Phosphorus Release from Sewage Sludge by Thermal Treatment and Recovery as Struvite

張, 明楊

https://doi.org/10.15017/1441212

出版情報：九州大学, 2013, 博士（工学）, 課程博士
バージョン：

Phosphorus Release from Sewage Sludge by Thermal Treatment and Recovery as Struvite

By

Ming Yang Zhang

Department of Urban and Environmental Engineering,

Graduate School of Engineering, Kyushu University

DEPARTMENT OF URBAN AND ENVIRONMENTAL ENGINEERING
KYUSHU UNIVERSITY
FUKUOKA, JAPAN

CERTIFICATION

The undersigned hereby certify that they have read and recommended to Graduate School of Engineering for acceptance of this dissertation entitled, "**Phosphorus Release from Sewage Sludge by Thermal Treatment and Recovery as Struvite**" by **Ming Yang Zhang** in partial fulfillment of requirements for the degree of Doctor of Engineering.

Dated: January, 2014

Thesis Supervisor:

Prof. Takahiro KUBA
Department of Urban and Environmental Engineering
Graduate School of Engineering
Kyushu University

Examination Committees:

Prof. Takayuki SHIMAOKA
Department of Urban and Environmental Engineering
Graduate School of Engineering
Kyushu University

Prof. Tsuyoshi HIRAJIMA
Department of Earth Resource Engineering
Graduate School of Engineering
Kyushu University

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Chapter 1

Chapter 1 Introduction of Research Background

Abstract

Phosphorus is a necessary nutrient element to all lives in the world. Distribution and phosphate rock reserves in the world disclose shortage crisis of phosphorus. In recent time, clean energy has been researched and applied in developed countries, especially large quantity of crops is demanded which means more phosphorus fertilizer should be required. This will aggravate the shortage crisis of phosphorus.

On the other hand, excess discharge of phosphate compounds into natural water bodies has induced many environmental problems, especially for eutrophication which makes much economic loss to society.

Thus phosphorus recovery has been a research hot spot in the world. Activated sludge applied in the wastewater treatment plant can accumulate lots of phosphorus resource inside its body by enhanced biological phosphorus removal technique. Therefore many researches use sewage sludge or sludge ash as the target for phosphorus recovery.

Some researchers [1] have introduced a new method named “heatphos” to recover phosphorus from sewage sludge during heating process. It seems that nearly all of the poly-phosphate (poly-P) and 87% of total phosphate (T-P) can be released from cultivated sludge by heating at 70˚C for 1 hour. Meanwhile, released poly-P can precipitate with Ca in neutral condition without any pH adjustment.

The purpose of this study aimed at testing the performance of thermal treatment at low temperature with sewage sludge collected from wastewater treatment plant (WWTP) to release phosphorus especially poly-P into liquid phase. Then whether poly-P can be crystallized as struvite had been investigated.

Keywords: phosphorus; shortage crisis; eutrophication; sewage sludge; recovery.

1.1 Importance of phosphorus

Phosphorus is an important constituent in every body tissue. The total amount constitutes about one percent of the body weight. The amount of phosphorus in the body is exceeded only by calcium. In bones the proportion of calcium to phosphorus is much higher than phosphorus to calcium. Most of the phosphorus is in organic combinations.

Phosphorus is one mineral that performs a number of important functions. It combines with calcium to form a relatively insoluble compound calcium phosphate, which gives strength and rigidity to bones and teeth. Phosphorus like calcium is needed not only for the growth of skeleton but also for its maintenance. The utilization of many nutrients that enter the body involves the formation and degradation of phosphorus containing compounds. The phosphorus-containing lipo-protein facilitates the transport of fats in the circulation. A series of phosphorus compounds are formed in the utilization of carbohydrates in the body. It is vital to the fundamental process of metabolism in the body. Phosphorus is a constituent of the nucleoproteins which can control heredity.

A deficiency of this element is very rare in human being because diets having sufficient cereals are seldom inadequate in this nutrient. The deficiency is common in animals. They develop stiff joints and bones become fragile and break easily [2].

It is a component of the complex nucleic acid structure of plants, which regulates protein synthesis. Phosphorus is, therefore, important in cell division and development of new tissue. Phosphorus is also associated with complex energy transformations in the plant.

Phosphorus is often recommended as a row-applied starter fertilizer for increasing early growth. University of Nebraska's starter fertilizer studies conducted in the 1980s showed early growth response to phosphorus in less than 40 percent of the test fields. Starter applications may increase early growth even if phosphorus does not increase grain yield. Producers need to carefully evaluate cosmetic effects of fertilizer application versus increased profits from yield increases [3].

1.2 Existence form of phosphorus in nature

Phosphorous is a multivalent nonmetal of the nitrogen group. It is found in nature in several allotropic forms, and is an essential element for the life of organisms.

Properties: The melting point of phosphorus (white) is 44.1˚C, boiling point (white) is 280˚C, and specific gravity (white) is 1.82, (red) 2.20, (black) 2.25-2.69, with a valence of 3 or 5. There are four allotropic forms of phosphorus: two forms of white (or yellow), red, and black (or violet). White phosphorus exhibits modifications, with a transition temperature between the two forms at -3.8˚C [4].

Ordinary phosphorus is a waxy white solid. When pure, it is colourless and transparent. It is insoluble in water, but soluble in carbon disulphide. It catches fire spontaneously in air, burning to P_4O_{10}, often misnamed as phosphorus pentoxide. When exposed to sunlight, or when heated in its own vapour to 250˚C, it is converted to the red variety. This form does not ignite spontaneously and it is a little less dangerous than white phosphorus. The red modification is fairly stable and sublimes with a vapour pressure of 1 atmosphere at 417˚C.

There are several forms of phosphorous, called white, red and black phosphorous, although the colours are more likely to be slightly different. White phosphorous is the one manufactured industrial; it glows in the dark, is spontaneously flammable when exposed to air and is deadly poison. Red phosphorous can vary in colour from orange to purple, due to slight variations in its chemical structure. The third form, black phosphorous, is made under high pressure, looks like graphite and has the ability to conduct electricity.

According to the properties of phosphorus, it has many applications in agriculture and farm industries. In particular, phosphorus is used extensively in fertilizers as concentrated phosphoric acid. Phosphorus is used in the production of special glasses, as a cleaning agent and as a water softener. Phosphorus is also used in production of phosphor bronze and steel.

Phosphorous in the environment

In the natural world phosphorous is never encountered in its pure form, but only as phosphate, which consists of a phosphorous atom bonded to four oxygen atoms. This can exists as the negatively charged phosphate ion (PO_4^{3-}), which is how it occurs in minerals, or as organophosphates in which there are organic molecules attached to one, two or three of the oxygen atoms.

The amount of phosphorous that is naturally present in food varies considerably but can be as high as 370 $mg \cdot 100\ g^{-1}$ in liver, or can be low, as in vegetable oils. Foods rich in phosphorous include tuna, salmon, sardines, liver, turkey, chicken, eggs and cheese (200 $mg \cdot 100\ g^{-1}$).

There are many phosphate minerals, the most abundant being forms of apatite. Fluoroapatite provides the most extensively mined deposits. The chief mining areas are Russia, USA, Morocco, Tunisia, Togo and Nauru. World production is 153 million tons per year. There are concerns over how long these phosphorous deposits will last. In case of depletion there could be a serious problem for the world's food production since phosphorus is such an essential ingredient in fertilizers [5].

Health effects of phosphorus

Phosphorus can be found in the environment most commonly as phosphates. Phosphates are irreplaceable nutrient materials for livings in the earth, because they are a part of DNA materials and they take part in energy distribution. Phosphates can also be found in plants.

Phosphates are dietary requirement, the quantity for everyone is 800 $mg \cdot day^{-1}$, a normal diet provides between 1000 and 2000 $mg \cdot day^{-1}$. This depends on the extent to the foods which contain phosphorus.

Because of the application of fertilizers containing phosphate and detergent, people have changed the natural phosphate supply radically. Phosphates were also added to a number of food stuffs, such as cheese, sausages and hams.

Phosphorus in its pure form has a white colour. White phosphorus is the most dangerous form of phosphorus that is known to us. When white phosphorus occurs in nature this can be a serious danger to our health. White phosphorus is extremely poisonous and in many cases exposure to it will be fatal.

In most cases people that died of white phosphorus exposure had been accidentally swallowing rat poison. Before people die from white phosphorus exposure they often experience nausea, stomach cramps and drowsiness.

White phosphorus can cause skin burns. While burning, white phosphorus may cause damage to the liver, the heart or the kidneys [5].

1.3 Distribution of phosphorus reserves in the earth

Geopolitical dimensions of phosphorus scarcity can also restrict the availability of phosphate for the use in food production in the short or long period. For example, while all farmers need access to phosphorus, most of the world's remaining phosphate rock reserves (approximately 85%) are controlled by four areas, the main players being Morocco, China, South Africa and Jordan.

In 2008 China imposed a 135% export tariff to secure domestic supply for food production, a move which essentially halted exports from the region over night and by 2009 the US and EU had gone to the WTO claiming China was exhibiting anti-competitive behavior. The EU is almost entirely dependent on imports of phosphorus. The US is expected to deplete its own high-grade reserves in the coming decades. This may threaten the stability of the market as soon as this becomes public knowledge. The market response could be similar to what happened during 2008 when prices spiked by 800%. The US increasingly imports phosphate rock from Morocco. However Morocco currently occupies Western Sahara and controls that region's reserves in defiance of UN resolutions. The contested nature of the ownership of the Western Sahara reserves means there is an ethical concern that companies, countries and consumers are knowingly or unknowingly supporting an occupation, and a practical concern that insecurity in the region could lead to a distribution in supply [6].

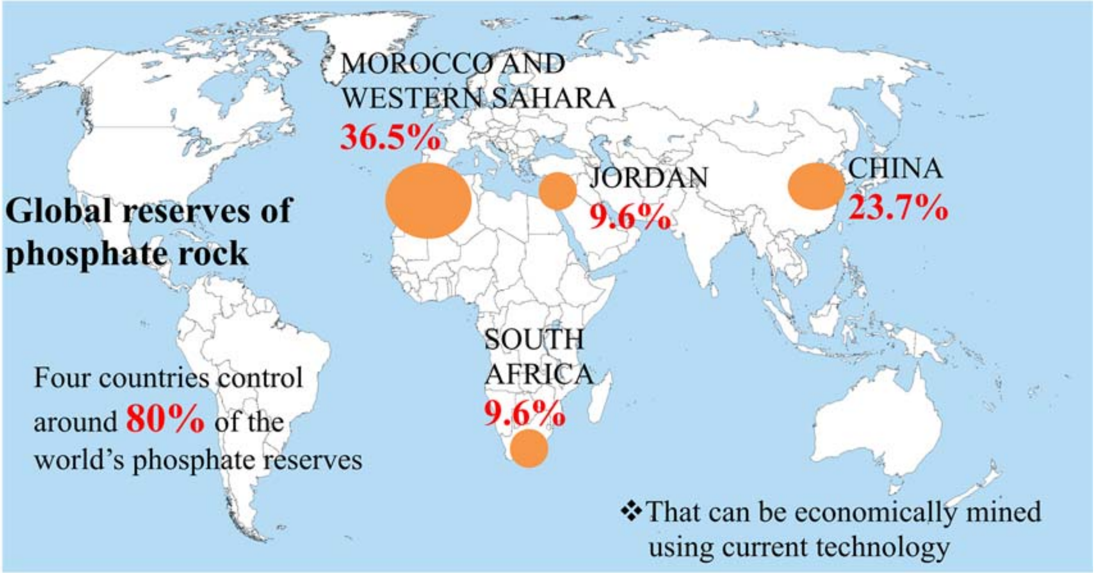

Fig.1.1 The distribution of phosphate reserves in the world

Table 1.1 indicates various estimates of the lifetime of reserves by different authors. Note that the term reserves pertain to the amounts that are currently considered economically and technically recoverable, and these amounts are smaller than total resources.

Approximately 90% of all phosphate demand is for food production- primarily for the production of agricultural fertilizer (82%) and a smaller fraction for animal feed additions (7%) and food additives (1-2%). The remaining 9% goes to industrial uses such as detergents and metal treatment and other industrial applications. The fraction used for detergents has decreased in recent years due to regulations in many countries in response to phosphate pollution of surface water which causes eutrophication, algae blooms, poor water quality and fish kills. With efficient flocculation steps in sewage treatment plants, it is possible to retain for potential reuse most of the phosphate originating from detergents.

Table 1.1 Estimate of availability of remaining phosphate rock reserves

Author	Estimated lifetime of reserves	Lifetime assumptions
Steen [7]	60-130 years	2-3% increase demand rates, most likely 2% increase until 2020 and 0% growth thereafter if efficiency and reuse measures are implemented
Smil [8]	80 years	At current rate of extraction
Smit et al. [9]	69-100 years	Assuming 0.7-2% increase until 2050, and 0% increase after 2050
Vaccari [10]	90 years	At current rates
Fixen [11]	93 years	At 2007-2008 production rates

1.4 Pollution of excess discharge of phosphate compounds to natural water bodies

Because more and more phosphate compounds have been discharged into natural water bodies, it results in many environmental problems which make many economic losses to our society, especially for algal blooms and eutrophication.

An algal bloom is a rapid increase or accumulation in the population of algae in an aquatic system, and this phenomenon can be found in freshwater as well as marine environments. There is a growing awareness that harmful blooms of cyanobacteria and planktonic protists, known as harmful algal blooms (HABs), have increased globally with serious implications for human health and economy.

There are two possible mechanisms which can explain the formation of HABs:

1. Toxic compounds defend a planker against pathogens, parasites or predators.

2. Active release of toxins may inhibit the growth or survival of competing series. [12]

When phosphates are introduced into water systems, higher concentrations cause growth of algae and plants. Algae tend to frow very quickly under high nutrient availability, but each alga is short-lived result in decay of dead organic matter. The decay process consumes dissolved oxygen in the water and makes hypoxic conditions. This phenomenon will endanger the water quality for animals and plants.

Eutrophication or more precisely hypertrophication, is the ecosystem response to the addition of artificial or natural materials, such as nitrates and phosphates, through fertilizer or sewage to an aquatic system shown in Table 1.2. [13] This phenomenon is usually found in lakes, rivers and ocean waters

Table 1.2 Causes and Effects of Eutrophication

Causes	• Natural run-off of nutrients from soil and weathering of rocks • Run-off of inorganic fertilizer • Run-off of manure from farms • Run-off from erosion • Discharge of detergents • Discharge of partially treated or untreated sewage
Effects	• Increase in plant and animal biomass • Increase in growth of rooted plants • Increase in turbidity of water • Increase in rate of sedimentation • Development of anoxic conditions • Decrease in species diversity • Change in dominant biota • Increase in the frequency of algal blooms

1.5 Phosphorus removal from wastewater by activated sludge

Generally speaking, phosphorus can be removed from three directions: physical treatment, chemical treatment and biological treatment. Nowadays, biological treatment has been mainstream method and widely applied in the world shown in Fig.1.2.

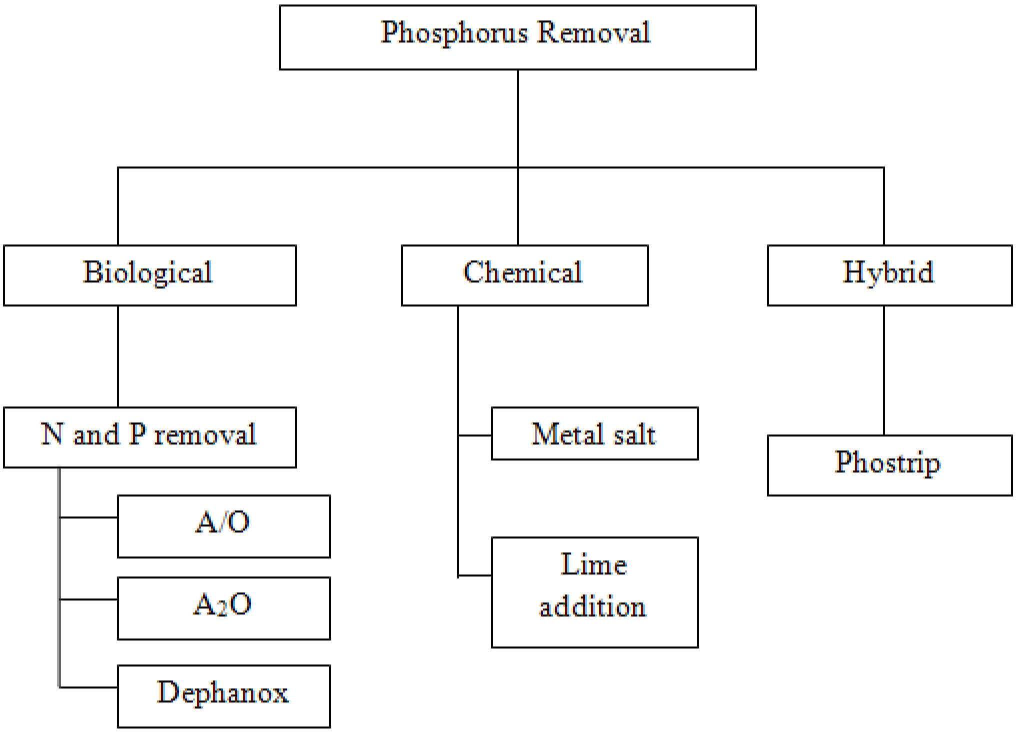

Fig.1.2 Overview of phosphorus removal processes

Phosphorus removal from wastewater has long been achieved through biological assimilation – incorporation of the P as an essential element in biomass, particularly through growth of photosynthetic organisms (plants, algae, and some bacteria, such as cyanobacteria).

