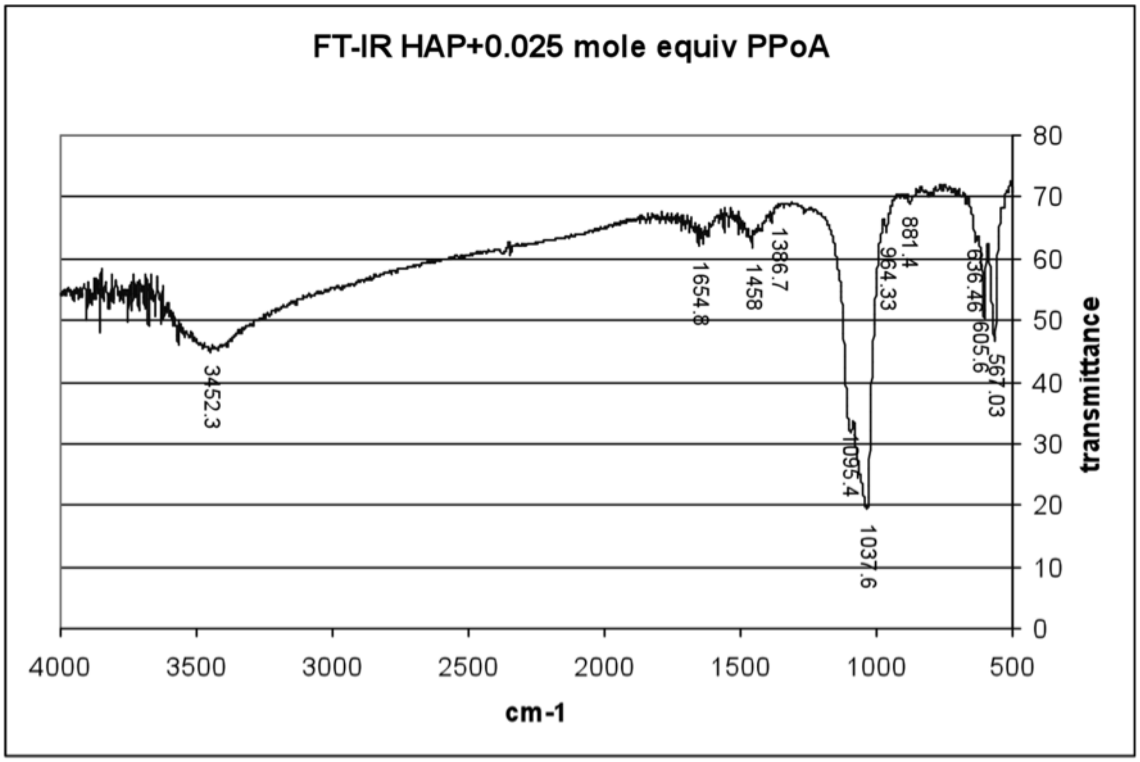


Figure B.10 FT-IR of pre-functionalized HAP + 0.025 equiv PPoA dried at 60 ^{o}C

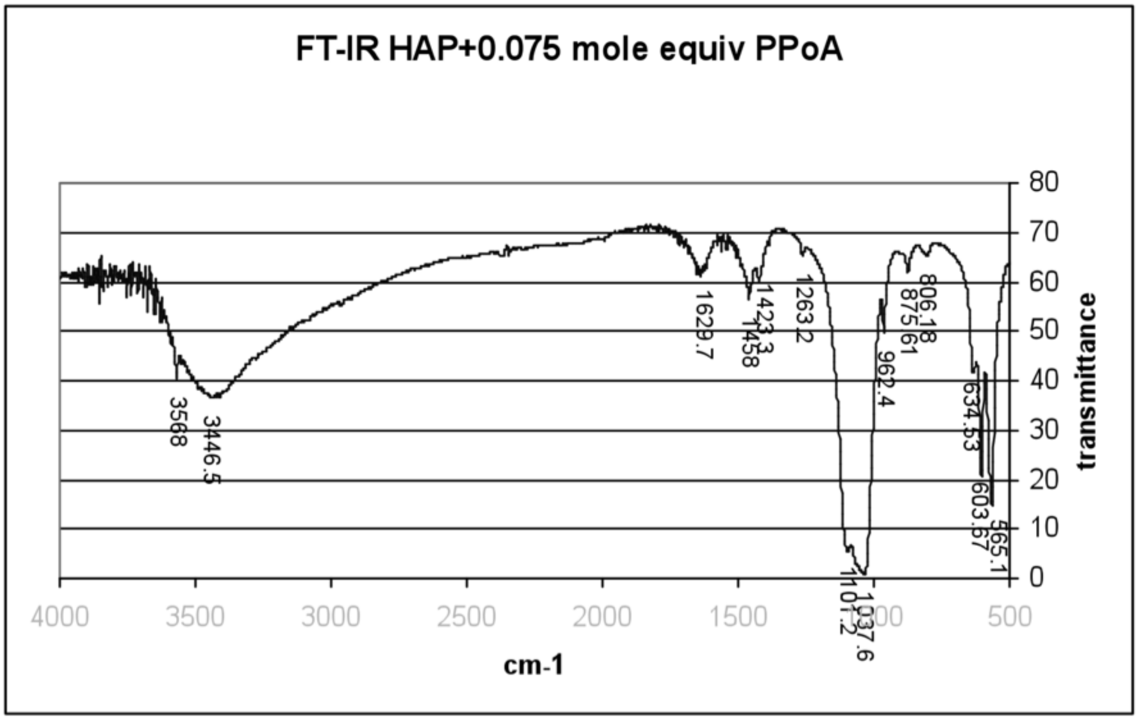


Figure B.11 FT-IR of pre-functionalized HAP + 0.075 equiv PPoA dried at 60 °C

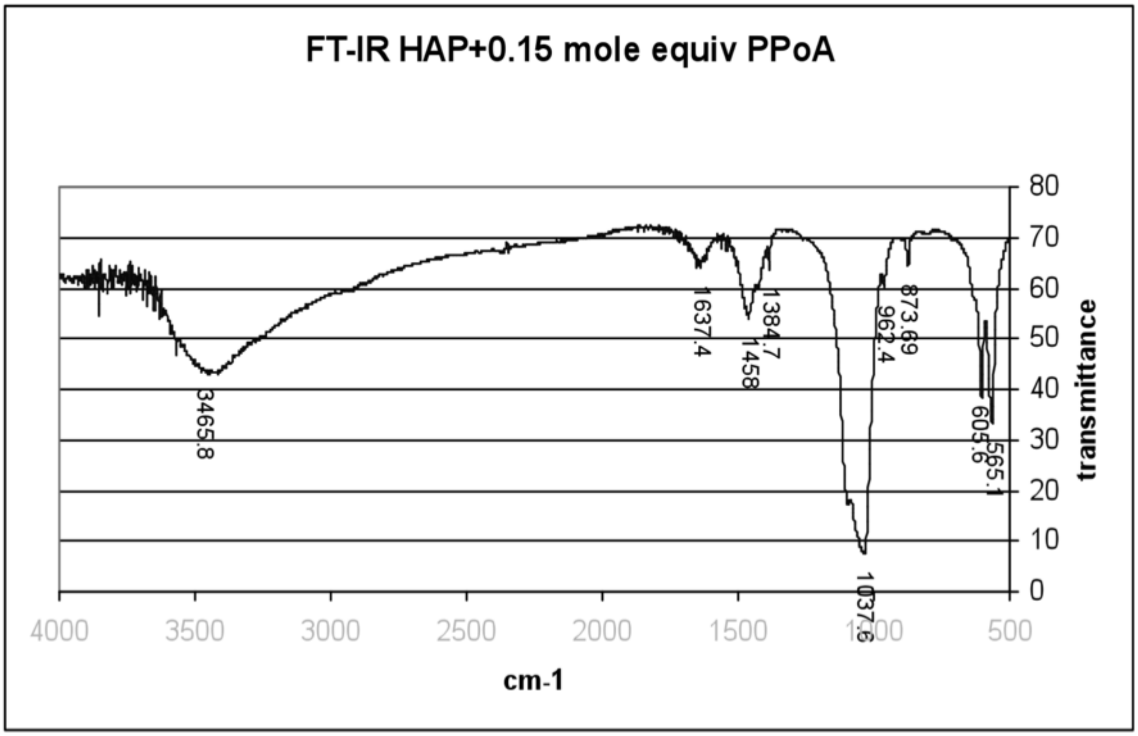


Figure B.12 FT-IR of pre-functionalized HAP + 0.15 equiv PPoA dried at 60 °C

ii. Post-functionalization

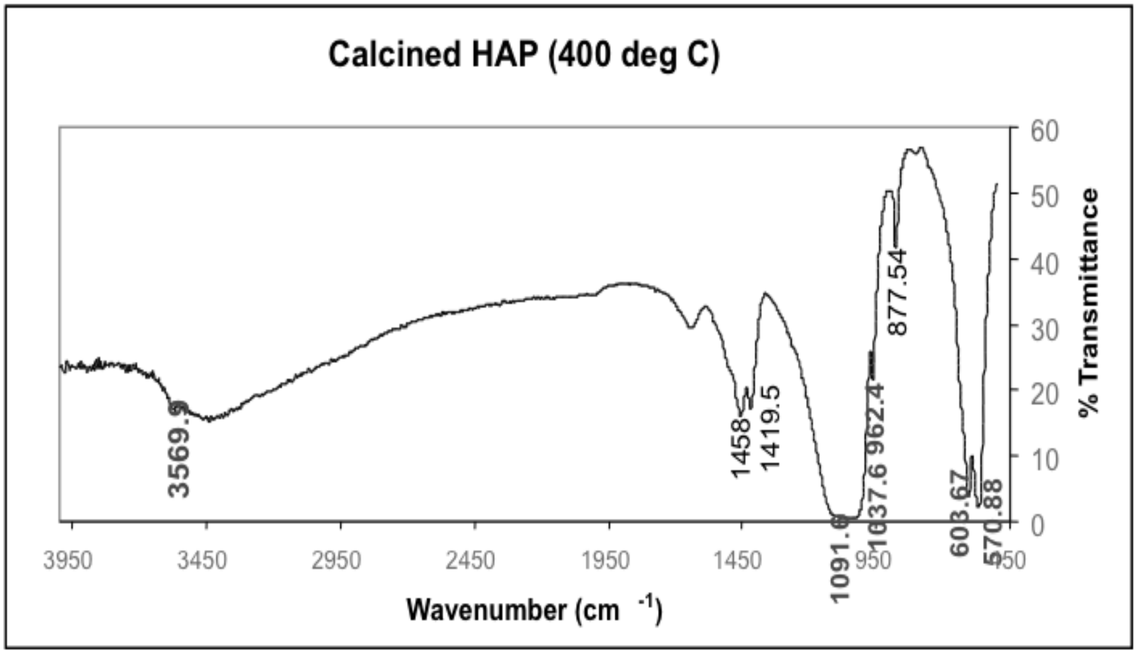


Figure B.13 FT-IR of unfuncitonalized HAP dried at 400 °C

