# Phosphorus enrichment in the treatment of pig manure in China using anaerobic digestion technology

## Dissertation

zur
Erlangung des akademischen Grades

Doktor-Ingenieur

an der Fakultät Bauingenieurwesen
der
Bauhaus-Universität Weimar

Vorgelegt von

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Weimar, März 2008

# Acknowledgements

I would like to express my special thanks to my supervisor, Prof. Dr.-Ing. Jörg Londong, for providing me with the opportunity to study with him, for his insight, patience and timely help throughout all stages of my PHD studies.

Many thanks to my colleagues Dr.-Ing. Jana von Horn, Dr.-Ing. Ralf Englert, Matthias Hartmann, Jan-Mauriz Kaub and Sten Meusel for their help in both academic and official matters. Their friendship will be remembered. I would also like to thank Johanna Scharf and Winfried Großmann for their assistance in analytical and instrumental work.

Sincere thanks are also due to the Bauhaus-Universität Weimar’s Institute of Waste Management for providing pilot plant and test materials. Many thanks to Thomas Haupt for his instruction and technical support during the experiments. The help of Laura Weitze on detailed lab work is also greatly appreciated.

My sincere thanks also go to Howard Atkinson, who kindly agreed to proofread the draft of the dissertation and correct any linguistic inconsistencies.

Finally I must give my thanks to my dear parents for their continued love and support.

# Kurzfassung

Phosphor (P) ist ein zentrales Element und ein unersetzbarer Nährstoff in allen Lebensformen. Phosphathaltige Mineraldünger werden aus Phosphaterz hergestellt. Ungefähr 80% des weltweiten Phosphaterzverbrauchs wird von der Düngemittelindustrie genutzt. Allerdings werden als eine endliche Ressource die weltwirtschaftlich abbaubaren Phosphatreserven für nur noch ca. 100-250 Jahre reichen. Die Ressource Phosphat in China ist ebenfalls begrenzt. Die verwertbaren Lagerstätten können noch 70 Jahre genutzt werden. Die Kosten für den Abbau steigen, es ist daher notwendig nach Recyclingmöglichkeiten zu suchen. Bilanzen zeigen, dass die größten wiedergewinnbaren Phosphatressourcen in China sich in tierischer Gülle befinden. Es wurde geschätzt, dass die potenzielle Phosphatressource in Massentierhaltungsanlagen 47% des gesamten Verbrauchs von Phosphaterz des Landes pro Jahr beträgt.

Das Ziel dieser Arbeit ist die Untersuchung der P-Fällung in der Schweinegülle, kombiniert mit anaerober Vergärung, um einen mit Phosphat angereicherten stabilisiersten Gülleschlamm zu erhalten, der landwirtschaftlich verwertet werden kann. Der Fokus liegt auf einem Einsatz in China.

Die anaeroben Vergärungsversuche deuteten darauf hin, dass die Gesamtkonzentrationen von Phosphor (TP) und Total-Kjeldahl-Stickstoff (TKN) im Wesentlichen konstant vor und nach der anaeroben Vergärung blieben. Allerdings veränderte sich die Bindungsformen von Stickstoff und Phosphor durch die Vergärung. 37,7% des Phosphors lag als $PO_4$-P in der rohen Gülle vor, während nur noch 20,8% als $PO_4$-P in der vergorenen Schweinegülle enthalten war. $NH_4$-N stellte 50,4% des gesamten TKN in der rohe Schweinegülle dar, während die größte Teil des TKN (79,3%) in der vergorenen Gülle aus $NH_4$-N bestand. Der pH-Wert von Schweinegülle stieg um 0,88 Einheiten nach der anaeroben Vergärung an. 45% des $PO_4$-P wurde während der anaeroben Vergärung reduziert. Die durchschnittlichen Molarverhältnisse von Mg/P und Ca/P betrugenen 1,3 und 1,7. Die Fest/Flüssig-Trennung hat wenig Einfluss auf die Änderung der Molarenverhältnisse. Es optimal ist die P-Fällung in der homogenen vergorenen Schweinegülle durchzuführen.

Der optimale pH-Bereich für die P-Fällung liegt zwischen 8,0 und 9,5. Im pH-Bereich von 8,8-9.5 wird die Fällungsreaktion der Struviteformation dominiert. Die Existenz von Calcium-Ionen führt zu einer konkurrierenden Reaktion mit Magnesium-Ionen. Im pH-Bereich von 8,0 bis 8,8 bildete sich tendenziell mehr Calciumphosphat. Sowohl $MgCl_2 \cdot 6H_2O$ als auch MgO können als Magnesiumquelle verwendet werden. MgO ist geeignet zur Zugabe in roher Gülle. Ohne den Zusatz von anderen Alkalinen stieg der pH-Wert an auf 8,5. Fast 85% des löslichen Phosphors ($PO_4$-P) konnte aus dem Flüssiganteil entfernt werden. $MgCl_2 \cdot 6H_2O$ ist gut löslich. Als $MgCl_2 \cdot 6H_2O$ mit einem pH-Wert von 9,0 verwendet wurde, betrug die Gleichgewichtszeit 30 Minuten. Das entsprechende Mg/P Molareverhältnis betrug 1,3.

Die P-Fällung in Kombination mit anaerober Vergärung eignet sich für den Einsatz in China. Mehr als 90% des löslichen Phosphors konnten aus dem Flüssiganteil der Schweinegülle durch P-Fällung entfernt werden. Mit Hilfe von Flockungsmitteln konnten bis zu 95,7% des gesamten Phosphors (TP) in das Gärrest-Endprodukt eingebunden werden.

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# Abbreviations and symbols

| | |
|---|---|
| ADP | Adenosine Diphosphate |
| AD | Anaerobic Digestion |
| ATP | Adenosine Triphosphate |
| BAT | Best Available Technique |
| BOD | Biological Oxygen Demand |
| Ca | Calcium |
| Ca/P | Calcium to phosphorus molar ratio |
| CEEP | The European Phosphate Industry’s Joint Research Association |
| CNY | China Yuan |
| COD | Chemical Oxygen Demand |
| CP | Calcium Phosphate |
| d | days |
| DCPA | Dicalcium Phoshphate Anhydrous |
| DCPD | Dicalcium Phosphate Dihydrate |
| DIN | Deutsche Industrie-Norm |
| DMIP | Direct Material Input |
| DNA | Dioxyribonucleic acid |
| EN | Europaeischen Normung |
| EU | European Union |
| FAO | Food and Agriculture Organization of the United Nations |
| g | grams |
| h | hours |
| ha | hectare |
| HAP | Hydroxyapatite |
| IAP | Ionic Activity Product |
| k | Boltzmann’s constant |
| kg | kilogram |
| km | kilometer |
| KMP | Potassium Magnesium Phosphate |
| Kmt (P) | Kilo metric tonnes of phosphorus |
| Ksp | Solubility product |
| L | Litre |
| m | metre |

| | |
|---|---|
| $m^3$ | cubic metres |
| MAP | Magnesium Ammonium Phosphate |
| mg | milligram |
| Mg | Magnesium |
| $MgCl_2$ | Magnesium chloride |
| MgO | Magnesium oxide |
| $Mg(OH)_2$ | Magnesium hydroxide |
| $MgSO_4$ | Magnesium sulfate |
| mg/L | milligram per litre |
| Mg/P | Magnesium to phosphorus molar ratio |
| min | minute |
| mL | millilitre |
| mmol | millimole |
| MOST | Ministry of Science & Technology |
| MP | Magnesium Phosphate |
| Mt | Million tons |
| n | number |
| N | Mole per litre |
| N | Nitrogen |
| NADPH | Reduced Nicotinamide Adenine Dinucleotide Phosphate |
| NDRC | National Development and Reform Commission |
| $NH_4$-N | Ammnonium Nitrogen |
| NPK | Nitrogen Phosphorus Potassium |
| OCP | Octacalcium Phosphate |
| OLR | Organic Loading Rate |
| OP | orthophosphate |
| P | Phosphate, Phosphorus |
| PLE | Polymeric Ligand Exchanger |
| $PO_4$-P | Orthophosphate |
| SBR | Sequenced Batch Reactor |
| SEPA | State Environmental Protection Administration |
| SP | Soluble Phosphorus |
| SRT | Sludge retention time |
| SS | Suspended Solids |
| TS | Total Solids |
| TSS | Total Suspended Solids |

| | |
|---|---|
| T, Temp | Absolute Temperature |
| TCP | Tricalcium phosphate |
| TP | Total phosphorus |
| UASB | Up-flow Anaerobic Sludge Bed |
| UBF | Up-flow Blanket Filter |
| USD | the United States Dollars |
| VFA | Volatile Fatty Acids |
| VS | Volatile Solids |
| $\alpha$ | ionic activity |
| ℃ | Degree Celsiums |
| Ω | Degree of saturation |
| μ | chemical potential |
| % | Percent |

# 1 Introduction

## 1.1 Problem

Phosphorus (P) is a key irreplaceable nutrient element in all known life forms. Almost all phosphorus used by society is mined from non-renewable phosphate rock. The most widespread use of phosphate rock is as mineral fertilizers for agricultural production. This accounts for approximately 80% of global consumption (Valsami-Jones, 2004). As a finite resource, the global phosphate reserve could be exhausted within the next 100-250 years (Shu et al., 2006). The phosphate resource is also limited in China. Current exploitable deposits could be used up in 70 years if used solely for domestic consumption.

Phosphorus has been recognized as a pollutant for a long time. It is for this reason that excessive phosphorus present in receiving water bodies is one of the main causes of eutrophication. In the past decade, it has been discovered that phosphorus could be recovered from waste streams in the form of struvite ($MgNH_4PO_4 \cdot 6H_2O$) and calcium phosphate (CEEP, 1998; 2001). As struvite could be used as slow-release fertilizer, it is regarded as the most ecologically efficient future method of P recycling.

Animal waste contains phosphorus and nitrogen in higher concentration than other waste streams. The forced precipitation of struvite from animal waste slurries prior to land application could reduce dissolved reactive P levels in manure slurries. It also offers the potential to recover excess phosphorus from manures and move it to cropping areas that require phosphorus fertilizer input.

China is the largest pig-breeding nation in the world, with approximately 50% of global production (Dong et al., 2007). In recent years, intensive animal breeding has resulted in the production of large amounts of manure waste, and treatment to reduce this has become a matter of priority. Moreover, as the world's largest developing country, China faces an energy crisis. In 2005, a "Renewable Energy Law" was passed in China. The government is paying a great deal of attention to the development of renewable energy.

In the light of these developments, it can be claimed that anaerobic digestion, combined with struvite precipitation, would be a suitable method of treating pig manure in China, as it could not only generate biogas energy, but also create valuable fertilizer as an end product.

## 1.2 Objective of this study

The objective of this study is to investigate forced P-precipitation in pig manure combined with anaerobic digestion. Phosphorus and nitrogen in the manure are not recovered as pure struvite, but precipitated in the digested manure, when biogas is generated, an enriched P-containing digested manure sludge can be obtained.

## 1.3 Dissertation Structure

This dissertation is divided into the following parts:

Chapter one has provided a brief introduction to the study and stated its objective.

Chapter two reviews all relevant information on phosphorus and phosphorus recovery.

Chapter three analyses the potential recoverable phosphate resource in China.

Chapter four reviews the situation of manure treatment on intensive scale animal farms in China.

Chapter five describes experimental materials and analytical methods.

Chapter six studies the performance of the pilot digester and the chemical properties of pig manure during the anaerobic digestion process.

Chapter seven investigates the conditions for phosphorus precipitation, including pH value, initial solution concentration, reaction time, the molar ratio of the reactant.

Chapter eight presents the conclusions of the study and offers some suggestions for the application of phosphorus recovery combined with biogas technology in China. The economic evaluation is also investigated.

Chapter nine summarizes the conclusions of the study.

# 2 Literature review: P-recovery

This chapter aims to review the background knowledge of phosphorus, the principles and technologies available for phosphorus recovery.

## 2.1 Background Knowledge: Phosphorus

### 2.1.1 The role of phosphorus in the natural world

Phosphorus (P) is the fifteenth element in the periodic table of elements. It has an atomic weight of 30.97376. Phosphorus has four allotropes: white, red, black and brown P. Phosphorus in its standard form is a waxy white solid which is highly poisonous and reactive in air. It ignites spontaneously in air, burning to pentoxide ($P_2O_5$) (Valsami-Jones, 2004). Phosphorus is seldom found as a free element in the natural world. Under most circumstances, phosphorus in natural systems occurs exclusively in the +5 oxidation state in the form of orthophosphates, polyphosphates, organophosphates and particulate phosphates (Morton, 2003).

Phosphorus is an essential element of life. Neither proteins nor carbohydrate polymers can be made without P (Westheimer, 1987). The conversion of ATP to ADP is the source of energy in most biochemical reactions. Cell membranes separate cells from each other and the surrounding environment and contain many phospholipids. The nucleic acids DNA and RNA have phosphate “backbones” forming the double helix structure (Menge, 2003). Phosphorus is abundant in vertebrate bodies because bones and teeth are comprised principally of hydroxyapatite, $Ca_{10}(PO4)_6(OH)_2$, which contains 18.5% P and makes up almost 60% of bone and 70% of dental-and fibrous collagen (Vaclav, 2000). Phosphate is also an important mineral macronutrient, governing the rate of growth of plants. Plants have an additional P requirement in NADPH, which is used in the light harvesting reactions of photosynthesis.

However, excessive phosphorus can be problematic, especially in aquatic systems. Phosphorus in the form of orthophosphate ($PO_4^{3-}$) is a direct factor in inducing eutrophication, which can be defined as the enrichment of waters by nutrients and the resulting deterioration of quality due to the luxuriant growth of plant life and its resultant effect on the ecological balance of the affected waters (Lester, 1999). In agriculture, superfluous loading of phosphate fertilizer or animal manure onto farm lands has also been recognized as a threat to ground water quality. When phosphorus input from fertilizer exceeds phosphorus output in crops, phosphate will tend to accumulate in the soil (Kuo et al., 2005) and leach out into the groundwater.

### 2.1.2 Impact of human activities on ecological P-recycling

The phosphorus cycle is shown in Fig. 2.1. In the natural environment, the phosphorus cycle starts with the release of phosphate minerals through rock weathering (Valsami-Jones, 2004). The erosion moves inorganic phosphate into soil and rivers, where it is absorbed by plants and incorporated into organic molecules (DNA, ATP, phospholipids etc.). When plants are eaten by animals and the human beings, phosphorus is incorporated into animal and human organisms. They ingest phosphorus as a nutrient, as well as excreting it with bodily wastes in their everyday lives. When the organisms die, phosphorus returns from their tissues back into soil and river. Apart from the phosphate absorbed by plants, the phosphate remaining in the soil enters streams and rivers, which then flow into the ocean. Along with the decomposition of aquatic organisms, it builds up in sediments and settles deep on the ocean bed. Over extremely long periods of time, the once-buried deposits are transformed into phosphate rock and brought up to the surface through violent geological shifts. Phosphate mineral rock could therefore be regarded as a non-renewable and limited resource.

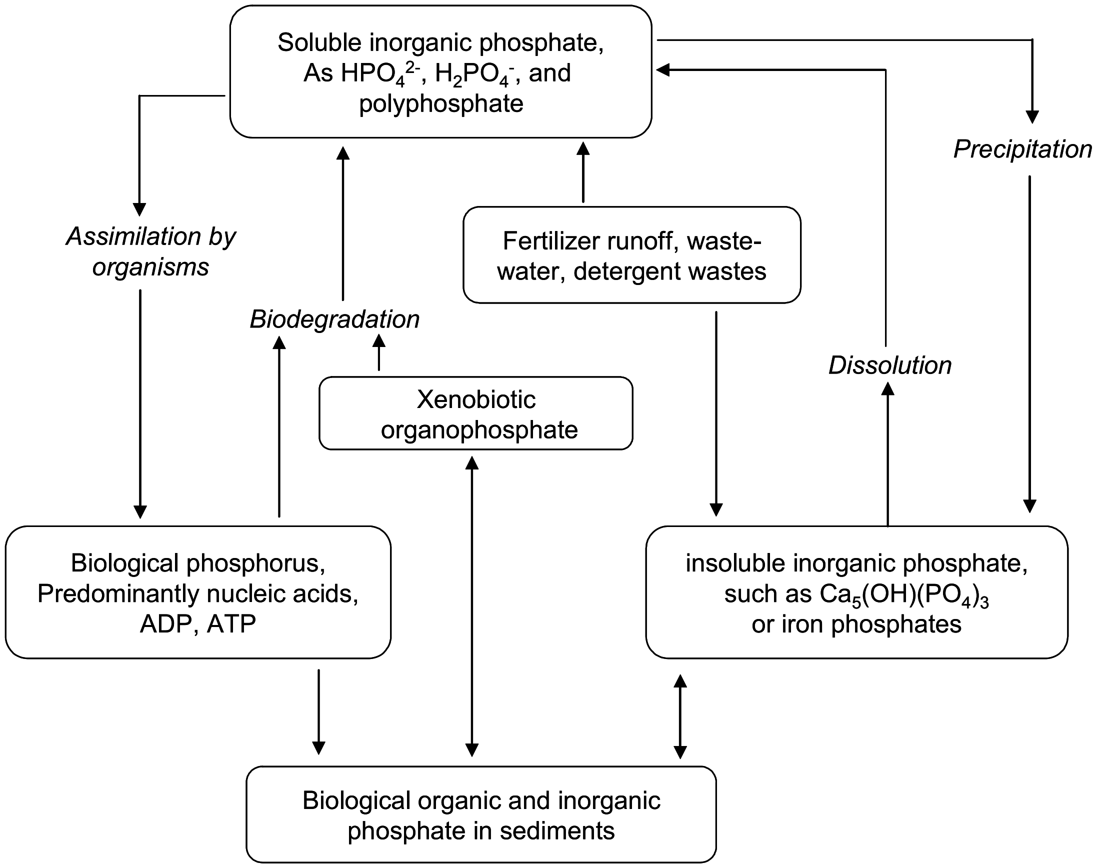

Fig. 2.1: The phosphorus cycle (Manahan. 2005)

Compared with other nutrient elements such as carbon and nitrogen, phosphorus has no common gaseous forms. Phosphorus is held largely in poorly soluble minerals. The most ecological route for phosphorus recycling is the agricultural application of bio-solids (sewage sludge, manures). Animal manure has been used by farmers to maintain crop production for thousands of years, but this is increasingly limited or impossible in many circumstances, for reasons of social acceptance, soil nutrient saturation or pollutant contamination/health issues (CEEP, 2001). However, the current urbanization of society is leading to intensive agricultural production and animal breeding, which diverts the natural cycle of phosphorus. The phosphorus cycle has thus largely been replaced by a complete linear system: phosphorus is extracted from a non-renewable resource (phosphate rock), passes through crops, animal and human life, and ends up either in landfill (of raw or incinerated sewage sludge) or in rivers and the sea (if sewage or animal wastes are not adequately treated). Meanwhile, in order to obtain high crop yields and to produce enough food for the growing population, intensive modern agricultural methods require large quantities of mineral fertilizer, which makes the limited resource even scarcer.

### 2.1.3 Phosphate reserve limitation in space and time

Phosphorus is the eleventh most abundant element in the lithosphere. However, the phosphate rock reserves are unevenly distributed throughout the world. Phosphate rock resources occur principally as sedimentary marine phosphorites. The largest deposits are found in northern Africa, China, the Middle East and the United States. Significant igneous occurrences are found in Brazil, Canada, Russia and South Africa. Large phosphate resources have been identified on the continental shelves and on seamounts in the Atlantic and Pacific Oceans, but they cannot be recovered economically using current technology (USGS, 2007)

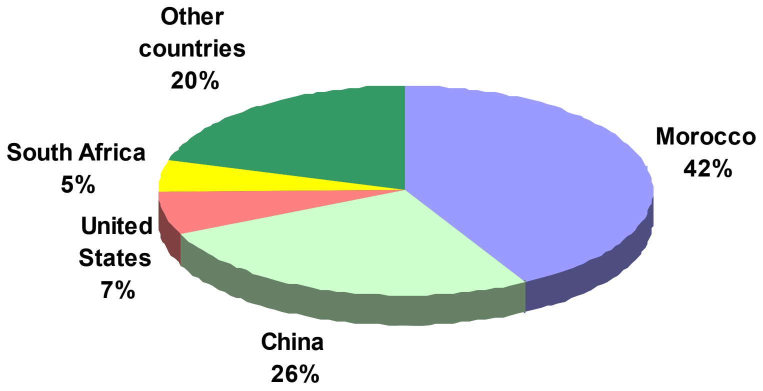

Fig. 2.2: Global phosphate rock reserve base in 2006

The basic reserve of phosphate rock resources in the world is estimated to be 50 billion tons (USGS, 2007). Over 30 countries currently produce phosphate rock for use in domestic markets or international trade. The world’s top 3 countries with phosphate rock, as shown in Fig. 2.2, account for over 80% of the world’s phosphate resource. Reserve data for China includes the deposit of low-grade ore. Of these countries, Morocco is the largest exporter of phosphate rock. The United Sates is the largest importer of phosphate rock and the leading consumer, producer, and supplier of phosphate fertilizers in the world (USGS, 2007), while the domestic phosphate rock of the United Sates has ceased to be exported.

Phosphate rock is an important material in chemical industries responsible for such products as fertilizers, food additives, medicines, explosives, friction matches, fireworks, toothpaste, detergents, etc. Of these applications, the most significant commercial use of phosphate rock is the production of fertilizers. A report complied by CEEP (Scope newsletter, 1997) stated that fertilizers account for 80% of overall phosphorus chemical production, the rest being used to produce detergents (12%), animal feeds (5%) and special applications (3%).

Global reserves of high-quality mined phosphate deposits are being gradually depleted (Shu et al., 2006). It is estimated that there are seven billion tons of phosphate rock as $P_2O_5$ remaining in reserves that could be economically mined. The human population consumes as much as 40 million tons of P as $P_2O_5$ each year and P demand will increase by 1.5% each year. It is predicted that the resource could be exhausted in as little as 100–250 years (Shu et al., 2006).

## 2.2 P-recovery in sewage work

### 2.2.1 The development of P-recovery

Deposition of struvite (MAP) in sewage works was first reported in 1963 at the Los Angeles Hyperion Wastewater Treatment Plant (Borgerding, 1972). Struvite was found to have accumulated in areas where there was an increase in turbulence, for example pipe bends, valves, pumps, and separating screens (Mohajit et al., 1989; Webb and Ho, 1992). Similar accumulation problems have also been found in anaerobic digestion sludge from animal farming liquid wastes (Booram et al., 1975). Steve (1998) subsequently presented the case of Slough sewage works in the UK, where struvite deposits have been causing considerable operating problems by blocking pumps and pipes. The methods used for the cleaning of struvite scale include acid washing, thermal treatment and jet washing (Borgerding, 1972; Williams, 1999). It is an extremely difficult and expensive operation in terms of replacing damaged equipment, system downtime and increased labor costs.

The concept of P-recovery has advanced in the past decade (CEEP, 1998; 2001). The substantial difference between traditional P-removal and P-recovery from wastewater is that P-removal stresses acquiring a P-free effluent by transferring P to sludge using chemical and biological processes, whilst P-recovery stresses acquiring a product containing P that can be reused in either agriculture or the P industry (Song, 2007).

Compared with traditional P-removal in sewage works, the advantage of P-recovery technology is obvious. First of all, P-recovery from waste streams enables industry to replace an imported non-renewable resource with a sustainable recycled raw material. An economic payback thus becomes feasible. Secondly, P-recovery can relieve certain operational problems in sewage works. Struvite precipitation in pumps and pipes can be prevented downstream of P-recovery. In addition, P-recovery offers the potential of significantly reducing sludge production compared with established P-removal processes (Uludag-Demirer et al., 2008).

Although some P-recovery technologies are currently being developed, most of them still in laboratory or pilot scale, this technology has not been widely adopted. The reasons are largely economic and technical. The investment and operational costs of P-recovery installations tends to be unacceptably high. Technical aspects requiring further improvement include the removal of heavy metal and reactor design, particularly in terms of efficiency and practicality. These need to be resolved as a matter of urgency before such an option becomes commercially viable.

The two common products in P-recovery process are Magnesium Ammonium Phosphate, $MgNH_4PO_4$ (MAP or struvite) and calcium phosphate compounds ($Ca_x(PO_4)_y$).

1. Struvite (MAP)

Magnesium ammonium phosphate hexahydrate (MAP), also known as struvite, is a white inorganic crystalline mineral. The properties of struvite as a slow-release fertilizer were tested as early as the 1960s in Germany and the USA (Schuiling and Andrade, 1999). Compared to other fertilizers, the benefits of using struvite are low leaching rates and the prolonged release of nutrients throughout the growth cycle of plants, with the possibility of only one single application (Gaterell et al., 2000). Moreover, struvite can also be used as a raw material in the fertilizer industry (Gaterell et al., 2000). Another advantage of P-recovery in the form of struvite is that not only phosphorus, but also equivalent molar ammonia can be removed from waste streams.

2. Calcium phosphate compounds

Calcium phosphate contains complex compounds of calcium phosphate salts with different crystal water contents. They include Hydroxylapatite (HAP), Tricalcium phosphate (TCP), Octacalcium phosphate (OCP), Dicalcium phoshphate anhydrous (DCPA) and Dicalcium phosphate dihydrate (DCPD) (see Tab. 2.3). The most frequently used method of phosphorus recovery in the form of calcium phosphate compounds is through crystallization. When mined, calcium phosphate is the same chemical as phosphate rock and can be reused in the phosphate industry (Valsami-Jones, 2004).

Tab.2.1 shows six forms of calcium phosphates, their molar ratios and solubility. Of these, HAP is the most stable, whilst DCPD is easiest to produce. The chemistry of calcium phosphate compound precipitation is complex, as it is not one molecule, but potentially a number of different compounds with different hydration complexes. The solubility and crystallization properties of these different molecules cause the balance between them to vary.