The common element in EBPR implementations is the presence of an anaerobic tank prior to the aeration tank. Under this condition, a group of heterotrophic bacteria, called poly-phosphate-accumulating organisms are selectively enriched in the bacterial community within the activated sludge. This process can accumulate more poly-P inside the cells thus the removal of phosphorus is said to be enhanced.

Mino et al. [14] introduced microbiological and biochemical aspects of the enhanced biological phosphate removal process. They discussed microorganisms responsible for EBPR, isolation of poly-P accumulating organisms and micro diversity of the EBPR sludge.

1.6 Methods of phosphorus recovery

There is still a long way to go to achieve a sustainable society. One aspect of sustainability is to economize with scarce resources. The known reserves of phosphorus are estimated to last 100 years with present utilization rate. The interest in recovery and reuse by sludge fractionation has increased in recent years, largely due to environmental and political considerations.

Methods to recover phosphorus from wastewater treatment plant:

In general, there are two possibilities to recover phosphate from municipal wastewater [15, 16];

- Recovery in wastewater treatment
- Recovery from produced sludge

Supercritical Water Oxidation (SCWO) is an innovative and effective destruction method for organics in sewage sludge. The SCWO process leaves slurry of inorganic ash in a pure water phase free from organic contaminants, which opens possibilities for a simple process to recover components like phosphates and/or coagulants from the sewage sludge, a process marketed as the Aqua Reci [17].

Stark and Hultman [18] present solutions of advanced technology system for a large wastewater treatment plant. This method has advantages because of use of enhanced biological phosphorus removal and fractionation of the sludge in two stages, thus it needs low necessary chemical, energy demands and recovery efficiency.

Svanström et al., [19] shown that the life cycle assessment (LCA) of a SCWO processing of sewage sludge is strongly dependent by the surrounding of the actual SCWO unit.

Another method to recover phosphorus from sludge is KREPRO [20].Because of lower phosphorus recovery demand, the project was postponed in 2002. Estimated investment cost in 1999 was 7.3 MEUR for the process. Full-scale experiments were conducted, producing ferric phosphate and tests show that its product has considerable fertilizing effect [21].

In contrast to this a study performed in Norway by Krogstad et al. [22] showed Fe rich sludge had the most negative value for plant uptake.

Another interesting method looked into is, for instance, Sulphate reducing bacteria (SRB) could effectively be used for phosphates release from Fe-P sludge [23].

Kuroda et al. [24] introduced a new method which can release most of poly-P saved inside the microorganism into liquid phase by thermal treatment. This method had very good performance on the release of poly-P with cultivated sludge in the lab; nearly 90% poly-P and 87% T-P can be released into liquid phase by heating at 70˚C for 60 minutes. In the precipitation process, most poly-P can be precipitated with Ca in neutral condition.

1.7 Objectives and Structure of this dissertation

Because abundant poly-P can be released into liquid phase from cultivated sludge by thermal treatment at low temperature, and compared with conventional methods for phosphorus recovery by Pi, poly-P can precipitate with Ca^{2+} in neutral condition, this is obvious advantage. Thus in this dissertation, the performance of activated sludge in WWTP by thermal treatment was observed.

Objectives:

1. Release phosphate especially for poly-P from sewage sludge collected in WWTP as much as possible during thermal treatment.

2. Find the parameters which can affect the poly-P release from sewage sludge in thermal treatment and identify the mechanism.

3. Recover poly-P with Mg and ammonium as struvite because N and P are both nutrient elements for plants.

Main structure of dissertation was shown in Fig.1.3:

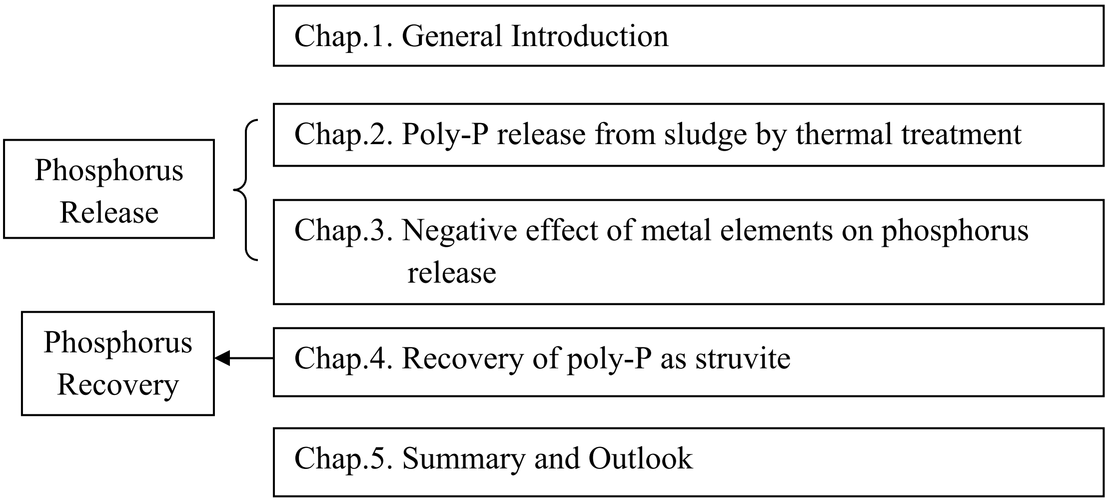

Fig.1.3 Structure of dissertation

1.8 Conclusions

Phosphorus element is an irreplaceable element to all lives in the world; it can be found in nature with different forms of existence. Phosphate compounds are widely used in agriculture as fertilizer and industry.

In recent years, increasing demand of phosphate compounds and uneven distribution in the world results in phosphorus shortage crisis. Therefore, price of phosphate rocks increases all the time. This makes lots of economic press to these countries which imports abundant phosphate rocks from world market, especially for Japan, nearly 100% phosphate rocks is imported.

On the other hand, excess discharge of phosphate compounds into natural water bodies has induced many environmental problems like algae blooms and eutrophication. This makes lots of economic losses to our society.

Activated sludge can accumulate most phosphorus existed in the waste water. In recent years, enhanced biological phosphorus removal technique is widely applied in many wastewater treatment plants all over the world.

It has very good performance and high efficiency to remove phosphorus in waste water.

Because activated sludge can accumulate abundant phosphate inside bodies, many researchers are trying different methods to recover phosphorus from wastewater and sludge.

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Chapter 2

Chapter 2 Poly-Phosphate and Ortho-phosphate Released from Sewage Sludge by Thermal Treatment

Abstract

In this chapter, the performance of phosphorus removal from wastewater by activated sludge will be briefly introduced. Similar research in the world will also be reviewed. Kuroda et al. [1] introduced a new method which can release most of poly-P saved inside the microorganism into liquid phase by thermal treatment at low temperature with cultivated sludge, and most poly-P can precipitate with Ca in neutral condition.

In this study, practical activated sludge collected from waste water treatment plant (WWTP) had been tested. In my research, 30% poly-P and 29% T-P could be released from sludge by heating at 70˚C. Different kinds of pretreatments had been tested to improve phosphorus release from activated sludge in thermal treatment; addition of chelating reagent at final concentration of 2 mM before thermal treatment could improve the phosphorus release obviously, 68% poly-P and 53% T-P could be released into liquid phase. Approximately 85% T-P could be precipitated with calcium at pH 11; it was interesting to find nearly 50% precipitation occurred in neutral condition without pH adjustment.

Keywords: temperature, heating time, thermal treatment, release

2.1 Introduction

As we known, heat treatment has been used to reduce volume of excess sludge as pretreatment because excess sludge presents a serious problem. In the temperature range from 40 to 180 ˚C [2, 3], the carbohydrates and the lipids of the sludge can be degraded easily, the proteins are protected from the enzymatic hydrolysis by the cell wall. Thermal pre-treatment in the low temperature range from 60 to 180 ˚C destroys the cell walls and makes the proteins accessible for biological degradation. The input of thermal energy is mostly realized by heat exchangers or by application of steam to the sludge.

Brooks [4] observed solubilization of organic matter from samples of waste activated sludge (WAS) in the order of 40-60% and a mixture of primary sludge in the order of 20-35%, respectively, when the treatment temperature is 170˚C. The highest yield of hydrolysis with municipal sewage sludge in experiments shows that can be achieved at 165–180˚C. The heating time (10–30 min) has little influence on the result. The dissolved components are readily degradable in a digestion process. In addition the dewaterability is increased [5].

The effect of high temperature on treatment of sewage sludge had been reported by Fisher and Swanwick [6]. In their research, a wide range of sludge dewaterability was improved at temperatures above 150˚C. The effect which temperature was above 180˚C became more pronounced. Unfortunately the formation of refractory COD compounds had been found in their work (the chemical oxygen demand (COD) is the amount of oxygen required to chemically destroy the organic compounds of wastewater). As part of the study they looked at some selected liquors and concluded that about a third of the liquor COD was not treatable [5].

The effect of heat treatment at lower temperatures to combine some of the benefits of dewaterability with improved digestibility and at the same time avoid the problems that occurred with higher temperature heat treatments had been researched by Haug and co-workers [7–9]. They showed that it was possible to obtain an improvement in dewaterability of undigested and digested sludge and that the temperature of 175˚C was about the limit for digestibility before digestion was inhibited (presumably because of the formation of inhibitory and/or refractory compounds) [5].

They showed that the largest effect on digestibility was for activated sludge but that all sludges tested dewatered better at 175˚C. At that temperature, digestion of the thermally pre-treated sludge resulted in an increase of 60–70% in methane production over not pre-treated sludge. Higher temperatures resulted in decreased gas production. Thermal hydrolysis as pre-treatment has hence given very good results on digester performance. The homogenization of the material goes further than in a mechanical process. The total surface of the particles is significantly increased, enhancing biological degradability [5].

From these literatures, we can find that thermal treatment will make some damage to the cell wall or membrane to sludge cells which means intracellular materials can be released into outside. It provides the potential possibility to release phosphorus inside cells by thermal treatment.

Kuroda et al. [1] researched the possibility of phosphorus recovery from cultivated sludge by heating. This method had very good performance on the release of poly-P with cultivated sludge in the laboratory; nearly 90% poly-P and 87% T-P can be released into liquid phase by heating at 70˚C after 60 minutes.

Because of the digestion process in waste water treatment plant (WWTP), the generated heat energy and inflammability gas can be used to satisfy energy demand in thermal treatment for the purpose of phosphorus release. If most poly-P can be released into liquid phase by thermal treatment at low temperature, and recovered with Ca at pH 7.5, it has a glorious prospect for application.

Therefore activated sludge collected from WWTP which used enhanced biological phosphorus removal (EBPR) technique to remove the phosphorus from wastewater had been tested with thermal treatment at low temperature in this study. To improve the phosphorus release from the sewage sludge, some pre-treatments had been used. Whether the mixture of poly-phosphate and ortho-phosphate can be precipitated with Ca at pH 7.5, the result was shown in this chapter.

2.2 Experiment

2.2.1 Experiment materials

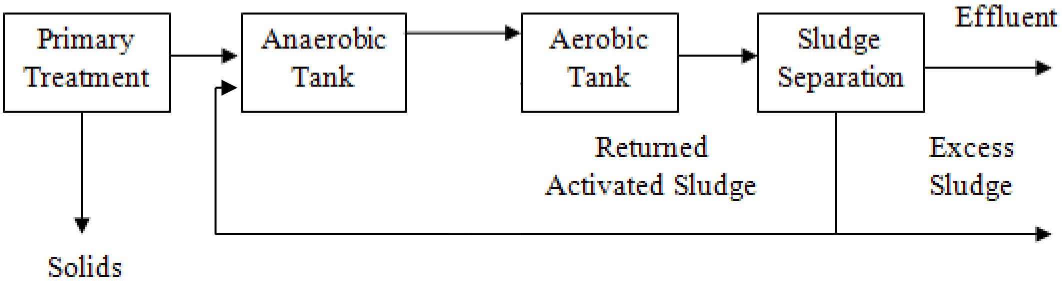

Fig.2.1 Main treatment process in WWTP

Activated sludge used in this research was collected from the aeration tank of WWTP in Fukuoka, Japan, which used anaerobic-aerobic (A/O) technique to remove phosphorus in the wastewater shown in Fig.2.1. Before the experiment, the sludge had been settled for 20 minutes and the mixed liquor suspended solids (MLSS) of settled sludge maintained at 4000-4500 mg·L^{-1}.

2.2.2 Pretreatments

Four kinds of the sludge samples had been prepared:

A. with centrifugation at 3000rpm for 5 minutes, the supernatant was instead of de-ionized water and then mixed de-ionized water with sludge by vortex oscillator, this sample was named as “cleaning sample”;

B. pH of suspending liquid was adjusted to 3 by addition of hydrochloric acid, named as “acid sample”;

C. pH of suspending liquid was adjusted to 10 by addition of sodium hydroxide, named as “alkaline sample”;

D. EDTA was inputted into suspended liquid at final concentration of 2 mM, named as “chelating sample”.

2.2.3 Thermal treatment and precipitation of Ca and P

The sludge samples were distributed into 10-mL test tubes and incubated in the thermostatic water baths which were used for providing constant temperature environment. The tubes were taken outside from the water bath every 20 minutes in 2 hours. The temperature was chosen at 50˚C, 60˚C, 70˚C, 80˚C. After the incubation in the water baths, the supernatant was separated from sludge sample by centrifugation at 3000rpm for 5 minutes and analyzed for the concentration of Pi, poly-P and T-P. The precipitation of phosphorus was studied by adding $CaCl_2$ into the supernatant at final concentration of 100 mM without pH adjustment and with pH adjustment to make the comparison.

2.2.4 Analytical methods

Pi was determined by ascorbic acid method; Intracellular Pi was extracted from the sludge biomass by cold 10% trichloroacetic acid solution. Poly-P was determined by heating in the autoclave for 30 minutes in acid condition. T-P was determined by persulfate digestion method [10].

Energy dispersive X-ray (EDX) (EDX-800, shimadzu) had been used to analyze the element quantity near the surface of sludge with an accelerating voltage of 20 kilovoltage. Sludge samples were washed by phosphate buffer solution at pH 7.2 and fixed by 2.5% glutaraldehyde for 2 hours. Samples were washed again by phosphate buffer solution, and then fixed by 1% osmic acid for 2hours. After this step, samples were dehydrated with series gradient ethanol (30%, 50%, 70%, 85%, 95% and 100%) then coated with lead by ion-coating instrument (JFC-1600, JEOL).

Inductive coupled plasma atomic emission spectrometry (ICP-AES) (Optima 5300dv, PerkinElmer) was applied to analyze the species and quantity of metal elements existed in the supernatant. Standard solution should be configured and pH of samples should be adjusted into weak acid condition.

2.2.5 Metal elements in Extracellular Polymeric Substances (EPS)

Because extracellular polymers can bind soluble metal [11], EPS (which are biosynthetic polymers from prokaryotic and eukaryotic microorganisms, which either form (loose or tight) slimes around the microbial cells or excreted as discrete gels to the surrounding environment) had been separated from sludge samples. 10 mL sludge sample was treated by EDTA (2%; at 4˚C for 3 h) [12]. Microbial cells and low molecular-weight metabolites maybe also can absorb metal, so membrane which can remove these materials didn't be used in this experiment. After the extraction, elements in the supernatant were analyzed by ICP-AES.

2.2.6 Metal elements inside cells

With enough agitation, 100 ml sewage sludge sample was inputted into the glass beaker, and then 1ml nitric acid and 0.5 ml hydrochloric acid were added into the sample before heating. The glass beaker was placed on the heating panel, stopped heating until the volume of sample condensed to 10-15 ml. When the sample cooled off, it was removed into 100 ml volumetric flask and diluted to 100ml with distilled water. After centrifugation at 3000 rpm for 10 minutes, supernatant was divided and filtered by glass filter with 1 μm aperture. Finally, it was analyzed by ICP-AES instrument.

The whole experiments were shown in Fig.2.2.