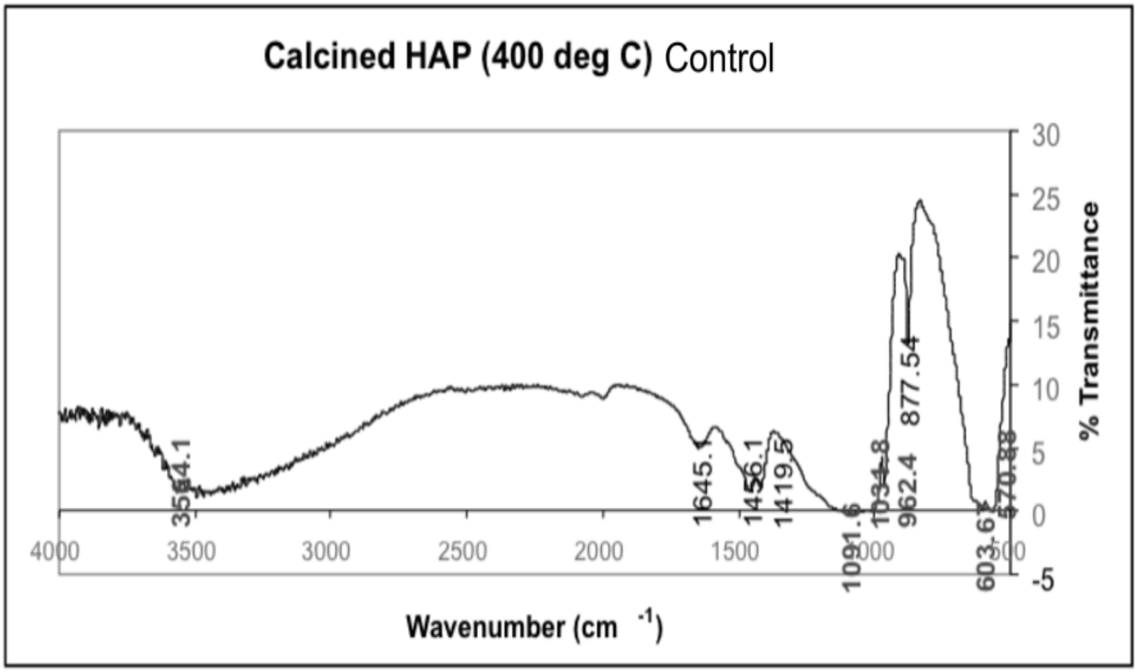


Figure B.14 FT-IR of HAP dried at dried at 400 °C and refluxed in water for 7 days

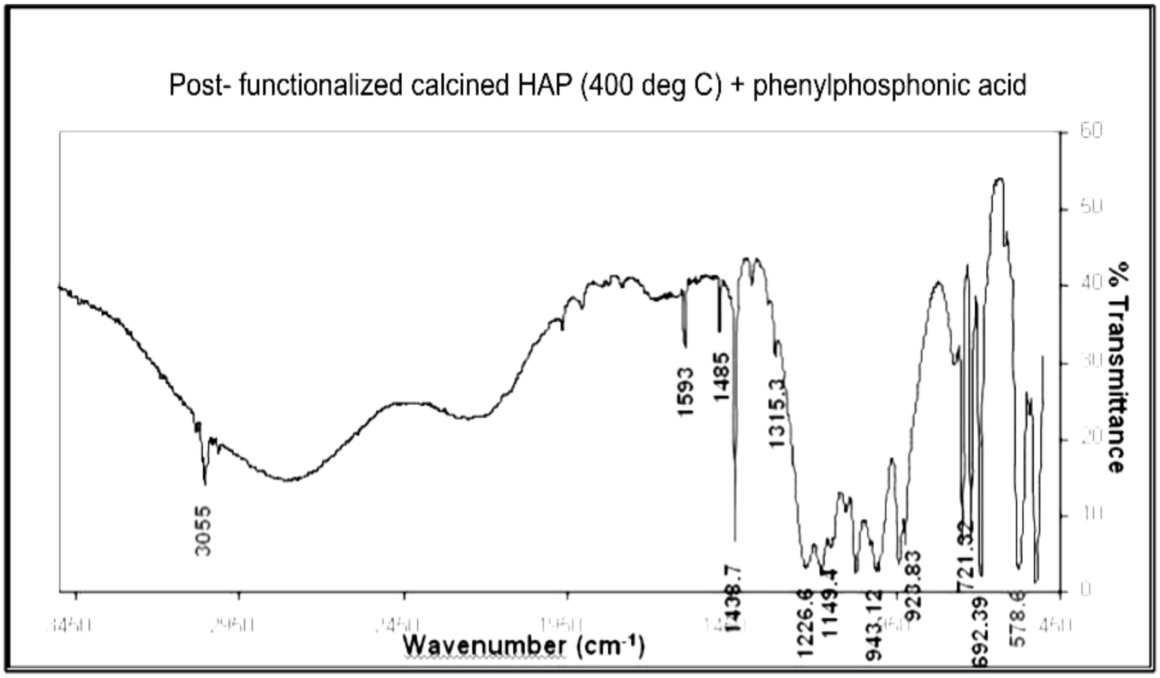


Figure B.15 FT-IR of HAP dried at 400 ^oC and post-functionalized with PPoA

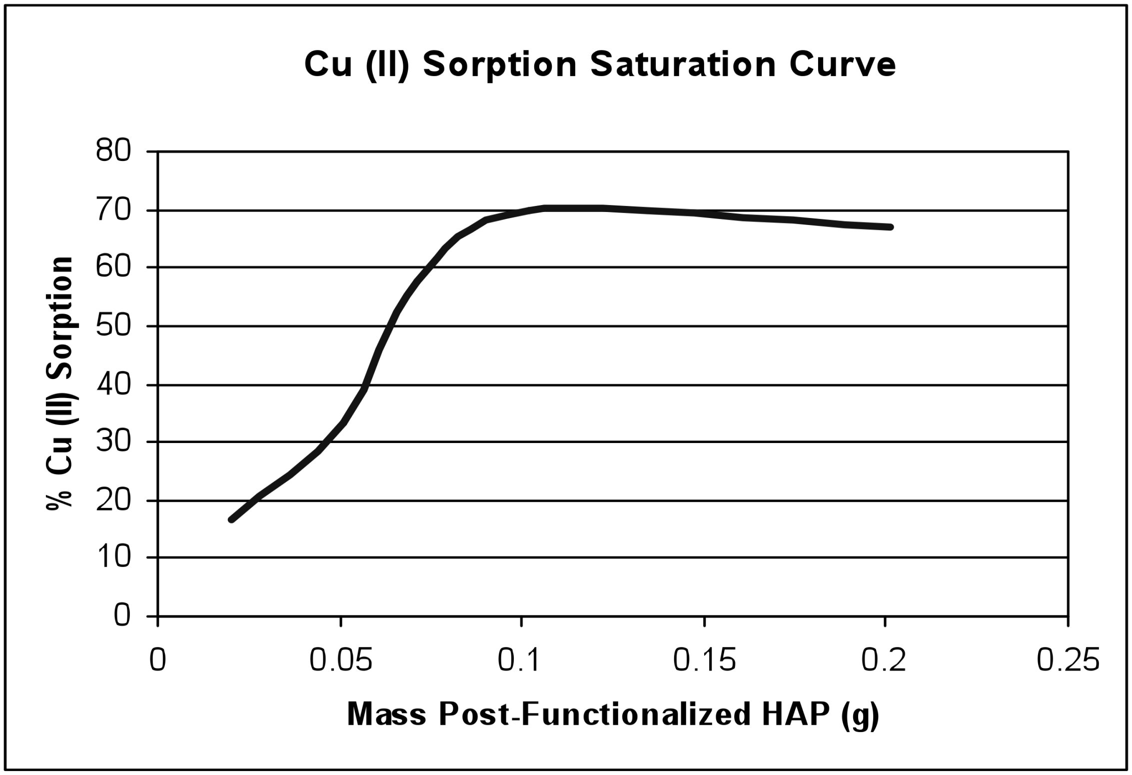


Figure B.16 Copper (II) saturation curve for post-functionalized HAP + PPoA

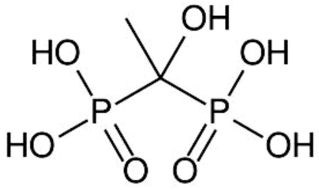
Table B.2 Copper sorption for HAP-400 and HAP-400 + PPoA