Tab. 2.1: Calcium phosphate crystalline phases, formulae and corresponding thermodynamic solubility products (Valsami-Jones, 2004)

| Solid Phase | Abbr. | Formula | Ca/P Molar ratio | Thermodynamic Solubility Product |
|---|---|---|---|---|
| Dicalcium phosphate Dihydrate | DCPD | $CaHPO_4 \cdot 2H_2O$ | 1.0 | $1.87 \times 10^{-7} (mol\ l^{-1})^2$ |
| Dicalcium phoshphate anhydrous | DCPA | $CaHPO_4$ | 1.0 | $9.2 \times 10^{-8} (mol\ l^{-1})^2$ |
| βTricalcium phosphate | TCP | $Ca_3(PO_4)_2$ | 1.5 | $2.8 \times 10^{-9} (mol\ l^{-1})^{15}$ |
| Octacalcium phosphate | OCP | $Ca_8H_2(PO_4)_6 \cdot 5H_2O$ | 1.33 | $2.5 \times 10^{-99} (mol\ l^{-1})^{16}$ |
| Hydroxylapatite | HAP | $Ca_{10}(PO_4)_6(OH)_2$ | 1.67 | $5.5 \times 10^{-118} (mol\ l^{-1})^{18}$ |

### 2.2.2 Techniques for P-recovery in sewage works

#### 2.2.2.1 Routes for P-recovery in sewage works

According to the analysis of Jardin (1995), phosphorus in the sewage plant can be recovered from the following three locations:

1. water phase (in the main stream or side stream);
2. sludge
3. sludge ash

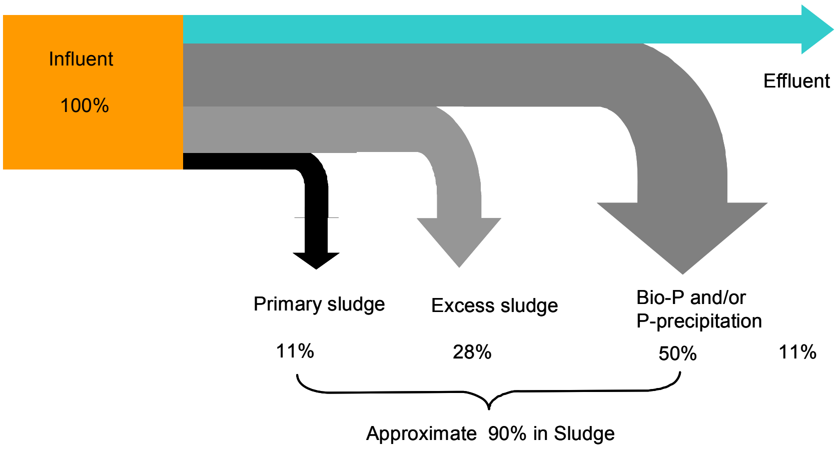

Fig. 2.3: Phosphorus balance in the conventional wastewater treatment plant (Jardin, 1995; Cornel and Schaum, 2005)

Fig. 2.3 shows the P balance in the conventional waste water treatment plant. It can be seen that the percentage of P is low in the water phase (11%) but high in sludge or sludge ash (about 91%). The methods for P-recovery from waste streams include direct precipitation, crystallization and ion exchange. Several major P-recovery technologies will be reviewed.

### 2.2.2.2 Crystallization

At present, there are two types of crystallization process which have been developed for P-recovery: fluidized bed crystalactor and fixed bed crystalactor. Most of the crystalactors enable P-removal and recovery by following process routes (Piekema and Gaastra, 1993).

1. Crystallization as calcium phosphate (CP)
2. Crystallization as magnesium phosphate (MP)
3. Crystallization as magnesium ammonium phosphate (MAP)
4. Crystallization as potassium magnesium phosphate (KMP)

#### 2.2.2.2.1 Fluidized bed crystalactor

A fluidized bed crystalactor usually consists of a vertical cylinder filled with suitable seed materials, which are brought to a fluidized state by means of reactant solutions fed into the bottom of the cylinder. Several materials such as sand, calcite sand and a variety of calcium phosphate crystals have so far been used as seed materials (Koutsoukos et al., 1980,1981; Moreno et al., 1981; De Rooij et al., 1984; Moriyama et al., 2001). Fig. 2.4 shows the structure of a DHV crystalactor.

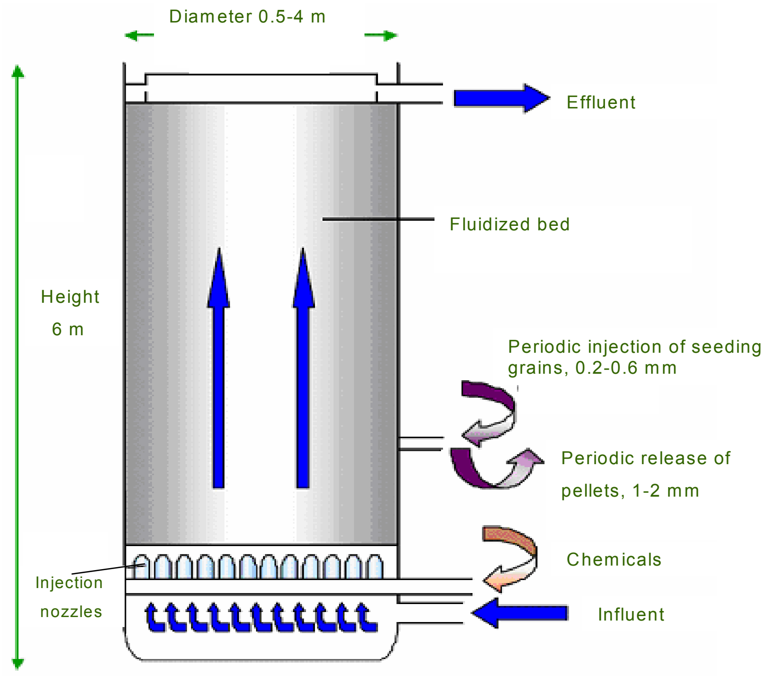

Fig. 2.4: The design principle of a DHV Crystalactor (Piekema and Gaastra, 1993)

Two further typical crystallization reactors are CSIR fluidized bed crystallization column and Unitika Phosnix.

The CSIR fluidized bed crystallization column has been developed in South Africa. Phosphate can be removed as either hydroxylapatite or struvite, according to the composition of the feed stream, resulting in retention times ranging from 3-10 minutes in over 90% of P-removal at pH controlled between 8.0 and 9.5.

The Unitika Phosnix process has been developed in Japan. It is a side-stream process, and treats rich phosphorus wastewater, such as the effluent from digesters, biological nutrient removal systems etc. Digester effluent is fed into the base of the tower, where it is mixed with magnesium chloride. Caustic soda is added in order to ensure a pH of 8.5–9.0. Thus the conditions for spontaneous nucleation and growth of struvite crystals are achieved.

One advantage of the P-recovery process using the fluidized bed reactor is that, because new MAP crystals are produced on the crystal surfaces fluidized in the reactor, the necessary reactions and solid-liquid separation can take place simultaneously (Graveland et al., 1983; van Dijk and Wilms, 1991). A problem, however, was that, in the case of conventional type fluidized bed reactors, the crystals are enlarged in diameter in the course of treatment in the reactor, and as a result, the reaction surface areas decrease, causing fluidization to be insufficient and the phosphorus recovery ratio to be decreased (Shimamura et al., 2003).

### 2.2.2.2.2 Fixed bed crystalactor

The Kurita fixed bed crystallization column is based on chemistry similar to the DHV crystalactor (Brett, 1997). It is designed to remove P from the secondary effluent of a sewage treatment plant. The recovery process is shown in Fig. 2.5. The structure consists of a fixed bed column reactor packed with phosphate rock seeding grains. Secondary effluent is fed into the base of the column and travels upwards through it. The phosphate-depleted effluents exit from the top of the column.

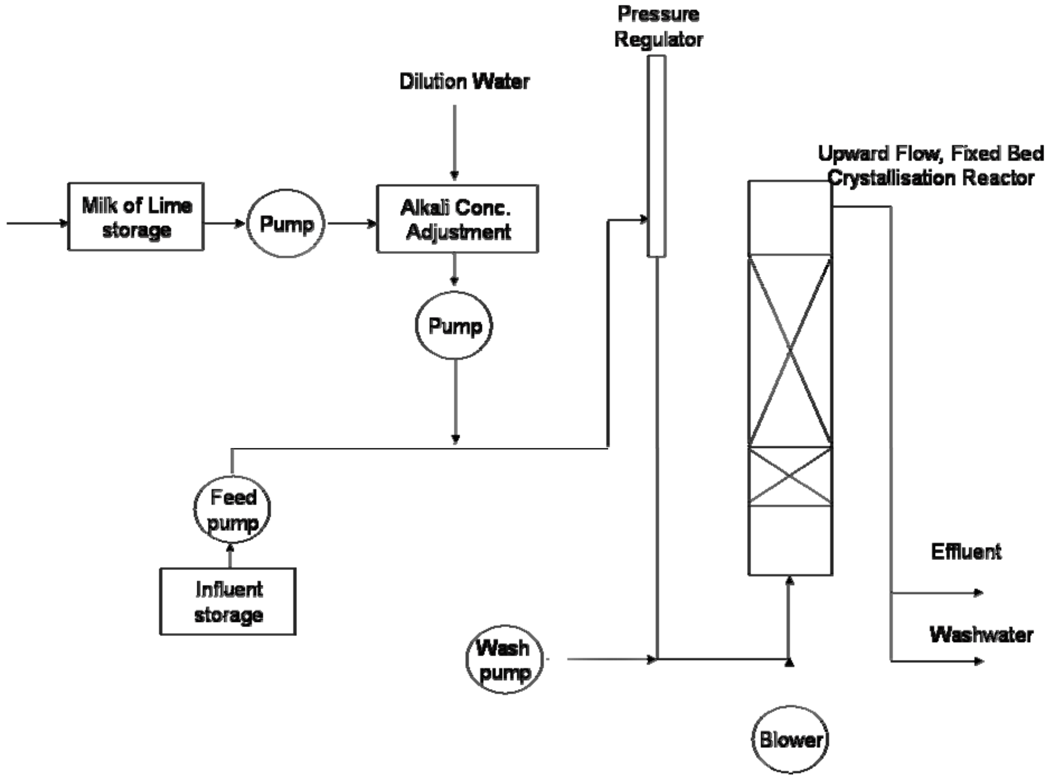

Fig. 2.5: The Kurita process

Parsons et al. (2001) found that recovery efficiency by crystallization could be enhanced by increasing the particle size of the precipitate. Particle formation is referred to as nucleation or induction. Facilities in Europe and Japan are seeking to increase particle size to enhance recovery (Battistoni et al., 2000, 2002; Kumashiro et al., 2001; Ueno and Fuji, 2001). Experiments using this technology on animal manures have not yet been performed.

All the aforementioned techniques have some worth, but they need the addition of chemicals to adjust the experimental conditions in order to facilitate the crystallization of phosphate salts. Song (2003) summarizes the reaction conditions of the above technology, shown as Tab. 2.2.

Tab. 2.2: Summary of crystallization technologies for phosphorus recovery

| Technology | Main reactor | Key process conditions | Product |
|---|---|---|---|
| DHV Crystalactor | Fluidized crystalactor | pH: 8.0-8.5;<br>Ca/P: ratio2-3;<br>hydraulic load: 40 m/h | CP, MP, struvite |
| CSIR fluidized be crystallization column | Fluidized column | pH: 8.0-9.5 for HAP;<br>pH>8.0 for struvite | HAP, struvite |
| Unitika Phosnix | Air-agitated column | pH: 8.0-9.0;<br>Mg/P ratio:1-1.3 | struvite |
| Kurita fixed bed crystallization column | Fixed bed column | Hydraulic load: 2.3 m/h | HAP |

#### 2.2.2.3 Ion exchange

An ion exchanger (Helfferich, 1995) consists of solid material into which anions or cations in the solution can be adsorbed. The ion exchanger can be made of a polymer with attached ionic groups. Sulfonic, phosphonic and carboxylic groups are examples of ionic groups suitable for cation exchangers. Amino groups were first used for anion exchangers. A cation exchanger is made from a material with a negative surface charge to which the metal cations in the solution can be attached.

The use of polymeric ligand exchange resins and adsorbents for P-removal from phosphate-rich waters has been reported by several authors (Zhao et al., 1995,1998; Petruzzelli et al., 2004). Kumar (2007) demonstrated that PLEs (polymeric ligand exchanger) can be successfully used to remove phosphate from reverse osmosis concentrate and to recover more than 85% of the adsorbed phosphate radical from the exhausted media , precipitated as a beneficial product (struvite).

The BioCon process shown in Fig. 2.6 (Schaum, 2002) is a technology-combined ion exchanger for the removal of phosphorus. It has been developed by a Danish company. In this process, ion exchange is used for phosphorus recovery after leaching with acid. The ion exchange process is performed in two sets of four columns. In the first column, which is a cation exchanger, the ferric ions are taken up. This column is regenerated with sulfuric acid, producing ferric sulfate $Fe_2(SO_4)_3$. The second column is an anion exchanger, which removes sulfate ions and is regenerated with potassium chloride, producing potassium bisulphate, $KHSO_4$. The third column is an anion exchanger, which removes phosphate ions and is regenerated with hydrochloric acid, producing phosphoric acid, $H_3PO_4$. The final column is a cation exchanger, which removes other metals and is regenerated hydrochloric acid, producing metal chloride.

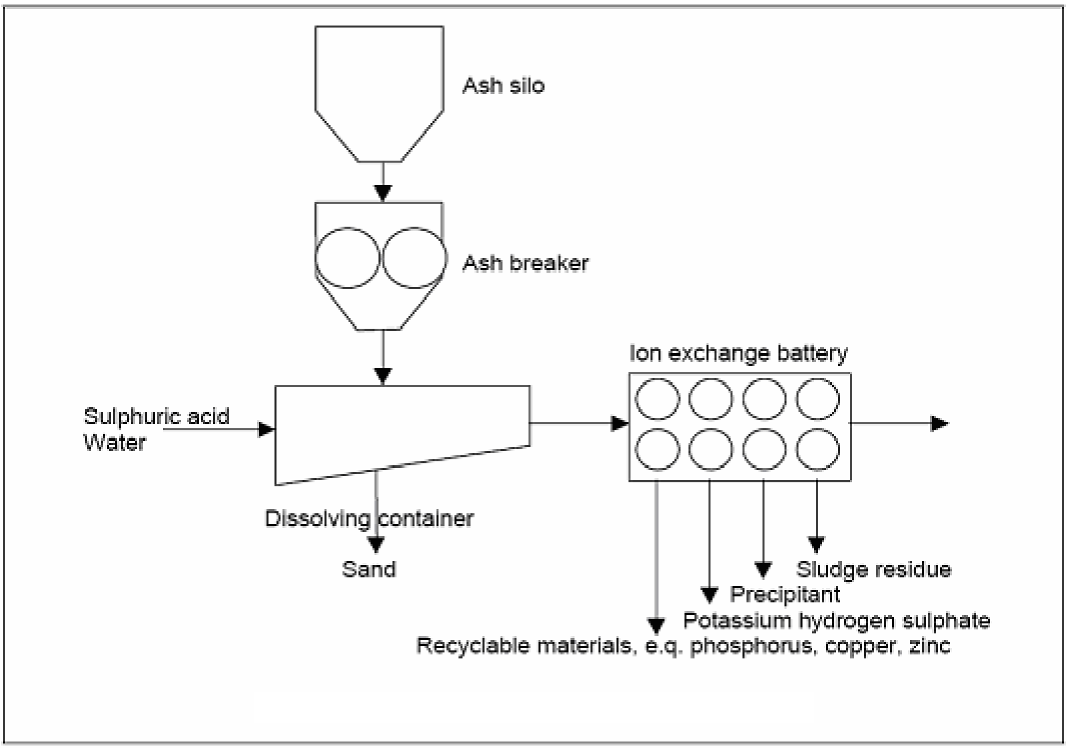

Fig. 2.6: Schematic drawing of the BioCon-Process (Schaum, 2002)

Liberti (Liberti et al. 1986; 2001) operated a mineral-precipitating pilot plant using the RIM-NUT process to remove constituent ions selectively onto resins, followed by the addition of with magnesium salts (at a stoichiometric ratio of $Mg:NH_4:PO_4 = 1:1:1$), to form struvite precipitation and thus separate them from the solution. The flow chart of the REM-NUT process is shown in Fig. 2.7. The RIM-NUT process consists of three stages: two columns of cationic resin, two columns of anionic resin and the nutrient precipitation process. A dual column system is adopted for each resin to allow for simultaneous regeneration and phosphorus removal.

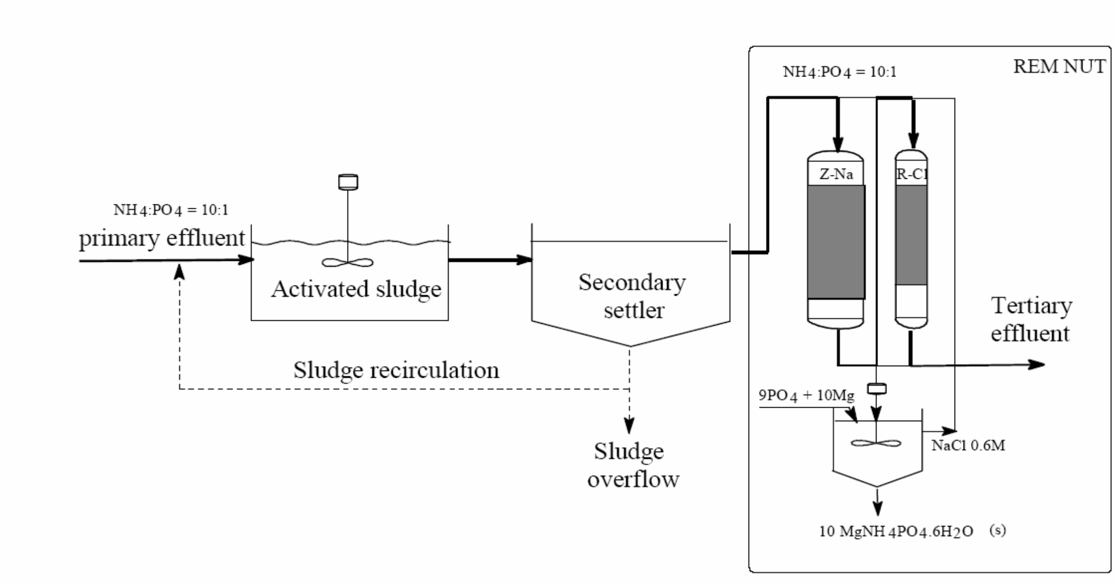

Fig. 2.7: Flow chart of the REM-NUT process

Tab. 2.3: List of P-recovery process in WWTP and its product, efficiency and cost (von Horn, 2007)

| **Verfahren** | **Wirkungsgrad* P-Rücklösung** | **Produkt** | **Aufwand** |
|---|---|---|---|
| **Rückgewinnungsansätze aus der flüssigen Phase (Abwasser, Prozesswasser)** | | | |
| DHV Crystalactor | max. 37 % | $CaPO_4$ | gering |
| P-Roc | ca. 40 % | $CaPO_4$ | sehr gering |
| Phostrip | ca. 30 % | $CaPO_4$ | gering |
| MAP-Fällung aus Prozesswasser | 50 - 65 % | MAP | sehr gering |
| PRISA | 35 - 45 % | MAP | sehr gering |
| RIM/NUT | keine Angaben | MAP | moderat |
| MAP-Ausschleusung bei der Schlammbehandlung | keine Angaben | MAP | sehr gering |
| **Rückgewinnung aus Klärschlamm** | | | |
| Seaborne | ca. 70 % | MAP | sehr hoch |
| Krepro | max. 65 - 70 % | $FePO_4$ | sehr hoch |
| Cambi | ca. 45 % | MAP | hoch |
| Aqua Reci | ca. 70 % | $CaPO_4$ | hoch |
| **Rückgewinnung aus Klärschlammasche** | | | |
| Nasschemische Verfahren | keine Angaben | MAP, $CaPO_4$ | sehr hoch |
| Ashdec | keine Angaben | Mehrkomponentendünger | moderat |
| Eisenbad | keine Angaben | Phosphatschlacke | moderat |

*Wirkungsgrad bezogen auf die Phosphatfracht im Zulauf zur Kläranlage

## 2.3 Chemical principles of struvite formation

### 2.3.1 Properties of struvite

The main physicochemical properties of struvite are shown below (Robert et al., 1990):

- Chemical formula: $MgNH_4PO_4 \cdot 6H_2O$
- Formula weight: 245.41
- Crystal System: Orthorhombic
- Colour: white, yellowish-white and brownish
- Specific density: 1.7
- Solubility: highly insoluble in water and alcohol, soluble in acid
- Melting point: at melting point it decomposes to form magnesium pyrophosphate ($Mg_2P_2O_7$)
- $\Delta H^{o} f$ (kcal/mole): −880.0

Struvite is found to be thermally unstable in temperatures over 50℃ (Sarkar, 1991). The ammonia and water molecules of struvite are lost depending on the time and temperature of the heat treatment, ultimately forming magnesium hydrogen phosphate trihydrate ($MgNPO_4 \cdot 3H_2O$). When struvite is further heated, monohydrate ($MgNPO_4 \cdot H_2O$) is formed.

### 2.3.2 Thermodynamics of struvite formation

In aqueous solution, struvite forms according to the general reactions shown below:

$$Mg^{2+} + NH_4^{+} + PO_4^{3-} + 6H_2O \Leftrightarrow MgNH_4PO_4 \cdot 6H_2O \downarrow \qquad (2\text{-}1)$$

$$Mg^{2+} + NH_4^{+} + HPO_4^{2-} + 6H_2O \Leftrightarrow MgNH_4PO_4 \cdot 6H_2O \downarrow + H^{+} \qquad (2\text{-}2)$$

$$Mg^{2+} + NH_4^{+} + H_2PO_4^{-}\ 6H_2O \Leftrightarrow MgNH_4PO_4 \cdot 6H_2O \downarrow + 2H^{+} \qquad (2\text{-}3)$$

Other possible side reactions include:

$NH_4^+ + OH^- \Leftrightarrow NH_3\uparrow + H_2O$ (2-4)

$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2\downarrow$ (2-5)

$3Mg^{2+} + 2PO_4^{3-} \rightarrow Mg_3(PO_4)_2\downarrow$ (2-6)

$Mg^{2+} + HPO_4^{2-} \rightarrow MgHPO_4\downarrow$ (2-7)

$Mg^{2+} + 2H_2PO_4^- \rightarrow MgH_2PO_4\downarrow$ (2-8)

According to the equation (2-1), the ionic activity product *IAP* is given by the following expression:

$$IAP = \alpha_{Mg^{2+}} \cdot \alpha_{NH_4^+} \cdot \alpha_{PO_4^{3-}} \tag{2-9}$$

where $\alpha$ is the ionic activity.

The driving force for the formation of struvite is the difference between the chemical potentials $\Delta\mu$ of the salt in the supersaturated solution $\mu_s$ from the corresponding value at equilibrium $\mu_\infty$ ( Kofina and Koutsoukos, 2005):

$$\Delta\mu = \mu_\infty - \mu_s \tag{2-10}$$

$$= [\mu_\infty^\circ + kT\ln(\alpha_{Mg^{2+}} \cdot \alpha_{NH_4^+} \cdot \alpha_{PO_4^{3-}})_\infty^{1/3}] - [\mu_s^\circ + kT\ln(\alpha_{Mg^{2+}} \cdot \alpha_{NH_4^+} \cdot \alpha_{PO_4^{3-}})_s^{1/3}]$$

where k is the Boltzmann's constant and T the absolute temperature.

Assuming that the chemical potentials of the standard states in the supersaturated solution and at equilibrium are equal, i.e. $\mu_\infty^\circ = \mu_s^\circ$ , the difference in chemical potentials is:

$$\Delta\mu = kT\ln\frac{(\alpha_{Mg^{2+}} \cdot \alpha_{NH_4^+} \cdot \alpha_{PO_4^{3-}})_\infty^{1/3}}{(\alpha_{Mg^{2+}} \cdot \alpha_{NH_4^+} \cdot \alpha_{PO_4^{3-}})_s^{1/3}}$$

$$= -\frac{kT}{3}\ln\frac{(\alpha_{Mg^{2+}} \cdot \alpha_{NH_4^+} \cdot \alpha_{PO_4^{3-}})_s}{(\alpha_{Mg^{2+}} \cdot \alpha_{NH_4^+} \cdot \alpha_{PO_4^{3-}})_\infty}$$

The supersaturation ratio $\Omega$ can described as:

$$\Omega = \frac{\alpha_{Mg^{2+}} \cdot \alpha_{NH_4^+} \cdot \alpha_{PO_4^{3-}}}{K_{sp}} = \frac{IAP}{K_{sp}} \qquad (2\text{-}11)$$

where $K_{sp}$ is thermodynamic solubility product of struvite, then the equation (2-10) is given by:

$$\Delta\mu = -\frac{kT}{3}\ln\Omega = -\frac{kT}{3}\ln(\frac{IAP}{K_{sp}}) \qquad (2\text{-}12)$$

The supersaturation ratio $\Omega$ is a measure of the driving force of the precipitation.

for $\Omega$<1; $IAP < K_{sp}$, the solution is undersaturated and dissolution may occur.

$\Omega$=1; $IAP = K_{sp}$, the solution is saturated (equilibrium).

$\Omega$>1; $IAP > K_{sp}$, the solution is supersaturated and precipitation may take place.