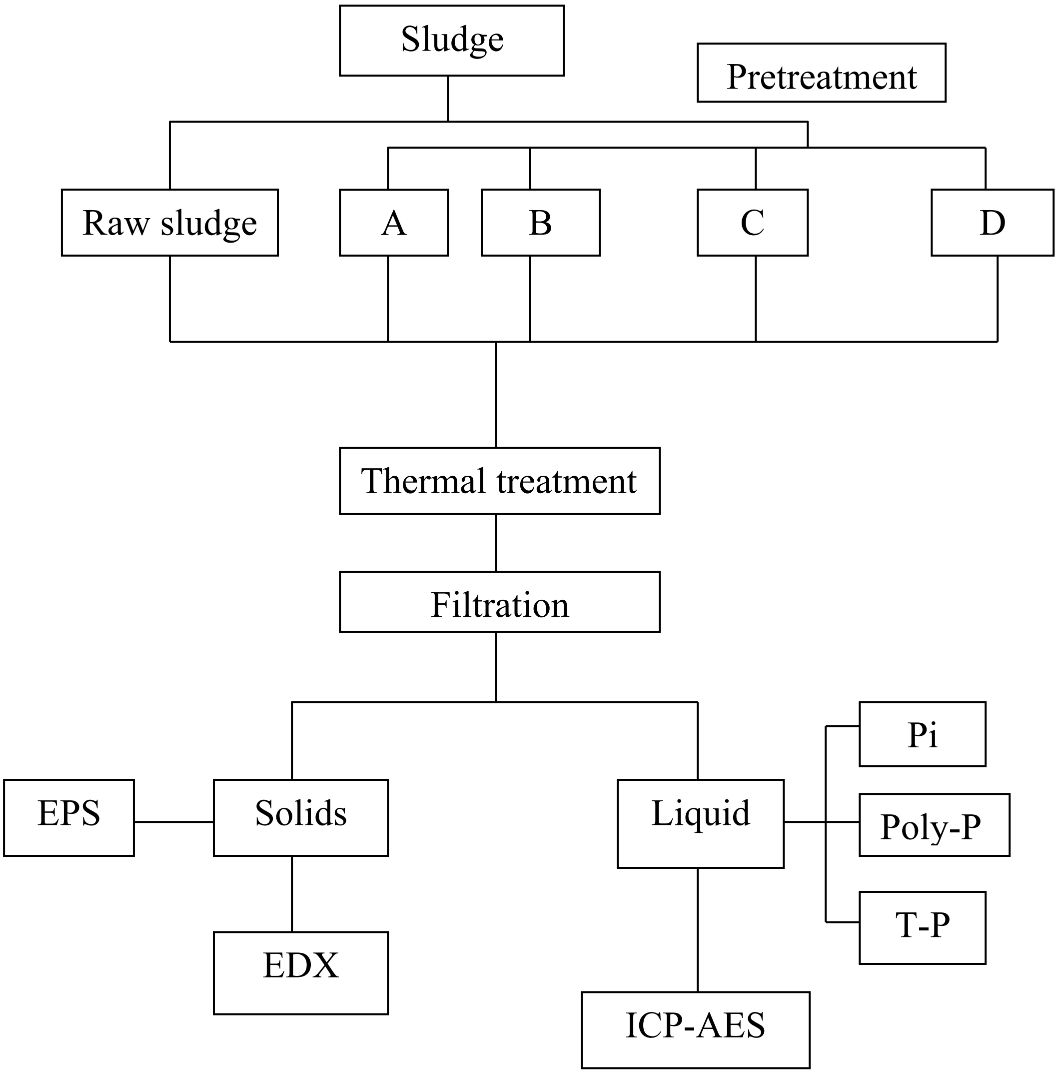

Fig.2.2 Experiment process in this study

2.3 Results

2.3.1 The effect of time and temperature on the release of poly-p in thermal treatment

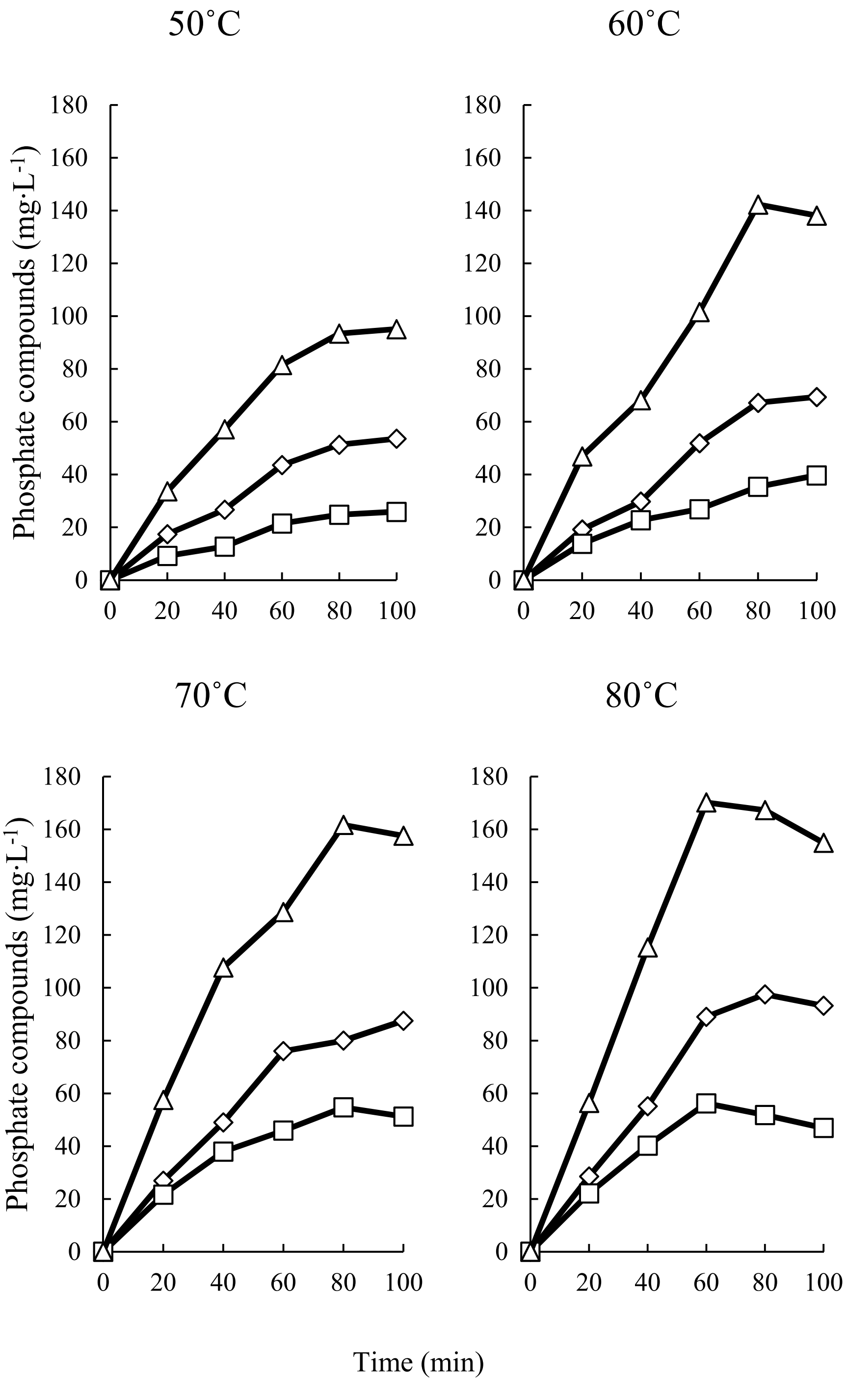

Fig.2.3 Phosphorus was released from sewage sludge in the thermal treatment at different temperature ranged from 50˚C to 80˚C. The concentrations of Pi (rhombus), poly-P (rectangle) and T-P (triangle) are analyzed

In order to find the influence of temperature and heating time on the phosphorus release, different temperature and heating time had been tested in this study. The performance of phosphorus release from sludge in thermal treatment was shown in Fig.2.3. With the increase of temperature, more T-P can be released into liquid phase. When temperature was higher than 50˚C, increase of phosphorus release was obvious, but the increase of phosphorus release could be negligible when temperature was higher than 70˚C, meanwhile, more poly-P can be released at high temperature, but there was a contradictory that higher temperature and longer heating time would induce the hydrolysis of poly-P. Thus 70˚C and 80 minutes were optimal parameters for phosphorus release by taking these factors into account.

2.3.2 The effect of pretreatments on the release of poly-P in the thermal treatment

In order to increase the release of poly-P and T-P, the sludge samples had been treated before the thermal treatment as shown in Fig.2.4. Cleaning sample (A) didn't have good performance on the release of poly-P compared with raw sludge samples without any pretreatment. Acid sample (B) had no different performance compare with raw sludge sample even a little decrease release of poly-P because poly-P was unstable in acid condition. Alkaline sample (C) had better performance because of 20% increase about poly-P release. It was very worth noting the chelating sample (D) had very good performance on release of poly-P compared with the raw sludge sample without any pretreatment, it nearly increased 100% release of poly-P shown in Fig.2.4.

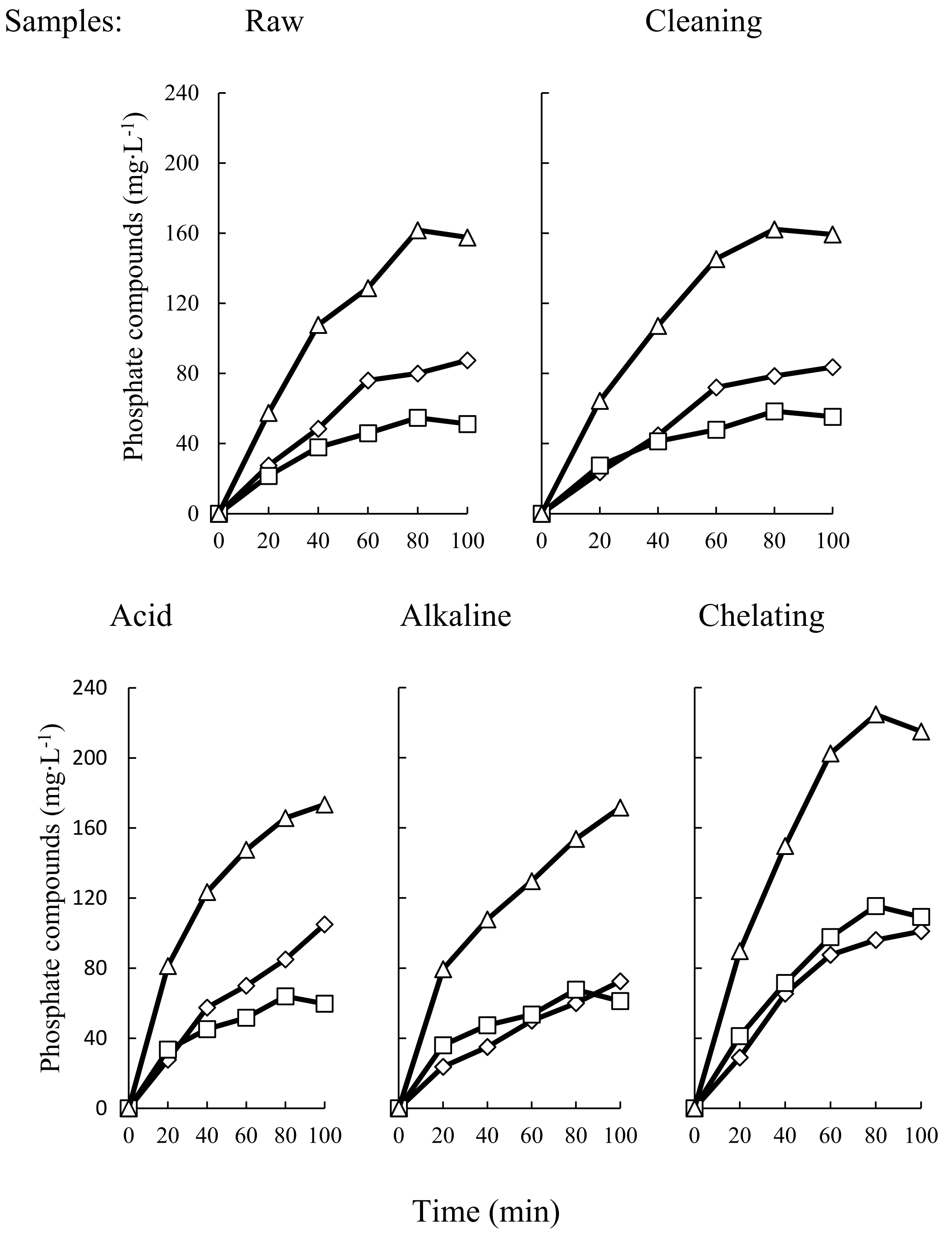

Fig.2.4 Phosphorus was released from sewage sludge in the thermal treatment at 70˚C with different kinds of pretreatments. The concentrations of Pi (rhombus), poly-P (rectangle) and T-P (triangle) are determined by the analytical methods

2.3.3 Different forms of phosphorus saved inside cell

Fig.2.5 depicted the performance of thermal treatment on releasing phosphorus from activated sludge. The activated sludge (1) working in the aeration tank can accumulate approximately 13% T-P as their dry weight because of EBPR technique. Activated sludge can accumulate large amounts of poly-P (approximately 6.5-7.4% as their dry weight). Sewage sludge (2) can release 30.0% poly-P and 28.8% T-P into liquid phase after the thermal treatment. With the addition of chelating reagent (EDTA) before thermal treatment, sludge sample (3) can release 67.5% poly-P and 52.5% T-P into liquid phase.

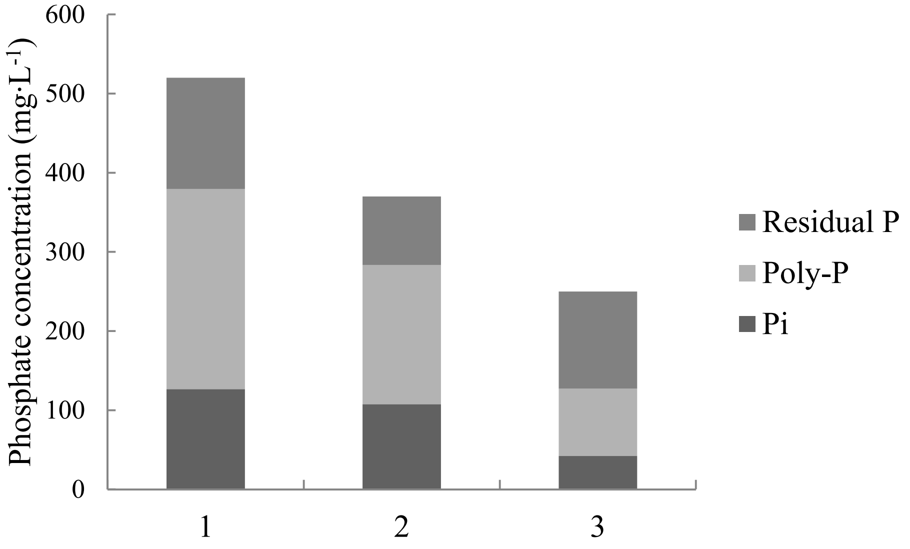

Fig.2.5 Different forms of phosphorus saved in activated sludge which taken from raw sludge sample (1), sludge sample after thermal treatment (2) and sludge sample which be added with EDTA at final concentration 2mM then heated (3) had been analyzed

2.3.4 The composition of elements near the surface of sludge biomass

The elements near surface of cells before the thermal treatment had been analyzed by EDX. The spectra of EDX showed the presence of various elements near the surface of bacteria. Every kind of elements can be distinguished by the peaks at characteristic spectra.

Table 2.1 The distribution of metal elements near the surface of sludge biomass shown as atom% by EDX

Element	a	b	c
Fe	3.33	3.25	2.76
Na	28.32	21.55	25.56
Mg	1.09	2.30	2.03
Al	5.90	5.91	7.00
Si	9.38	11.14	10.29
P	39.59	43.74	37.29
S	3.58	6.06	4.84
K	0.46	0.32	0.59
Ca	1.49	1.04	2.09
Cu	4.02	2.60	3.38
Zn	2.83	2.10	4.08

a-sewage sludge; b-sewage sludge after thermal treatment; c-sewage sludge after thermal treatment with addition of EDTA.

Strong signals had been obtained for P, Na, Si, Cu; weak signals for Fe, Mg, Al, K and Ca had been detected in Table 2.1. Through the comparison of atom percentage of elements near the surface of sludge biomass before (a), after the thermal treatment (b) and with the addition of EDTA (c), it was worth noting that the quantity of phosphorus increased from 39.59% to 43.74% after the thermal treatment, but with the addition of EDTA, it decreased from 39.59% to 37.29% shown in Table 2.1. The addition of EDTA before the thermal treatment made this difference.

2.3.5 Elements existed in liquid phase

By comparing data before and after thermal treatment, the elements released into supernatant during the thermal treatment can be found. Many kinds of elements existed in the wastewater (data not shown), but the attention had been paid on alkaline and transition elements as Al, Ca, Fe and Mg which can combine with P. The results of ICP-AES were shown in Fig.2.6. Metal elements such as Al, Ca and Fe couldn’t be released into liquid phase obviously by thermal treatment except Mg. When chelating reagent EDTA was inputted into sludge samples before thermal treatment, the release of elements Al and Fe increased 274% and 358% respectively after thermal treatment compared with the samples before thermal treatment.

The origin of metal elements had been analyzed by EPS extraction and cell lysis shown in Table 2.2. Most phosphorus was saved inside the cells, but there is a small part of phosphorus saved near the surface of cells. A large quantity of Mg and Al was existed in the wastewater, especially, little Ca was saved inside the cells. The quantity of heavy metal such as Cu and Zn saved inside the cells can be negligible.