Sample	**Mass** (g)	**Cu (II) Sorption** (%)
Unmodified HAP-400	0.10	32
HAP-400 + PPoA (post-functionalized)	0.10	71
Control	0.11	33

E. Conclusion

There was no difference among the FT-IR spectra of HAP pre-functionalized with PPoA. HAP-400 was used for post-functionalization experiments because at the time of the experiment, this was taken to be thermodynamically stable compared to HAP-60. The post-functionalized HAP-400+PPoA showed new bands corresponding to PPoA indicating that post-functionalization was a valid route for modification. The Cu(II) isotherm for HAP-400+PPoA revealed that saturation began near 0.1 g and no more copper was removed with added sample. This mass was therefore used in all subsequent metal ion sorption experiments to ensure maximum efficiency and reproducibility.

B.4 1-hydroxyethane-1, 1-diphosphonic acid (HEDP)



Molecular weight: 206.028 g/mole
Molecular formula: $C_2H_8O_7P_2$

Figure B.17 Structure of HEDP

A. Pre-functionalization

i. Crush 3.859 g $Ca(OH)_2$
ii. Add 140 ml dH_2O
iii. Add 0.1 moles modifier corresponding to the amount of $Ca(OH)_2$ added using the ratio in part iv
iv. H_3PO_4 was added in the following format, adding ~0.2ml per min and stirred:

$$\frac{1.783 \text{ moles } Ca(OH)_2}{1 \text{ mole } H_3PO_4 - 0.1 \text{ moles organophosphate}}$$

v. After 4 h, adjust the pH to 8.0-8.2 if not at that pH already
vi. Check the pH after 17 and 24 h and adjust the pH to 8-8.2 if necessary
vii. Check the pH after 48 h and turn off stirrer
viii. Filter
ix. Vacuum oven dry for 8 h at 60 ^{o}C
x. Wash in the soxhlet for 24 h and vacuum oven dry again for 60 ^{o}C for 3 h
xi. Split the sample into 2 portions and dry one half at 400 ^{o}C
xii. Obtain FT-IR
xiii. Prepare HAP in the same manner without HEDP as a control

B. FT-IR

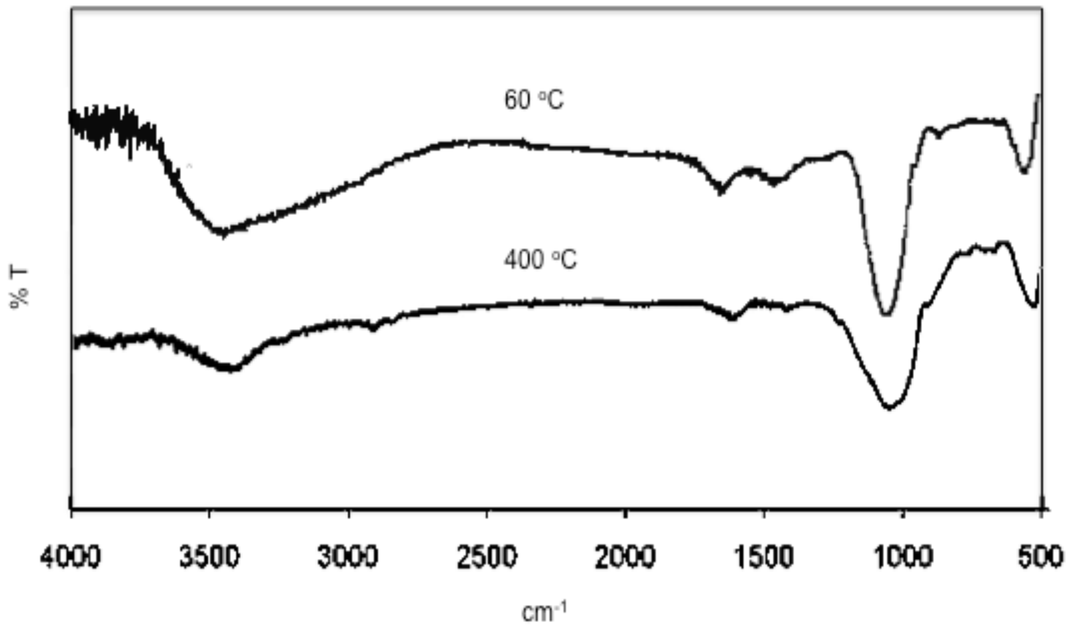


Figure B.18 FT-IR of HAP pre-functionalized with HEDP then dried at 60 °C and 400 °C.

C. Copper (II) sorption

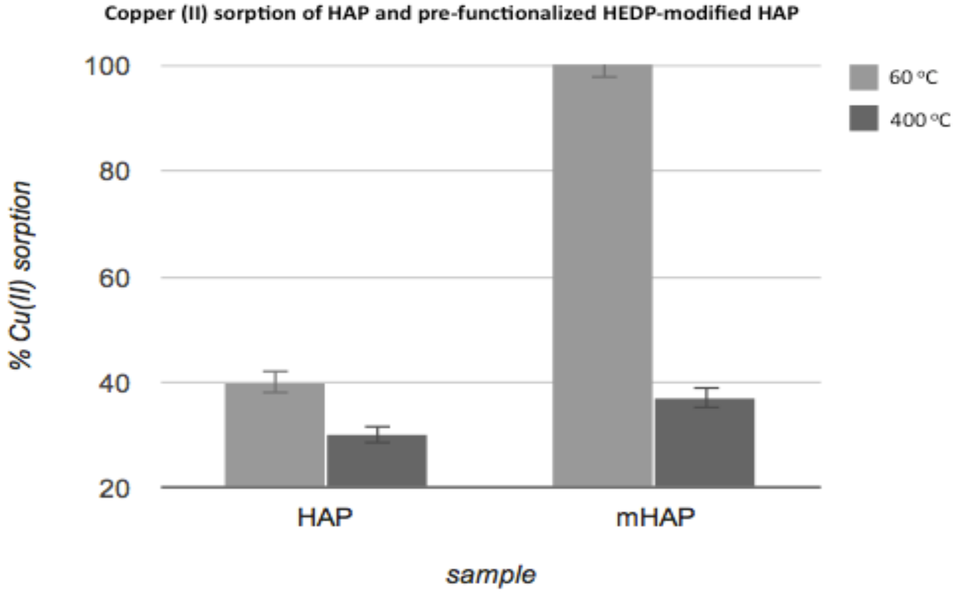


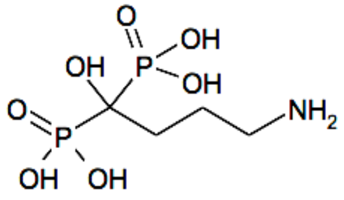
Figure B.19 Copper (II) sorption of HAP and HAP pre-functionalized with HEDP, dried at 60 °C and 400 °C.

D. Conclusion

HAP was pre-functionalized with HEDP and dried at 60 ^{o}C. A similar sample was prepared where drying took place at 400 ^{o}C to determine whether thermodynamically stable HAP+HEDP could be obtained from pre-functionalization. Neither sample showed new FT-IR bands (Figure B.18). Cu(II) sorption studies revealed that HAP+HEDP dried at 60 ^{o}C removed 100% Cu(II) and HAP+HEDP dried at 400 ^{o}C removed less than 40%. This led to two important conclusions: (1) The newly modified HAP pre-functionalized with HEDP has an FT-IR spectrum similar to unmodified HAP and (2) HEDP may be decomposed when dried at 400 ^{o}C since sorption decreased. Therefore in order to use a thermodynamically stable HAP, post-functionalization is suggested.