A number of thermodynamic solubility product values of struvite, $K_{sp}$, have been measured (Tab. 2.4). In practice, however, as wastewater composition will vary from one to another, each wastewater is likely to have a distinct $K_{sp}$ value. Any variation in water chemistry will result in a change in ion activity.

Tab. 2.4: Reported solubility products for struvite in aqueous solution

| $K_{sp}$ | $pK_{sp}$ | References |
|---|---|---|
| $7.08X10^{-14}$ | 13.15 | Taylor et al., 1963 |
| $4.36X10^{-13}$ | 12.6 | Stumm et al., 1970 |
| $3.98X10^{-10}$ | 9.4 | Borgerding, 1972 |
| $7.58X10^{-14}$ | 13.12 | Burns, 1982 |
| $1X10^{-13}$ | 13.0 | Mamais et al., 1994 |
| $2.51X10^{-13}$ | 12.6 | Loewenthal et al., 1994 |
| $4.36X10^{-13}$ | 12.36 | Buchanan et al., 1994 |
| $1.16X10^{-13}$ | 12.94 | Aage et al., 1997 |
| $5.50X10^{-14}$ | 13.26 | Ohlinger et al., 1998 |

### 2.3.3 Factors influencing struvite precipitation

Struvite formation occurs when the concentrations of magnesium, ammonium and phosphate in solution reach and exceed supersaturation levels. Supersaturation is a function of the pH value of the solution and the constituent ions. Possible factors influencing struvite precipitation, therefore, include the pH value, the concentrations of reactant ions, temperature and the presence of other ions such as calcium in the solution.

#### 2.3.3.1 pH value

The reaction of struvite precipitation is highly dependent on pH value. This is firstly due to the struvite solubility. Struvite is soluble in an acid environment and highly insoluble in an alkaline environment. Struvite precipitation can thus be controlled by pH adjustment (Booram et al. 1975; Doyle and Parsons. 2002). Secondly, reactant ions forming the struvite are all pH-dependent. It is known that, with a change in pH value, phosphate radical exists in different forms (Fig. 2.8). The concentration of ammonium ion varies with the change in pH value (equation 2-4). In the presence of phosphate, magnesium forms the complexes $MgPO_4^-$ and $MgHPO_4$, depending on the pH and concentrations of species in solution (Ohlinger 1999). When pH is over 12, $Mg^{2+}$ ion has priority to react with the alkali to form $Mg(OH)_2$.

The pH range within which struvite can precipitate has been identified as 7 – 11 (Regy et al., 2001).

Rettmer (1991) specified the pH range at 8-10. Webb and Ho (1992) found struvite solubility to decrease throughout the pH range of 6.5-8.2. Liao et al. (1995) tested various pH levels in combination with other factors, and found an optimum of 7.5 for piggery wastewater and an optimum of 10.0 for synthetic wastewater. Ohlinger et al. (1998) predicted (but did not measure) the pH for minimum struvite solubility to be just over 10. Beal et al. (1999) reported phosphorus removal at pH 8.5 and slightly less than 9.0. Miles and Elli (2001) conducted bench experiments on treating digested pig waste with the addition of supplemental magnesium and phosphate; the optimum pH was determined to be 9.0 for struvite precipitation. Nelson et al. (2003) found that minimum concentrations of $PO_4$-P occurred between pH 8.9 and 9.25 at all Mg/P ratios in the treatment of anaerobic pig lagoon liquid. Burn et al. (2003) used 64% magnesium chloride ($MgCl_2$) solution to force the P-precipitation in pig wastes, the best soluble P-removal efficiency was achieved at a pH of 8.6.

The pH can be adjusted according to dosing base. NaOH was regarded as the most effective chemical (Fujimoto, 1991). Another method of pH adjustment that has been applied is the aeration of liquids. Aeration strips carbon dioxide and thus alters the carbonate chemistry of the liquids, resulting in an increase in pH.

#### 2.3.3.2 Reactant ions

##### 2.3.3.2.1 Magnesium

Magnesium is generally the limiting nutrient for struvite recovery (Westerman et al., 1985; Buchanan et al., 1994). According to equation (2-1)-(2-3), the theoretical molar ratio of dissolved magnesium to dissolved phosphorus is 1:1. Literature has shown that most waste streams are magnesium deficient and lack the minimum necessary molar ratio of 1:1. Besides, $Mg(OH)_2$, $Mg_2(PO_4)_3$, $MgHPO_4$ and $MgH_2PO_4$ could possibly be formed during struvite formation. Magnesium additions exceeding the stoichiometric rate are therefore required. It was also found that additional amounts of $Mg^{2+}$ are required to overcome the effects of complex agents that can bind to magnesium, such as organic materials (Schulze-Rettmer, 1991; Burns et al., 2001). Animal waste slurries often contain high concentrations of organic matter and solids. The minimum required magnesium dosing rate was reported as a magnesium to phosphorus molar ratio of 1.3:1.

Various magnesium salts, such as Magnesium hydroxide ($Mg(OH)_2$), magnesium oxide (MgO), magnesium chloride ($MgCl_2$) and magnesium sulfate ($MgSO_4$), have been used as a magnesium source. The advantage of using $MgCl_2$ and $MgSO_4$ is their faster dissolution in solution. The supplementation of MgO and $Mg(OH)_2$ can increase the pH of the solution. They are normally less expensive than $MgCl_2$ and $MgSO_4$. However, as MgO and $Mg(OH)_2$ are insoluble in water, longer disassociation times may require a longer time for the reaction to attain equilibrium. A fine particle size and vigorous agitation are needed when using MgO or $Mg(OH)_2$ for struvite precipitation (Zeng and Li, 2006).

In order to reduce the cost of chemical addition, alternative sources of magnesium have been investigated. Chimenos et al. (2003) adopted low grade MgO instead of pure MgO as their magnesium source. Seawater and bittern were also recommended as a source of magnesium if the wastewater works was near the coastal area (Fujimoto et al., 1991; Shin and Lee, 1997; Lee et al., 2003).

#### 2.3.3.2.2 Phosphate radical

Orthophosphate acid is a ternary acid, and, several orthophosphate species therefore exist in aqueous solution at any given pH value. Fig. 2.8 shows that, in the pH range of 7-11 in which struvite forms, $HPO_4^{2-}$ is the dominant phosphate ion. The reaction of struvite precipitation is mainly based, therefore, on equation 2-2.

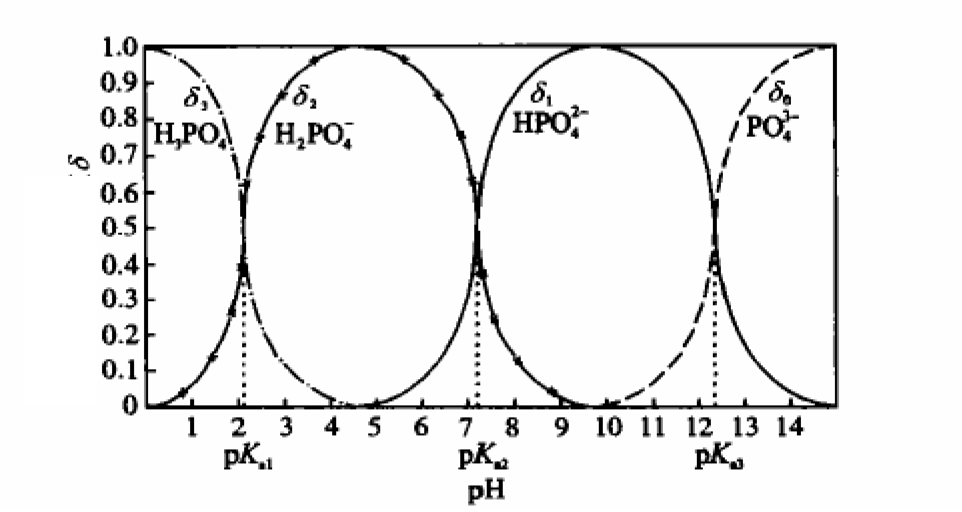

Fig. 2.8: Relation between distribution coefficients of three species of phosphoric acid and pH value of solution

#### 2.3.3.2.3 Ammonium

In general, ammonium concentration in waste streams is in excess of phosphate and magnesium. The proportion of ammonium ion present in a solution depends on its equilibrium with ammonia. Ammonia in solution exists in two forms: ammonium ions ($NH_4^+$) and ammonia ($NH_3$). The equilibrium of ammonium in solution is pH-dependent. As shown in equation 2-4, the equilibrium tends to move towards leftwards at lower pH. More ammonium ions are available in an area of low pH. Ammonium is not available when the solution pH exceeds 11 (Burns and Moody, 2002).

Stratful et al. (2001) demonstrated that an excess of $NH_4^+$ relative to $Mg^{2+}$ and $PO_4^{3-}$ could drive the reaction to form a relatively pure precipitate in terms of struvite composition. Münch and Barr (2001) reported that P-removal rate improves with higher ammonium concentration.

### 2.3.3.3 Influence of other ions

The existence of the calcium ion also influences struvite precipitation by competing for phosphate ions (Le Corre et al., 2005). When the calcium ion reacts with phosphate, it can form different type of calcium phosphate (Tab. 2.3).

Abbona and Madsen (1986) reported that the chemical contents of P-precipitates in terms of calcium, magnesium and phosphate were affected by the calcium to magnesium molar ratio. The crystallization of calcium phosphates was not affected by the presence of magnesium in the pure calcium solution until Ca/Mg became less than 1.3. Research by Battistoni et al. (1998) has shown that HAP and MAP could be formed when both calcium and magnesium ions were present in the solution. 80 to 100% of the struvite was obtained when the Ca/Mg molar ratio was 1.8. Lind et al. (2000) reported that small amounts of Ca may act as a substitute for Mg in struvite by means of P-recovery from urine. Musvoto et al. (2000) discovered that struvite will precipitate in the presence of the calcium ion at $Mg^{2+}/Ca^{2+}$ molar ratios of >0.6. Yi and Lo (2003) have found that the contents of precipitates were affected by Ca/Mg ratio. The higher calcium contents were obtained with wastewaters with a high Ca/Mg ratio.

In addition, potassium often exists at a considerable level in manure effluents and can act as a substitute for $NH_4^+$ to form K-struvite ($MgKPO_4 \cdot 6H_2O$). K-struvite has a similar structure to struvite (Mathew and Schroeder, 1979). It is also, as a mineral source of both potash and phosphate, an excellent fertilizer. Yi and Lo (2003) conducted a study of P-precipitation from greenhouse wastewater and found that K-struvite precipitated with MAP and HAP. However, it was not the major product in the precipitate; the potassium contents in the precipitates were not even affected by the addition of magnesium.

#### 2.3.3.4 Suspended solid and mixing energy input

Struvite precipitation can be separated into two stages: nucleation and growth (Doyle and Parson, 2002). Nucleation occurs when ions combine to form crystal embryos. Growth is the process of incorporating constituent ions into the crystal lattice of the embryos to form detectable crystals. Crystal growth continues until equilibrium is reached (Ohlinger et al., 1999). Nucleation can be divided into primary nucleation (homogeneous and heterogeneous) and secondary nucleation, as shown in Fig. 2.9 (Mullin, 2001). In homogeneous nucleation, nucleus forms spontaneously with the precipitating substance itself, while heterogeneous nucleation is induced by foreign particles.

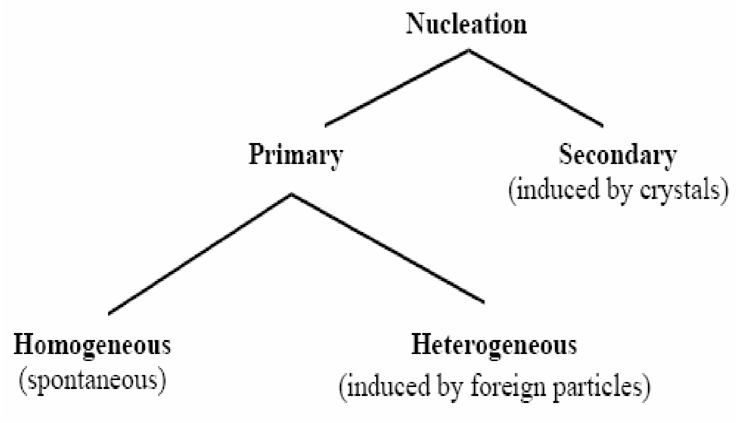

Fig. 2.9: Classification of nucleation

As homogeneous nucleation occurs only in highly purified and/or highly supersaturated solutions, heterogeneous nucleation is usually the predominant nucleation mechanism in wastewater treatment environments (Ohlinger et al., 1999). Theoretically, the existence of a proper quantity of suspended particles can be provided as the nuclei of heterogeneous nucleation and increase the specific surface area of contact. Zhou (2005) also reports that the existence of suspended solids helps to increase the precipitation rate. However, Schuiling and Andrade (1999) suggested that total suspended solids interfere with the precipitation process at total suspended solid concentrations of over 1000 mg/ $L^{-1}$.

According to reports, quartz sand, borosilicate glass grindings, phosphate rock and parent struvite have been used as seed materials in the crystallization process (Joko, 1984; Münch and Barr, 2001; Valsami-Jones, 2004). The experiments of Ali and Schneider (2005) have shown that mother crystals (struvite) were more effective as seeds for struvite crystallization.

Borgerding (1972) reported that struvite is prone to form in locations with the greatest surface to volume ratio: rough surfaces and locations of energy input. Momberg and Oellerman (1992) have proved that, under stagnant conditions (without mixing) when the pH less than 8, struvite precipitation proceeds very slowly and the reaction may last many days. Ohlinger et al. (1999) concluded that nucleation can be shown to be primarily controlled by supersaturation. Growth rates were shown to be primarily controlled by mixing energy, a factor that varies from system to system. In addition, mixing of the solution can significantly shorten the precipitation time.

### 2.3.3.5 Temperature

The solubility product of struvite increases with an increase in temperature (Tab. 2.5). Thus struvite recovery theoretically decreases with an increase in temperature. Salutsky et al. (1972) reported that lower residual phosphate concentration was obtained at higher temperatures for the chemical precipitation of struvite from the digested effluent in a sewage plant. However, Aage et al. (1997) found that, compared with other known factors (such as pH, molar ratio and interference ions), temperature has a less pronounced effect on struvite recovery. Zeng and Li (2006) reported that the influence of temperatures between 5 and 50℃ on struvite precipitation from digested cattle manure effluents is less significant. They also suggest that the operation temperature can be set at 15-35℃.

Tab. 2.5: Thermodynamic solubility product of struvite at various temperatures (Aage et al., 1997)

| Temperature ℃ | Solubility product *La $\times$ $10^{-14}$ |
|---|---|
| 10 | 5.42 |
| 15 | 6.90 |
| 25 | 11.65 |
| 30 | 15.80 |
| 40 | 30.2 |
| 50 | 37.3 |

*La denotes the solubility product in terms of activity.

## 2.4 Previous work on P-recovery from animal waste

Animal manure has been recognized as the most promising source of future P-recovery (CEEP 1998; 2001); animal manure contains abundant nutrients, magnesium and calcium. In addition, it is well known that animal waste should be properly controlled. Otherwise it could cause serious environmental pollution. P-recovery techniques have been applied to various animal wastes, most of them used to treat pig and calf manure.

### 2.4.1 Aeration

Pig manure has a relatively higher water content in comparison to other animal manures. Especially in some countries, manure in piggeries is cleaned by flushing water, which produces large amounts of wastewater. Most studies of P-recovery combined with the aeration method have been made by Japanese researchers (Suzuki et al., 2002; 2004; 2005; 2007). The purpose of aeration is to provide suitable mixing of the contents in the reaction zone. This will also help increase the pH of the reactor contents by stripping out carbon dioxide.

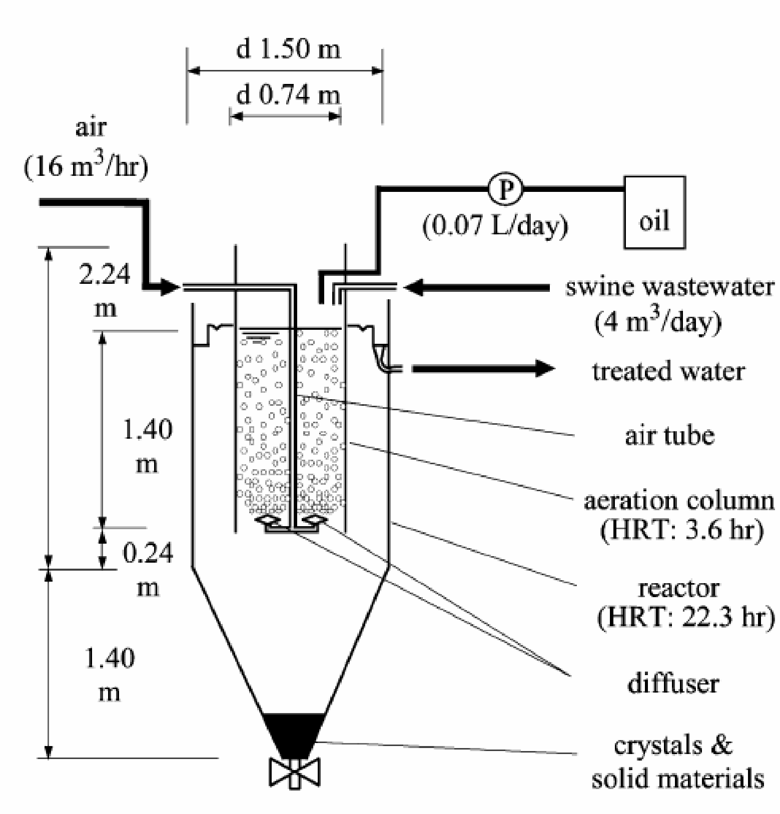

Fig. 2.10: Layout of pilot-scale crystallization reactor (Suzuki et al. 2007)

Fig. 2.10 shows a pilot-scale crystallization reactor for P-recovery in Japan. In most Japanese pig-farming facilities, faeces, urine and washing water are separated into solid and liquid forms (Suzuki et al., 2002). The pH value was increased by aeration, and the concentrations of total P and soluble $PO_4$-P were reduced by means of struvite crystallization. The reaction was conducted under a high pH condition. A 30% addition of $MgCl_2$ proved effective in enhancing the struvite crystallization reaction. The recovered struvite required only air-drying before use, since it was approximately 95% pure, even without washing.

The reactor was designed with dual functions crystallization through aeration, and separation of formed struvite by means of settling. The piggery wastewater was screened by a 1.5 mm mesh from a piggery. Then it was continuously fed into the aeration column of the reactor (4.0 $m^3$/day) and aerated at 15.6 $m^3$-air/h. Air was sent to diffuser units via a stainless-steel air tube (2.8 cm in outer diameter). The device has a struvite-accumulation surface, which is made of stainless-steel wire mesh (1 mm in diameter, 1 $cm^2$ square) to reduce its total weight. After 30 days of submersion, the device was taken from the aeration column, and struvite was then scraped from the struvite accumulation surface.

### 2.4.2 Anaerobic digestion (AD)

From a waste-treatment and nutrient-recovery point-of-view, anaerobic digestion has some obvious advantages in the treatment of animal manure. Microbial action in the anaerobic digestion process substantially reduces chemical and biological oxygen demand (COD and BOD, respectively), total solids (TS), and volatile solids (VS). The total nitrogen and phosphorus contents are not substantially changed by anaerobic digestion. However, the nitrate nitrogen and much of the organic nitrogen are converted to ammonia. Because phosphorus and nitrogen are necessary nutrients for plant growth, the digested residues from AD can be used as fertilizer. A potential of nutrients and energy recovery through AD technology is illustrated below in Fig. 2.11 (Lens et al. 2001).

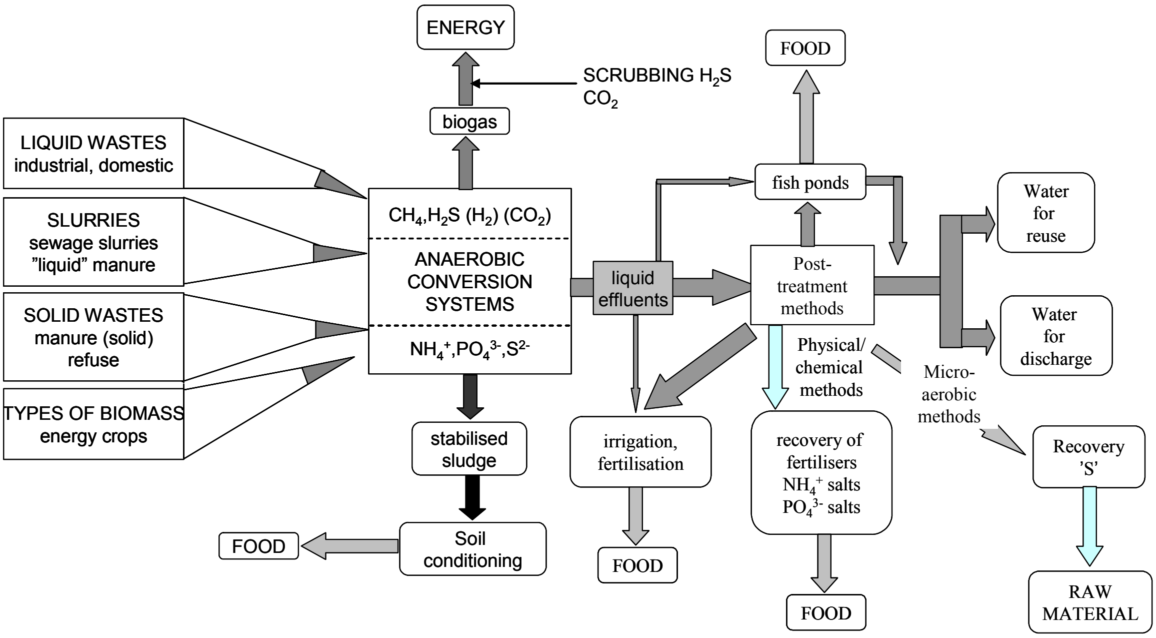

Fig. 2.11: Potential of nutrient and energy recovery through the implementation of AD

Magnesium, ammonium and phosphate can be released as the result of solids degradation in anaerobic digestion. Literature shows that most research has focused on the removal and recovery of soluble phosphorus from liquid anaerobic effluent.

Wrigley et al. (1992) used $MgSO_4$ as magnesium source to precipitate soluble phosphorus from the anaerobic effluent of piggery wastewater (TS of 0.3%) at a pH of 9, achieving a $PO_4$-P decrease of 75%.

Nelson et al. (2000) conducted experiments to precipitate struvite from anaerobic piggery effluent. Soluble P concentrations were decreased by 60-95% at the pH value of 9.0 and a Mg/TP ratio of 1.6:1 with the addition of $MgCl_2$.

Miles and Ellis (2001) noticed that MgO was better than $Mg(OH)_2$ for struvite precipitation from digested pig wastes after they experienced insolubility problems with $Mg(OH)_2$.

Nelson et al. (2003) reported that struvite precipitation decreased the $PO_4$-P concentration in anaerobic piggery liquid from an initial concentration of 51 mg/L to one of 7.6 mg/L in approximately 30 minutes at a pH of 9.0 and a Mg:P ratio of 1.2:1.

Uludag-Demirer (2005) investigated the removal of $NH_4^+$ when struvite precipitation from the effluents of anaerobic reactors digested the dairy manure. The manure was pretreated by means of screen separation. The $NH_4^+$ removal efficiency rates achieved were above 95% when excess amounts of $Na_2HPO_4$ and $Mg^{2+}$ were added. $MgCl_2 \cdot 6H_2O$ proved to be a more efficient magnesium source than $Mg(OH)_2$. It was also observed that the initial pH adjustment to 8.50 using NaOH did not result in any significant increase in the $NH_4^+$ removal rate.

Asif et al. (2006) reported that the subsequent anaerobic digestion of the diary manure led to the recovery of the removed phosphorus in a form sufficiently concentrated as to be suitable for recovery as struvite. The preliminary pilot-scale experiment indicated that 91% of $NH_4$-N and 59% of $PO_4$-P were removed from the dissolved phase. Zeng and Li (2006) studied nutrient removal (N, P) by means of struvite precipitation from anaerobically-digested cattle manure. It was found that the ammonium removal was not highly efficient, as the removal rate reached only 56%, even at a $Mg/PO_4^{3-}/NH_4^+$ molar ratio of 1.5:1.25:1. In addition, various magnesium salts were tested for struvite precipitation. Their relative suitability for phosphate removal was as follows: $MgCl_2 > MgSO_4 > MgO > Mg(OH)_2 > MgCO_3$.

Ipek et al. (2007) found that it is only possible to significantly reduce the quantity of orthophosphate (OP) from liquid pig manure by increasing the pH value. However, experimental and model data indicate that the addition of a magnesium source ($MgCl_2 \cdot 6H_2O$) is required for optimum recovery of OP.

The physical-chemical conditions for the precipitation of phosphate with calcium have been investigated by House (House, 1999). A 60% magnesium hydroxide $Mg(OH)_2$ slurry was used for a controlled struvite crystallization experiment aimed at removing phosphate from anaerobic digester side streams (Münch and Barr, 2001).

Struvite has been found in anaerobic digestion sludge of animal wastes (Booram et al. 1975).

There are only a few published studies in which struvite precipitation has been carried out during digestion or in a digester (Lee et al., 2004). The results of Lee's (2004) study indicate that struvite precipitation obtained by the addition of $Mg^{2+}$ during AD led to 67% and 73% N and P-removal rates respectively.