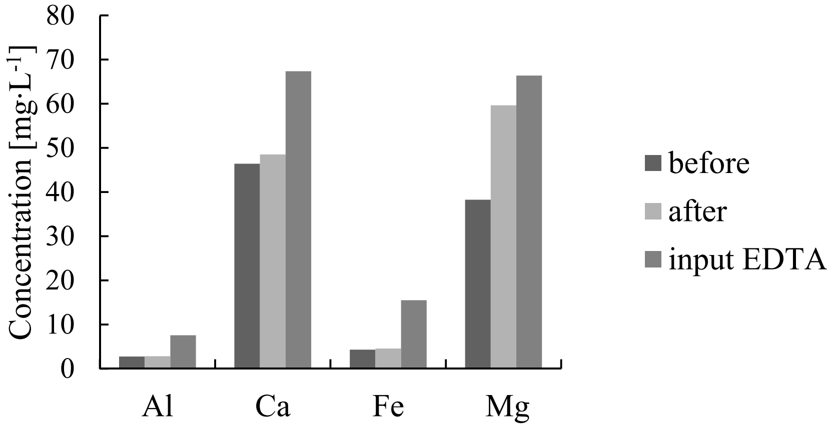

Fig.2.6 Metal elements existed in supernatant before thermal treatment ("before"), after the thermal treatment ("after") and after thermal treatment with the addition of chelating reagent EDTA ("input EDTA") had been analyzed

Table 2.2 The distribution of metal elements in raw sludge flocs

Position / Elements	Wastewater [mg·L^{-1}]	Near surface of sludge cell [mg·L^{-1}]	Inside sludge cell [mg·L^{-1}]
P	6.60	34.59	108.31
Al	3.43	0.65	2.57
Mg	20.19	4.10	18.62
Ca	27.00	17.60	1.06
Fe	2.72	2.39	3.55
Cu	3.23	0.02	0.16
Zn	2.74	0.35	0.16

2.3.6 The precipitation of phosphorus and calcium

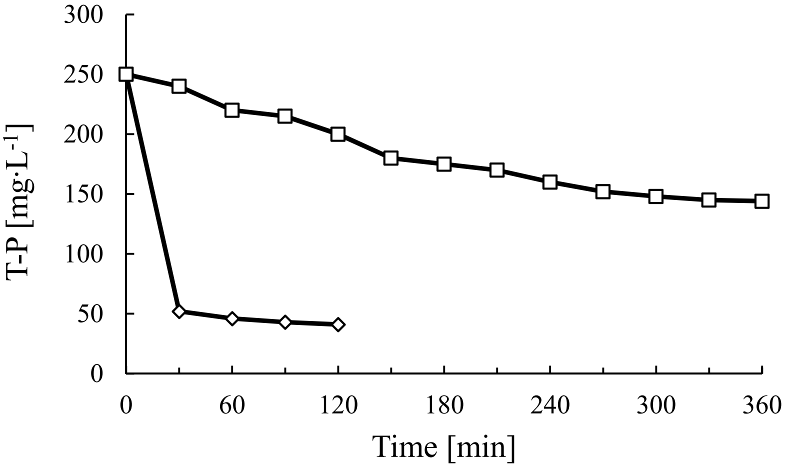

Fig.2.7 The precipitation of P and Ca without pH adjustment (rectangle) and at pH 11 (rhombus). $CaCl_2$ was inputted into the supernatant separated from sludge sample with addition of EDTA, which was obtained from the sludge samples after thermal treatment by centrifugation at a final concentration of 100mM

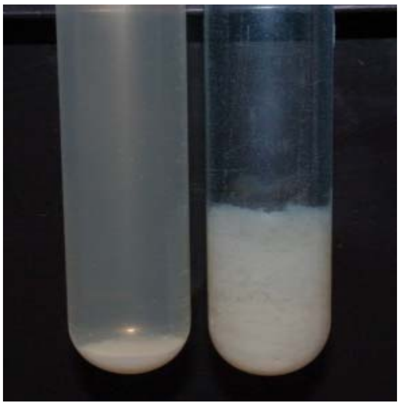

Fig.2.8 Phosphates can precipitate with Ca^{2+} without pH adjustment shown in the left test tube; nearly total phosphorus can be precipitated with Ca^{2+} at pH 11 shown in the right test tube

After the thermal treatment, $CaCl_2 \cdot 2H_2O$ was inputted into the supernatant separated from sludge sample with addition of EDTA at the final concentration of 100mM. The precipitation can be observed immediately at pH 11 and the precipitation process nearly ceased after 40 minutes, most of phosphorus in the supernatant can be precipitated shown in Fig. 2.7 and Fig. 2.8, but a little precipitation can be observed in the supernatant without pH adjustment. Oppositely, 75% T-P can be precipitated in 2 hours without pH adjustment in Kuroda's research [1], he emphasized that the Ca-P precipitation was significantly influenced by the concentration of poly-P in the supernatant.

2.4 Discussion

2.4.1 Phosphorus release from sewage sludge

Temperature and heating time are very significant for the release of phosphorus from sewage sludge. Higher temperature and longer heating time can release more phosphorus into liquid phase, but poly-P is not stable at high temperature, it will be hydrolyzed into Pi. Consideration for existence of poly-P and energy saving, 70˚C and 80 minutes are recommended for the thermal treatment by using activated sludge collected from WWTP.

Kuroda et al. [1] said approximately 90% of Poly-P saved in the cultivated sludge was released into the liquid phase by 60 min at 70˚C and about 87% of T-P was released by heating at 70-90˚C. However, only 30% poly-P and 29% T-P could be released into liquid phase from activated sludge by heating at 70˚C for 80 minutes in this study, shown in Fig.2.4. The source of sludge samples possibly resulted in the obvious difference. With cultivated sludge in lab, only necessary metal elements and nutrients for living activities should be added into liquid phase, but wastewater includes many kinds of organic, inorganic materials and metal elements shown in Table 2.2, even though toxic materials, the living condition for sewage sludge is more complicated than the cultivated sludge. In Fig.2.5, nearly 50% of T-P in activated sludge was poly-P; this was very different observed in Kuroda's cultivated sludge, most of T-P was poly-P in their research thus more poly-P can be released into outside during thermal treatment.

Because of this low release extent, some kinds of pretreatments had been tested shown in Fig.2.4. The increase of phosphorus release from cleaning sample can be negligible; this suggested the soluble materials in the wastewater possibly can't make the negative effect on the phosphorus release during the thermal treatment or the materials which can prevent the phosphorus release had been absorbed by the activated sludge. The acid and alkaline samples had better performance because of 20% increase about Poly-P release, but poly-P would be hydrolyzed in acid condition. Moreover acid and alkaline supernatant should be treated before the discharge, this method can't be recommended. Chelating reagent like EDTA had very good performance on the poly-P release during the thermal treatment. EDTA is usually used to sequester metal cations in industry, thus the metal cations must be the significant factor for the phosphorus release from sewage sludge during the thermal treatment.

2.4.2 The effect of metal elements on phosphorus release from sewage sludge in thermal treatment

The kinds of metal elements which can be released into liquid phase can be distinguished by ICP-AES. The release of Al, Ca and Fe from sewage sludge can be negligible during thermal treatment, but with the addition of EDTA, these elements can be released into liquid phase obviously shown in Fig.2.6. Poly-P complexed by divalent metals such as Ba^{2+}, Pb^{2+} and Mg^{2+} are poorly soluble. The low solubility of these complexes possibly causes the precipitation inside the poly-P granules inside the cell [13]. These metal elements existed in the poly-P granules have been demonstrated by the use of energy dispersive analysis of X-rays (EDX). On the other hand, metal phosphates are highly insoluble and will precipitate on the cell surface of activated sludge [14, 15]. The hydrolysis of poly-P in thermal treatment may promote the precipitation of metal phosphates on the cell surface. These precipitated phosphates possibly can't be easily released into liquid phase only by thermal treatment. With the addition of chelating reagent as EDTA, the metal elements which can precipitate with poly-P or Pi can be sequestered by EDTA and poly-P anions can be easily released into liquid phase by heating. The assumption may explain the phenomenon activated sludge treated by

EDTA can release more phosphorus into liquid phase after thermal treatment.

2.4.3 Precipitation of poly-P and Pi with Ca

Fig.2.7 depicted different process of P and Ca in neutral condition and at pH 11. Higher pH condition could improve precipitation speed and precipitation quantity. But in conventional research, we couldn't find so much precipitation (nearly 50%) with Pi and Ca^{2+} in neutral condition. Poly-P existed in the supernatant possibly promote the precipitation in neutral condition. But in Fig.2.8, suspended white micro precipitant can be found and it couldn't settle down with gravity. This means the size of precipitant was not big enough.

2.5 Conclusions

With the comparison of cultivated sludge, only 30% poly-P and 29% T-P can be released into liquid phase after thermal treatment at 70˚C for 80 minutes from sewage sludge collected from WWTP. Different characteristics of cultivated sludge and sewage sludge possibly induce the different performance about phosphorus release. In order to improve poly-P release, kinds of pretreatments had been used in this study. Chelating reagent had very good performance through comparison.

Because chelating reagent can improve poly-P release obviously, we can assume that metal cations existed in the waste water possibly prevented phosphorus release.

Poly-P can precipitate with Ca in neutral condition had been demonstrated by the precipitation experiment. But compared with the performance at high pH condition, quantity of precipitant was not abundant and lots of micro white precipitant suspended in the liquid phase; but little precipitant can be found by conventional method with ortho-phosphate, this may illustrate the advantage of poly-P about recovery.

2.6 References

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Chapter 3

Chapter 3 Impediment of Metal Cations on the Phosphorus Release from Sewage Sludge during Thermal Treatment

Abstract

In chapter 2, sewage sludge collected from a WWTP released less poly-P and T-P into liquid phase compared with cultivated sludge. Nearly 90% poly-P and 87% T-P can be released into liquid phase from the cultivated sludge by heating at 70˚C after 60 minutes, but only 30% poly-P and 29% T-P can be released into liquid phase after thermal treatment at 70˚C for 80 minutes from sewage sludge collected from the WWTP.

In this chapter, parameters which would affect phosphorus release during thermal treatment would be tested, and the mechanism of interference about phosphorus release by metal cations would also be discussed.

The purpose of this chapter was aimed at identifying the influence of metal cations like Mg^{2+}, Ca^{2+}, Al^{3+} and Fe^{3+} on poly-P and T-P release from sewage sludge collected from the WWTP during thermal treatment. With addition of chelating reagent as EDTA, release of poly-P and T-P was improved obviously during thermal treatment. Inhibitory effect of metal cations on phosphorus release was apparent by adding each metal cation into sludge sample respectively. Most of released Ca, Al and Fe from inner of cell were concentrated in extracellular polymer substance (EPS); oppositely, large quantity of Mg could be released into liquid phase and not concentrated in EPS. Performance of sewage sludge on phosphorus release in summer and winter was different; precipitation and temperature possibly result in this phenomenon.

Keywords: metal cations, chelating reagent, mass conservation, impediment

3.1 Introduction

The complexity of the microorganism's structure implies that there are many ways for the metal to be captured by the cell. Biosorption mechanism is therefore various and in some cases they are still not very well understood. They may be classified by the following different criteria [1].

According to the dependence on the cells' metabolism, biosorption mechanisms can be divided into:

1. Metabolism dependent;
2. Non-metabolism dependent.

According to the location where the metal removed from solution is found biosorption may be classified as:

1. Extracellular accumulation/ precipitation;
2. Cell surface sorption/ precipitation;
3. Intracellular accumulation.

In the case of physicochemical interaction between the metal and functional groups of the cell surface, based on physical adsorption, ion exchange and complexation. Cell surface of microbial biomass, mainly composed of polysaccharides, proteins and liquids, offers particularly abundant metal-binding functional groups, such as carboxylate, hydroxyl, sulphate, phosphate and amino groups.

In the case of precipitation, the classification is not unique. In fact the precipitation of the metal may take place both in solution and on the cell surface [2]. Furthermore, it may be dependent on the cells' metabolism if, in the presence of toxic metals, the microorganism produces compounds which favour the precipitation process. On the other hand, precipitation may not be dependent on the cells' metabolism, occurring after a chemical interaction between the metal and the cell surface.

Limited basic metal salts would be provided to cultivated sludge, but activated sludge in municipal wastewater would adsorb many kinds of metal ion because of the biosorption activity. This may resulted in the different performance on phosphorus release during thermal treatment with these two kinds of sludge samples.

The purpose of this chapter is to identify the effect of kind and concentration of chelating reagent on the poly-P release from sewage sludge during thermal treatment. In order to study the impediment effect of every kind of metal elements on poly-P release, each kind of metal element had been artificially added into sludge sample to check respective impediment effect on poly-P release. Finally, movement of metal cations at different positions of sludge biomass (inner of cell, EPS and outside of cell) had been researched by series experiments.

3.2 Experiment

3.2.1 Thermal treatment

Activated sludge used in this research was collected from the aeration tank of WWTP in Fukuoka of Japan, which used anaerobic-aerobic (A/O) technique to remove phosphorus from the wastewater. Before the experiment, the sludge had been settled for 20 minutes and the mixed liquor suspended solids (MLSS) of settled sludge maintained at 3500-4000 $mg\cdot L^{-1}$. The sludge samples were distributed into 10-mL test tubes and incubated in the thermostatic water baths which were used for providing constant temperature environment. After incubation in the water baths at 70°C for 80 minutes, the supernatant was separated from sludge sample by centrifugation at 3000 rpm for 5 minutes and filtration; then analyzed for the concentration of Pi, poly-P and T-P.

3.2.2 Analytical methods

Pi was determined by ascorbic acid method; Intracellular Pi was extracted from the sludge biomass by cold 10% trichloroacetic acid solution. Poly-P was determined by heating in the autoclave for 30 minutes in acid condition. T-P was determined by persulfate digestion method [3].

Energy dispersive X-ray (EDX) (EDX-800, Shimadzu) had been used to analyze the element species and quantity near the surface of sludge cells with an accelerating voltage of 20 kilovoltage. The sludge samples were washed by phosphate buffer solution at pH 7.2 and fixed by 2.5% glutaraldehyde for 2 hours. The samples were washed again by phosphate buffer solution, and then fixed by 1% osmic acid for 2 hours. At last, samples were dehydrated with series gradient ethanol (30%, 50%, 70%, 85%, 95% and 100%) then coated with lead by ion-coating instrument (JFC-1600, JEOL).

Inductive coupled plasma atomic emission spectrometry (ICP-AES) (Optima 5300dv, PerkinElmer) was applied to analyze the species and quantity of metal elements existed in the supernatant. Standard solution should be configured and pH of liquid samples should be lower than 7.

3.2.3 Addition of different kinds of chelating reagents

In order to find the optimal kind of chelating reagent, four kinds of complexing reagents had been added to the sludge samples before thermal treatment (EDTA, citrate, $Na_2S_2O_3$ and KF) with different concentration ranged from 2 mM to 10 mM.

3.2.4 Extraction of metal elements saved inside Extracellular Polymeric Substances (EPSs)

Because extracellular polymeric substances can bind soluble metal cations [4], EPSs had been separated from sludge samples. 10 ml sludge sample was treated by EDTA (2%; at 4˚C for 3 h) [5]. Microbial cells and low molecular-weight metabolites maybe also can absorb metal cations, thus membrane which can remove these materials were not be used in this experiment. After the extraction and centrifugation, elements in the supernatant were analyzed by ICP-AES.

3.2.5 Metal elements inside the cells

With enough agitation, 100 ml sewage sludge sample was inputted into the glass beaker, and then 1ml nitric acid and 0.5 ml hydrochloric acid were added into the sample before heating. The glass beaker was placed on the heating panel, stopped heating until the volume of sample condensed to 10-15 ml. When the sample cooled off, it was removed into 100 ml volumetric flask and diluted to 100ml with distilled water. After centrifugation at 3000 rpm for 10 minutes, supernatant was divided and filtered by glass filter with 1 μm aperture. Finally, it was analyzed by ICP-AES instrument. Thus, total metal elements in sludge biomass (liquid phase, EPS and inner of cell) can be identified.

3.2.6 Artificial addition of metal elements into sewage sludge

In order to find the effect of every kind of metal elements on phosphorus release in thermal treatment, $MgSO_4$, $CaCl_2$, $Al_2(SO_4)_3$ and $FeCl_3$ had been distributed into the four sludge samples respectively at the same final concentration of 5mM for Mg^{2+}, Ca^{2+}, Al^{3+} and Fe^{3+}.

3.2.7 Position analysis of metal cations in sludge biomass during thermal treatment

In order to identify the movement of cations at different position of sludge biomass during thermal treatment, experiments and quantity calculation had been introduced.

The quantity of cations in EPS before and after thermal treatment can be analyzed with the method introduced in section 3.2.4. The quantity of cations in liquid phase can be analyzed by ICP-AES.