B5. Alendronic acid

A. Structure and Properties



Molecular weight: 243g/mol
Molecular formula: $C_4H_7NO_7P_2$

Figure B.20 Structure of alendronic acid

B. Post-functionalization

i. Add 0.2 g of HAP-700 to a plastic vial
ii. Add 10 ml of 0.5 M alendronic acid
iii. Contact (stir) for 1 h at RT
iv. Repeat steps i-ii to obtain 3 new samples contacted for 2 h, 3 h, and 4 h
v. Centrifuge, wash 3x with dH_2O
vi. Air dry for 48 h

C. Characterization

i. FT-IR

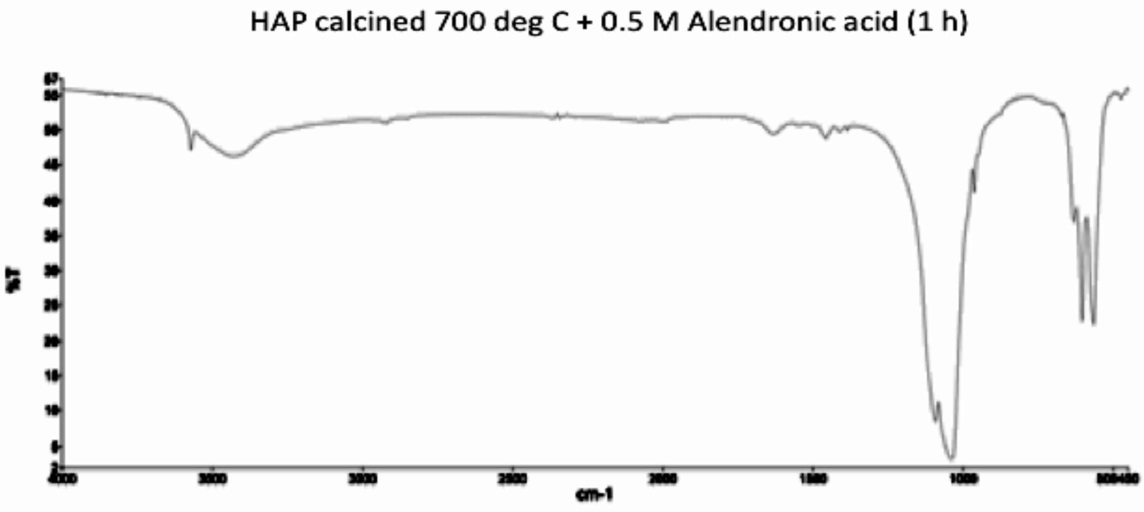


Figure B.21 FT-IR of HAP-700 modified with 0.5 M alendronic acid (1 h)

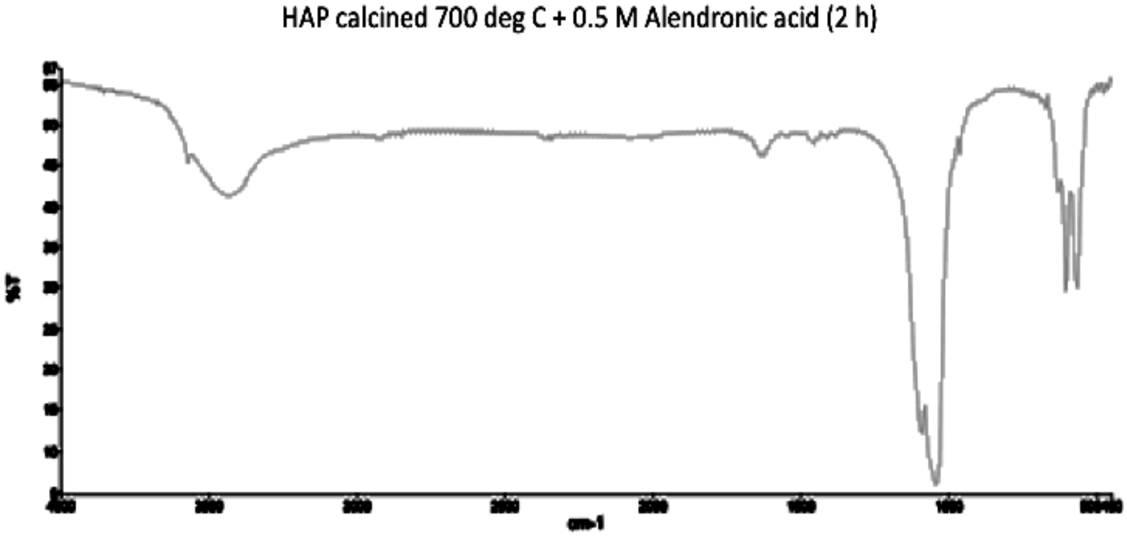


Figure B.22 FT-IR of 700 ^{o}C calcined HAP modified with 0.5 M alendronic acid (2 h)

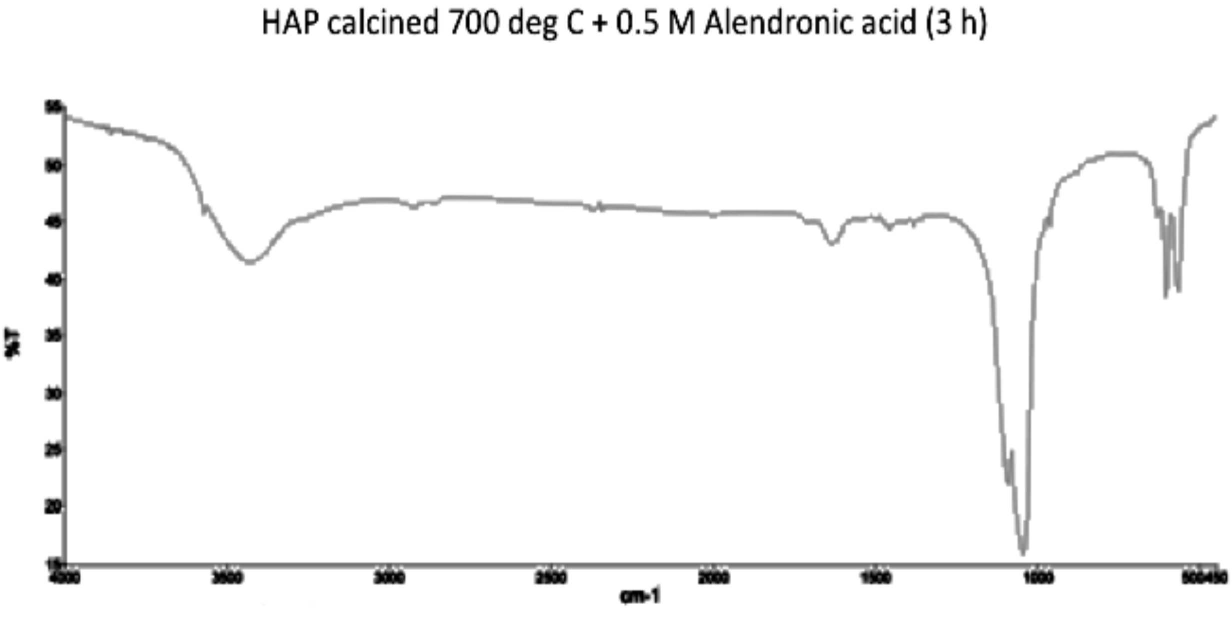


Figure B.23 FT-IR of 700 ^{o}C calcined HAP modified with 0.5 M alendronic acid (3 h)