As animal manure contains rich nutrients, including phosphate, ammonium, calcium, magnesium and potassium, the P-precipitate product is a compound of different types of phosphate salt. Wrigley et al. (1992) found that the precipitate formed from piggery wastewater was comprised of struvite, apthitatite ($K_3Na(SO_4)_2$) and thermardite ($Na_2SO_4$). Burns et al. (2003) detected $CaPO_3(OH)\cdot 2H_2O$ (brushite) in precipitates from the struvite precipitation of pig-manure slurries. Michalowski and Pietrzyk (2006) report that $MgHPO_4\cdot 3H_2O$ (newberyite), $Mg_3(PO_4)_2\cdot 8H_2O$ (bobierrite) and $Mg_3(PO_4)_2\cdot 22H_2O$ (cattiite) can be formed during the struvite crystallization or dissolution process.

## 2.5 Chapter summary

This chapter has reviewed the following points on the basis of the relevant literature:

1. Phosphorus (P) is an essential element of life. The phosphate rock resource is limited in space and time and could be exhausted within 100–250 years. Phosphorus recovery can contribute to the closing of society's resource cycles, making sustainable development possible.

2. Phosphorus could be recovered through struvite and calcium phosphate compounds from different waste streams. There are three recovery principles: chemical precipitation, crystallization and ion exchange.

3. Manures are rich sources of phosphorus, containing complex mixtures of organic and inorganic, soluble and insoluble phosphorus compounds. Pig manure must be seriously considered because of its abundant content of N, P, Mg and Ca.

4. Aeration and anaerobic digestion are common methods for the treatment of animal manure. In comparison with the aeration method, anaerobic digestion is more cost-effective and sustainable. However, anaerobic digestion combined with P-recovery would be the better choice, as it could reduce the energy cost, produce biogas to offset the expense and create a valuable end product.

# 3 Analysis of the potential P resource in China

## 3.1 Phosphate rock reserve in China

The reserve of phosphate rock in China is 13.3 billion tons. The reserve is mainly distributed in the southwestern and central-southern regions of the country, including Yunnan, Guizhou, Hubei and Hunan provinces. The phosphate ore in China contains large contaminants (Fe, K, Si, etc.). High-grade phosphate ores ($P_2O_5$ content ≥ 30%) account only for 8.4% of the total reserve, and it is gradually being depleted (Jiang et al., 1990). Based on the domestic consumption of phosphate rock (11.1-11.6 million tons per year), it can be estimated that the phosphate reserve could be used up within about 70 years. The high-grade phosphate reserve will be used up in about 10~15 years.

According to the statistics of the USGS (2007), the phosphate reserve in China constitutes 26% of the world's total, second only to Morocco (USGS, 2007). Tab. 3.1 shows the state of the phosphate reserve in China, the United States and Morocco.

Tab. 3.1: Comparison of phosphate rock reserves in China, the United States and Morocco

| Country | Reserve of $P_2O_5$>30% (100Mt) | Mine centrality (%) | Average content ($P_2O_5$ %) | Transport distance (km) |
|---|---|---|---|---|
| China | 11.08 | 28.6 | 23 | >900 |
| United States | 10 | 57.9 | >30 | <300 |
| Morocco | 57 | >70 | >33 | 98 |

Note: 1. Mine centrality means the production percentage of the largest mining area in relation to the whole country.
2. Transportation distance means the distance from the mine area to the nearest port.

The following aspects of China's phosphate reserves can be summarized on a comparative basis:

1. The quality of phosphate rock in China is lower than in the other two countries.

2. The distribution of the phosphate reserve in China is decentralized.
3. Phosphate rock is relatively difficult to exploit and transport in China.

Considering China's large population and the development of its economy, the country will surely face a phosphorus crisis in the near future. Phosphate is on the list of 20 critical minerals which could not satisfy the demands of economic development in China after 2010 (Liu, 2005). The Chinese government has taken measures to keep down the quantity of phosphate ore exports.

## 3.2 The application and consumption of phosphate in China

China is a large agricultural country. The use of chemical fertilizer has been drastically increased. Fig 3.1 shows the rapid growth in the amount of chemical fertilizer used in arable land compared with the rest of the world. In China, mineral phosphate rock is consumed primarily as a principal component of chemical fertilizers. About 73% of the total amount of phosphate rock is used in phosphate fertilizer manufacture. 6% is used to produce animal food feed (Lin, 2005).

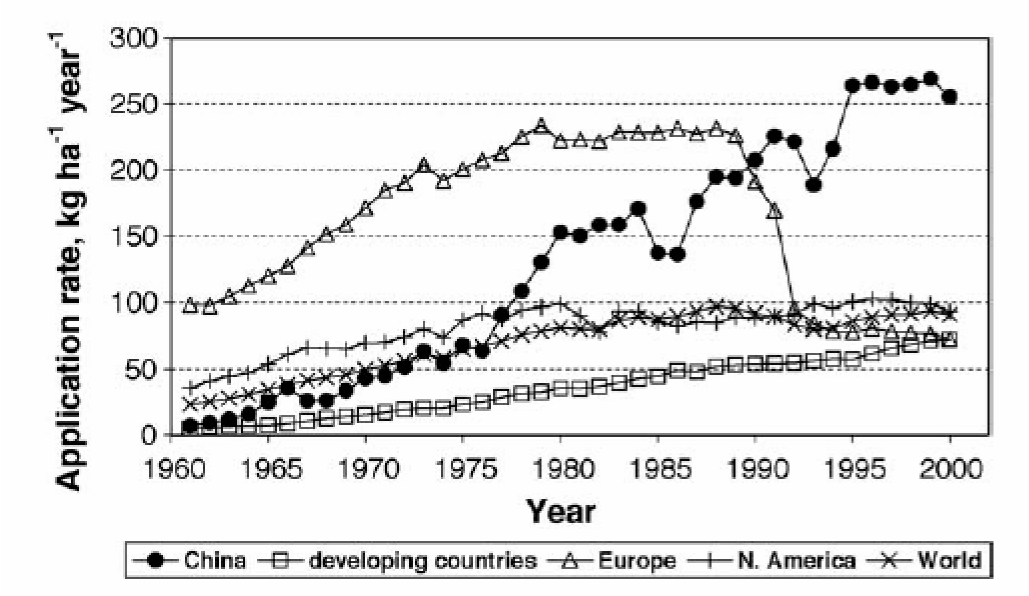

Fig. 3.1: Rate of chemical fertilizer use in arable land (including permanent crop land) in China compared with other developing countries, Europe, North America and the world (FAO, 2002)

The rates are based on N for nitrogen, $P_2O_5$ for phosphorous, and $K_2O$ for potassium.

Liu et al. (2007) describe a flow chart of China's national phosphorus metabolism on the basis of the data of 2000, shown as Fig 3.2. The national direct material input (DMIP) amounted to 5,984,000 metric tons of phosphorus.

Domestic extraction played a dominant role in DMIP, being responsible for 82%. Most of the extracted ores were consumed domestically, and only 9%, amounting to 451 kmt (P), were exported. Movement of minerals involves the removal and processing of raw ores, during which a huge quantity of gangue is discarded. This is classified as “hidden flow”. According to the estimate of Liu et al. (2007), 45% of raw ores were lost in the production of marketable ore yield as a result of the washing and flotation processes. In 2000, phosphorus commodity imports were 1099 kmt (P), while exports were 713 kmt (P), accounting for 18% and 12% of DMIP respectively. The net import of phosphorus (i.e. 386 kmt (P) in 2000) was processed, utilized and eventually accumulated in domestic environments via various routes. The huge gap in the phosphorus budget of international trade was mainly attributed to the huge import quantity of chemical fertilizers. Since domestic demand for high-quality compound fertilizers has been increasing annually (Liu et al., 2004), the international trade deficit in terms of phosphorus flux is likely to remain relatively stable. This will result in an increase in the total quantity of phosphorus accumulation in Chinese soils and waters.

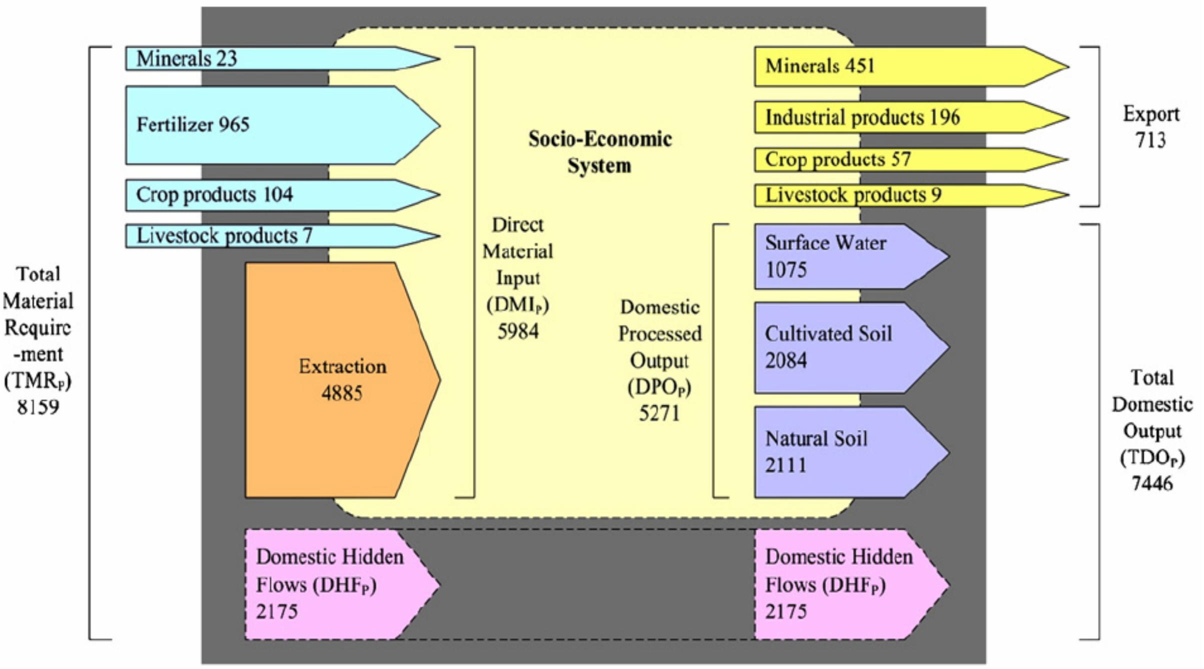

Fig. 3.2: Aggregate phosphorus metabolic structure in China, 2000

[unit: kmt (P)] (Liu et al., 2007)

## 3.3 Potential of the recoverable P in China

There are three potential P resources in China: human excrement and animal manure in rural areas; wastewater in municipal sewage plants; animal manure in intensive-scale animal plants.

### 3.3.1 Human excrement and animal manure in rural areas

China is an agricultural country, the rural population accounts for about 70% of the total population (China statistical year book, 2006). There are no sewage treatment facilities in rural areas. Human excrement and animal manure are used for cropland application.

In the past 20 years, biogas technology has been applied in rural areas. More than 8 million household biogas digesters and 800 large biogas plants have been built. It is regarded as a way of enabling rural households to gain access to “free” energy while utilizing all organic residues. The family biogas digester is mainly connected to latrines and the pig sties human excrement, pig and cow dung and crop residues are used as raw materials for the digester. The gas from a biogas tank can be used for cooking, temperature control in greenhouses. It can also be used for the preservation of agricultural products. The solid residue is used as fertilizer; the liquid effluent from the digester could be discharged into fishery ponds, or it could irrigate plants.

In rural areas or other areas where sufficient farmland is locally available for agricultural waste or manure spreading, it is better to retain the traditional method of nutrient recycling, because it is more convenient and economical.

### 3.3.2 Wastewater in municipal sewage plants

According to statistics (Zhang, 2000), the average total content of phosphorus in municipal sewage plants is 10g/m$^3$. The total annual amount of municipal wastewater is 46 billion cubic meters (China statistical year book, 2004). According to the phosphorus balance of Jardin (1995), there would be 64.4 thousand tons of potential $P_2O_5$ in municipal wastewater streams and 580 thousand tons $P_2O_5$ in sewage sludge or ash in China.

### 3.3.3 Animal manure in intensive-scale animal plants

With the urbanization and population growth of the past two decades, many large and medium-sized intensive-scale animal plants have been built close to the peripheries of cities and towns. In 2000, a nationwide survey of intensive livestock and poultry breeding was carried out by SEPA (SEPA, 2002), in which a total of 32,564 intensive livestock and poultry farms were investigated in 23 provinces and autonomous regions in China. The composition of the intensive livestock and poultry farms is shown in Fig 3.3.

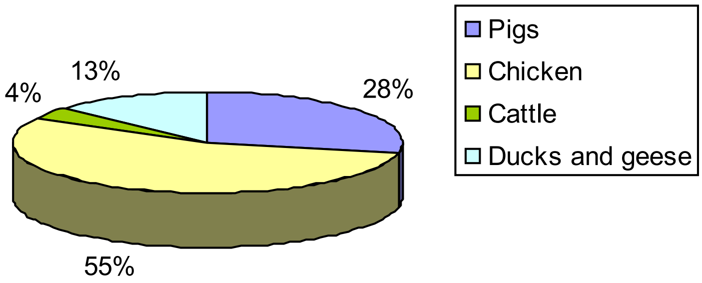

Fig. 3.3: Composition of intensive livestock and poultry farms in China

On the basis of the 2002 SEPA report and the statistics of the China Animal Husbandry Yearbook (2004), the amount of potential phosphate ($P_2O_5$) in various animal wastes is calculated. The results are shown in Tab. 3.2. The total potential of $P_2O_5$ is 6.1 million tons.

Tab. 3.2: Amount of potential phosphate ($P_2O_5$) in various animal wastes

| Category | | Description | Number (1000) | TP (kg/year.head) | $P_2O_5$ ($10^7$ kg/year) |
|---|---|---|---|---|---|
| Cattle | | Faeces | 129,349 | 8.61 | 298.28 |
| | | Urine | | 1.46 | |
| Pigs | | Faeces | 472,896 | 1.36 | 184.1 |
| | | Urine | | 0.34 | |
| Poultry | Chickens | Faeces | 3974,748 | 0.115 | 128.07 |
| | Ducks | | 660,361 | | |
| | Geese | | 227,987 | | |
| Total | | | | | 610.45 |

From the above analysis, it can be demonstrated (Fig 3.4) that the greatest recoverable phosphate resource is formed by animal manure. Around 13.09 million tons of $P_2O_5$ per year are used to produce fertilizer (Zhang, 2005). If the total $P_2O_5$ is assumed to be 100%, then the potential phosphate in sewage plants could replace 5% of the raw phosphate rock, and the potential phosphate in intensive-scale animal plants may provide nearly half of whole amount. The remaining 48% could be filled by the phosphate resource currently in use. If these potential phosphorus resources could be properly utilized, the life expectancy of the natural phosphate reserve would be doubled.

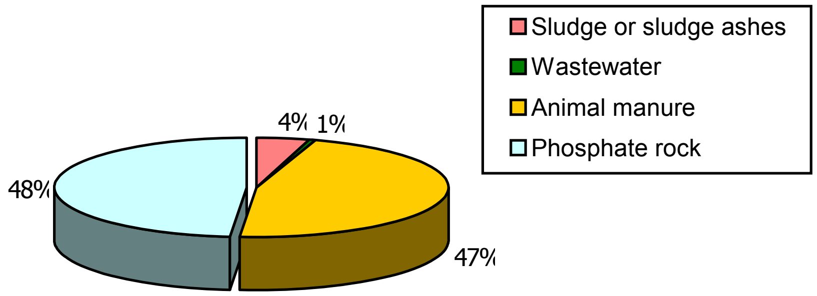

Fig. 3.4: Estimation of the proportion of recoverable phosphate and the new demand for phosphate rock in China

## 3.4 Prospects for the application of the recovered P

According to the chemical properties of the two P-recovery products demonstrated in Chapter two, struvite and calcium phosphate compound can be used in agriculture and the phosphate industry (Li, 2003; De-Bashan, 2004). The application of recovered phosphates includes reuse as a raw material as a substitute for mined phosphate rock in the phosphate industry, direct reuse as a fertilizer or, after further processing, the manufacture of higher-value fertilizer products.

### 3.4.1 Use as fertilizer

Struvite has been reported to display excellent fertilizer qualities under specific conditions when compared to standard fertilizers. This is because of its low solubility and non-burning features (Salutsky et al., 1970; Buchanan, 1993). Ghosh et al. (1996) confirmed that struvite displays excellent fertilizer qualities under specific conditions when compared with standard fertilizers. Other factors that support struvite use as a fertilizer include the low heavy metal content of the product when compared to the phosphate baring rocks mined and supplied to the fertilizer industry (Driver et al., 1999). However, the N:P:K ratio in struvite available to plants has yet to be researched (Burns et al., 2003). Struvite may require supplementation with potassium in order to meet the NPK (nitrogen: phosphorus: potassium) requirements of certain specific crops (Gaterell et al., 2000).

Zheng et al. (2004) stated that generation of 1 kg of struvite per day is enough to fertilise 2.6 ha of arable land at an application rate of 40 kg phosphorus at $P_2O_5$/ha/yr. in Japan, Struvite recovered from sewage is sold for $250 per ton, which is sufficient to recover the costs of production (Zhou, 2005).

Use of recovered P in agriculture is a particularly important strategy for China, a large agricultural country. It could not only conserve the mineral phosphate resource, it could also compensate nutrient removals and losses, as well as helping to maintain soil fertility and thus increase crop production.

### 3.4.2 Use as raw material in the phosphate industry

As calcium phosphate has a similar composition to natural phosphate rock, it can readily be incorporated into industrial processes for recycling-subject to obtaining an appropriate material quality (reasonably high phosphate content, limited levels of certain heavy metal contaminants, low water and organic content, physical and handling properties (CEEP, 2001). However, there seems to be little possibility that struvite could be a useful raw material for the phosphate (non-fertilizer) industry because it is incompatible with current industrial processes. There are two ways of producing phosphate in the phosphate industry: the thermal process and the wet-acid process. The thermal process is for the production of elemental phosphorus, whilst the wet-acid process is for generating phosphoric acid. Minerals are treated with phosphoric or sulfuric acids to produce more soluble superphosphate. The reactions are shown as follows:

$$2Ca_5(PO_4)_3F(s)+14H_3PO_4+10H_2O=2HF(g)+10Ca(H_2PO_4)_2\cdot H_2O \qquad (3\text{-}1)$$

$$2Ca_5(PO_4)_3F(s)+7H_2SO_4+3H_2O=2HF(g)+3Ca(H_2PO_4)_2\cdot H_2O+7CaSO_4 \qquad (3\text{-}2)$$

If recovered phosphates are to be reused in the phosphate industry, they are subject to certain requirements and constraints, which are addressed below.

1. Phosphate content

In order for reuse to be viable, the recovered phosphate product should have a reasonable P-content. The typical $P_2O_5$ content of phosphate rock is 30-40% (=13-17.5%P).

2. Impurities

The amount of certain impurities should not exceed a critical value. The impurities include iron, zinc, chloride, copper, lead, cadmium and tin.

3. Water content

Wet material should not be used in the thermal process because of technical limitations (mixing, milling, interference with internal sludge processing capacity). Phosphate rock is usually supplied as a dry material. Dry material could reduce waste of the heat source. On the other hand, it is also feasible to be transported if it has a low water content.

4. Organic material and ammonium

The presence of significant amounts of organic material leads to a decreased pellet strength after sintering. This will limit the capacity of the plant, which is unacceptable. The material should therefore consist of inorganic phosphate only (max. 5% carbon).

## 3.5 Chapter summary

The reserve of mineral phosphate ore in China is 13.3 billion tons. On the basis of current consumption, these reserves could be exhausted in about 70 years. High-grade phosphate reserves will be exhausted in about 10~15 years.

Wastewater and animal manure are the main potential sources of phosphorus. In rural areas, where the animals are raised comfortably and there is sufficient farmland, it is better to retain the traditional way of bringing nutrients back to the cropland. Phosphorus is more suitably recovered in municipal sewage plants and intensive-scale animal plants.

The greatest recoverable phosphate resource is found in animal manure. The potential phosphate in intensive-scale animal plants accounts for 47% of the total consumption of phosphate rock in China. It has been estimated that, if the potential phosphorus resources in municipal sewage plants and intensive-scale animal plants could be properly utilized, the life expectancy of the natural phosphate reserve would be doubled.

# 4 Situation of manure treatment on intensive scaled pig farms in China

There are two basic methods of animal breeding: traditional and concentrated. The traditional method, natural feeding, is mainly suitable for family- and small-sized farms. With this feeding method, excrement is scattered in grasslands or fields and thus difficult to collect. Concentrated feeding on large and medium-sized farms for pigs, cattle sheep and poultry, has increased dramatically in recent years. These livestock are generally reared in pens, with the result that the excrement can be treated intensively. This chapter seeks to review the current situation of manure treatment on intensive-scale pig farms.

## 4.1 The nature of intensive livestock and poultry breeding

China has a long history of using animal manure as a fertilizer and soil conditioner. In the past, crop and livestock production were intimately associated with each other. Today, in order to pursue efficiency and economic benefit, livestock production has tended to shift away from small diversified family farms, which produced livestock as well as crops, in favor of a larger, more concentrated scale of production.

With the rapid population growth of the 1980s, the Chinese government launched the “shopping basket project” in an attempt to solve the meat, egg and milk problem in the cities. The output of livestock increased rapidly, as shown as Fig. 4.1. Transportation costs meant that most of the livestock and poultry plants were built conveniently in the urban suburbs. With the subsequent urban development and population growth, some plants have already moved close to the peripheries of cities and towns, or have even become integrated into residential areas. This has led to the current situation of intensive animal plants around large and medium-sized cities.

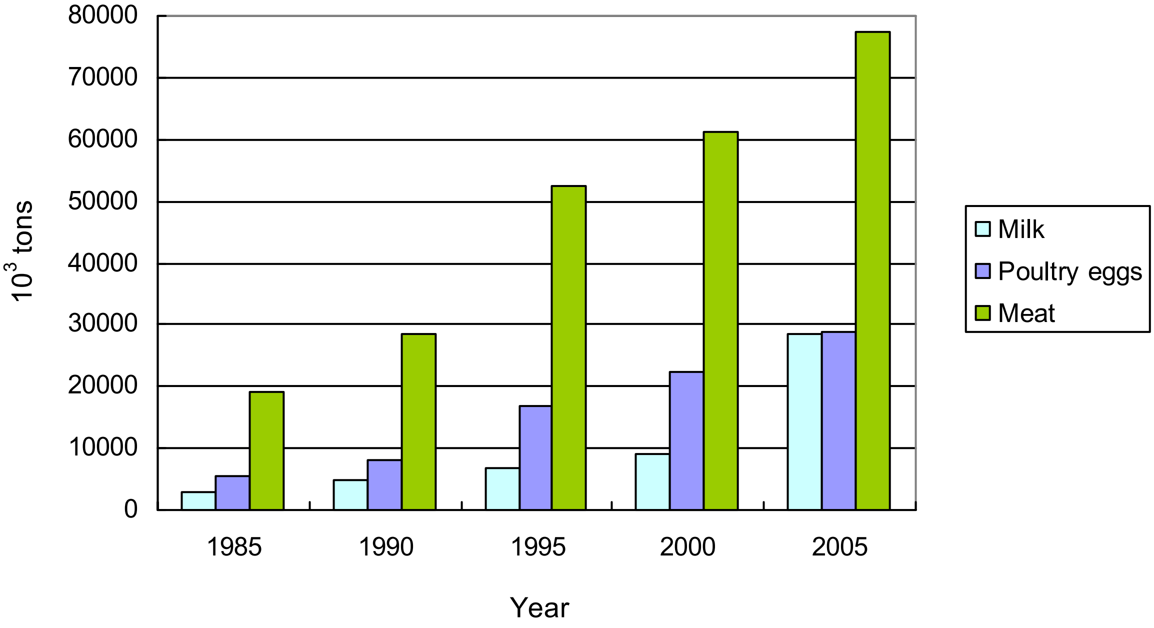

Fig. 4.1: Output of livestock product (China Statistical Yearbook, 2006)

According to the statistics of the Ministry of Agriculture, the amount of large and medium-sized intensive animal breeding plants in eastern China accounts for 51.6% of the total. Central China accounts for 41%, and the western region only accounts for 8% (Fig. 4.2). The intensive-scale animal farms are mainly located in the populous southeastern area, the coastal area and around large and medium-sized cities (SEPA, 2002).

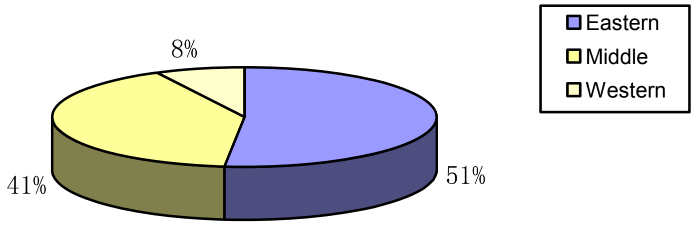

Fig. 4.2: Distribution of the intensive livestock and poultry farms

## 4.2 Characteristics of pig manure

The composition of pig manure includes water, organic matter, nutrients (N, P), salts (Na, K, Ca, Mg and $CO_3^{2-}$) and pathogenic organisms.

Pig manure has a higher water content (faeces 82%; urine 94%) than other types of animal manure, such as poultry and dairy (Wang et al., 2004). The solid concentration of pig manure also varies with different management systems; for example, the feeding and watering system, the amount of wash water and the manure storage system all affect the nutrient level in the manure and the choice of waste treatment method.

Solid manure is produced in farms that use bedding under pig sties. This kind of manure can be easily stacked and treated using conventional methods (composting). Today, more and more pig production plants are adopting slatted floor pens with no bedding. Pig manure is either stored in pits beneath the floor or drained from gutters into outside storage tanks. Because the manure contains urine as well as faeces, and because extra wash water is used to clean the piggery, this type of manure management produces liquid manure. Liquid manure is stored below pig sties and is either transferred periodically to outside holding tanks, removed and applied directly to the land or diluted and placed in lagoons before eventually being applied.