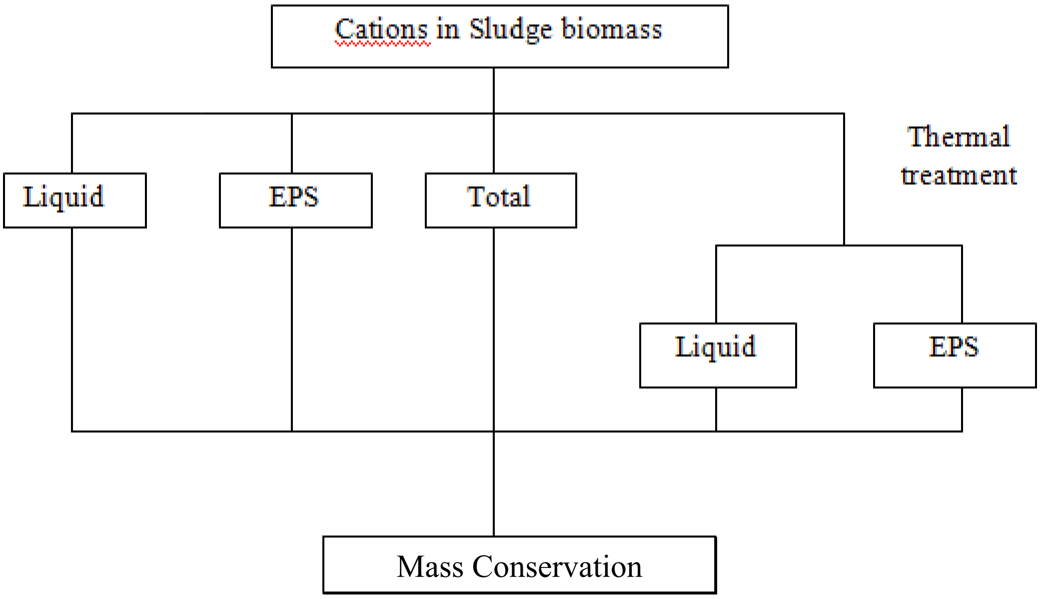

Fig.3.1Experiments structure of position analysis with metal cations during thermal treatment

Because of conservation of mass, the quantity of cation inside cell can be calculated by this equation:

Inner of cell =Total quantity- Liquid phase - EPS

Whole experiments in this chapter can be shown in Fig.3.1.

3.3 Results

3.3.1 Phosphorus release in thermal treatment

Due to the application of EBPR technique in WWTP, activated sludge accumulated large amount of phosphorus inside body. Approximately 520 mg·L^{-1} T-P and 250 mg/L poly-P could be found as shown in Fig.2.5. After thermal treatment, nearly 140-150 mg·L^{-1} T-P could be released into supernatant; Poly-P was predominant in the released T-P. With addition of chelating reagent like EDTA before the thermal treatment, approximately 290 mg·L^{-1} T-P could be released, 170 mg·L^{-1} T-P consisted of poly-P. Meanwhile, the release of Pi had also increased more 30 mg·L^{-1} into liquid phase.

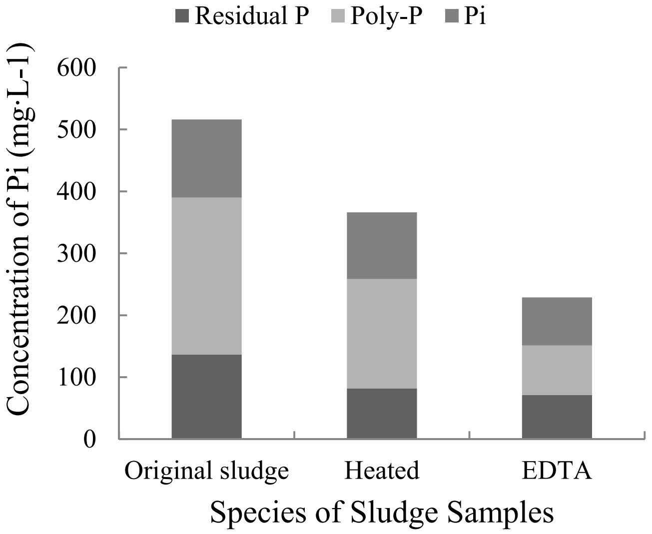

Fig.2.5 Different forms of phosphorus saved inside three kinds of activated sludge: original sludge without thermal treatment; after thermal treatment at 70˚C for 80 minutes; with addition of EDTA in thermal treatment at 70˚C for 80 minutes

3.3.2 Effect of different kinds and concentration of chelating reagents on phosphorus release in thermal treatment

Effect of different kinds and concentration of chelating reagents on phosphorus release from sewage sludge in thermal treatment had been tested shown in Fig.3.2. The performance of organic chelating reagents for phosphorus release was better than inorganic chelating reagents. Release tendency for different forms of phosphate compounds accorded with each other. When concentration was varied from 1 mM to 2 mM, the increase of phosphorus release with addition of citrate, EDTA and $Na_2S_2O_3$ was obvious, but with further increase of concentration, no obvious increase of poly-P and T-P could be found thus optimal concentration for chelating reagent in present study was 2 mM. By taking these factors into account, the sequence of efficiency for phosphorus release with addition of chelating reagents was EDTA>Citrate>$Na_2S_2O_3$>KF.

From Table 3.1, released phosphorus existed in the supernatant had been detected by ICP-AES. The data about released phosphorus showed the coherence with the information in Fig.3.2. The sequence for phosphorus release with chelating reagents was EDTA>Citrate>$Na_2S_2O_3$>KF. Inorganic chelating reagents as $Na_2S_2O_3$ and KF couldn’t combine Fe and Al ions in the liquid phase, but organic chelating reagents as EDTA and Citrate could combine them which can form poorly soluble compounds with phosphorus. Because of strong complexation ability, Ca^{2+}, Al^{3+} and Fe^{3+} could be combined by it obviously, special for Ca^{2+} ions which had a large amount in the waste water.

Table 3.1 Metal elements existed in supernatant after thermal treatment with addition of chelating reagents

Element	original sludge	EDTA	Citrate	$Na_2S_2O_3$	KF
	mg·L^{-1}				
Mg	46.1	32.1	35.5	40.8	30.8
Ca	23.6	42.7	30.6	27.3	22.8
Al	0	2.0	1.1	0	0
Fe	0	4.4	0	0	0
P	75.3	109.4	97.5	91.2	88.3

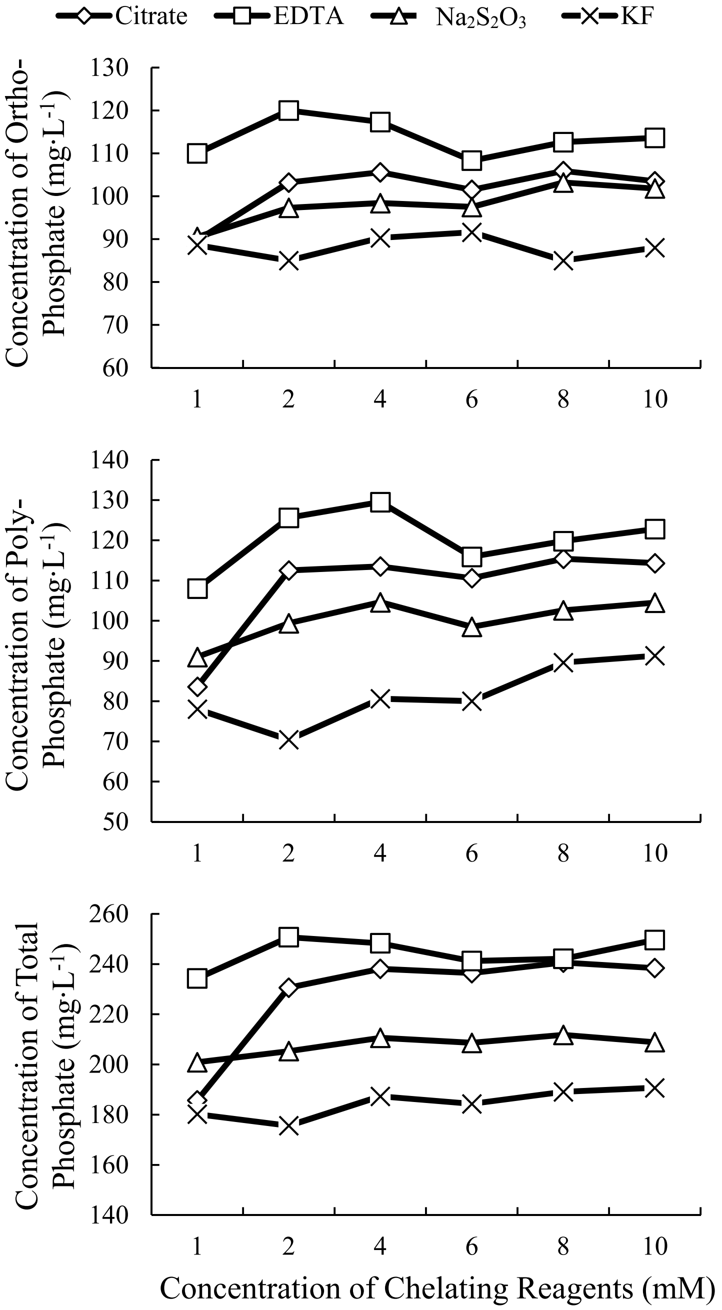

Fig.3.2 Release of Pi, poly-Phosphate and total phosphate in thermal treatment with addition of chelating reagents at different concentrations

3.3.3 Analysis of elements distribution near the surface of sludge biomass

Lots of metal elements had been found near the surface of biomass shown in Table 3.2. Every kind of metal elements was investigated by the presence of peaks at characteristic spectra. Main metal elements near the surface of biomass were P, Na and Si; Fe, Mg, Al, K and other metal elements had also been detected near the surface of biomass by analyzing three sludge samples collected at different time in the same place. No obvious difference in these 3 samples only a little increase of P nearly 4% can be found in sample B and 2% decrease in sample C compared with sample A.

Table 3.2 The distribution of metal elements near the surface of sludge biomass shown as atom% by EDX

Element species	A	B	C
Fe	3.33	3.25	2.76
Na	28.32	21.55	25.56
Mg	1.09	2.30	2.03
Al	5.90	5.91	7.00
Si	9.38	11.14	10.29
P	39.59	43.74	37.29
S	3.58	6.06	4.84
K	0.46	0.32	0.59
Ca	1.49	1.04	2.09
Cu	4.02	2.60	3.38
Zn	2.83	2.10	4.08

*: A-sewage sludge; B-sewage sludge after thermal treatment; C-sewage sludge which was added with EDTA at final concentration 2mM then treated by thermal treatment.

3.3.4 Effect of addition with metal elements on the phosphorus release from sewage sludge

In order to find the effect of metal elements on phosphorus release, four kinds of metal elements had been added artificially. Fig.3.3 depicted the effect of artificial addition with Mg, Ca, Al and Fe at final concentration of 5 mM on phosphorus release from sewage sludge in thermal treatment. Compared with original sludge without any chelating reagent, the addition of metal elements seemed preventing phosphorus release from sewage sludge. The sequence of negative effect on phosphorus release from sewage sludge was Fe>Al>Ca>Mg. With the addition of Fe, phosphorus could hardly release into outside of sludge biomass.

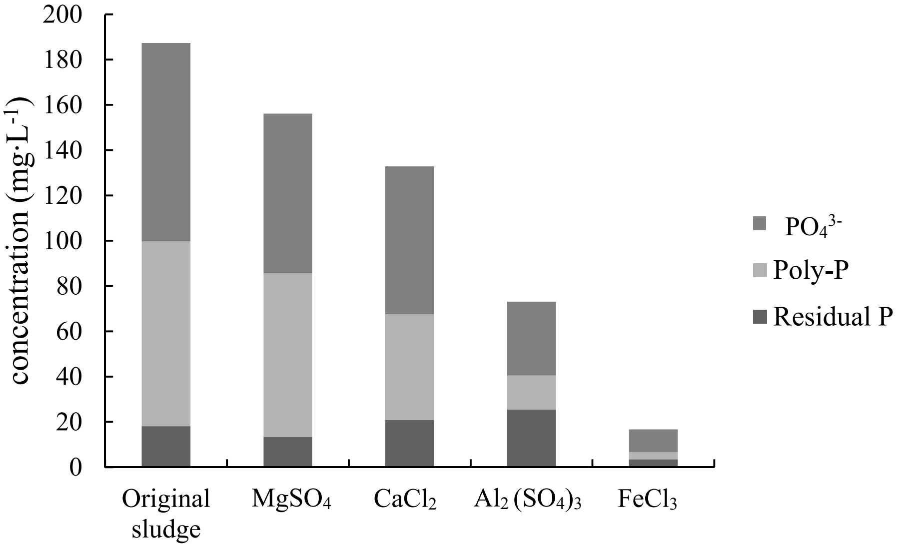

Fig.3.3 Influence of metal elements on phosphorus release from sewage sludge in thermal treatment. Each metal salt was added into sludge sample at final concentration of 5mM before thermal treatment

After the thermal treatment with addition of metal elements at final concentration 5mM, elements existed in the supernatant had been analyzed by ICP-AES. With the respective addition of Mg and Ca, Al and Fe couldn't be released into supernatant and a little increase for Mg and Ca release could be found in Table 3.3. Oppositely, lots of Mg and Ca could be released into supernatant accompanied the respective addition of Fe and Al. Because each kind of metal elements was added into sludge sample, the release of this kind of metal element was affected artificially, thus the concentration for this kind of element was not analyzed. From Table 3.3, we can find that the addition of metal element would inhibit P release compared with original sludge. This depicted existence of metal elements made negative effect to P release from sewage sludge during thermal treatment.

Table 3.3 Metal elements existed in the supernatant with addition of metal elements after thermal treatment

Element	Original sludge	Mg	Ca	AL	Fe
			mg·L^{-1}		
Mg	43.91	–	47.28	59.62	57.74
Ca	26.61	32.53	–	55.49	54.11
Al	0	0	0	–	3.24
Fe	0	0	0	0.34	–
P	60.23	51.23	41.73	26.39	8.16

3.3.5 The fluxion of metal elements in sludge biomass during thermal treatment

The data in Table 3.4 depicted the positions and new trend of moving for different kinds of metal elements saved inside sludge biomass. Analysis methods of metal elements in supernatant, EPS and total quantity had been introduced in section 3.2.6; because of mass conservation for every kind of elements, the concentration of intracellular metal elements had been calculated with equation in section 3.2.6. A big amount of Mg and Ca existed in the supernatant consisted of influent waste water. Lots of Ca was saved in the EPS not inside the cell, oppositely, main part of Mg was saved inside the cell. Dissociation ions of Fe and Al couldn't be found in the supernatant, and mainly concentrated in EPS and intracellular materials.

After thermal treatment without addition of chelating reagents, the situation was changed. Large amount of Mg was released into supernatant by thermal treatment, but released Ca was accumulated in EPS; thermal treatment couldn't drive Al and Fe transferring from intra-cellular to extracellular liquid phase.

With the addition of chelating reagents as EDTA and citrate, lots of Ca, Al and Fe could be released from EPS of sludge biomass and a bit from inner of cell, it also promoted the release of phosphorus; a part of Fe could be released from intracellular, chelating reagent couldn't promote the release of Mg.

3.3.6 Element release after thermal treatment in different seasons

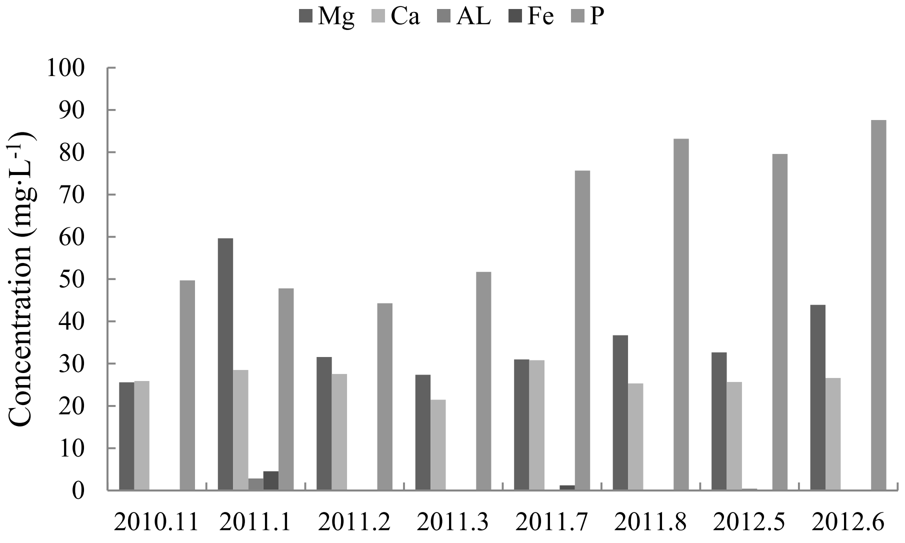

Fig.3.4 Release of different kinds of metal elements from sewage sludge during thermal treatment without addition of chelating reagents in different seasons

From Fig.3.4, the performance of element release from sewage sludge after thermal treatment was obvious in different seasons. In summer, sludge sample can release high quantity of phosphorus compared with in winter. It was assumed lots of rainfall in summer dilutes the concentration of metal cations in waste water, thus the inhibit effect for P release was not obvious like in winter.