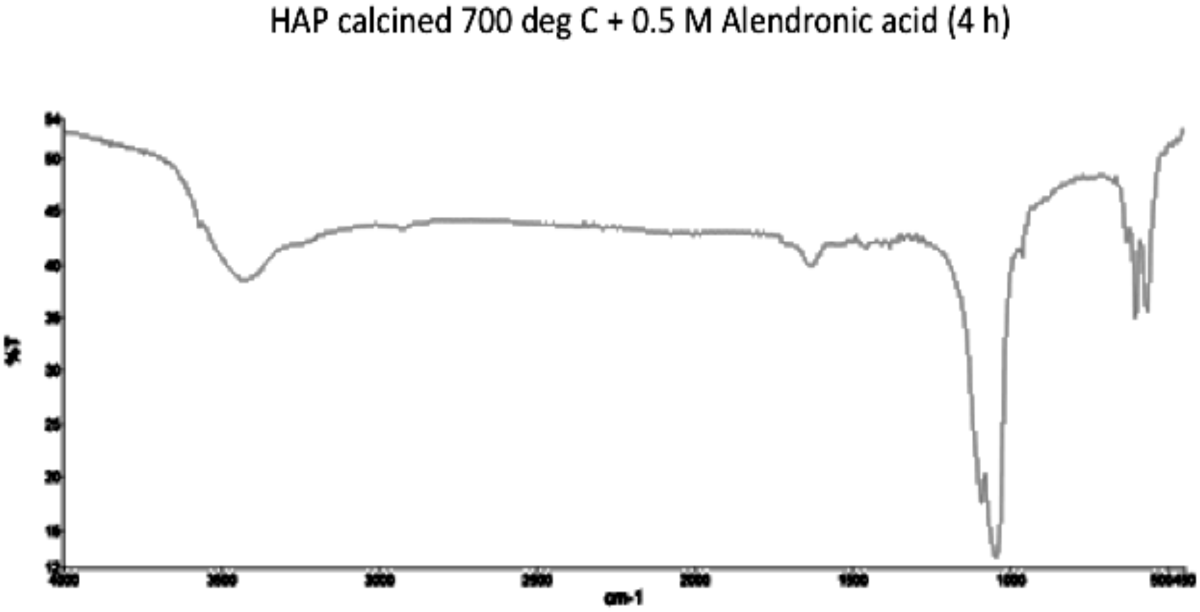


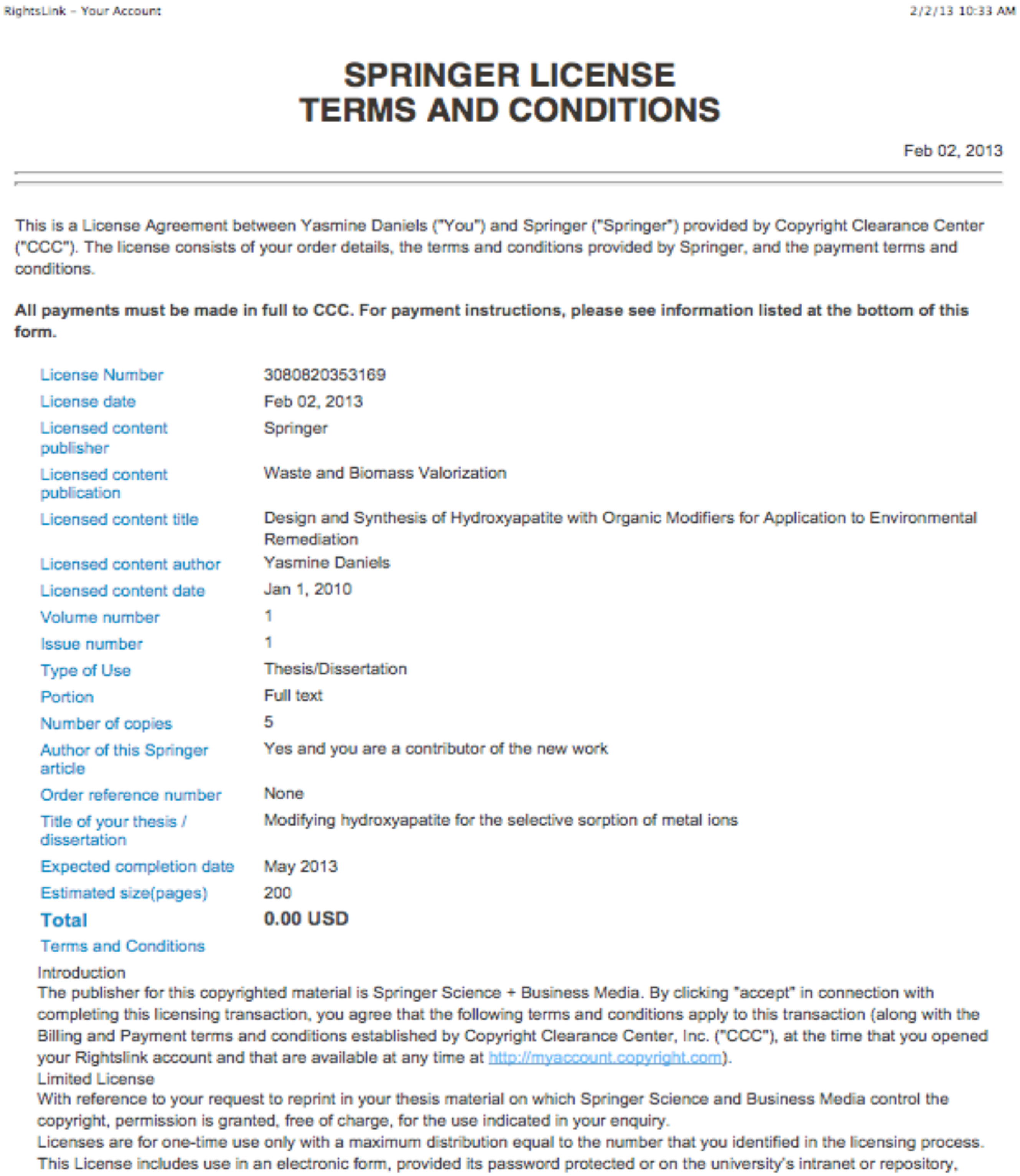
Figure B.24 FT-IR of 700 ^{o}C calcined HAP modified with 0.5 M alendronic acid (4 h)

D. Conclusion

HAP was reported to have a very high affinity for the bisphosphonate alendronic acid[198] therefore this was used in a post-functionalization study. Modification via the post-functionalization method was expected to produce samples showing new bands in the FT-IR, similar to results obtained from HAP post-functionalization with PPoA (Figure B.15). FT-IR spectra of HAP+alendronic acid did not show new bands for any of the samples prepared therefore post-functionalization with the HEDP bisphosphonate was later attempted. Results from post-functionalized HAP+HEDP are presented in chapter 6.

Appendix C

C. 1 LETTERS OF PERMISSION FROM SPRINGER



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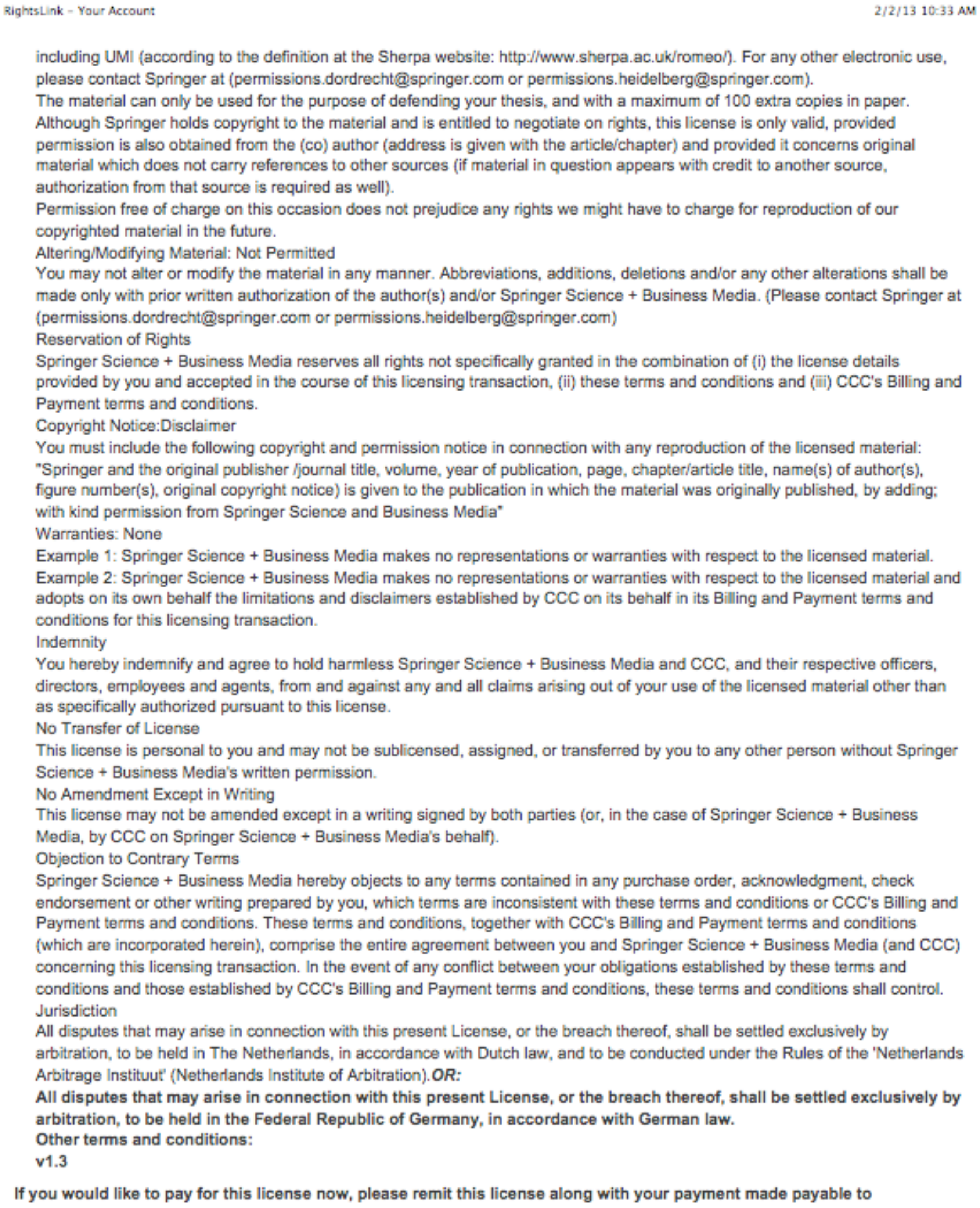

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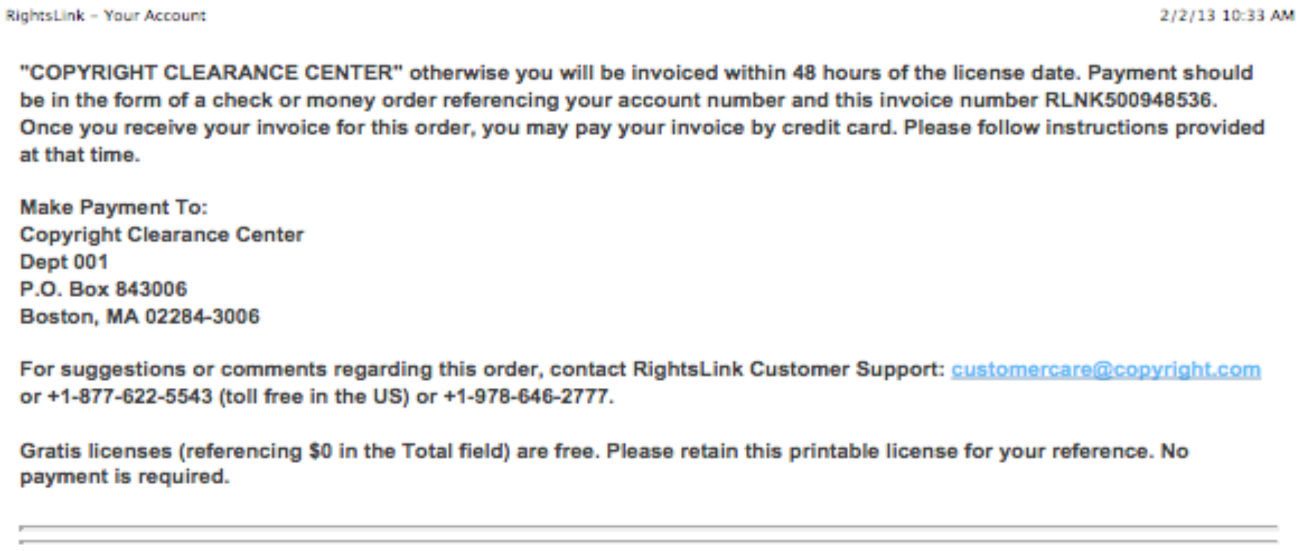