Pig manure is much more readily biodegradable. The biological oxygen demand (BOD) of pig manure is about twice as high as that of dairy manure. The decomposition of the organic compounds in pig manure is mostly due to the high BOD content in faeces. According to the data of the Agriculture Ministry of China in 2001, fresh pig faeces contain about ten times more BOD than the urine component (pig faeces 63,000 BOD; pig urine 5,000 BOD). The anaerobic decomposition of the biodegradable organic solids produces gases such as carbon dioxide ($CO_2$), methane ($CH_4$), ammonia ($NH_3$) and hydrogen sulfide ($H_2S$). It also produces short-chain volatile fatty acids and other volatile organic compounds.

## 4.3 Manure management and environmental pollution

In 2000, a nationwide survey of intensive livestock and poultry breeding was carried out by SEPA (State Environmental Protection Administration). The investigation revealed that about 80% of the country’s intensive livestock and poultry farms lacked the necessary pollution control facilities, whilst 60% lacked basic solid liquid separation facilities. Tab. 4.1 shows detailed data on manure management pig farms of various sizes.

Tab. 4.1: Situation of manure management at pig farms of various sizes

| Item | | 200-500 | 501-1,000 | 1001-5,000 | 5001-1,0000 | 10001-50,000 | > 50,000 |
|---|---|---|---|---|---|---|---|
| National average (%) | Rate of liquid-solid separation | 36.02 | 37.75 | 47.85 | 48.43 | 52.56 | 60.0 |
| | Rate of mechanical separation | 24.71 | 22.95 | 18.85 | 13.82 | 19.51 | 66.67 |
| | Rate of possessing solid waste treatment facilities | 8.38 | 10.73 | 20.49 | 25.98 | 28.21 | 40 |
| | ate of possessing waste water treatment facilities | 12.46 | 15.71 | 27,18 | 34.65 | 50.0 | 40 |
| Beijing (%) | Rate of liquid-solid separation | 27.78 | 18.79 | 26.32 | 19.05 | 12.5 | 50 |
| | Rate of mechanical separation | 31.43 | 25.0 | 37.14 | 25.0 | 0 | 100 |
| | Rate of possessing solid waste treatment facilities | 12.7 | 9.4 | 9.02 | 4.76 | 25 | 0 |
| | Rate of possessing waste water treatment facilities | 13.49 | 6.71 | 9.02 | 0 | 0 | 0 |
| Guang-zhou (%) | Rate of liquid-solid separation | 33.09 | 31.97 | 53.38 | 59.26 | 55.0 | 100.0 |
| | Rate of mechanical separation | 31.84 | 31.23 | 16.9 | 28.13 | 45.45 | 100.0 |
| | Rate of possessing solid waste treatment facilities | 6.32 | 6,69 | 24.44 | 29.63 | 30.0 | 100.0 |
| | Rate of possessing waste water treatment facilities | 9.29 | 13.01 | 34.98 | 55.56 | 70.0 | 100.0 |

Poor technology and facilities represent one of the reasons for poor manure management. Other potential challenges identified with manure management include: high water content in manure waste, excessive nutrient loading or insufficient cropland for assimilation, gas and odor emission and non-compliance with national regulations. There are certain constraints that also affect management at given pig farms. These include location and size, local economic conditions, manure volume and composition, surrounding soil type, crop selection, climate and the availability and technical skills of farm workers. Although manure contains valuable plant nutrients, their concentrations are also much lower than those in commercial fertilizers, especially when they are diluted. Because of transportation and land application costs, farmers tend to buy commercial fertilizer which can be handled easily.

SEPA (2002) estimated that the whole country's output of excrement and urine was about 1,900 million tons in 1999, which was 2.4 times that of industrial solid waste in the same year. From this, the emission of COD amounted to as much as 71,180,000 tons, which exceeded the emission of the sum of industrial and domestic wastewater. Untreated manure discharged directly into rivers and lakes causes serious environmental pollution. Lakes south of the Yangtze River area were found to be choked with dense algal growth. Nitrogen and phosphorus levels in Chaohu Lake and Dianchi Lake exceeded the maximum safety limits by 200-800 % (Wang et al., 2004). The most serious location for pollution was the outskirts of large cities.

Beijing:

There are more than 800 concentrated livestock farms in Beijing. The total waste in 2000 was as much as 304.42 million tons, including 93,434 tons COD, 8,759 tons $NH_4$-N, 18,460 tons TN and 7,030 tons TP. Based on the monitoring of some densely-populated areas in Beijing, the concentration of COD was 53 times, the concentration of BOD 76 times and the concentration of SS 14 times over the limit.

Shanghai:

In Shanghai, there are more than 1,600 large and medium-sized animal-breeding farms. The annual waste in 2000 was 700 million tons. Manure pollution has already become the most serious problem in the suburbs of Shanghai.

Guangzhou:

In Guangzhou, the annual waste in 2000 was 473,193 million tons. Though the amount of wastewater from animal-breeding farms was just 1.25% of domestic wastewater, the amount of COD was 1.5 times that of domestic wastewater.

## 4.4 Manure treatment technology

### 4.4.1 Manure storage and removal

4.4.1.1 Dry clearing

The dry clearing process means that solid and liquid manure wastes are treated separately. Excrement is collected, cleaned and transported artificially or by machinery. Urine and a certain amount of wash water flows into the sewer. In this process, little nutrition in the excrement is lost, with the result that the manure has higher fertilizer efficiency. The dry-clearing process is mainly used in chicken and cattle farms.

The traditional clearing tools are shown in Fig. 4.3.There are two types of machinery tools: a shoveling and scraping. Clearing machinery can lighten the intensity of labour, economize in terms of the workforce and improve working efficiency. The shortcoming is that the noise of clearing is loud, and it is not good for the growth of the animal.

Fig. 4.3: Artificial excrement clearing tools

4.4.1.2 Water flush

The water flush process was introduced in the 1980s from abroad. In this process, excrement, urine and wastewater enter the excrement ditch under the chink floor and mingle. In some plants, the manure is washed by water pipe (Fig 4.4), in others the flush water turns over automatically from the end of the ditch several times a day.

The water consumption involved in this process is large. After solid and liquid are separated, most soluble organic matter remains in the water. The isolated solid part has a low fertilizer efficiency.

Fig. 4.4: Water valve (left) and pipe (right)

### 4.4.1.3 Soaking in pens

This process is derived from the water flush process. A certain amount of water is first injected into the ditch under the animal housing. Excrement, urine and wash water flow into the ditch under the chink floor. After storage for time when the excrement ditch is full, the gate is opened and the wastewater discharge into the manure lagoon. However, although the water use involved in this process is not as much as in the above process, the excrement and urine stay in the animal housing for a long time, producing a large amount of harmful gases such as sulphurating hydrogen, methane etc., which are dangerous for the animals and workers.

Fig. 4.5: Slatted floor in pig sty

The dominant method of storing the waste until land application is permissible depends on the size of the operation. For smaller operations (2,000 - 10,000 heads) below-floor slurry or deep pits are mainly used (70%) whereas anaerobic lagoons without cover are mainly used for large pig operations (81%). Deep pits are 6 to 8 feet deep and allow for up to 6 months storage under the animal housing. The slurry is removed from the pit twice a year for surface application or subsurface injection, or else it is pumped into an over ground steel storage tank or earthen storage facility.

### 4.4.2 Solid manure treatment

#### 4.4.2.1 Direct spraying onto land

After storing the manure in the manure pit for a period of time, the waste is sprayed directly onto the land or used as base fertilizer. Oxidation causes the microorganism to decompose in the soil. Though this kind of treatment method is simple, it is apt to cause environmental pollution and lead to the spread of disease.

#### 4.4.2.2 Drying treatment

Drying treatment includes mechanical drying and dehydration with heating power. Mechanical drying with a solid-liquid separation machine could make the moisture content fall to 50%. The dehydration method involves drying in the air, drying by heat, thermal spraying, bulking and microwave treatment, which could make the moisture content fall to 12%.

As chicken excrement is drier than other animal manures, the excrement from the chicken coop could be dried and dealt with directly. In the late 1980s, the drying treatment was used widely in chicken-breeding farms. But it was later found that high temperatures cause effective elements such as nitrogen to be lost in the process. The stench gas produced when entering the atmosphere causes serious air pollution; residents near the chicken fields have been known to complain. Fig. 4.6 shows a farm in Huokou, which adopted this method to deal with chicken excrement.

(a) Drying machine (b) Drying square (c) Storage pit

Fig. 4.6: Chicken excrement treatment in Huokou

### 4.4.2.3 Composting

#### 1) Natural composting

Natural composting basically utilizes natural environmental conditions. The excrement is piled up alone or mixed with soil or crop straw. Using the energy produced by anaerobic reaction to kill bacteria, it could be applied to the field after fermentation and further drying. This method does not need special equipment or extra energy, but its reaction time is relatively long (the traditional method used in rural areas takes more than 300 days).

#### 2) Compost in a canopy

Excrement is put on the excrement bed in a plastic or glass-fiber reinforced canopy. The excrement in the canopy ferments due to aerobic bacteria; on the other hand, it can be dried with the aid of ventilation and solar energy. After about 25 days, the moisture content of the excrement usually drops to below 20%. The temperature can be up to 70℃, killing most germs and worms.

Fig. 4.7 shows the treatment of chicken excrement using the method of natural composting and compost in a canopy in an organic fertilizer plant in Bei Langzhong. Because solar energy can be utilized efficiently with this method, it is more suitable for northern China, which is a dry area.

(a) Natural composting (b) Compost with solar energy in a canopy

Fig. 4.7: Organic fertilizer plant in Bei Langzhong

At present, most treatment facilities in animal farms are simple. The manure is piled up in the open field and fermented naturally. There is usually no facility for leak - roofing, which makes it likely to cause surface water and underground water pollution. The main function of the animal manure is as organic fertilizer, which is then returned to the field. Most cattle and poultry production plants adopt the dry-clearing process because the moisture content of manure is low and it is easy to clean and transport. The manure is generally used on vegetable gardens and orchards. The drying time depends on the local crop cultivation. As a rule, it takes a long time in winter and on rainy days in summer.

### 4.4.3 Wastewater treatment

4.4.3.1 Direct return-to-field mode

1) Process description

This process is a traditional and economic method of animal manure disposal. It is mostly used in dispersive animal breeding or small-scale intensive animal breeding. Fig. 4.8 shows the simple process of the return-to-field mode. The excrement (or straw cushion used to absorb urine) is artificially removed from the animal housing. The remaining excrement and urine is cleaned using small amount of water. Dry excrement is sold or used to produce organic fertilizers, while the wash water is stored in the manure pit. In the irrigation season, it can be applied to the farmland.

Manure return-to-field can achieve nutrient recycling in the “animal-soil-plant” ecosystem. In some contexts, it could reduce the consumption of chemical fertilizer. However, there are two relevant regulations that should be established by the government. The first is a breeding balance policy; the amount of manure applied to farmland should respond to the affordable load of nutrients, taking account of the local soil type. The second is an agreement with the farmers; liquid manure should be applied to the farmland only in seasons of cultivation. At times when application to farmland is forbidden, the manure should be stored in a manure pit.

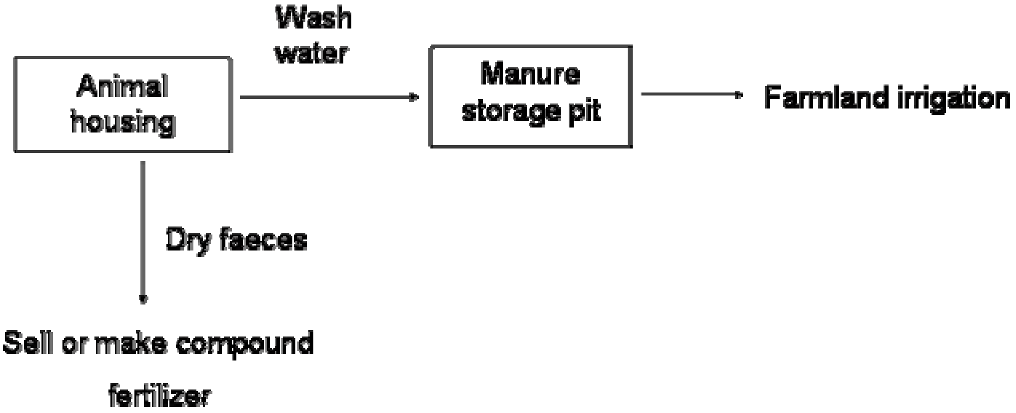

Fig. 4.8: Flow chart of direct return-to-field process

2) Characteristics of the process

Advantages:

a) It can be used as fertilizer.

b) The operation is simple and requires little investment. For a pig farm of 5,000 livestock, the capital of investment is about 10,000 CNY (100 Euro).

Shortcomings:

a) There is a danger of disease propagation.

b) Unreasonable or excessive use could cause heavy metal pollution to the soil and groundwater.

c) The release of harmful gases such as $NH_3$ and $H_2S$ causes air pollution.

This process is used far away from cities and towns, in economically underdeveloped areas where the local workforce rates are low and the land is extensive enough to dissolve the manure, especially in areas where crops grow throughout the year. Furthermore, the scale of the pig farm should not be too large (generally under 5,000 livestock).

### 4.4.3.2 Anaerobic digestion plus natural treatment

1) Process description

In this process, anaerobic digestion is the main component, combined with natural treatment systems such as pool, artificial wetland, etc. This can enable the effluent to reach the discharge standard. The residue from the digestion tank can be returned to the field.

As shown in Fig. 4.9, the dried excrement is sold or to make organic fertilizer. The wastewater enters to the digestion system, in which organic matter is digested. Parasitic worms and pathogens are degraded or killed in the digestion tank. Finally, the effluent is discharged into the natural process system. If there is enough farmland, it can be used directly as liquid fertilizer.

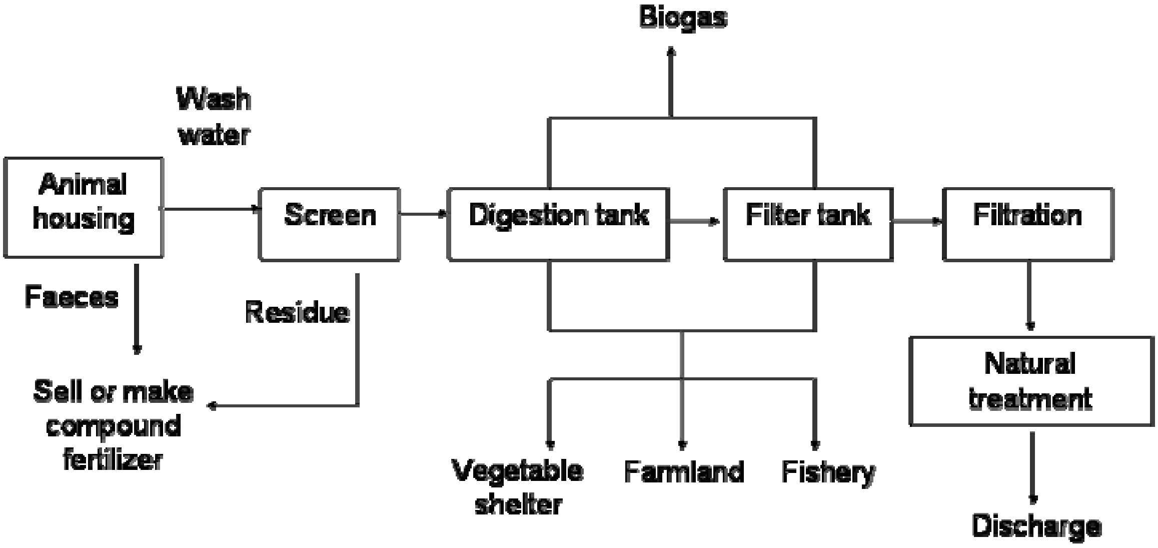

Fig. 4.9: Anaerobic digestion - natural treatment mode

2) Characteristics of the mode

<u>Advantages:</u>

a) Little sludge is produced, so a complicated sludge treatment system is unnecessary.

b) Methane can be retrieved as energy. There is relatively little negative impact on the surrounding environment.

Shortcomings:

a) The treatment takes up a large amount of land.

b) High expenses for operation and administration.

This mode is adopted in areas where the economy is comparatively well-developed, the local government can to some extent afford the investment and subsidies for the farmers, the land is extensive, the price of land is relatively low and, best of all, there are forested areas, low-lying or invalid land that can be used as natural process systems. The scale of pig-breeding farm is medium-size (generally 5,000-10,000 livestock).

#### 4.4.3.3 Industrial treatment process

1) Process description

This process consists of pre-treatment, anaerobic and aerobic treatment, sludge treatment and biogas utilization. The process is complicated and comprehensive. Compared with the above two modes, the technological element of this mode is the most extensive, requiring staff with greater technical knowledge to operate and maintain it. The water quality of the effluent is able to achieve the industrial discharge standard.

The simple process can be seen in Fig. 4.10. After pre-treatment, the wastewater is treated using the industrial mode, as in a sewage plant. The usual anaerobic method involves anaerobic digestion, UASB, UBF, etc. Aerobic treatment involves the active sludge and SBR methods. If the animal farm is located near a municipal sewage plant, the wastewater from the digestion tank could be mixed with the municipal sewage and the two treated together.

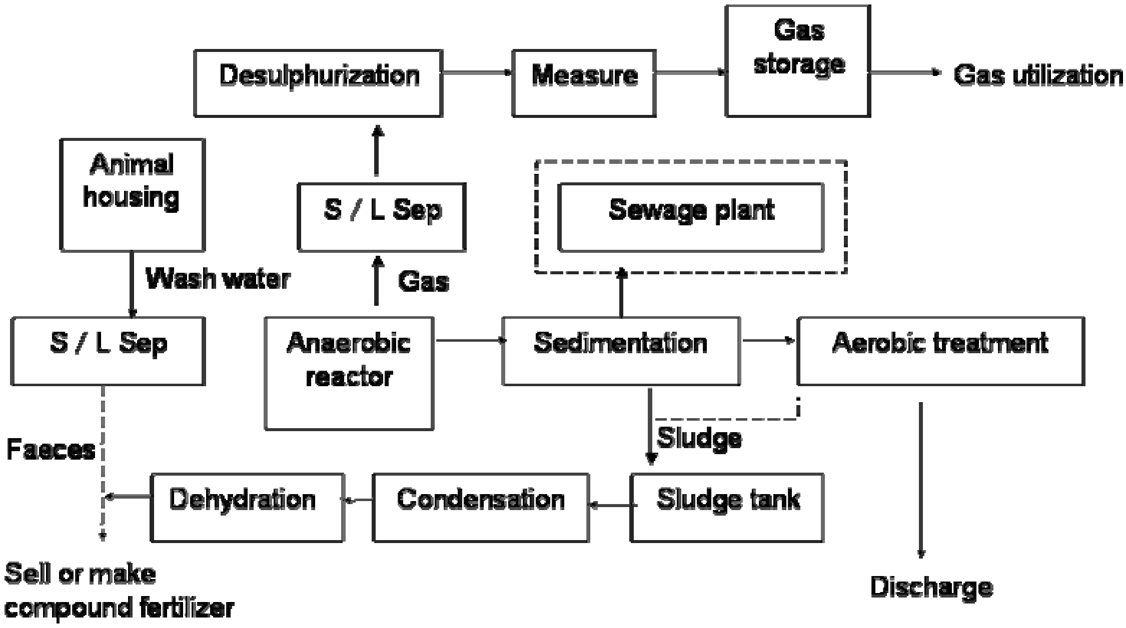

Fig. 4.10: Industrial treatment process

2) Characteristic of the process

Advantages:

a) This process is not constrained by geographical position.

b) The effluent can achieve the industrial discharge standard.

Shortcomings:

a) Considerable investment is required for construction.

b) High energy consumption, operational costs and equipment maintenance.

This kind of farm is located in the suburbs of big cities, where the economy is well-developed, the land is in short supply, the local workforce is expensive and the volume of wastewater is large. There is no large-scale farmland, or forested areas or fishponds which can be utilized. The scale of such pig farms is over 10,000 livestock.

## 4.5 Intensive pig manure management in Germany

15 EU countries account for approximately 20% of world pork production, with Germany the most prolific (20%) (Grimm et al., 2002). The central environmental issue in intensive livestock farming is manure. In September 1996, the 96/91/EG Council Directive determined that intensive pig and poultry

livestock management facilities within the scope of the directive (>40,000 poultry locations >2,000 fattening pig locations and >750 pig-breeding locations) had to make provisions against environmental pollution by using the “Best Available Techniques” (BAT).

The BAT relates to the entire chain of animal production processes, from basic farm operations (housing, manure removal, ventilation) and feeding (food storage, processing, rationing and delivery) to the storage, treatment and field application of farm-produced manure.

1) Watering system

Water is used for cleaning purposes and for providing the animals with nourishment. In processes involving water, the BAT is to reduce water use by carrying out all of the following:

- cleaning animal housing and equipment with high-pressure cleaners after each production cycle or batch. In the case of pig housing, wash-down water typically enters the slurry system, and it is therefore important to find a balance between cleanliness and using as little water as possible;
- carrying out a regular calibration of the drinking-water installation in order to avoid spill;
- keeping a record of water use by monitoring consumption;
- detecting and repairing leakages.

2) Manure storage system

The BAT is to design storage facilities with sufficient capacity for animal manure until further treatment or application to land can be carried out. The BAT for the storage of solid manure and pig slurry is shown as follows:

Solid manure

For a heap of pig manure that is always situated in the same location, either at the installation or in the field, the BAT is to:

- use a concrete floor with a collection system and a tank for run-off liquid;
- locate any new manure storage areas where they are least likely to cause annoyance to sensitive receptors for odour, taking into account the distance to the receptors and the prevailing wind direction.

For a temporary heap of pig or poultry manure in the field, the BAT is to position the manure heap away from sensitive receptors such as residents, as well as watercourses (including field drains) that liquid run-off might enter.

Liquid manure

- a stable tank is able to withstand any likely mechanical, thermal and chemical influences;
- the base and walls of the tank are impermeable and corrosion-resistant;
- the store is emptied regularly for inspection and maintenance, preferably once a year;
- double valves are used on any valved outlet from the store;
- the slurry is only stirred just before emptying the tank, for example, immediately prior to land application.

To cover slurry tanks, one of the following options is used:

- a rigid lid, roof or tent structure;
- a floating cover, such as chopped straw, natural crust, canvas, foil, peat, light expanded clay aggregate (LECA) or expanded polystyrene (EPS).

To cover lagoons where slurry is stored, one of the following options is used:

- a plastic cover;
- a floating cover, such as chopped straw, LECA or natural crust.

3) On-farm treatment processing

In general, the on-farm processing of manure is the BAT only under certain conditions (i.e. a conditional BAT). The conditions of on-farm manure processing that determine whether a technique is the BAT relate to conditions such as the availability of land, local nutrient excess or demand, technical assistance, the marketing opportunities for green energy and local regulations. Tab. 4.2 gives some examples of the conditions for the BAT for pig manure processing.

Tab. 4.2: Examples of conditional BATs for on-farm pig manure processing (Grimm et al., 2002)

| **under the following conditions** | **example of a BAT:** |
|---|---|
| ● farm situated in an area with nutrient surplus but sufficient land in the vicinity to spread the liquid component (with decreased nutrient content)<br>● solid component can be spread over remote areas with a nutrient demand or can be applied using other processes | mechanical separation of pig slurry using a closed system (e.g. centrifuge or press-auger) to minimise ammonia emissions |
| ● farm situated in an area with nutrient surplus but with sufficient land in the vicinity to spread treated liquid component | mechanical separation of pig slurry using a closed system (e.g. centrifuge or press-auger) to minimise ammonia emissions, followed by aerobic |

| | |
|---|---|
| ● solid component can be spread over remote areas with a nutrient demand<br>● farmer gets technical assistance for running aerobic treatment installation | treatment of the liquid component where the aerobic treatment is well-controlled, so that ammonia and N2O production are minimized |
| ● there is a market for green energy<br>● local regulations allow co-fermentation of (other) organic waste products and land-spreading of digested products | anaerobic treatment of manure in a biogas installation |

## 4.6 Policies on manure pollution control in China

The Chinese government is currently taking the following three measures to control manure pollution.

### 4.6.1 Regulation and law

From 2001, two regulations have been launched to control manure pollution.

2001.12.19
“Technical standard of preventing pollution for livestock and poultry breeding”

2001.12.28
“Discharge standard of pollutants for livestock and poultry protection administration“

In this regulation, the scale of the intensive-scale animal-breeding farm was defined and the discharging standard of waste was regulated.

### 4.6.2 Financial support for renewable energy

The Chinese government has paid much attention to the development of renewable energy. In 2005, “The renewable energy law” was passed. Renewable energy technologies include biogas, solar PV, wind energy, hydropower, etc. Major financial support for renewable energy includes subsidies and tax-related incentives.

Subsidies are provided bye central and local government, representing the most important support for renewable energy development.

Central government subsidizes research and development on key renewable energy technologies through the National Development and Reform Commission (NDRC) and the Ministry of Science & Technology (MOST).

Funds provided by the MOST during the tenth Five-Year Plan period (2000-2005) amounted to 28 million CNY (3.4 million USD).

Based on collection and distribution rights, tax can be classified as central government, local government and shared tax. Biogas and wind energy are eligible for specific tax incentives at central government level.

### 4.6.3 The development of biogas

China's biogas development dates from the 1970s, and three phases can be identified.

**Phase 1** (pre-1990) During this period, biogas development fluctuated greatly and the overall development was s low.

**Phase 2** (1990s) Technical breakthroughs were made and processes improved. Several models were developed, including 'pig-biogas-fruit' in Southern China, 'four-in-one' in Northern China and 'five-supplements' in Northwest China. With better technologies, biogas developed steadily. By the end of 2000, there were 9.8 million household digesters throughout China, 55% of which conducted integrated utilization. Large and medium-sized biogas plants on husbandry farms began to be built for demonstration purposes.