Table 3.4 Fluxion of metal elements in sludge biomass during thermal treatment

Element	Liquid				EPS				Intracellular				Total
	Before heating	Thermal treatment			Before heating	Thermal treatment			Before heating	Thermal treatment			
		No addition	EDTA	Citrate		No addition	EDTA	Citrate		No addition	EDTA	Citrate	
	$mg\cdot L^{-1}$												
Mg	15.33	36.72	30.10	33.07	7.70	6.13	5.19	5.57	36.84	17.02	24.58	21.23	59.87
Ca	25.41	27.33	42.34	31.57	23.12	27.56	12.57	20.94	15.76	9.40	9.38	11.78	64.29
Al	0	0	3.27	1.51	2.59	3.06	0.42	1.39	7.89	7.42	6.79	7.58	10.48
Fe	0	0	5.41	0.67	2.25	2.59	0.19	1.78	3.83	3.49	0.48	3.63	6.08
P	3.34	51.60	87.25	92.68	24.34	34.6	16.43	18.59	156.42	87.9	70.42	62.83	174.1

3.4 Discussion

3.4.1 Different forms of phosphate accumulated inside activated sludge

In the present study, activated sludge accumulated a large amount of phosphorus because the sludge sample was collected from the end of aeration tank of WWTP which used EBPR technique to remove phosphorus. The concentration of T-P was 4.3-5.0% as phosphorus of its dry weight; half part of phosphorus was saved as poly-P, approximately 2.2-2.5% as its dry weight. This phenomenon was different from that observed in the research of Kuroda et al. [6]. In their research, nearly 4.3-6.9% T-P and 3.5-5.0% poly-P was accumulated in the cultivated sludge in the laboratory, thus it was higher than the sludge sample used in this study, especially, and the ratio of poly-P to T-P was much higher than the sample used in this study. The reason for this difference may be attributable to the presence of metal phosphate saved inside the sludge sample collected from WWTP in this study. After the thermal treatment, only approximately 150 $mg{\cdot}L^{-1}$ T-P as Pi was released into supernatant, but with the addition of EDTA, 290 mg/L T-P could be released from sewage sludge during thermal treatment. The increase of T-P release was very obvious, and we all know that main function for chelating reagent used in industry was occultation of metal ions, thus it could be judged metal ions sequestered by EDTA made negative effect on the phosphorus release from sewage sludge during thermal treatment.

3.4.2 Effect of different kinds and concentration of chelating reagents on phosphorus release

Figure.3.2 depicted the improvement performance of different kinds of chelating reagents on the phosphorus release from sewage sludge after thermal treatment. When the concentration was higher than 2 mM, phosphorus release tendency was similar; with more chelating reagents, no more phosphorus can be released into supernatant during thermal treatment. Thus the optimal concentration with addition of chelating reagents for phosphorus release was 2 mM in present study.

The elements existed in the supernatant with addition of chelating reagents after thermal treatment had also been analyzed. It seemed that organic chelating reagents could complex lots of metal elements which can form poorly soluble compounds with phosphate, and special for Ca which existed in the supernatant with large quantity shown in Table 3.1. This possibly explains why the most quantity of phosphorus could be released into supernatant after thermal treatment with the addition of EDTA, because it can sequester most metal ions which can combine phosphate, thus the poly-P and Pi anions could be released easily into supernatant.

3.4.3 Elements distribution near the surface of sludge biomass

Many kinds of elements could be found near the surface of sludge biomass by EDX analysis. The quantity of phosphorus and sodium was much higher than other metal elements. There was not a distinct difference which could be identified before and after thermal treatment.

3.4.4 Negative effect of excess metal elements on phosphorus release

The concentration of released poly-P (with addition of Mg, Ca, Al and Fe) reduced 11.4%, 42.9%, 81.6% and 96.1% respectively, and the concentration of released T-P reduced 7.9%, 28.1%, 68.8% and 93.6% compared with original sludge sample in thermal treatment shown in Fig.3.3. It seemed that metal elements obviously prevented the release of poly-P and T-P from sewage sludge.

There was an interesting phenomenon found in Table 3.3. After the addition of Al and Fe, lots of Mg and Ca could be found in the liquid phase after thermal treatment. Oppositely, with the addition of Mg and Ca, Al and Fe couldn’t be found in liquid phase. Thus it can be assumed there was a competition among these metal ions combined Pi and poly-P, Al and Fe can combine phosphate easily than other two kinds of metal elements.

3.4.5 Migration of metal elements in different positions of sludge cells during thermal treatment

In order to identify release source of metal elements and transferring orientation, different kinds of analysis methods had been researched in this study. The main quantity of Mg, Al and Fe was saved inside the cell, but main quantity of Ca was existed in the EPS and supernatant shown in Table 3.4. Because of the thermal power, metal elements were released from inner of cell to supernatant. Without addition of chelating reagents, large quantity of Mg could be released into supernatant because of thermal treatment, but the released Ca from inner of cell accumulated inside EPS, the same condition had also been found with Al and Fe. Attention should be paid on this phenomenon that more metal elements were released from EPS not inner of cell with addition of EDTA after thermal treatment shown in Fig.3.5. Without these metal compounds in EPS, more intracellular phosphorus was able to release into supernatant. This data provided collateral evidence that the main interference of metal elements on phosphorus release was formation of compounds with low solubility in the EPS and blocked the pathway or transfer system which can be used for releasing intracellular materials into extracellular condition.

From Fig.3.4, the quantity of released metal elements and phosphorus was different in summer and winter seasons. Without addition of EDTA, activated sludge collected in summer could release large amount of phosphorus easily after thermal treatment; but the situation for activated sludge collected in winter was opposite, phosphorus release was limited obviously. With the addition of EDTA, sludge sample collected in winter could release much more phosphorus than it collected in summer. The rainfall in summer was higher than other seasons because it was rainy season in Fukuoka. Large amount of rain possibly diluted the concentration of Ca^{2+} which can combine phosphate anion and from poorly soluble compounds; these compounds may prevent phosphorus release from sewage sludge by thermal treatment.

Moreover, temperature in summer and winter varied obviously, higher amounts of EPS were produced at lower temperature with higher concentration of extra-cellular phosphorus content [7], more quantities of EPS will absorb more cations which can combine phosphate anions and form poorly soluble compounds.

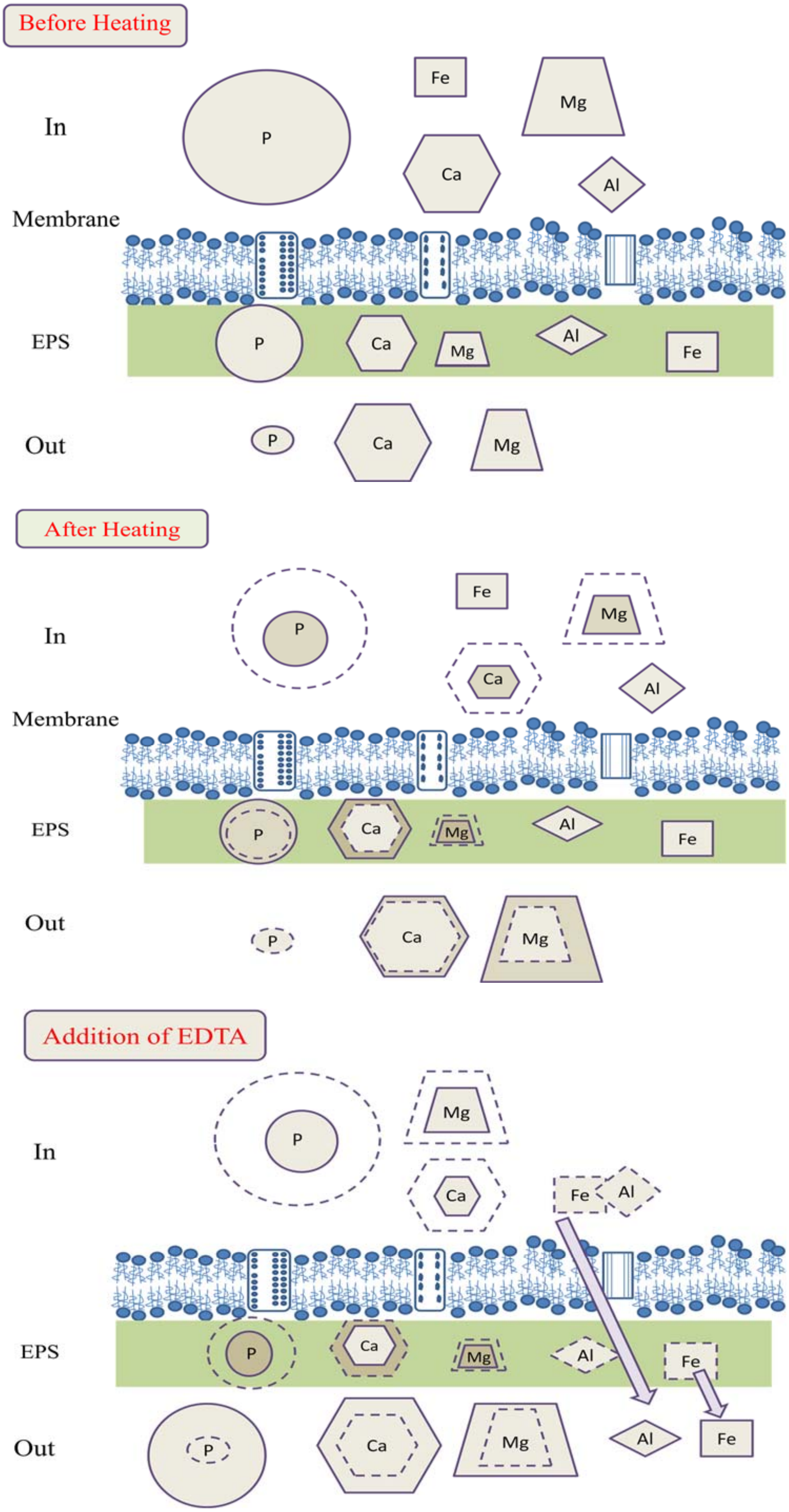
Before Heating
In
Membrane
EPS
Out
P
Fe
Mg
Ca
Al
P
Ca
Mg
Al
Fe
P
Ca
Mg
After Heating
In
Membrane
EPS
Out
P
Fe
Mg
Ca
Al
P
Ca
Mg
Al
Fe
P
Ca
Mg
Addition of EDTA
In
EPS
Out
P
Mg
Ca
Fe
Al
P
Ca
Mg
Al
Fe
P
Ca
Mg
Al
Fe

Fig.3.5 Migration of metal elements in sludge biomass during thermal treatment

Altogether, poly-P complexed by divalent metals such as Ba^{2+}, Pb^{2+} or Mg^{2+} are poorly soluble [8]. The low solubility of these complexes probably causes precipitation of poly-P-metal complexes within the cell resulting in poly-P granules [9]. This immobilized poly-P couldn’t be released into supernatant from sewage sludge after thermal treatment. Metal phosphates are highly insoluble and will precipitate on cell surfaces [10, 11]. It can be assumed this process will prevent phosphorus release because these precipitants on cell surface maybe interferes tunnel or transfer system which can be used for releasing phosphates. As poly-P was unstable in the heating process, it will be hydrolyzed and provide more phosphate, this process maybe promote the precipitation between metal ions and phosphate anions. Some researchers reported the hydrolysis of poly-P may lead to precipitation of the metal-phosphates intracellular or extracellular [12]. From the data in present study, released phosphate could also concentrated or precipitated in EPS not liquid phase, this phenomenon made also challenge to phosphorus release from sewage sludge. Because of these reasons, sewage sludge cultivated in laboratory could release much more poly-P into liquid phase after thermal treatment than that collected from WWTPs.

3.5 Conclusions

The complexity of the microorganism’s structure implies that there are many ways for the metal to be captured by the cell. Sewage sludge collected from WWTP would uptake many kinds of metal ions and save in different positions of biomass, these metal ions possibly immobilize poly-P and Pi molecules inside sludge biomass, therefore increased the difficulty to release phosphorus from sewage sludge by thermal treatment.

Through addition of different kinds of chelating reagents, we can find not every kind of chelating reagent can improve phosphorus release, only EDTA and citrate can have good performance. And with addition of

EDTA, nearly 68% poly-P and 53% T-P could be released into liquid phase from sewage sludge during thermal treatment.

With artificial addition of excess metal ions, the interference of phosphorus release by metal ions can be found apparently. During thermal treatment, Mg and P were transferred from inner of cell to outside of cell; but released Al, Fe and Ca were concentrated in EPS of sludge biomass. At last, the effect of seasons about rainfall should also be taken into account because the rainfall will dilute the concentration of metal elements in the wastewater which can prevent poly-P release during thermal treatment.

3.6 References

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Chapter 4

Chapter 4 The Crystallization of Struvite by Recycling Poly-Phosphate Released from Sewage Sludge after Thermal Treatment

Abstract

Sustainability is an important environmental concern increasingly reflected in corporate strategy, government policy and international agreements. Phosphorus is an important element, making a major contribution to agricultural and industrial application.

In chapter 3, sewage sludge can release nearly 70% poly-P and 55% T-P into liquid phase after thermal treatment with addition of EDTA. With separation, liquid phase including abundant phosphate compounds can provide exuberant phosphorus source for recovery.

Many researchers have reported that ortho-phosphate can be precipitated as phosphate hexahydrate (struvite) with Mg and ammonium. Because P and N are both nutrient element in agriculture, recovery as struvite shows advantage as calcium phosphate. However little information mentions poly-P can be also crystallized as struvite.

In this study, poly-P released from sewage sludge after thermal treatment could be recovered successfully as struvite. This is a novel finding, and poly-P shows impressive performance on struvite formation compared with ortho-phosphate, because it can be precipitated at lower pH condition even neutral condition, with less addition of magnesium element.

Keywords: struvite, recovery, advantage, poly-Phosphate

4.1 Introduction

Each day, up to 2 g of phosphorus is discharged to wastewater by each individual. Released to the aquatic environment this may contribute to the environmental problem of eutrophication and the potential for recycling is lost. However, wastewater phosphorus represents a considerable renewable resource ready for technological exploitation [1].

Struvite is an ortho-phosphate, containing magnesium, ammonium, and phosphate in equal molar concentrations. The general formula for minerals of the struvite group is $AMPO_4 \cdot 6H_2O$, where *A* corresponds to potassium (K) or ammonia (NH_3) and *M* corresponds to magnesium (Mg), cobalt (Co), or Nickel (Ni). Struvite in the form of a magnesium ammonium phosphate hexahydrate crystallizes as an orthorhombic structure.

Struvite scale deposits are a significant concern in wastewater treatment plants [2]. The problem is not necessarily new, as struvite was first observed as a crust of crystalline material in 1937 in a multiple-stage sludge digestion system [3].

In the past decade, struvite precipitation has gained interest as a route to phosphorus recovery [2]. Its composition (i.e., nitrogen [N], P, and magnesium [Mg] ions in equal molar concentrations) makes it a potentially marketable product for the fertilizer industry, proved that its nucleation and the quality of crystals recovered can be controlled [4]. Research in struvite formation is now widespread and includes studies toward the prevention of scaling, alternative phosphorus removal and recovery from wastewater effluents, and potential exploitation to the benefit of wastewater companies and industries as a fertilizer [5].

Several studies have been carried out to assess potential methods of phosphorus recovery as struvite with Pi at a bench and pilot scale, and few processes, integrated in treatment plants, already exist and are effective in Japan [6], The Netherlands [7] and Italy [8,9], shown in Table 4.1.

Crystal formation is a complex process leading to the occurrence of a solid phase made of regular structures named crystals. Despite its complexity, crystallization is commonly used in industrial applications aiming to separate a desirable solid phase [5].

This chemical engineering process can be divided in two parts:

- *Nucleation* corresponds to the crystal birth into a liquid or a gaseous media. Ions combine together to form crystal embryos, which are the first state of crystals. Nucleation is mostly governed by kinetics of reaction.
- *Crystal growth* corresponds to the development of crystals until the equilibrium is reached. The crystal growth determines the final size of crystal according to the crystallization kinetics (rate of growth).

The purpose of this chapter focused on whether poly-P mixed with Pi can be recovered as struvite. Optimal parameters like pH, reaction time and molar ratio about crystallization with poly-P as struvite had been analyzed by series experiment.