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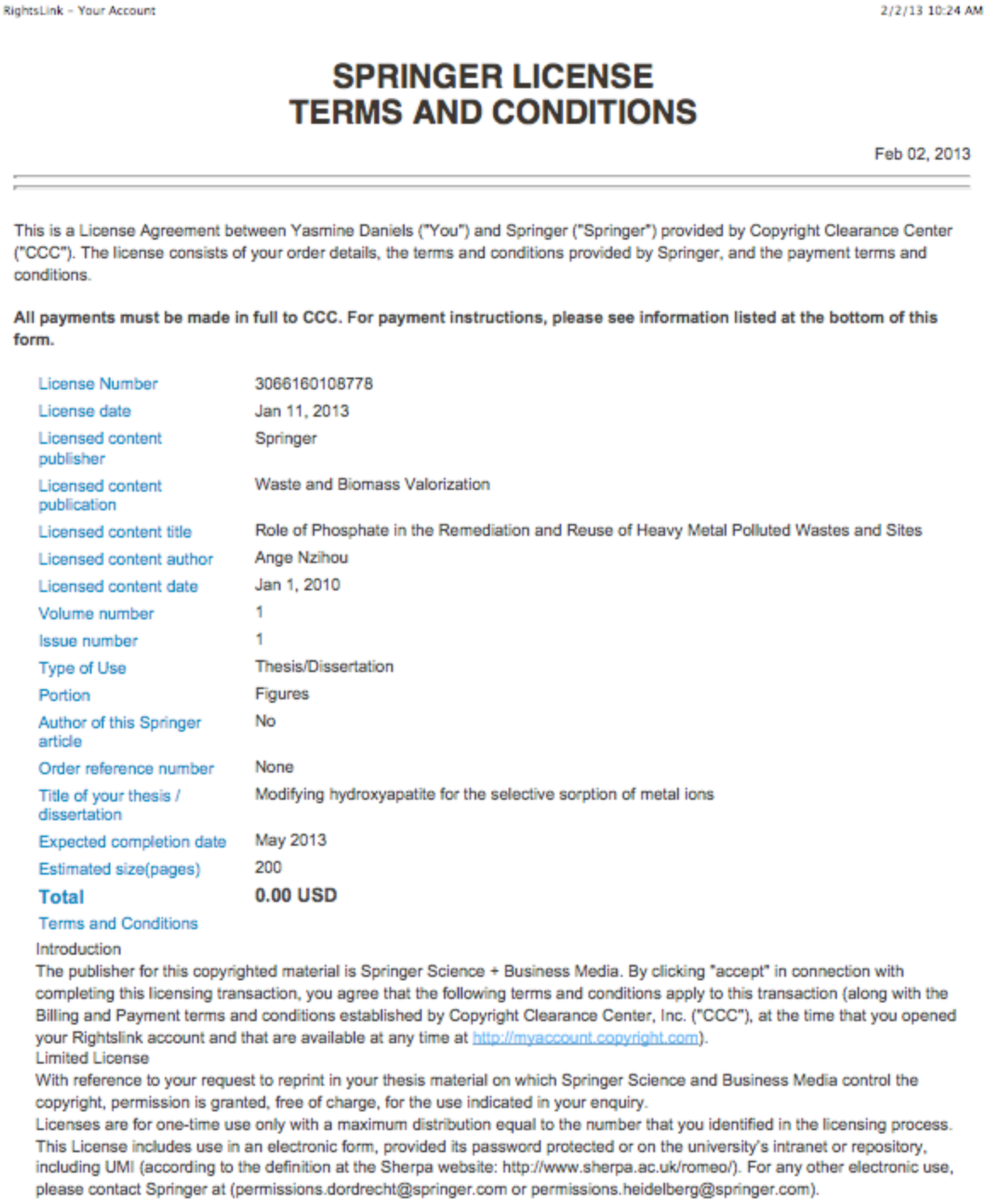

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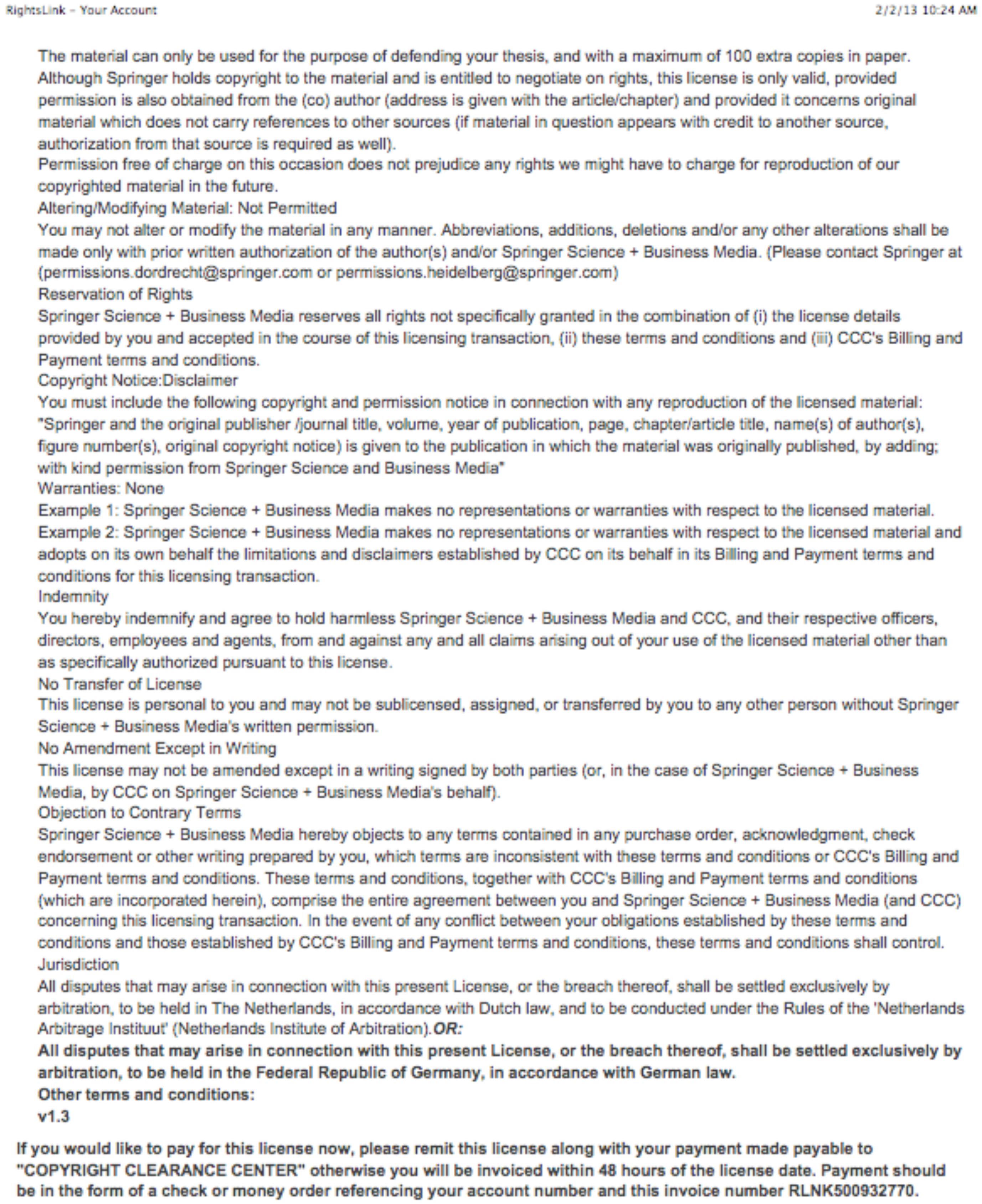