**Phase 3** (post-2000) This has been a period of accelerated development. Since 2000, the Ministry of Agriculture has begun to implement the Bio-household Program. Central government increased its investment in rural biogas development. From 2001 to 2006, the total investment was over 6 billion CNY, benefiting 6 million households. In recent years, about 2 million household biogas digesters have been newly built every year. State subsidies have supported about 200 biogas plants on large and medium-sized husbandry farms. By the end of 2005, 18 million households had adopted biogas technologies, producing 7 billion $m^3$ biogas annually. There are now 3,556 biogas plants treating 87 million tons of animal waste.

## 4.7 Chapter summary

This chapter has reviewed the following current aspects of manure treatment on intensive-scale pig farms in China today.

In China, most intensive-scale animal farms are located in the populous southeast area, in the coastal area and around large and medium-sized cities.

Animal manure was found to be poorly managed on intensive-scale farms in

China. About 80% of the country's intensive livestock and poultry farms lacked the necessary pollution control facilities, whilst 60% lacked basic solid liquid separation facilities.

China is a country with relatively low water resources. Water flush cleaning is not suitable for use in China.

Animal manure would best to be used in local agriculture without negatively impacting the environment. However, it is impossible for all the manure to be produced in today's concentrated animal production operations. Pig manure has a relatively large water content. The transportation of untreated slurry to locations where it can be treated or utilized is not economically advisable. A method for concentrating the high content of nutrients in solid manure is therefore more worthwhile for long-distance transportation.

The Chinese government is paying a great deal of attention to renewable energy. Both administrative and economic means have been adopted in order to control manure pollution. Biogas technology has been supported in China and developed rapidly in the last 20 years.

# 5 Materials and methods

## 5.1 Sample materials

### 5.1.1 Raw pig manure

Pig manure was obtained from a pig farm in Mörsdorf. All samples were collected from under the slatted floor of the pig sty. The manure was composed of faeces, urine and spillage water. Because of the inevitable variations in the composition of the feedstock, the most relevant chemical characteristics of the manure were analyzed every time the sample was collected.

Fig. 5.1: Source of the raw pig manure, Mörsdorf pig farm

### 5.1.2 Substrate of the pilot anaerobic digester

The substrate for the pilot anaerobic digester was taken from an efficiently functioning biogas plant in Mörsdorf, which uses the same pig manure as this study for its raw material.

## 5.2 Chemicals and apparatus

### 5.2.1 Chemicals

Magnesium Oxide ($MgO$) and Magnesium Chloride ($MgCl_2 \cdot 6H_2O$) were used as the magnesium source in order to adjust the molar ratio of Mg/P in the solution.

NaOH reagent (4 N) was used to adjust the pH value of the solution.

The chemicals and reagents used in the experiments were all chemically pure.

### 5.2.2 Apparatus

pH meter: ECM Multi, Dr Lange
electronic balance: Sartorius Basic
refrigerator: Alaska KS315 refrigerator control
centrifuge: SiGma 6K10
sludge dryer: Linn Elektro Therm
grinder: Fritsch mortar grinder

**Cell test:**
hosphate cell test: Merck KGaA
Ammonium cell test: Merck KGaA
Calcium cell test: Dr. Lange
Magnesium cell test: Dr. Lange
COD cell test: Dr. Lange; Merck KGaA

## 5.3 Analytical methods

The Phosphate cell test (DIN EN 1189, 1996) was used for the determination of orthophosphate ($PO_4$-P) and total phosphorus (TP). In sulfuric solution, orthophosphate ions react with molybdate ions to form molybdophosphoric acid. Ascorbic acid reduces this to phosphomolybdenum blue (PMB), which is then determined photometrically.

The ammonium cell test (DIN EN ISO 7150/1) was used to determine ammonium nitrogen ($NH_4$-N). Ammonium nitrogen ($NH_4$-N) occurs partly in the form of ammonium ions and partly as ammonia. A pH-dependent equilibrium exists between the two forms. Ammonium nitrogen is present in strongly alkaline solution almost entirely in the form of ammonia; this reacts with hypochlorite ions to form monochloramine. This in turn reacts with a substituted phenol to form a blue indophenol derivative, the concentration of which is determined photometrically.

Calcium (Ca) and Magnesium (Mg) were analyzed by means of a cell test (LCK 327, Firma Dr. Lange) in accordance with the standard methods DIN 38 406-E 3-1. Other chemical analyses included pH, chemical oxygen demand (COD) (DIN 38 409-H 41-1), 5-d biochemical oxygen demand ($BOD_5$) (DIN 38 409-H 51) and Kjeldahl N (TKN) (DIN 38 409-H 28). These routine analyses were measured in the analysis laboratory of the Sanitary Engineering department of Bauhaus-University Weimar.

Total solids (TS) and volatile solids (VS) were analyzed on the basis of standard method DIN 38414 part 10 (DEV-S2, S3). Total solids are the solids remaining after the evaporation of a sample to constant weight at 105℃. Total solids comprise total suspended solids (TSS) and dissolved solids (DS). Volatile solids (VS) represent the fraction of the solid lost on ignition in a muffle furnace at 550℃ over a period of 2 hours.

The composition of the end solid product was analyzed in analysis laboratory of materials research and testing institute (MFPA) at the Bauhaus-University Weimar.

## 5.4 Experimental setup

### 5.4.1 Facilities for manure storage

The raw pig manure used for anaerobic digestion was stored in a climate chamber room at a temperature of Bauhaus-University Weimar 4±2□ (shown in Fig. 5.3). The construction of manure storage tank is shown in Fig. 5.2. Before using raw pig manure, the stirring motor should be operated for 15min in order to make sure the manure is mixed completely.

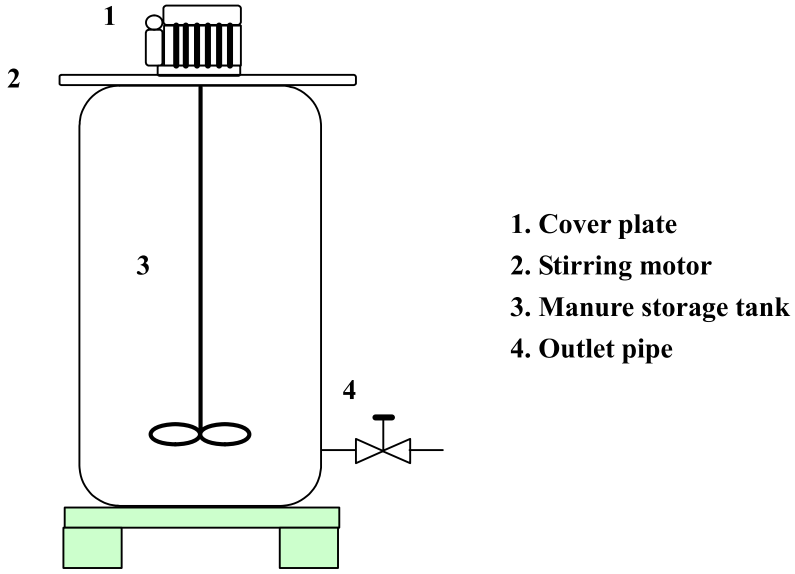

Fig. 5.2: Manure storage tank

Fig. 5.3: Illustration of manure storage facility

### 5.4.2 Anaerobic digestion system

The anaerobic digestion system included two anaerobic reactors (Fig. 5.4). The construction of the anaerobic digestion reactor is shown diagrammatically in Fig. 5.6. The total volume of the reactor was 30 litres. 25 litres of manure were added in each reactor. The space above the manure (5 litres) was kept free for gas emission. Manure was discharged from the outlet at the bottom of the reactor. Raw manure was added from the upper inlet of the reactor (No.7 in Fig. 5.6). The reactors were heated to a temperature of 37±2℃ using recycling water fed in through the base of the digester. The two anaerobic reactors R1 and R2 were operated in accordance with the parameters shown in Tab. 5.1. R1 represents the anaerobic digester with a sludge retention time (SRT) of 25 days. The SRT value of R2 was 15 days. The performance of the reactors was monitored by measuring the quantity and quality of the biogas through the gas meter and the gas analysis apparatus (shown in Fig. 5.5). Gas production and composition could be accessed online.

Tab. 5.1: Design and operational characteristics of the anaerobic digesters

| Reactor | Temperature | pH | Volume (Litres) | SRT (d) | | Stirring |
|---|---|---|---|---|---|---|
| | | | | 12.07.06-19.10.06 | 20.10.06-31.01.07 | |
| R1 | 37±2℃ | 6,5-8,5 | 25 | 25 | 15 | 15min/hour |
| R2 | 37±2℃ | 6,5-8,5 | 25 | 25 | 25 | 15min/hour |

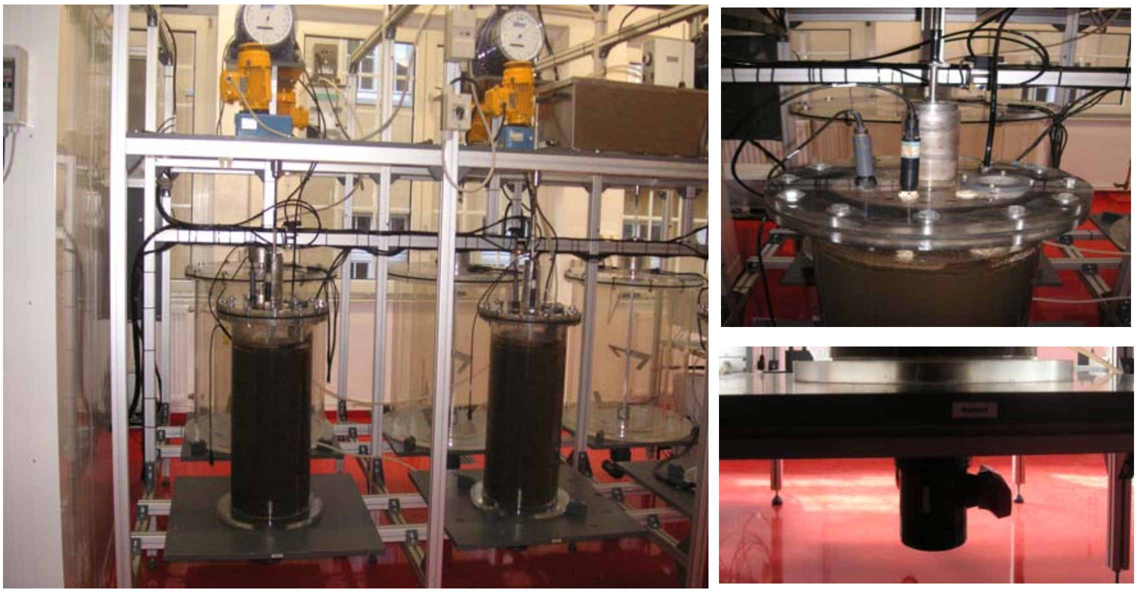

Fig. 5.4: Illustration of the anaerobic reactors (Digester system)

Fig. 5.5: Apparatus for the measuring, storage and analysis of gas

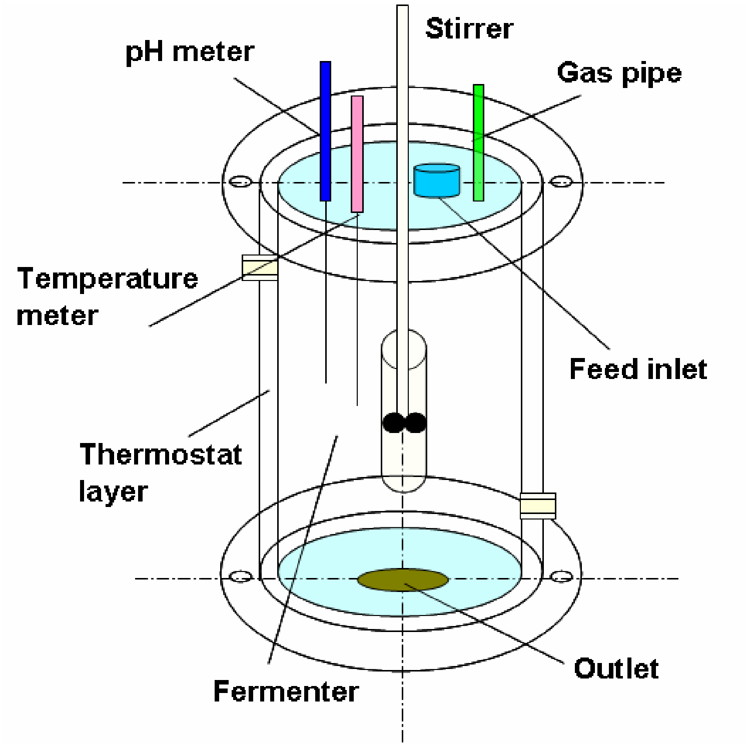

Fig. 5.6: Diagram of the anaerobic digestion reactor

### 5.4.3 Design of the P-precipitation system

The P-precipitation experiments were conducted in a batch reactor (Fig. 5.7). The batch system consisted of a water bath, a thermometer, a stirrer and a pH controller.

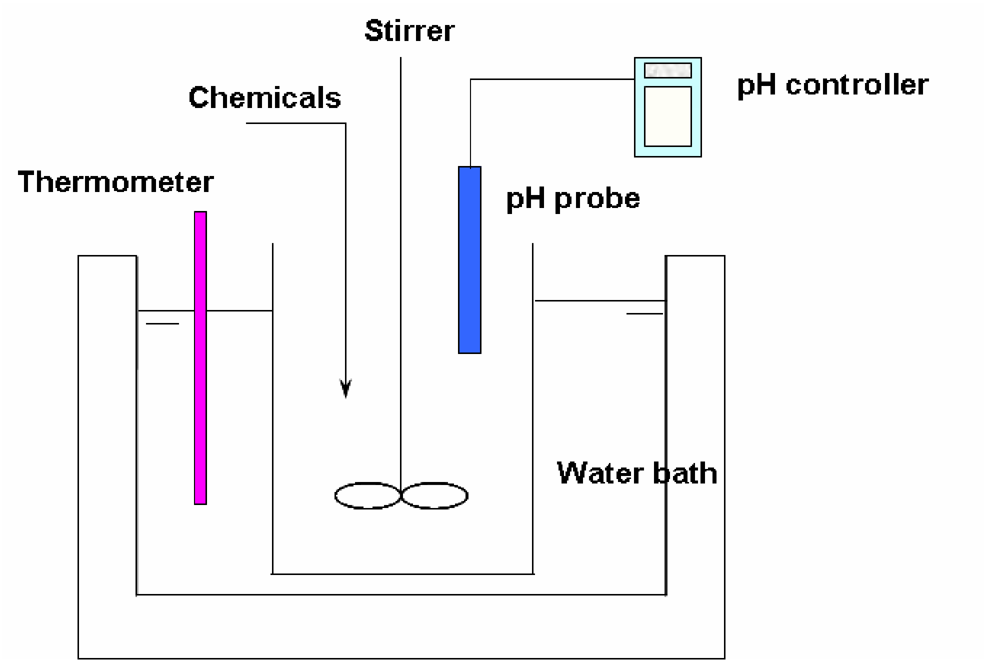

Fig. 5.7: Schematic diagram of the P-precipitation reactor

## 5.5 Experimental procedures

1. Manure characterization

Pig manure samples were refrigerated at 4℃ prior to use and analyzed within 7 days of collection.

2. Set-up, testing and operation of the anaerobic reactor

First, the two anaerobic reactors were filled with substrate. In the initial stages of operation, one litre of substrate was discharged from the reactor every day, and one additional litre of fresh raw manure was added to the reactor. The anaerobic reactors were operated under the conditions shown in Tab. 5.1.

3. Investigation of the ideal location for P-precipitation

Possible locations for P-precipitation during pig manure treatment include:

1.) P-precipitation in raw manure
2.) P-precipitation during anaerobic digestion
3.) P-precipitation after anaerobic digestion

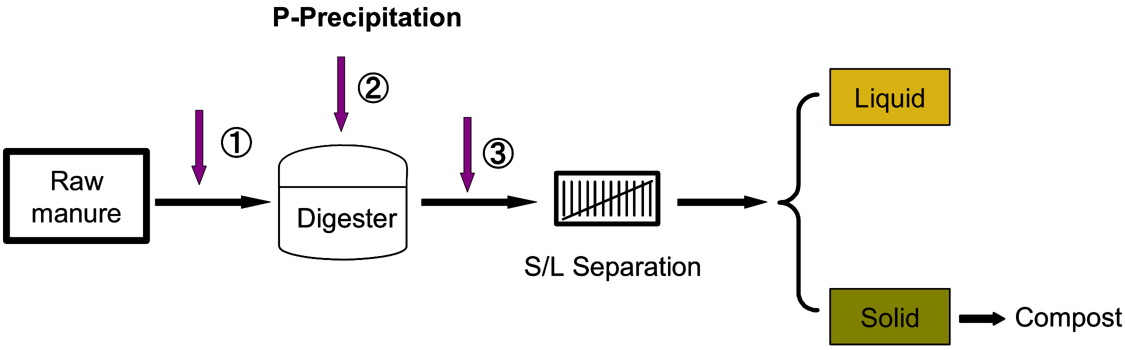

Fig. 5.8: Possible locations for P-precipitation in the pig manure treatment process

4. Investigation of precipitation conditions in the batch system

The conditions for phosphorus precipitation include the pH value, initial solution concentration, reaction time and molar ratio of the reactants.

5. Identification of the ideal process conditions for P-precipitation, combined with AD technology.

# 6 Experimental studies on the effect of anaerobic digestion

A pilot anaerobic digestion system was established in order to investigate the influence of anaerobic digestion on pig manure composition. The results are dealt with in this chapter. Two anaerobic reactors with different sludge retention times were operated at the same time for comparative purposes. The intention was to study the operating performances of the two reactors and the chemical performances of the pig manure during the digestion, and ultimately to determine a suitable position for P-precipitation.

## 6.1 Principle of anaerobic digestion

Anaerobic digestion (AD) is a biological process in which biodegradable organic matter is converted by bacteria into biogas, consisting of $CH_4$ (50-70%), $CO_2$ (30-50%) and small amounts of other gases (such as $H_2$ and $H_2S$).

The aims of pig manure digestion in this study include:
1. generating biogas for energy
2. reducing greenhouse gas emissions(methane, nitrous oxide)
3. reducing offensive odor and pathogens in the raw manure
4. reducing the mass of manure sludge
5. concentrating the nutrients in the final solid product for storage or export

### 6.1.1 Stages of anaerobic digestion

Anaerobic digestion is a microbiologically complex process. Four stages of anaerobic digestion have been recognized: hydrolysis, acidogenesis, acetogenesis and methanogensis. The entire process is illustrated in Fig. 6.1. Though AD is divided into four stages, their reactions occur simultaneously and synergistically.

#### 6.1.1.1 Hydrolysis

Hydrolysis is the stage in which complex organic molecules are broken down into monomers. Proteins are converted into amino acids, fats into fatty acids, glycerol into triglycerides, while complex carbohydrates such as polysaccharides, cellulose, lignin and starch turn into simple sugars (glucose or monosaccharides). The bacteria responsible for this process are hydrolytic bacteria.

### 6.1.1.2 Acidogenesis

The acidogenesic stage is also called fermentation; the organic monomers are fermented to form different types of organic acids. An important intermediate in the fermentation of amino acids is pyruvate, from which lactate, propionate, butyrate, formate and acetate are formed. Acetate, propionate, butyrate, caproate, caprylate, valerate and heptanoate constitute the group of compounds traditionally known as volatile fatty acids (VFA). Sugars are usually fermented to form alcohols and acetic acid. The decomposition reactions of glucose are shown as follows:

$$C_6H_{12}O_6 \rightleftharpoons 2CH_3CH_2OH + 2CO_2 \qquad (6\text{-}1)$$
(glucose converted into ethanol)

$$C_6H_{12}O_6 + 2H_2 \rightleftharpoons 2CH_3CH_2COOH + 2H_2O \qquad (6\text{-}2)$$
(glucose converted into propionate)

### 6.1.1.3 Acetogenesis

Acetogenesis is the stage in which the simple fermentation products of acidogenesis are converted mainly into acetate by the hydrogen-producing acetogenic (OHPA) bacteria. The acetate formation reactions are shown as follows:

$$C_6H_{12}O_6 + 2H_2O \rightleftharpoons 2CH_3COOH + 2CO_2 + 4H_2 \qquad (6\text{-}3)$$
(glucose transformed into acetate)

$$CH_3CH_2OH + 2H_2O \rightleftharpoons CH_3COO^- + 2H_2 + H^+ \qquad (6\text{-}4)$$
(ethanol transformed into acetate)

$$2HCO_3^- + 4H_2 + H^+ \rightleftharpoons CH_3COO^- + 4H_2O \qquad (6\text{-}5)$$
(bicarbonate transformed into acetate)

### 6.1.1.4 Methanogenesis

Methanogenesis is the stage in which acetate and hydrogen are converted into methane by methanogenic bacteria. The methanogenic bacteria prefer a neutral or slightly alkaline environment. Because these bacteria are the slowest in the entire AD process, the kinetics of the overall reaction are "controlled" by the kinetics of methanogenesis. The following reactions can be performed during this stage:

$$2CH_3CH_3OH + CO_2 \rightleftharpoons 2CH_3\ COOH + CH_4 \tag{6-6}$$

(ethanol converted into acetate)

$$CH_3COOH \rightleftharpoons CH_4 + CO_2 \tag{6-7}$$

(acetate converted into methane)

$$CH_3OH + H_2 \rightleftharpoons CH_4 + H_2O \tag{6-8}$$

(methanol converted into methane)

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O \tag{6-9}$$

(carbon dioxide converted into methane)

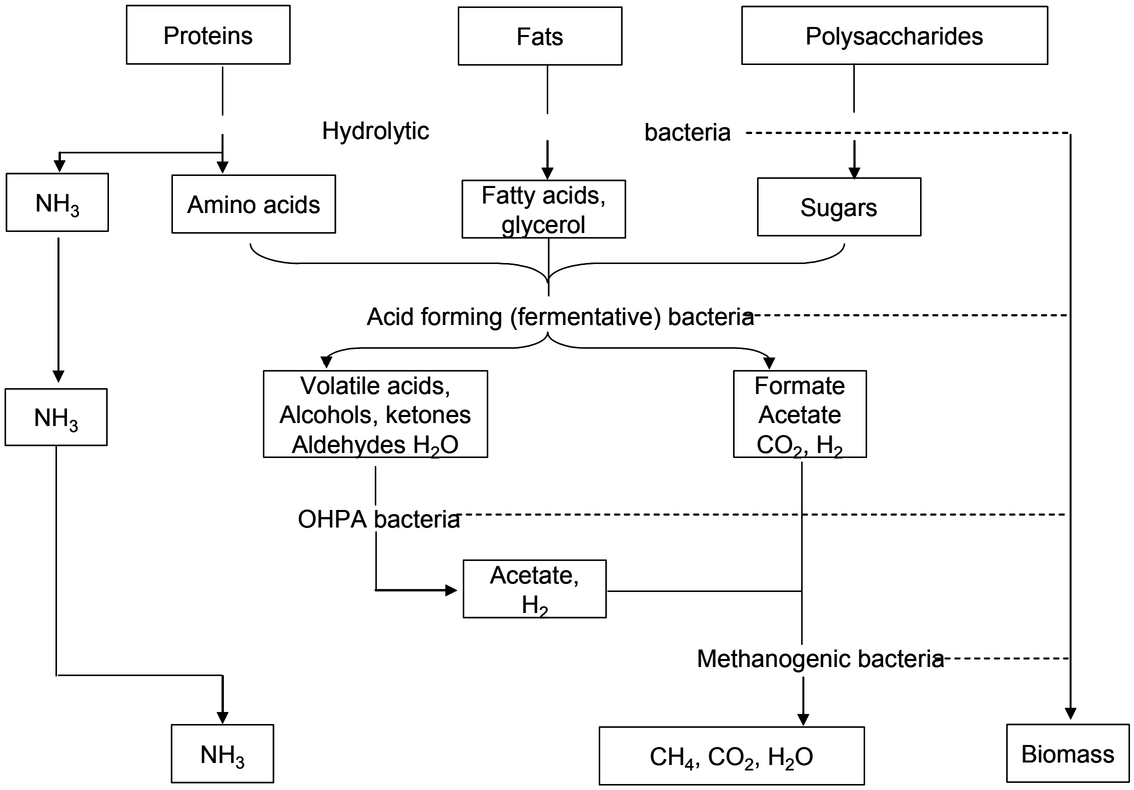

Fig. 6.1: The biochemistry of anaerobic digestion (Lester, 1999)

### 6.1.2 Important conditions influencing AD

#### 6.1.2.1 Temperature

Three temperature intervals have been explored for anaerobic digestion. The temperature ranges of psychrophilic, mesophilic and thermophilic digesters are shown in Tab. 6.1.

Tab. 6.1: Temperature ranges for various anaerobic populations (Prescott et al. 1999)

| | Temperature range (℃) |
|---|---|
| Psychrophilic | 0-20 |
| Mesophilic | 15-45 |
| Thermophilic | 45-75 |

Temperature is an important factor for microbial activity. In psychrophilic digestion, the microorganisms have a somewhat lower activity rate. The psychrophilic digester is primarily used in the form of a covered lagoon digester, which operate sat ambient temperatures (Stevens and Schulte, 1979). Thermophilic digestion has a faster reaction rate and better pathogen-killing effect than mesophilic digestion. However, when the economic factor is taken into consideration, mesophilic digesters are more commonly used in practice.