Table 4.1 Crystallization technology for P recovery (modified from [5])

References	Process/technology	Scale	Source	P removal	Recovered form
Liberti et al. [10]	Selective ion exchange	Full scale	Chlorinated secondary	≥90%	MAP
Fujimoto et al. [11]	Aeration, stirring and crystallization in a stirred reactor.	Bench and pilot	Supernatant from anaerobic digester	60 to 70%	MAP
Brett et al. [12]	CSIR Fluidized bed crystallization column seeded with quartz sand	Bench	Anaerobic digester supernatant, pond effluents, abattoir wastes	90%	MAP/HAP
Giesen [13]	DHV Crystalactor	Full scale	Supernatant from anaerobic sludge	–––	CaP
Battistoni et al. [14]	FBR, seeded with sand	Bench	Anaerobic supernatants after belt press	62 to 81%	MAP, or mixed MAP/HAP
Ueno and Fujii [15]	FBR	Full scale	Dewatered liquors from anaerobic sludge digestion	≥ 90%	MAP
Von M¨unch et al. [16]	Air-agitated column reactor	Pilot scale	Centrate from anaerobically digested sludge	94%	MAP
Suzuki et al. [17]	Aeration column	Pilot scale	Swine waste water	65%	MAP/HAP
Adnan et al. [18]	FBR	Pilot scale	Synthetic liquors	90%	MAP
Seco et al. [19]	Stirred reactor	Pilot	Supernatant from sludge digestion	90%	MAP/CaP
Battistoni et al. [20]	FBR	Full scale	Anaerobic supernatants after belt press	64–69%	MAP/HAP

4.2 Experiment

4.2.1 Experiment materials

Activated sludge was collected from the end of aeration tank of wastewater treatment plant located in Fukuoka, Japan, which used anaerobic-aerobic technique to remove phosphorus in the wastewater. After the collection of sludge sample, sewage sludge was aerated for an hour because it was saved in plastic bottles during the transportation. After the settlement, mixed liquid suspended solids (MLSS) of sewage sludge maintained at 3000-3500 $mg \cdot L^{-1}$. Pretreated sludge sample was distributed into glass bottles with addition of chelating reagent (EDTA) at final concentration of 2 mM. Then these glass bottles were placed in the thermostatic water baths and incubated at 70˚C for 80 minutes. After the thermal treatment, supernatant was separated from the solid phase by centrifugation at 3000rpm and filtered with filter paper which pore size was 0.45μm. Finally the supernatant had been prepared for the following experiments.

4.2.2 Experiment methods

A series of batch investigations were conducted to identify the fact whether the supernatant contained poly-P can form struvite. Magnesium sulphate ($MgSO_4$) and ammonium chloride (NH_4Cl) were used to adjust the molar ratio of Mg^{2+}:NH_4^+ in the liquid phase. The pH value of supernatant was controlled by addition of sodium hydroxide (6N NaOH). All precipitation experiments had a reaction time of 3 hours and at room temperature unless otherwise illustrated. The precipitant formed in the experiments was collected after the filtration through 0.45 μm membrane filter then dried in an oven at 40˚C for 2 days.

4.2.3 Analytical methods

Pi was measured by ascorbic acid method; ammonium was analyzed by salycilate method, both photochemical analyses used HACH DR/2400 spectrophotometer. Poly-P was analyzed by heating in the autoclave for 30 minutes in acid condition [21]. Magnesium and calcium were measured by inductive coupled plasma atomic emission spectrometry (ICP-AES) (Optima 5300dv, PerkinElmer). Energy dispersive X-ray (EDX) (EDX-800, SHIMADZU) was used to identify the quantity of elements existed in the dried precipitant. X-ray diffraction (XRD) was used to analyze the quality of precipitant whether it was struvite. Both EDX and XRD analyses were used at the center of advanced instrumental analysis, Kyushu University. All chemical reagents used were analytical grade.

4.3 Results

4.3.1 Characteristics of ions existed in the supernatant separated from sewage sludge

Many kinds of ions can be released from sewage sludge after thermal treatment at 70˚C for 80 minutes accompany phosphorus release [22]. Lots of poly-P had been found in the supernatant separated from sewage sludge. With addition of chelating reagent (EDTA), the release of poly-P and other ions can be improved which provides sufficient phosphorus source for recovery, lots of ammonium and magnesium also can be found in the supernatant B shown in Table 4.2.

Table 4.2 Characteristics of supernatant after thermal treatment

Parameter	Supernatant A	Supernatant B
	mg·L^{-1}	
T-P	157.3	230.6
Pi	74.1	90.5
poly-P	55.2	125.8
Mg^{2+}	36.7	30.1
NH_4^+	22.1	23.5
Ca^{2+}	27.4	42.3

*Supernatant A was separated from the sewage sludge after thermal treatment; supernatant B was separated from sewage sludge after thermal treatment with addition of chelating reagent.

Because chelating reagent can improve the release of poly-P and other useful ions for phosphorus recovery from sewage sludge during thermal treatment, thus supernatant B was always used in this study.

4.3.2 Confirmation of struvite appearance in the liquid phase contained poly-p

In order to testify the assumption which poly-P can also be recovered as struvite, a series experiment had been tested. Because the molar ratio of Mg:N:P in struvite is 1:1:1, the same element ratio had been used in first phase. The initial concentration of phosphate was 230.6 mg·L^{-1}, thus concentrations of Mg^{2+} and NH_4^+ should reach 59.5 mg·L^{-1} and 44.6 mg·L^{-1} respectively with the addition of chemical reagents. Because the effect of pH on the struvite formation with poly-P was unknown, thus a series experiment had been tested at pH ranged from neutral condition (7.5) to pH 10.0 with addition of alkaline.

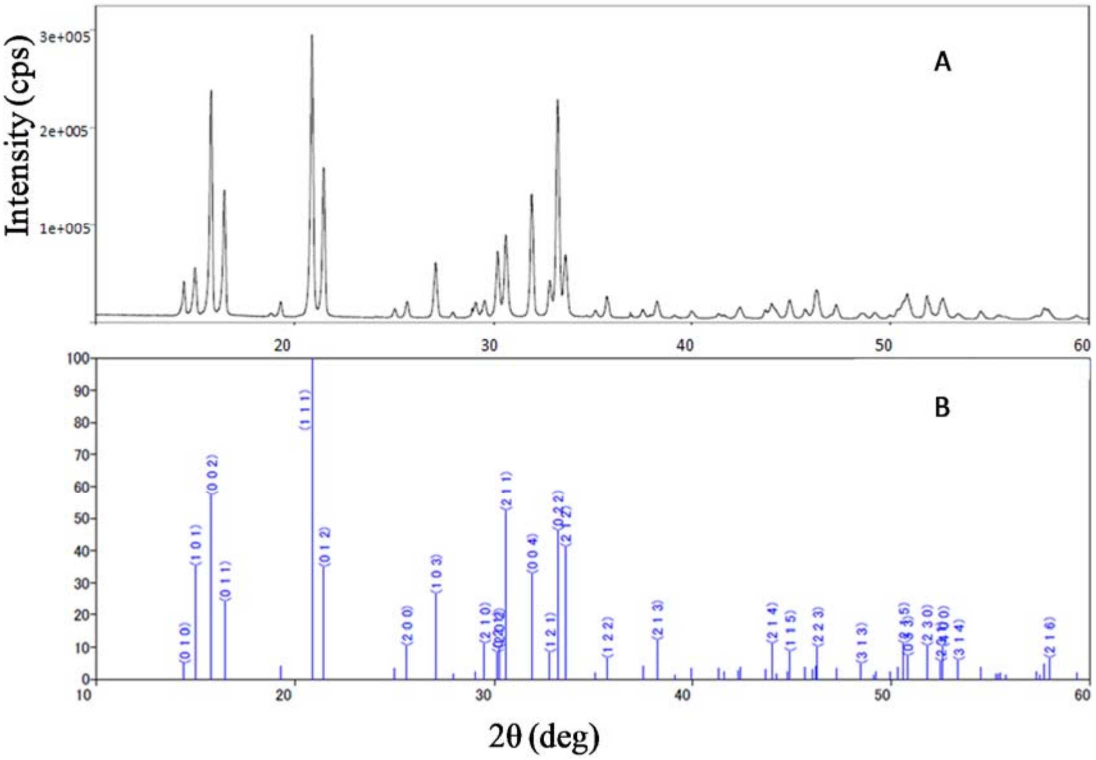

Fig.4.1 X-ray spectrum: A-precipitant formed in solution; B-struvite information in database

After 3 hours at 25˚C, white precipitant formed in the solution had been separated and dried. With the XRD analysis, a typical XRD spectrum of precipitant formed in solution had been shown in Fig.4.1A, and the spectrum of struvite in data base had also been shown in Fig.1B, they were matched. This XRD spectrum provided obvious proof to demonstrate the white precipitant was struvite.

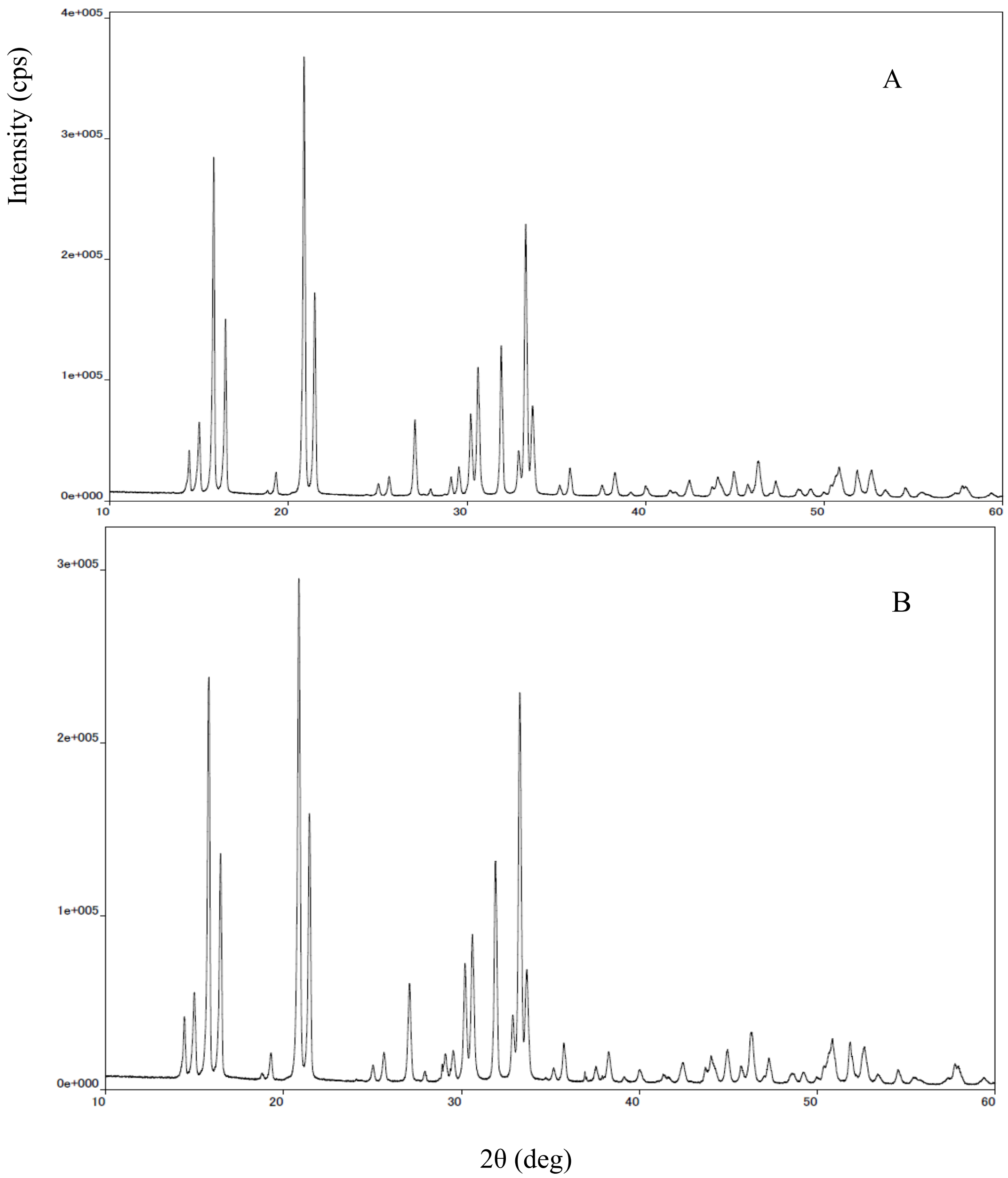

Fig.4.2 X-ray spectrum: A-struvite collected from WWTP; B-struvite crystallized from experiment

Struvite collected from a WWTP was compared with precipitant in this study. With XRD analysis, we can find the spectrum of these two kinds of struvite was the same shown in Fig.4.2.

Further information about elements quantity in the precipitant had been investigated by EDX analysis. From Table 4.3, the quantity percentage of main elements existed in precipitant and struvite indicated similar component. This can also provide collateral evidence the precipitant was struvite.

Table 4.3 EDX analysis of element quantity in precipitant and struvite sample

Elements	Struvite	Precipitant
	[wt%]	
N	3.93	4.12
O	35.74	33.56
Mg	22.35	21.41
P	36.78	40.45
Ca	1.23	0.61

Through the analysis of XRD and EDX, poly-P released from sewage sludge after thermal treatment can be recovered as struvite with existence of Pi. This beneficial phenomenon provides possibility to recover lots of poly-P, Pi, Mg^{2+} and NH_4^+ released from sewage sludge as struvite in industrial and agricultural application.

4.3.3 Parameters affected struvite formation in solution contained lots of Pi and poly-p

- Effect of pH on Struvite Formation

A series experiment about effect of pH on struvite formation had been analyzed and data were shown in Fig.4.3. The molar ratio of Mg:N:P in this experiment was 1:1:1. Poly-P had a good performance on removal percentage at low pH condition (pH 7.5 to 8.5); approximately 80% poly-P can be removed and precipitated as struvite at pH 8.5. When pH was higher than 8.5, the increase of pH couldn't improve removal percentage of poly-P apparently. Oppositely, removal percentage of Pi increased along with pH increase, only 45% Pi can be precipitated at pH 7.5, but nearly 85% Pi can be precipitated at pH 10.0. These data indicated the advantage of poly-P compared with Pi on phosphorus recovery as struvite because most of poly-P can be precipitated at pH 8.5, and 68% poly-P can even be precipitated in neutral condition. Removal percentage of magnesium and ammonium increased obviously with pH increase.

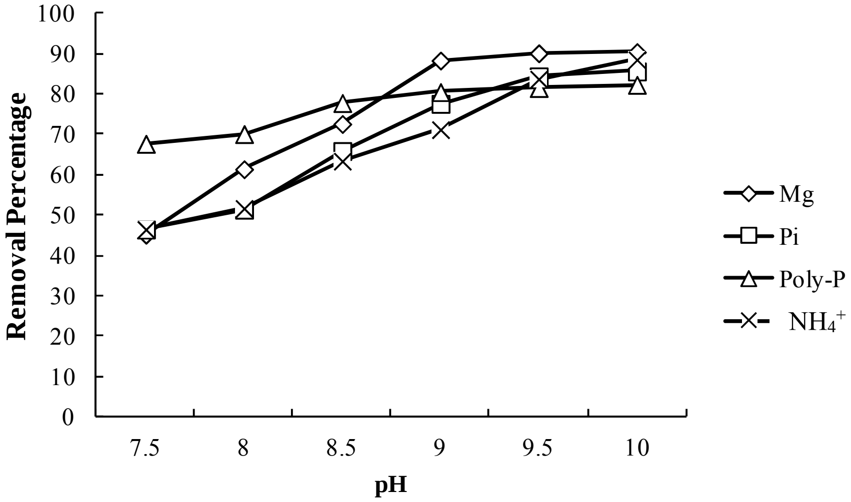

Fig.4.3 Removal percentage of different ions varied in different pH condition

- Effect of Reaction Time on Struvite Formation

In this study, adopted reaction time was 3 hours; removal rate of the constituent ions of struvite had been investigated at pH 8.5 shown in Table 4.4. Poly-P can be removed fast in the first hour, 51.2% poly-P can be removed. Oppositely, only 17.2% Pi can be removed in the first hour. In the last 2 hours, only approximately 20% poly-P was removed.

Table 4.4 Removal Efficiency of Ions in Liquid Phase with Time

Time [min]	Mg removal [%]	NH_4^+ removal [%]	Pi removal [%]	poly-P removal [%]
60	31.4	29.8	17.2	51.2
120	54.9	48.6	43.1	68.4
180	72.6	63.4	65.4	77.9

- Effect of Molar Ratio of Mg: P and N: P on Struvite Formation

When molar ratio of Mg: P was lower than 1, precipitation of Pi and poly-P was both inhibited obviously. When molar ratio was higher than 1, removal percentage of poly-P was not increased compared with molar ratio of 1Mg: 1P, but removal percentage of Pi increased obviously compared with this molar ratio, it increased nearly 10%, this indicated molar ratio of Mg:P can be limiting factor on struvite formation with Pi shown in Fig.4.4. When molar ratio of N: P was higher than 1, removal percentage didn’t change for both Pi and poly-P compared with molar ratio of 1N: 1P.