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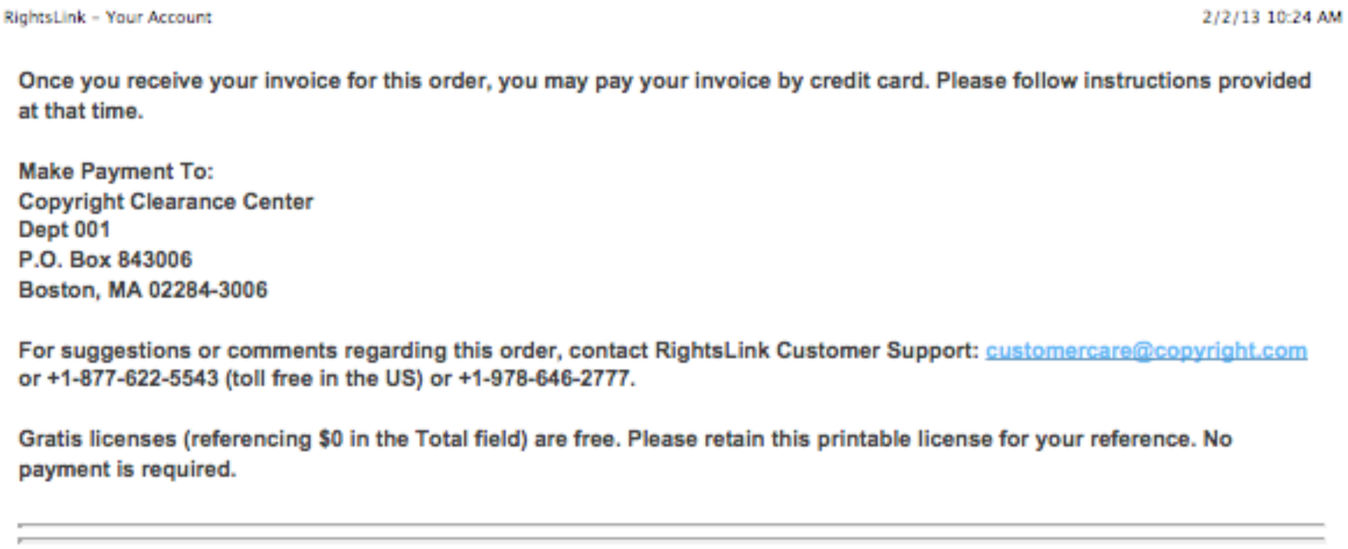

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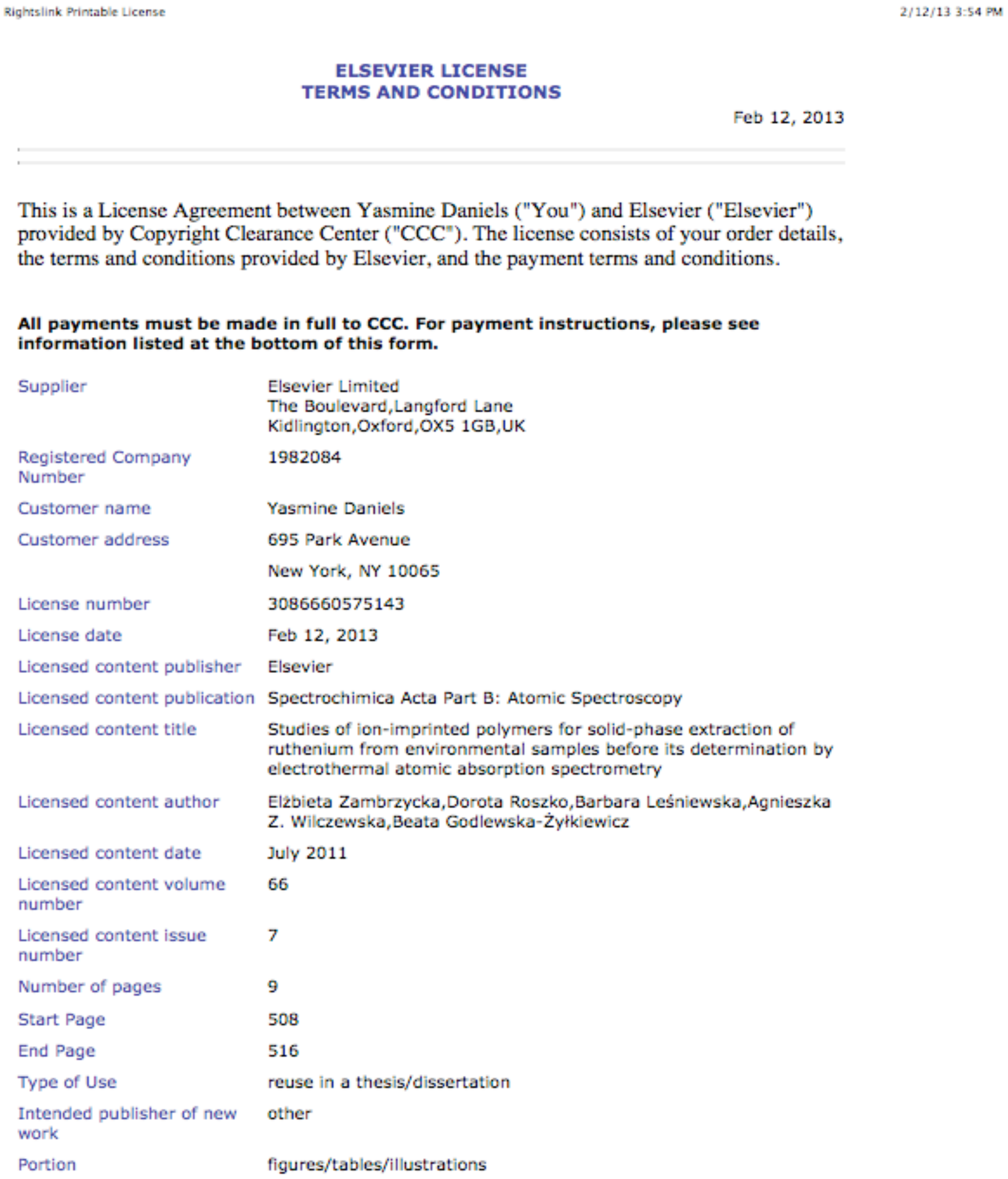

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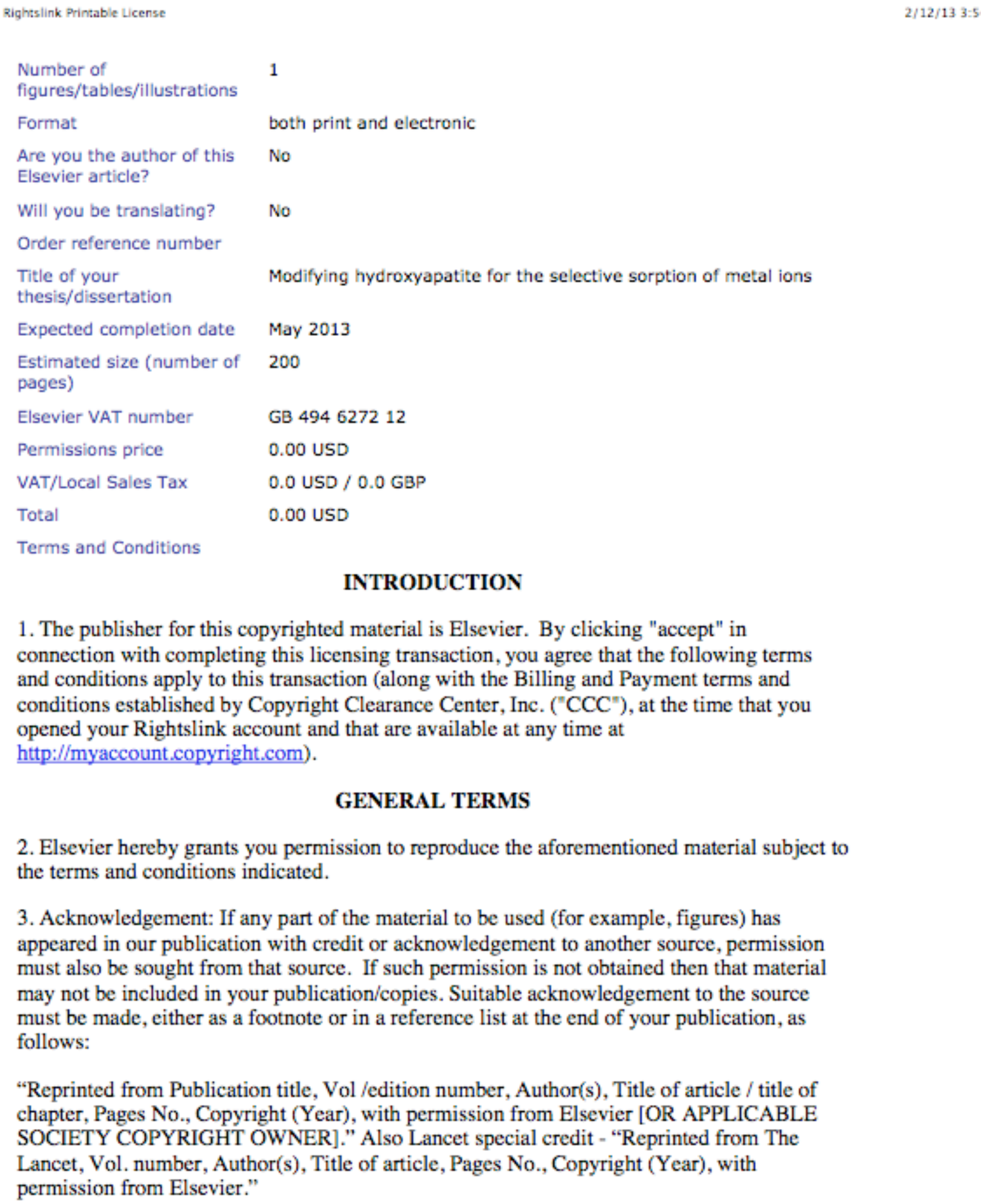