#### 6.1.2.2 pH value

In general, the pH value of the fermentation substrate lies between slightly acidic (ca. pH 6) and slightly alkaline (ca. pH 8). A low pH can inhibit acidogenesis, whilst a pH below 6.4 can be toxic for methane-forming bacteria (Van Velsen,1981). During the acidogenesis process, acids are formed which cause a drop in pH value. The methanogenic process consumes hydrogen ions, and thus the pH rises. To maintain stable methanogenic activity, a pH value between 7 and 8 is desirable (Lens et al. 2004).

#### 6.1.2.3 Sludge retention times (SRT)

The SRT represents the time that the feedstock spends in the digester: the longer, the better. Sludge retention time is an important factor in controlling the conversion of solids to gas and maintaining digester stability. The SRT is defined as equation 6-10:

$$\text{SRT} = \frac{\text{Total mass of sludge in digester (kg)}}{\text{Mass of sludge discharged each day (kg/d)}} \tag{6-10}$$

A sufficient SRT should be available for the bacteria to grow and replace the bacteria lost in the effluent. If the SRT is lower than a "critical SRT", when the rate of bacterial loss exceeds the rate of bacteria growth, the anaerobic digester cannot be operated properly. SRT varies according to waste composition and process temperature. For manure digestion, the SRT of mesophilic digesters operates typically between 25 and 35 days. The minimum SRT range is as low as 12-15 days (Lester, 1999).

#### 6.1.2.4 Nutrients and inhibitor

Nutrients such as nitrogen and phosphorus are needed for bacteria requirements in anaerobic digesters. The relationship between the amount of carbon and nitrogen present in organic materials is represented by the C:N ratio. The optimum C:N ratios in anaerobic digesters are between 20 and 30 (Hawkes 1980). Animal manure usually contains adequate nutrients of nitrogen and phosphorus for AD (Hong, 2005). However, it has been found that higher ammonia concentration (up to 5 g/L) can be toxic for the bacteria metabolism (Karakashev et al., 2005), especially in combination with a high pH that favors the volatile $NH_3$ form.

In addition, methanogenesis is sensitive to several groups of inhibitors, including alternate electron acceptors (oxygen, nitrate and sulfate), sulfides, heavy metals, halogenated hydrocarbons, volatile organic acids, ammonia and cations (Speece, 1996). The inhibitory concentration is dependent upon a number of variables, including pH, retention time, temperature and the ratio of toxic substance to bacterial mass concentration.

#### 6.1.2.5 Mixing

Stirring within the digester improves the contact between the micro-organisms and substrate, as well as improving the bacterial population’s ability to attract nutrients. Mixing also prevents the formation of scum and the development of temperature gradients within the digester. However, excessive mixing can disrupt the micro-organisms. For this reason, slow and intermittent stirring is preferable.

## 6.2 Anaerobic reactor performance

Anaerobic reactor performances were evaluated in terms of the following three criteria: biogas yield, methane content and organic matter reduction.

### 6.2.1 Gas production

During the anaerobic digestion experiment, the digester system was operated in two stages: a start-up phase (12.7.06-19.10.06) and a regular operational phase (20.10.06-31.01.07). In the start-up period, the whole system was tested by operating two reactors in parallel. Both reactors were fed with the same type and quantity of manure influent, so the amounts of cumulative gas produced from R1 and R2 were similar during this period (Fig. 6.2). When the digester system began to run steadily, the two reactors were distinguished by different SRT times (SRT1=15d; SRT2=25d). R1, with its higher loading rate, produced more gas than R2. Organic loading rates (OLRs) in Fig. 6.3 and 6.4 were expressed in terms of the weight of added COD per cubic meter per day (e.g., $m^3$/kg $COD_{added}$). The OLR value is calculated in relation to not only the sludge retention time, but also the manure composition. During the whole AD operation, the anaerobic reactors were successively fed with four types of raw pig manure. The chemical composition of feed 3 and feed 4 are shown in Tab. 6.2., whilst Fig. 6.2 shows that gas accumulates faster with a greater COD input.

Fig. 6.3 illustrates biogas productivity in terms of specific gas production. In the course of this stage, the specific gas productions of R1 were generally lower than those of R2. . The average biogas yield of R1 and R2 was calculated as 0.3 and 0.4$m^3$/kg $COD_{added}$ respectively. Fig. 6.3 reflects that a higher OLR rate may not result in a greater biogas yield. High OLR values require more bacteria, but an SRT of 15 days (R1) seems to be insufficient for bacteria to grow and regenerate, compared with an SRT of 25 days (R2). Furthermore, a high OLR could encourage acid production, which in turn could decrease the pH value and influence the normal functioning of methanogenic bacteria (Poliafico, 2007). This is one of the factors which explain the lower specific gas production in R1 and a slight pH drop in the 20.10.06-20.12.07 period. In accordance with the pH variation in the reactors, it is also influenced by the degradation of organic nitrogen and the appearance of the ammonium ion. Fig. 6.3 shows that the pH value fluctuated by at most 0.5 pH units. The results were still within the 6.9-8.0 range typical of anaerobic digestion (Hobson et al., 1974).

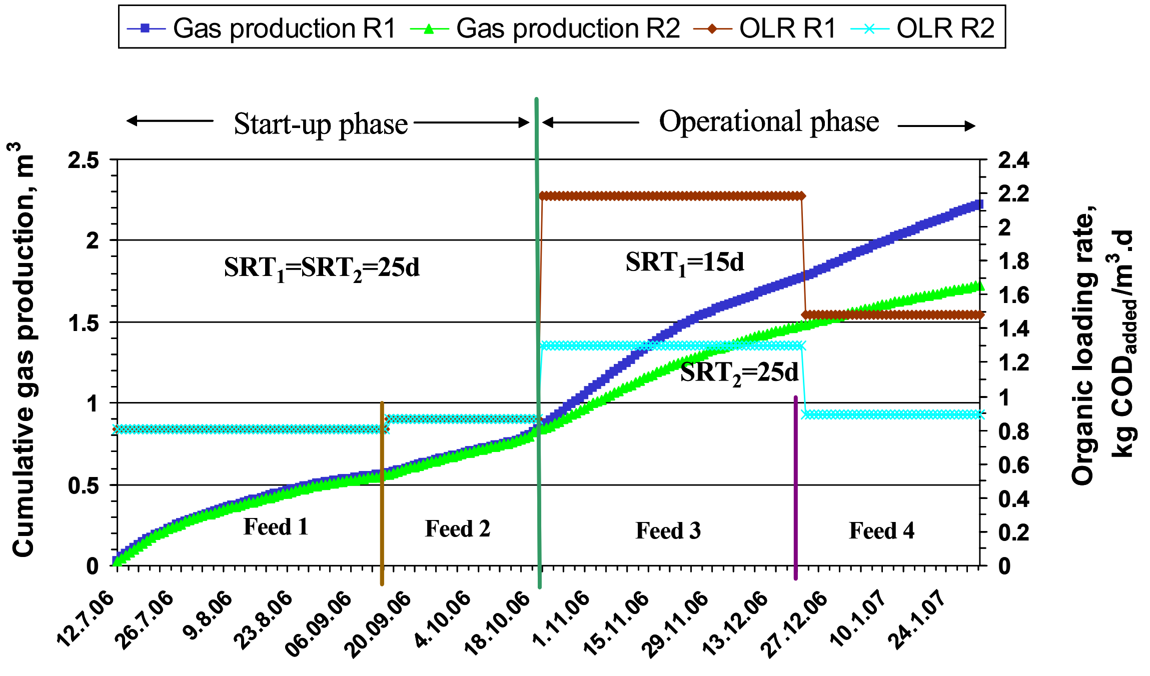

Fig. 6.2: Cumulative gas production and input COD loading rates in R1 and R2

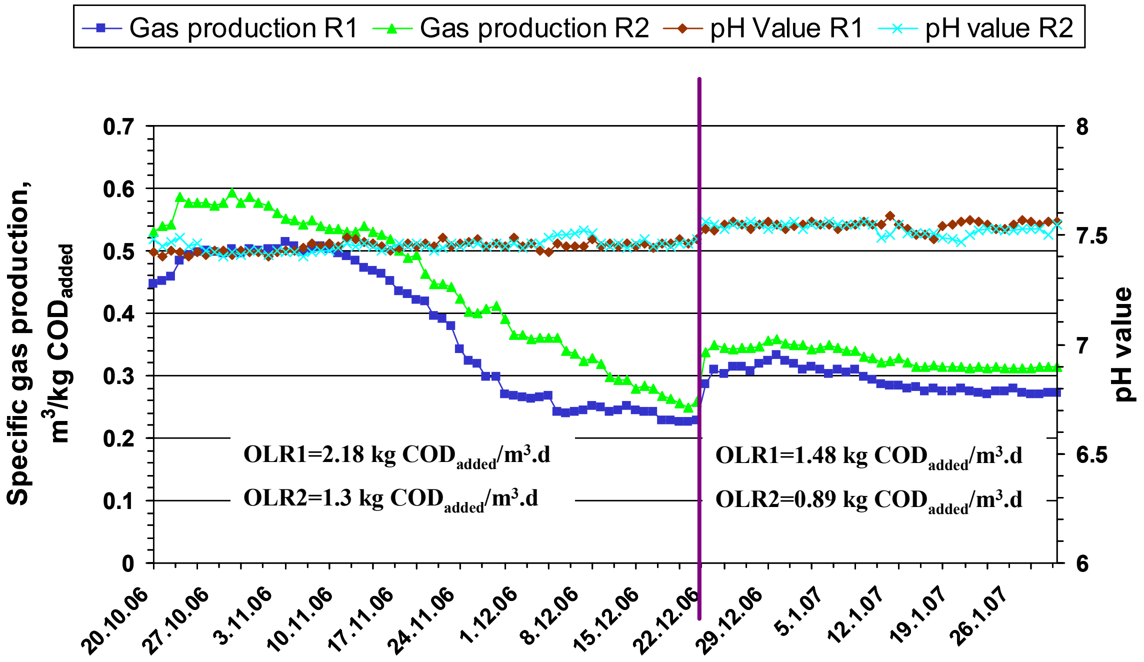

Fig. 6.3: Specific daily gas production in R1 and R2 during operational period

### 6.2.2 Methane content

The methane content of the biogas is an important indicator of the degree of degradation. In certain circumstances, using only gas yield as an indicator of degradation is not sufficient. This is because the pH variation in the AD reactor can induce changes in release or uptake of carbon dioxide that are unrelated to degradation (Chynoweth et al., 1998). In addition, a higher percentage of methane in biogas means improved fuel quality. Fig. 6.4 shows the methane and carbon dioxide concentration produced by Reactor 1 and Reactor 2. The biogas composition obtained was basically within the value ranges found in the literatures: 45-70% methane and 20-35% carbon dioxide. In general terms, the methane content falls as the carbon dioxide percentage in the biogas rises. On average, Reactor 2 produced a higher methane value (60.6%) than R1 (56.2%). This result indicates that the AD process in R2 has a better performance, with an SRT of 25 days.

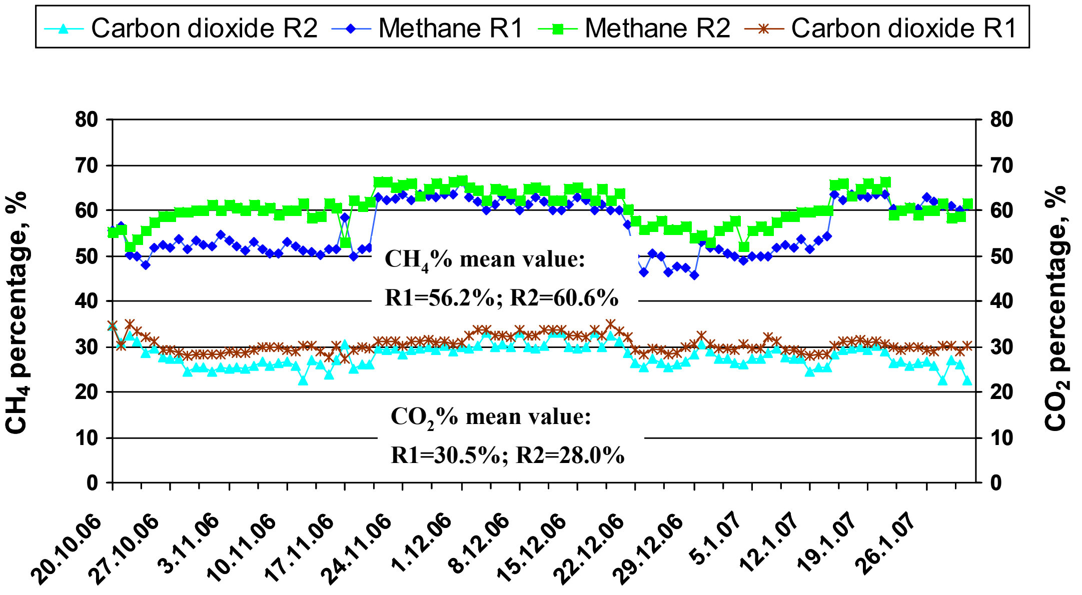

Fig. 6.4: Percentage of methane and carbon dioxide in biogas during operational period

### 6.2.3 Organic matter reduction

Pig manure is rich in biodegradable matter. This is composed principally of proteins, carbohydrates and fats. The conversion of biodegradable matter into biogas results in a lower required quantity of digested sludge. Biodegradability under anaerobic conditions is ultimately measured in terms of the reduction in organic matter (Chynoweth et al., 1998). Fig. 6.5 shows the Volatile Solid (VS) reduction rate during the operational period. On the whole, a longer sludge retention time is better for degradation. An average rate of 57.2% of the VS was reduced during the digestion of R2, while a VS reduction rate of 52.0% was achieved in R1. The gradients in Fig. 6.5 also reflect that VS reduction depends on feed composition and organic loading rate. When a different pig manure feed was added after 21.12.2006, the VS reduction rates of both R1 and R2 were to some extent decreased. The main reason was the inherent lower biodegradability of feed 4, compared with feed 3 (Fig. 6.2).

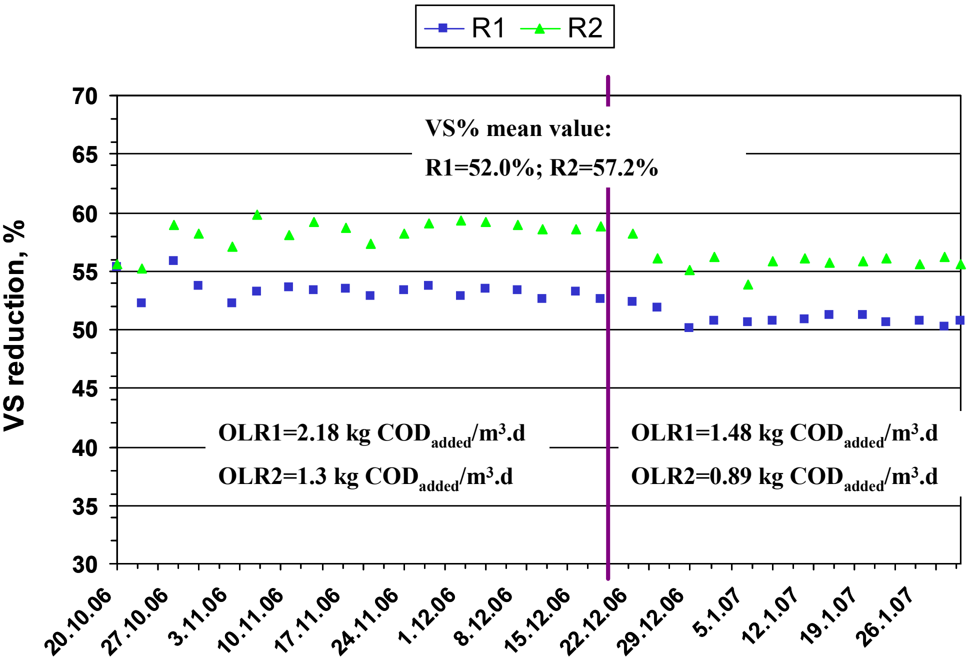

Fig. 6.5: VS reduction rate of R1 and R2 during operational period

## 6.3 Characteristics of pig manure before and after AD

The chemical characteristics of pig manure before and after AD are presented in Tab. 6.1. Considering the unstable operational factors in the start-up phase, the mean value was calculated using data from the 20.10.06 - 31.01.07 period. In order to compare the change in ion concentration, the data of Tab. 6.1 was analyzed and presented in Tab. 6.2.

The pH value of raw manure was generally found to be lower than that of digested manure. Tab. 6.3 shows an average rise of 0.88 units of pH value after anaerobic digestion. Anaerobic digestion is a process converting nutrients from organic form to gaseous and inorganic constituents. The conversion of organic nitrogen results in an increase in $NH_4$-N concentrations, which was the main reason for pH enhancement in this experiment. The data in Tab. 6.3 show that the concentration of $NH_4$-N in digested manure was 725 mg/L higher than in raw manure. The pH value may also be influenced by the dissolution of $CO_2$ in solution, although the effect of $CO_2$ is not comparable to $NH_4$-N in this experiment because of the presence of large amounts of $NH_4$-N.

The concentration levels of TP and TKN basically remained constant before and after anaerobic digestion. However, the proportions of soluble P (primarily as $PO_4$-P) and soluble N (primarily as $NH_4$-N) in raw and digested pig manure are quite different. Organic nitrogen and inorganic nitrogen (ammonium) are the two main forms of nitrogen found in animal manure. Digested manure contains larger proportions of ammonium ($NH_4$-N) because of the decomposition of organic matter. $NH_4$-N constituted 50.4% and 79.3% of TKN in raw and digested manure respectively. For phosphorus, $PO_4$-P took 37.5% TP in raw manure and 20.8% in digested manure, which indicates that part of soluble phosphorus was removed from the liquid portion during anaerobic digestion. The reduced phosphorus was thought to be in the form of inorganic precipitant and cellular material. The average $PO_4$-P reduction rate was calculated as 45%.

During anaerobic digestion, the concentration of $Mg^{2+}$ and $Ca^{2+}$ decreased by 21.1% and 3.3% respectively. The molar ratio of Ca/P increased from 1 to 1.7, whilst the molar ratio of Mg/P increased from 0.9 to 1.3.

Tab. 6.2: Comparison of pig manure characteristics before and after anaerobic digestion

| Operational phase | Mean value | | 20.10.06 - 20.12.06 (feed 3) | | 21.12.06 - 31.01.07 (feed 4) | |
|---|---|---|---|---|---|---|
| | Influent | Effluent | Influent | Effluent | Influent | Effluent |
| pH | 6.92 | 7.80 | 6.92 | 7.79 | 6.91 | 7.81 |
| TP (mg/L) | 264.1 | 263.9 | 265.0 | 266.2 | 263.2 | 261.6 |
| TKN (mg/L) | 2420 | 2450 | 2620 | 2660 | 2220 | 2240 |
| $PO_4$-P (mg/L) | 99.6 | 54.8 | 119.0 | 56.6 | 80.2 | 53.0 |
| $NH_4$-N (mg/L) | 1219 | 1944 | 1289 | 1905 | 1140 | 1983 |
| $Ca^{2+}$ (mg/L) | 128.8 | 124.5 | 135.1 | 133.1 | 122.6 | 122.5 |
| $Mg^{2+}$ (mg/L) | 71.6 | 56.5 | 72.6 | 59.1 | 70.5 | 53.9 |

Tab. 6.3: Analysis of ion concentration changes before and after anaerobic digestion

| Parameter | Raw pig manure | Digested pig manure | Difference (reduction rate) |
|---|---|---|---|
| pH | 6.92 | 7.80 | -0.88 |
| $PO_4$-P (mg/L) | 99.6 | 54.8 | 44.8 (45%) |
| $NH_4$-N (mg/L) | 1219 | 1944 | -725 (59.5%) |
| $Ca^{2+}$ (mg/L) | 128.8 | 124.5 | 4.3 (3.3%) |
| $Mg^{2+}$ (mg/L) | 71.6 | 56.5 | 15.1 (21.1%) |
| $PO_4$-P% in TP | 37.5% | 20.8% | - |
| $NH_4$-N% in TKN | 50.4% | 79.3% | - |
| Molar ratio **$Mg^{2+}$:$PO_4$-P**:$NH_4$-N | **0.9:1**:27.1 | **1.3:1**:77.1 | - |
| Molar ratio **$Ca^{2+}$:$PO_4$-P**:$NH_4$-N | **1:1**:27.1 | **1.7:1**:77.1 | - |

## 6.4 Influence of AD on $PO_4$-P and $Mg^{2+}$

Figs. 6.6 and 6.7 compare the degrees of concentration reduction between $PO_4$-P and $Mg^{2+}$ during anaerobic digestion. The entire period was divided into two periods before and after 21.12.06. The values of $PO_4$-P and $Mg^{2+}$ concentration (as well as the Mg/P molar ratio) in each stage are presented in Figs. 6.6 and 6.7 (and in Tab. 6.2). The concentration reduction is expressed as mmol/L.

Both Fig 6.6 and Fig. 6.7 show that, regardless of R1 or R2, higher $PO_4$-P reduction vales were achieved in the 20.10.06-20.12.06 period. The influent during this period had higher $PO_4$-P concentrations (119.0 mg/L). The reduction value of R1 varied from 1.6 to 1.8 mmol/L, whilst the value of R2 remained at approx. 2.0 mmol/L. This reflects the steady operation of R2 (SRT=25d).

Fig. 6.6 and Fig. 6.7 reflect that the $PO_4$-P reduction value was much higher than the $Mg^{2+}$ reduction value. In addition, the concentrations of $PO_4$-P and $Mg^{2+}$ were not decreased by the same molar quantities. These two points prove that the reduction in $PO_4$-P was not only due to its reaction with $Mg^{2+}$. Soluble phosphorus reduction can be caused by two main factors; the physical absorption and aggregation between molecules, and chemical precipitation.

The constituents of this solid part were not analysed as part of this experiment. The insoluble phosphorus is assumed to be composed of phosphate salts and organic phosphorus.

Although there is no particular relationship between the two changes in concentration, the residual Mg/P molar ratios generally remained constant, regardless of the SRT and influent concentrations. The average Mg/P molar ratios in both R1 and R2 can reach 1.3. In reality, as Chapter 2 explains, a molar ratio of 1.3 is a fundamentally required stoichiometric rate. In order to enforce P-precipitation as struvite under theses circumstances, either the pH value should be elevated or magnesium ions added. From this point of view, forced struvite precipitation in the anaerobic digester seems to be inappropriate, as AD operates under a strict temperature range. In contrast, P-precipitation could be more suitable for taking place after anaerobic digestion. Digested pig manure has higher pH value and a more suitable Mg/P molar ratio than raw manure. Although the additional magnesium source needs to be supplemented, the absolute amount of chemicals added will be lower. This is because soluble phosphorus is reduced after anaerobic digestion.

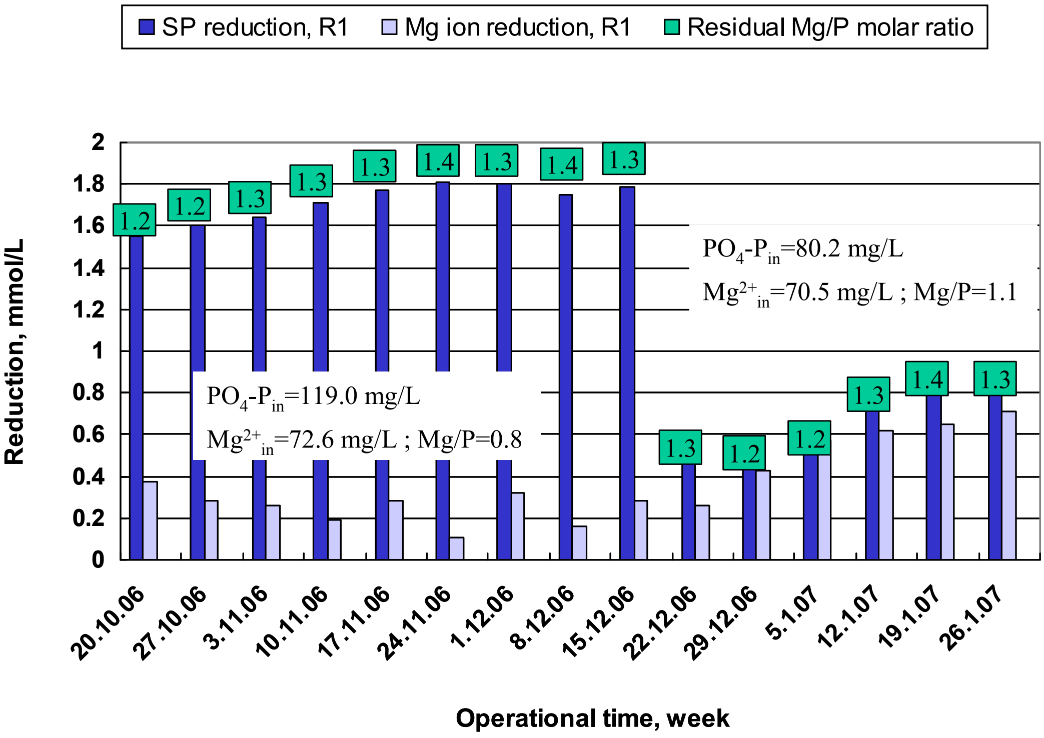

Fig. 6.6: $PO_4$-P, $Mg^{2+}$ reduction and residual Mg/P molar ratio of R1 effluent

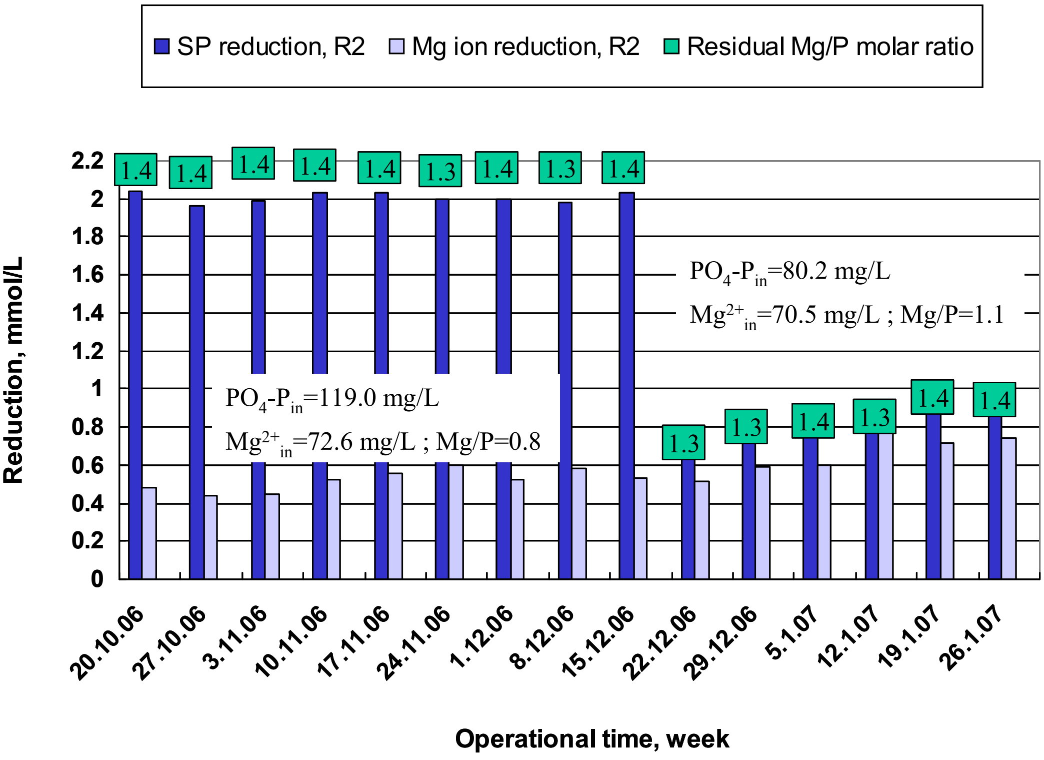

Fig. 6.7: $PO_4$-P, $Mg^{2+}$ reduction and residual Mg/P molar ratio of R2 effluent

## 6.5 Influence of solid-liquid separation on the composition of pig manure

The influence of solid-liquid separation on manure composition is shown in Tab. 6.4. In this experiment, manure effluent from the anaerobic reactor is separated by centrifuge. In the case of raw pig manure, about half of the COD, TP and TKN were removed from the homogeneous pig manure, whilst 54.5% of the COD, 49.2% of the TP and 48.8% of the TKN remained in the liquid phase. As for digested manure, 47.7% of the COD, 30.3% of the TP and 76.5% of the TKN remained in the liquid phase. After solid-liquid separation, The pH value increased by an average of 0.2 units; the concentration of $NH_4$-N contained in the liquid phase of both raw and digested pig manure decreased by 100 mg/L. The concentration of $PO_4$-P, $Ca^{2+}$ and $Mg^{2+}$ remained constant.