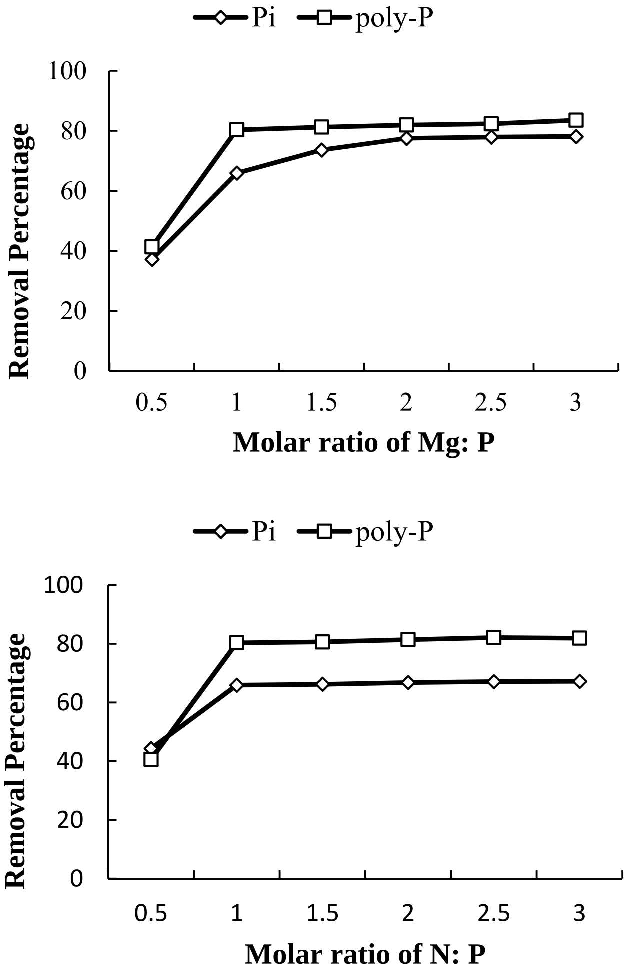

Fig.4.4 Removal percentage of Pi and poly-P with different molar ratios of Mg: P and N: P

4.4 Discussion

4.4.1Confirmation of poly-P can be precipitated with Mg and Ammonium as MAP

With analysis of XRD technique, we can find the typical spectrum of struvite formed in the liquid phase which included abundant poly-P was matched with spectrum of struvite in database. This can provide obvious proof that poly-P can also be precipitated as struvite with addition of magnism and ammonium.

EDX analysis depicited quantity of necessary element for struvite formation in struvite collected from the WWTP and precipitant formed in the experiment was very similar, and the quantity of interference element Ca was low shown in Table 4.3.

Struvite collected from the WWTP was formed in the liquid phase after digestion with excess sludge, thus main componant was Pi; however precipitant was formed in the liquid phase which included much poly-P compounds in this study. Little information mentioned this phoenomenon, it was the first time to find poly-P can be precipitated with magnesim and ammonium as struvite. Because we know that N and P were both recoverd as struvite, they are nutrient elements for crops and struvite can be used as fertilizer, this is advantage compared with HAP recovery.

4.4.2 Affect parameters on struvite formation

Predicting and controlling nucleation and crystal growth become all the more complex, as they depend on a combination of factors, such as the initial crystal states of the compounds, phenomena of matter transfer between solid and liquid phases, thermodynamics and kinetics of reactions, as well as several physico-chemical parameters, including pH, supersaturation level, mixing energy, temperature, and the presence of foreign ions in the precipitating solution.

In this chapter, attention was focus on the parameters of pH value, reaction time and molar ratio of Mg:P and N:P.

The pH at which struvite may precipitate is one of the main factors influencing the crystallization process, as it is linked to the notion of solubility and supersaturation. It can then control the rate of precipitation and, the induction period.

Several authors have studied the effects of pH on struvite crystallization with Pi. For instance, Borgerding [24] reported that struvite solubility could decrease from around 3000 $mg \cdot L^{-1}$ to less than 100 $mg \cdot L^{-1}$ for pH rising from 5 to 7.5, while Buchanan et al. [25] identified pH 9 as the pH of minimum solubility for struvite.

Solution pH is also important in the sense that it causes the transformation of NH_4^+ ions into gaseous ammonia, thus reducing the nitrogen concentration and affecting the molar ratio Mg:N:P (minimum value 1:1:1) necessary to form struvite.

From Fig.4.3, we can find the maximum quantity of struvite formation by poly-P can be obtained at pH 8.5 which is close to neutral condition; but only at high pH condition, most Pi can be precipitated as struvite. Therefore, limitation of pH to poly-P was not obvious compared with Pi.

Reaction time possibly affected struvite nucleation and crystal growth. In the first hour, nearly 50% poly-P can be recovered; compared with Pi, this was very fast crystallization rate. This phenomenon may be resulted by different chemical characteristics of poly-P and Pi.

Thus it seems poly-P can form crystal seed of MAP easily and fast compared with Pi, seed formation is the first step of MAP formation, it is very significant for MAP formation. This may be the important factor to analyze different performances of poly-P and Pi in MAP formation.

Several researchers mentioned the molar ratio of Mg and NH_4^+ can affect the precipitation of struvite with Pi, thus series experiment was also used to test poly-P. From Fig. 4.4, excess magnesium and ammonium couldn’t increase quantity of struvite crystallization which means it was not necessary to input more metal Mg into liquid phase for poly-P recovery compared with Pi recovery. This was beneficial for application in industry because cost of magnesium occupies big percentage for phosphorus recovery.

4.5 Conclusions

Poly-P existed in the solution separated from heated sewage sludge can form white precipitate at the molar ratio of 1Mg: 1N: 1P in neutral pH condition. Through XRD and EDX analysis, the precipitant had been confirmed as struvite. This was the first time to find poly-P released from sewage sludge can be recovered as struvite.

After a series analysis, pH and reaction time can affect precipitation process of poly-P. Approximately 80% poly-P can be precipitated as struvite at pH 8.5 after 3hours. Poly-P performed advantage compared with Pi because it can form lots of struvite at lower pH condition 8.5 and lower molar ratio of 1Mg: 1P. This new method indicated possibility to recover poly-P released from heated sewage sludge as struvite in practical application.

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Chapter 5

Chapter 5 Summary and Outlook

Through different experiments analysis, poly-P can be released during thermal treatment and recovered as MAP, this was very important for P recovery. In this chapter, total information about poly-P will be summarized and the application of recovered materials will be estimated.

5.1 Conclusions about phosphorus release from sewage sludge by thermal treatment

Poly-P and T-P accumulated inside activated sludge could be released by thermal treatment at low temperature as introduced in chapter 2, 30% poly-P and 29% T-P could be released from sludge by heating at 70˚C for 80 minutes. This performance of phosphorus release in this study was not ideal as Kuroda et al. introduced; nearly 90% poly-P and 87% T-P can be released into liquid phase by heating at 70˚C after 60 minutes [1]. Since excess sludge generated by the WWTP contained a variety of metal elements such as Al, Ca, Fe and Mg, it is likely that the presence of these elements negatively affected the P release from heated sludge [2].

Different kinds of pretreatments had been tested to improve phosphorus release from activated sludge in thermal treatment; addition of chelating reagent at final concentration of 2 mM before thermal treatment could improve the phosphorus release obviously, 68% poly-P and 53% T-P could be released into liquid phase. Approximately 85% T-P could be precipitated with calcium at pH 11 after 30 minutes; it was interesting to find precipitation occurred in neutral condition without pH adjustment.

Chelating reagent as EDTA could improve poly-P release during thermal treatment obviously, this depicted metal elements adsorbed by activated sludge in wastewater prevented the phosphorus release because of complicated mechanisms.

Poly-P complexed by divalent metals such as Ba^{2+}, Pb^{2+} or Mg^{2+} is poorly soluble [3]. The low solubility of these complexes probably causes precipitation of poly-P-metal complexes within the cell resulting in poly-

P granules [4]. This immobilized poly-P couldn't be released into supernatant from sewage sludge after thermal treatment. Metal phosphates are highly insoluble and will precipitate on cell surface [5, 6]. It can be assumed this process will prevent phosphorus release because these precipitants on cell surface maybe interferes tunnel or transfer system which can be used for releasing phosphate. As poly-P was unstable in the heating process, it will be hydrolyzed and provide more phosphate, this process maybe promote the precipitation between metal ions and phosphate anions. Some researchers reported the hydrolysis of poly-P may lead to precipitation of the metal-phosphates intracellular or extracellular [7]. From the data in present study, released phosphate could also concentrated or precipitated in EPS not liquid phase, this phenomenon made also challenge to phosphorus release from sewage sludge. Because of these reasons, sewage sludge cultivated in laboratory could release much more phosphorus into liquid phase after thermal treatment than that collected from the WWTP.

5.2 Phosphorus recovery as struvite with poly-P

Because N and P are both nutrient elements for plants growth, if poly-P can be recovered as struvite, it was an ideal path to reuse it as fertilizer. In order to testify the assumption which poly-P can also be recovered as struvite, a series experiment had been tested.

Initial parameters were utilized based on the performance of Pi.

Because the molar ratio of Mg:N:P in struvite is 1:1:1, thus the same element molar ratio had been used in first phase. Initial concentration of phosphate was 230.6 $mg \cdot L^{-1}$, thus concentrations of Mg^{2+} and NH_4^+ should reach 59.5 $mg \cdot L^{-1}$ and 44.6 $mg \cdot L^{-1}$ respectively with the addition of chemical reagents. Sewage sludge can also release Mg and ammonium into liquid phase, which means we can use it as raw materials for struvite formation. To avoid the limitation effect for struvite formation, pH of liquid phase was adjusted to 10. After 3 hours at 25°C, white precipitant formed in the solution had been separated and dried.

With XRD analysis, the typical spectrum of white precipitant formed in liquid phase which included lots of poly-P in this study was very similar compared with typical spectrum of struvite in database. This can provide obvious proof which can demonstrate the white precipitant was struvite.

Meanwhile, EDX analysis provided collateral evidence for this conclusion because similar element quantity percentage in precipitant and struvite sample collected from the WWTP were the same. This was the first to find novel phenomenon poly-P can also be precipitated with magnesium and ammonium as struvite.

In following experiments, difference of poly-P and Pi for phosphorus recovery had been found shown in Table 5.1. Poly-P can be recovered in low pH condition and with low quantity of Mg compared with Pi.

Table 5.1 Optimal parameters for struvite formation with poly-P and Pi

Parameters	Poly-P	Pi
pH requirement	8.5	10
P Removal in first hour	51%	17%
Molar ratio of Mg: P	1:1	1.6-1.8:1
Molar ratio of NH_4: P	1:1 (high purity)	1:1 (low purity)

5.3 Environmental impacts of P recovery

Phosphorus recovery from wastewater has become a necessity for sustainable development because phosphorus is a non-renewable essential resource; meanwhile excess discharge of phosphate compounds into natural water bodies has induced many environmental problems. If phosphorus in wastewater can be recovered and used as fertilizer, it will be ideal way to relieve this problem. The cost for phosphorus recovery had also been discussed in this section compared with mining.

5.3.1 Potential pollution reduction

Eutrophication typically occurs in aquatic environments when levels of nutrients (P and N) increase significantly and lead to an excessive growth of algae, which can cause the death of fish and other living organisms and reduce the availability of water resources. In their study on removing phosphorus from wastewater effluent, Pretty et al. [8] mentioned that the costs generated by this form of pollution to the water industry in the UK is estimated to $77 million per annum. Examples of harmful effect by algal bloom was summarized as: the production of neurotoxins which cause mass mortalities in fish and aquatic animals; human illness induced by eating polluted fish and other species as food; damage to whole ecosystem; oxygen depletion in water column during bacteria degradation.

5.3.2 Use as a fertilizer

Agronomic properties of struvite as fertilizer had been discussed in Radhakrishman's research. It seems struvite can provide three kinds of nutrient elements for growth of crops [9] and have similar effect as monocalcium phosphates [10].

Its low solubility in water (0.018 g·100 ml at 25°C; see [11]) also presents the advantage of prolonging the release of nutrients during the growing season [12] without danger of burning roots of crops treated [13]. To date, struvite has only been commercialized in Japan as a fertilizer for growing rice and vegetables [14]. Shu et al. [14] suggested that struvite is not widely applied as a fertilizer because of its limited availability to farmers and the lack of communication on its applicability and benefits [15].

5.4 Economics of phosphorus recovery

The success of the implementation of struvite crystallization processes to WWTPs depends on their economical sustainability. Because of these reasons, the main challenge is to make P recovery as struvite cost effective by taking into account costs of production and compared with struvite mining from phosphate rocks on the market of fertilizing products.

Costs of struvite production mainly depend on amounts (hence the costs) of chemicals to be injected in the process [16, 17], as well as on the energy required to ensure mixing during the crystallization [18].

By traditional research, in order to get more quantity of struvite formation, lots of Mg was inputted to promote formation. But Mg was expensive metal and constituted main portion of cost for phosphorus recovery. To illustrate, in their pilot scale study, Jaffer et al. [19] emphasized the effect of pH on struvite formation, at high pH condition, more quantities can be achieved (Slough Sewage Treatment Works, UK) as one of the principal sources of struvite production costs. In order to save cost, air stripping was used to adjust pH for struvite formation in Battistoni's research [20].

Moreover, some studies have looked at alternative ways to reduce costs associated with Mg dosing by, for example, using $Mg(OH)_2$, which is cheaper than $MgCl_2$ and simultaneously helps to increase the pH [17].

Estimation of profitability for phosphorus recovery by struvite depends on the price. After the comparison between the cost of recovery and mining, it seems very hard to assess, because it should be affected by many factors like rate of production, regional demand and relational policy.

Some researchers had reported phosphorus recovery as struvite had been applied in Japan, it had been sold as fertilizer at price of 250€.t^{-1} [21]. Based on this value, Jaffer et al. [17] estimated that for a process treating 400 $m^3 \cdot d^{-1}$of centrate liquors issued from a sewage treatment work, including a conventional activated sludge system and a BNR, the potential income generation from the sell of their struvite production would be around 25,000€ under optimum dosing regime (i.e., 90% P removal) [15].

In this research, lots of T-P and polyphosphate can be released by thermal treatment at low temperature of 70°C, and in WWTP, much quantity of heat and inflammable gas can be generated during digestion process. Thus problem for energy can be resolved easily. Because of advantages by using poly-P to recover phosphorus, lower quantity of Mg can be inputted and at lower pH condition, poly-P can form pure struvite than ortho-phosphate. From these advantages, we can find application of phosphorus recovery with poly-P will further decrease the cost compared with these conventional methods.

Overall, struvite recovered from sewage sludge needs more cost than phosphate rocks in market. Molinos-Senante et al. [22] said there were no economic incentives for the implementation of phosphorus recovery technologies because the selling price was lower than struvite recovery. However, with their new assessing method, the economic feasibility analysis taking into account the environmental benefits shows phosphorus recovery was viable not only from sustainable development but also from an economic point of view. Besides, with the force of policy, P product from recovery has bright future prospects.

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Appendix I

Table Lists

Appendix II

Figure Lists

Appendix III

Abbreviation

COD	Chemical oxygen demand
DNA	Deoxyribonucleic acid
EBPR	Enhanced biological phosphorus removal
EDTA	Ethylene diamine tetraacetic acid
EDX	Energy dispersive X-ray
EPS	Extracellular Polymeric Substance
FBR	Fabric bioreactor
HAP	Hydroxyapatite
ICP-AES	Inductive coupled plasma atomic emission spectrometry
MAP	Magnesium Ammonium Phosphate
MLSS	Mixed liquor suspended solids
PHA	Polyhydroxyalkanoate
PHB	Poly-β hydroxybutyrate
Pi	ortho-phosphate
Poly-P	Poly-phosphate
SRB	Sulphate reducing bacteria
SCWO	Supercritical Water Oxidation
T-P	total phosphate
WAS	Waste activated sludge
WWTP	Waste water treatment plant
XRD	X-ray diffraction

Acknowledgement

This research was carried out in the Urban and Environmental Engineering Laboratory, Graduate School of Engineering, Kyushu University in Japan. The author is supported by China Scholarship Council (CSC) and Kyushu University as student of International Special Course on Environmental Systems Engineering. I want to thank all these faculties.

I would like to express my sincere appreciation to my supervisor Professor, Dr. Kuba, Dept. of Urban and Environmental Engineering, Kyushu University. During these 4 years, he gave me many good suggestions and ideas, which were very helpful for my research. Especially, he gave me very important help for living which allowed me to continue my research.

I sincerely appreciate two reviewers of my dissertation, Mr. Shimaoka and Mr. Hirajima. They made comments about my dissertation very detailed; I found the disadvantages of my thesis and improved my dissertation.

I would also like to express my special gratitude to Ms Watanabe, Dept. of Center of Advanced Instrumental Analysis. She illustrated EDX and XRD analysis to me very patiently, thank you so much.

I would like to extend my heartfelt thanks to Ms Kubota, she introduced ICP-AES to me very carefully, and I want to appreciate for her help.

I would like to thank Project assistant professor, Dr. Hao, Dept. of Urban and Environmental Engineering. She gave me so much help for my research and living in these four years.

I would like to express my special gratitude to all members in my laboratory, thanks for their help and cooperation. In the first year when I came to Japan, they introduced culture, custom and famous spots to me. This was very wholesome for me to understand Japanese traditions.

Finally, I would like to express sincere appreciation to my parents supporting me silently always. Thank you for their understanding.