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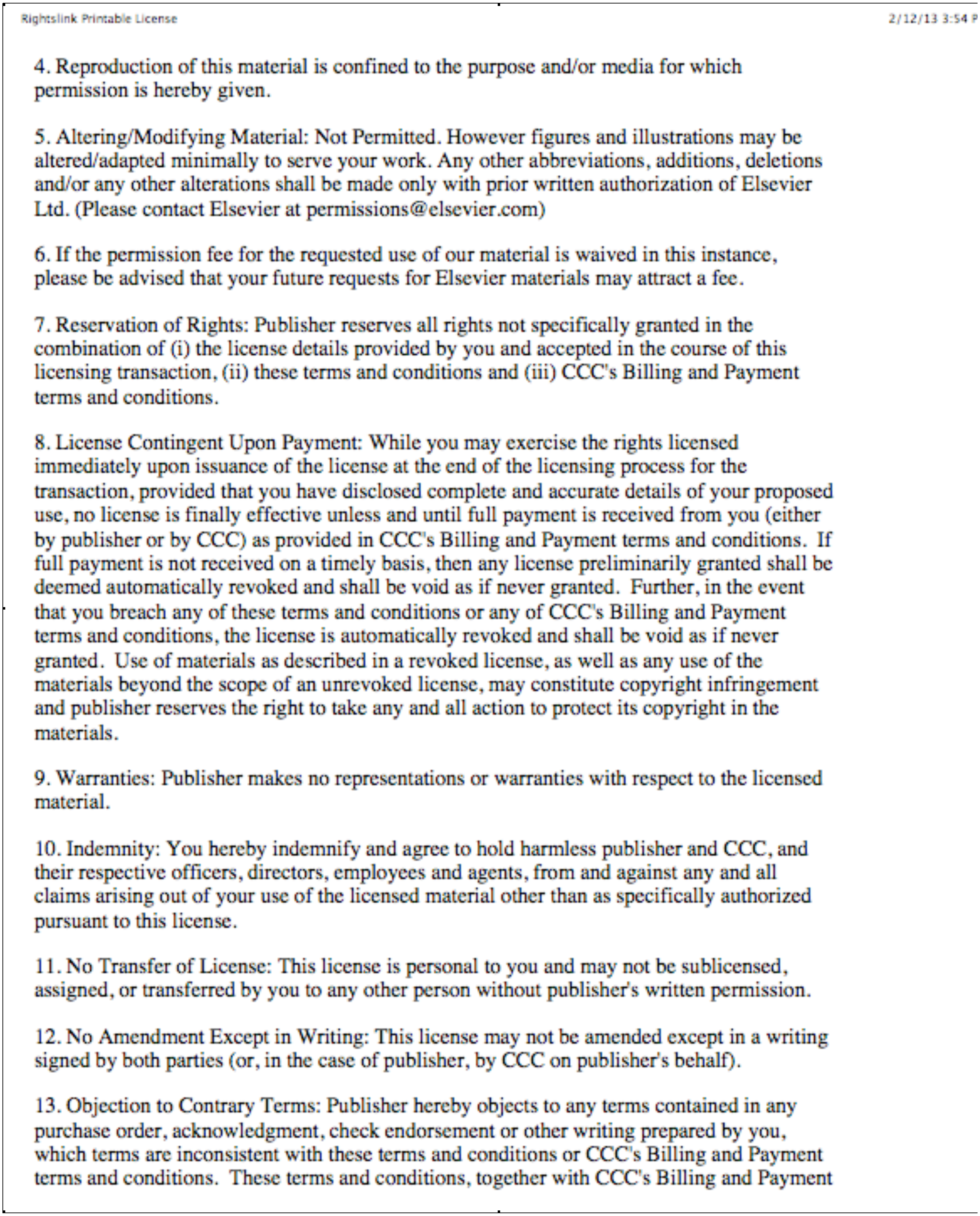

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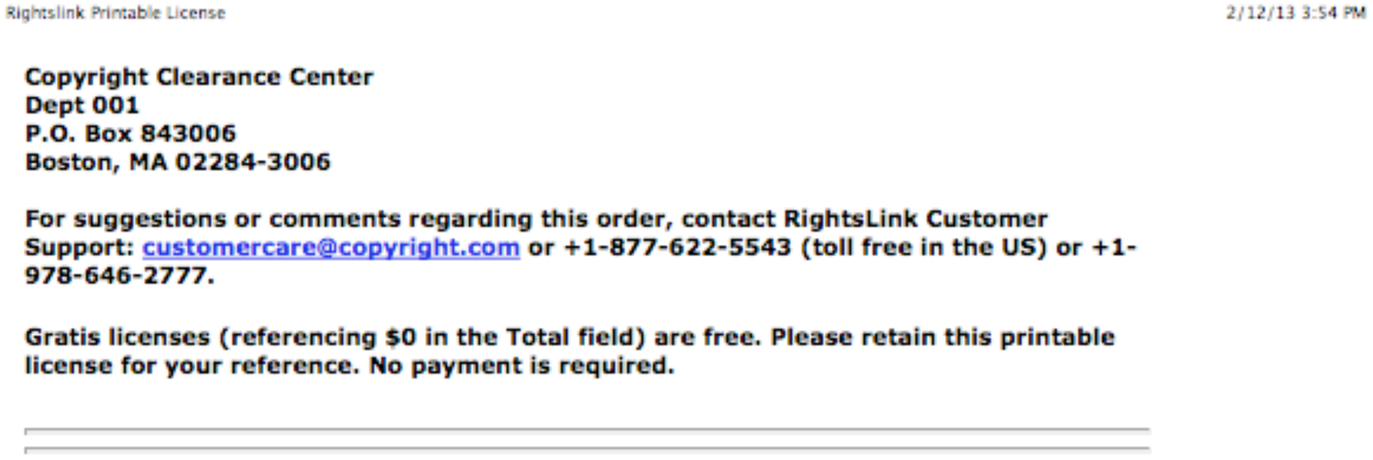

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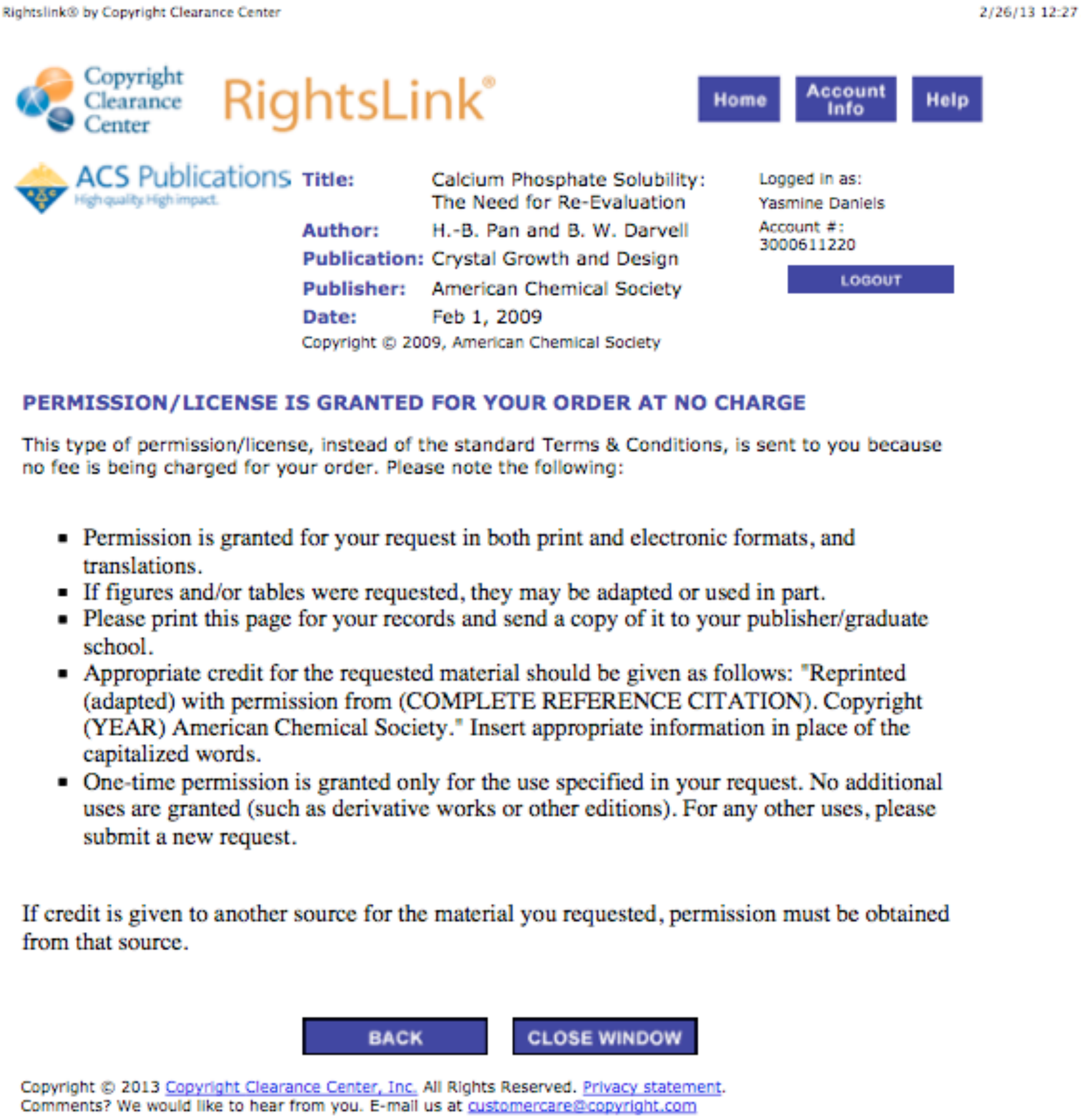

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