Tab. 6.4: Characteristics of raw and digested pig manure before and after solid-liquid separation

| Parameter | Raw manure | | Digested manure | |
|---|---|---|---|---|
| | homogeneous | after solid-liquid separation | homogeneous | after solid-liquid separation |
| pH | 6.90 | 7.16 | 7.81 | 8.01 |
| COD | 19220 | 10480 (54.5%) | 10260 | 4890 (47.7%) |
| TP (mg/L) | 261.9 | 128.8 (49.2%) | 265.0 | 80.2 (30.3%) |
| TKN (mg/L) | 2580 | 1260 (48.8%) | 2600 | 1990 (76.5%) |
| $PO_4$-P (mg/L) | 115.2 | 113.6 | 55.2 | 55.0 |
| $NH_4$-N (mg/L) | 1260 | 1160 | 1890 | 1790 |
| $Ca^{2+}$ (mg/L) | 133.3 | 133.0 | 132.4 | 131.6 |
| $Mg^{2+}$ (mg/L) | 70.6 | 69.8 | 58.6 | 58.0 |

The above were average values for 4 samples collected separately during the October 20, 2006 - December 21, 2006 period.

## 6.6 Chapter summary

According to the data analysis, the most suitable position for P-precipitation is after anaerobic digestion.

The reasons are as follows:

1. After anaerobic digestion, 45% of $PO_4$-P was reduced, whilst the pH value rose by 0.88 units. The cost of chemicals (alkaline and magnesium) will be less for P-precipitation in digested manure than for P-precipitation in raw manure.

2. Regardless of the SRT and feed concentrations, an average Mg/P molar ratio of 1.3 was achieved after anaerobic digestion. This is more suitable for struvite precipitation.

3. The solid-liquid separation has only a slight influence on the concentration of $PO_4$-P, $Ca^{2+}$ and $Mg^{2+}$. For this reason, struvite can be precipitated in the homogeneous pig manure and separated all at once at the end.

4. In addition, experiments also indicated that a shorter SRT (15 days) leads to higher biogas production but lower methane concentration and lower overall manure degradation. The R2reactor, with an SRT of 25 days, ran more steadily. The digested pig manure effluent from R2 can be used as a sample material for the P-precipitation experiment that will be conducted in the next chapter.

# 7 Experimental studies on P-precipitation

The three significant parameters which should be investigated in P-precipitation are: the solution pH value, molar ratio and equilibrium time of the reaction. Batch experiments were conducted at room temperature (approximately 20℃） to study the influence of these reaction conditions on P-precipitation. The results of these experiments, the objective of which is to predict conditions for optimum struvite precipitation, are reported in this chapter. Both raw and digested pig manure were used as sample materials in order to further investigate and determine a valuable ultimate route for P-recovery from pig manure.

## 7.1 Characterization of the sample pig manure

Before the study of the P-precipitation reaction is carried out, the chemical characteristics of the sample manure should be investigated. The important parameters for P-precipitation in different types of pig manure are listed in Tab. 7.1. The values given for the raw manure are by means of influent samples of the continuous anaerobic reactors. The values given for the digested manure are by means of effluent samples from Reactor 2 during the October 20-December 21, 2006 period. The values of digested manure were selected from Reactor 2 because this reactor was always operated using the same sludge retention time, and it ran relatively steadily in the October 20-December 21, 2006 period.

As discussed in Chapter 5, concentrations of $PO_4$-P and $Mg^{2+}$ were significantly reduced after anaerobic digestion. The more degraded ammonium resulted in an increase in $NH_4$-N concentration and pH value. However, $Ca^{2+}$ concentration changed only slightly after anaerobic digestion. It can be also seen from Tab. 7.1 that solid/liquid separation has little influence on the ion concentration of $PO_4$-P, $Ca^{2+}$ and $Mg^{2+}$. The molar ratio of $Ca^{2+}$ to $PO_4$-P and $Mg^{2+}$ to $PO_4$-P remained constant after centrifugal solid/liquid separation. In order to analyse the constituents of the solution better, the mole number of $PO_4$-P was set at 1. It can be seen from Tab. 7.1 that the molar ratios of $Ca^{2+}$ to $PO_4$-P and $Mg^{2+}$ to $PO_4$-P in raw pig manure were 1 and 0.9 respectively, whereas in digested manure the two ratios increased to 1.7 and 1.3. Tab. 7.1 shows that the concentration of ammonium nitrogen is much higher than that of dissolved phosphorus in the liquid phase. The variation of the $NH_4$-N concentration could lead to the change in pH value.

Tab. 7.1: Characteristics of sample pig manure

| Parameter | Raw manure | | Digested manure | |
|---|---|---|---|---|
| | homogeneous | filtrated after separation | homogeneous | filtrated after separation |
| pH | 6.92 | 7.13 | 7.80 | 8.01 |
| $PO_4$-P (mg/L) | 99.6 | 96.6 | 54.8 | 54.2 |
| $NH_4$-N (mg/L) | 1219 | 1197 | 1944 | 1892 |
| $Mg^{2+}$ (mg/L) | 71.6 | 68.5 | 56.5 | 55.2 |
| $Ca^{2+}$ (mg/L) | 128.8 | 123.2 | 124.5 | 122.5 |
| Molar ratio of **$Mg^{2+}$:$PO_4$-P**:$NH_4$-N | **0.9:1**:27.1 | **0.9:1**:27.8 | **1.3:1**:77.1 | **1.3:1**:77.2 |
| Molar ratio of **$Ca^{2+}$:$PO_4$-P**:$NH_4$-N | **1:1**:27.1 | **1:1**:27.8 | **1.7:1**:77.1 | **1.7:1**:77.2 |
| Molar ratio of **$Ca^{2+}$: $Mg^{2+}$** | **1.1:1** | **1.1:1** | **1.3:1** | **1.3:1** |

## 7.2 Study of the effect of pH value

In the experiments conducted in this section, the pH values were enhanced by the addition of NaOH solution (1N). The initial pH values of the homogeneous manure samples were adjusted to 8, 9, 10, 11 and 12 respectively. The volume of each manure sample was 2.5 liters. The reaction was conducted by stirring at a temperature of 20℃. The concentrations of $PO_4$-P, $NH_4$-N, $Mg^{2+}$ and $Ca^{2+}$ were measured initially and after 90 minutes.

### 7.2.1 Effect of pH on $NH_4$-N

Fig. 7.1 shows that the removal rate of $NH_4$-N increased with the enhancement of pH value. The $NH_4$-N removal rate increases from 5% to 35% when the pH rises from 8 to 12. As the ammonium content in pig manure is much higher than the content of phosphate and magnesium ion because of the limited amount of phosphate and magnesium ion in the solution (Tab. 7.1), it can be calculated that the ammonium ion removed by struvite precipitation in the course of the experiment accounts for only a small part of the total ammonium ion. The reduction of the ammonium ion is mainly due to the formation of ammonia gas, with a rise in pH value (Equation 2-4).

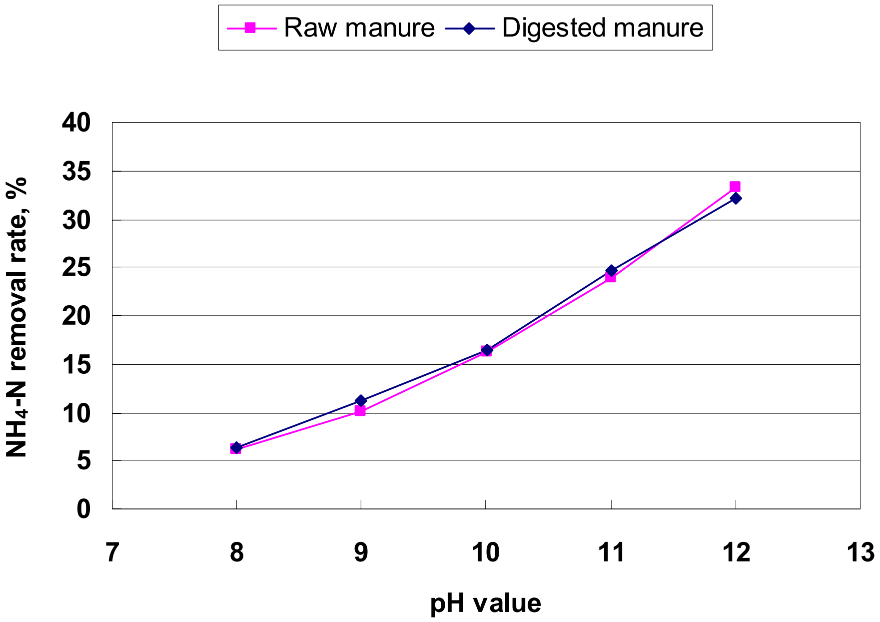

Fig. 7.1: Removal efficiency of $NH_4$-N in raw and digested pig manure at various pH values

### 7.2.2 Effect of pH on $Ca^{2+}$ and $Mg^{2+}$

As shown in Figs. 7.2 and 7.3, the $Ca^{2+}$ and $Mg^{2+}$ removal rate increased with a rise in pH. Over 80% of the calcium and magnesium ions can be removed from the liquid manure phase when the pH is raised to 9.0. However, the composition of the precipitate is impossible to verify. Fig. 7.13 shows that about 77% of calcium ions have been precipitated out at a pH of 8, whilst the magnesium ions do not basically react at the same pH value. Large quantities of the magnesium ion are precipitated at a pH value of 9.0, which is in accordance with the given theoretical pH value for struvite precipitation.

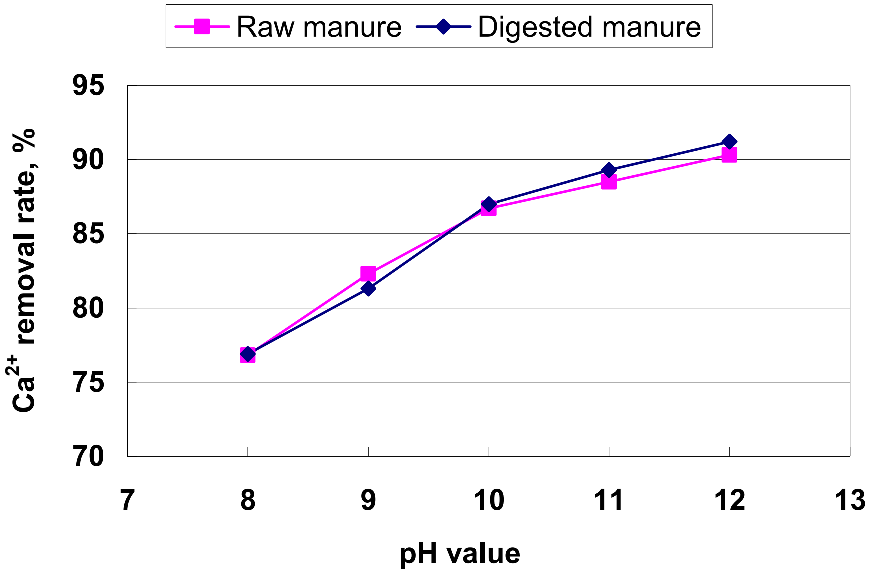

Fig. 7.2: Removal efficiency of $Ca^{2+}$ in raw and digested pig manure at various pH values

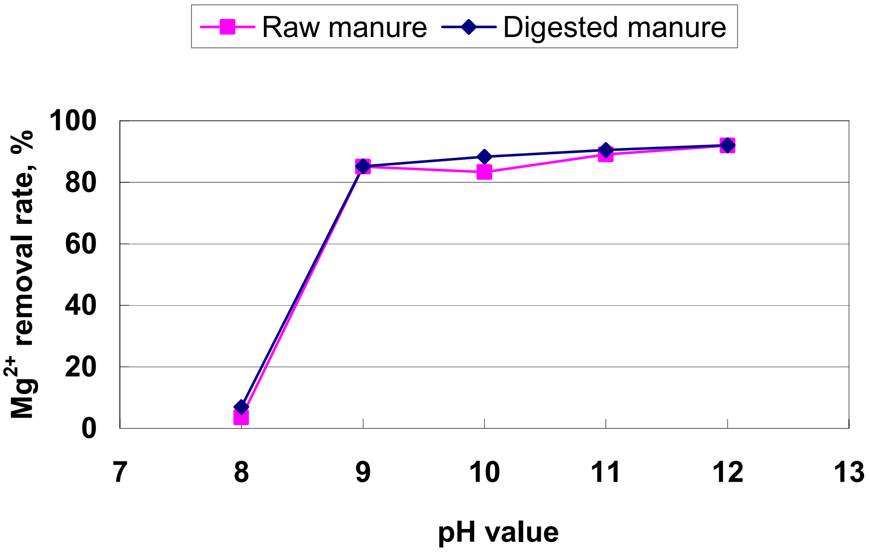

Fig. 7.3: Removal efficiency of $Mg^{2+}$ in raw and digested pig manure at various pH values

### 7.2.3 Effect of pH on soluble P-removal

The removal of soluble phosphorus from the liquid phase is the major objective of this study. The ideal pH value for P-precipitation can be determined by the curve of the $PO_4$-P removal rate at different pH values. Fig. 7.4 shows that the ideal pH values for P-precipitation were 9 and 10. As the removal rates at the two pH values were similar, the P-precipitation reaction conducted at pH=9 become more valuable, as less NaOH is used. At a pH value of 9, the removal rate of $PO_4$-P was about 90%. Comparing raw and digested manure, it was found that the removal rates of digested manure were slightly higher than that of raw manure at various pH values. As the initial pH value of raw manure is lower than that of digested manure, greater volumes of alkaline also need to be consumed in raw manure in order to attain the same pH value as that of digested manure.

Using the results shown in Figs. 7.2 and 7.3, it can be concluded that the favorable pH range both for struvite and calcium phosphate compound precipitation is from 8 to 10. Whereas the $Ca^{2+}$ and $Mg^{2+}$ removal rates are still higher when the pH value exceeds 10 (cf. Figs. 7.2, 7.3), Fig. 7.4 shows that the $PO_4$-P removal rate declines from a pH value of 10. This must mean that the $Ca^{2+}$ and $Mg^{2+}$ have combined with another anion to precipitate out, but not react with, the soluble phosphorus.

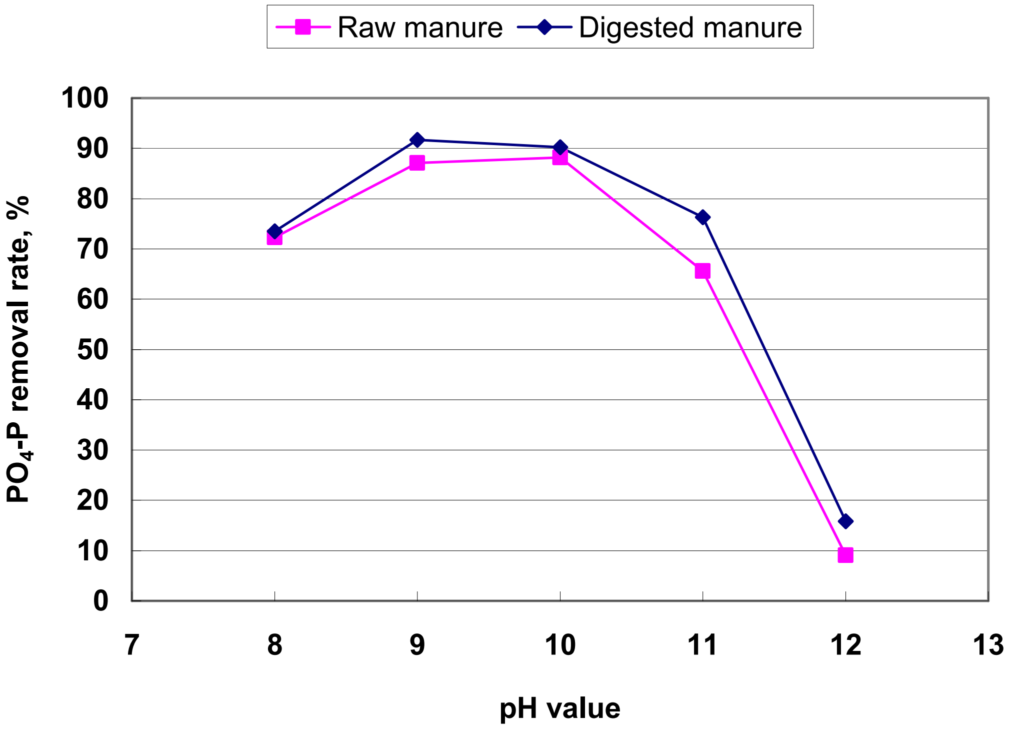

Fig. 7.4: Removal efficiency of $PO_4$-P in raw and digested pig manure at various pH values

## 7.3 Study of the effect of the $Ca^{2+}/Mg^{2+}$ molar ratio

In order to investigate the effect of the $Ca^{2+}/Mg^{2+}$ molar ratio on soluble P-removal from pig manure, $MgCl_2$ and $CaCl_2$ were added to the digested pig manure in order to achieve the desired Ca/Mg molar ratios of 0.6, 1.3 and 2.0. The total mole numbers of $Mg^{2+}$ and $Ca^{2+}$ were constant in each manure sample: $n(Mg^{2+}+Ca^{2+})$ =6 mol/L. The pH was raised with the addition of the NaOH solution. The relationship between the $PO_4$-P removal rate and the pH value at the different Ca/Mg molar ratios (0.6, 1.3, 2.0) is shown in Fig. 7.5. Fig. 7.6 shows a comparison of the three $PO_4$-P removal curves.

In general, $PO_4$-P removal rate first rises, then declines within the pH range of 8-10. When the pH value is between 8.8 and 9.5, more than 90% of the $PO_4$-P can be precipitated, regardless of the Ca/Mg molar ratio. When the pH value is less than 8.8, the $PO_4$-P removal rate increases rapidly with the rise in pH. The variation of Ca/Mg=0.6 is the most obvious, whilst Ca/Mg=1.3 and Ca/Mg=2.0 become gradually less obvious. When the pH is greater than 8.8, the slope of the curves become moderate and the discrepancy between the three curves is less significant.

From the above analysis, the influence of Ca/Mg molar ratio on P-precipitation can be determined. In the pH range of 8.0-8.8, over 70% of soluble phosphorus can be removed. Most of the precipitate is composed of calcium phosphate. At a certain pH value within this pH range, increasing the molar ratio of Ca/Mg can help improve the P-removal rate. It also means that the major reaction in this pH range is calcium phosphate precipitation. When the pH value is raised to above 8.8, most of the calcium ions have been precipitated with the phosphate ions. For this reason, struvite formation dominates the P-precipitation reaction in the pH range of 8.8-9.5. The supplementation of magnesium ion is beneficial to P-precipitation. Moreover, the most P-removal rate is also achieved in this pH range (>90%). When the pH is further raised (>9.5), the calcium and magnesium ions are more apt to combine with other anionic ions and less apt react with phosphate ions, thus resulting in the decline of the P-removal rate.

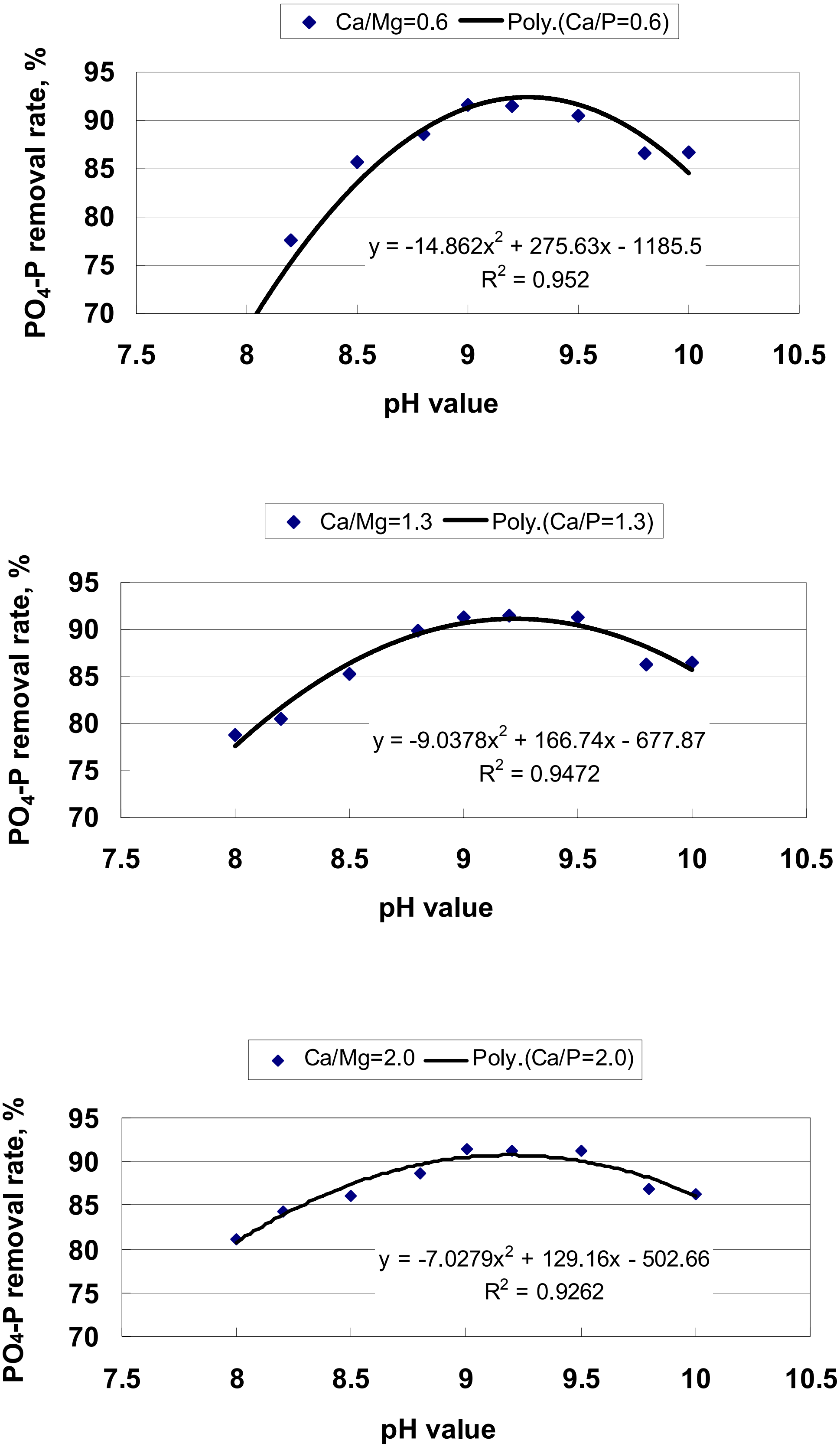

Fig. 7.5: The relationship between $PO_4$-P removal rate and pH value at various Ca/Mg molar ratios

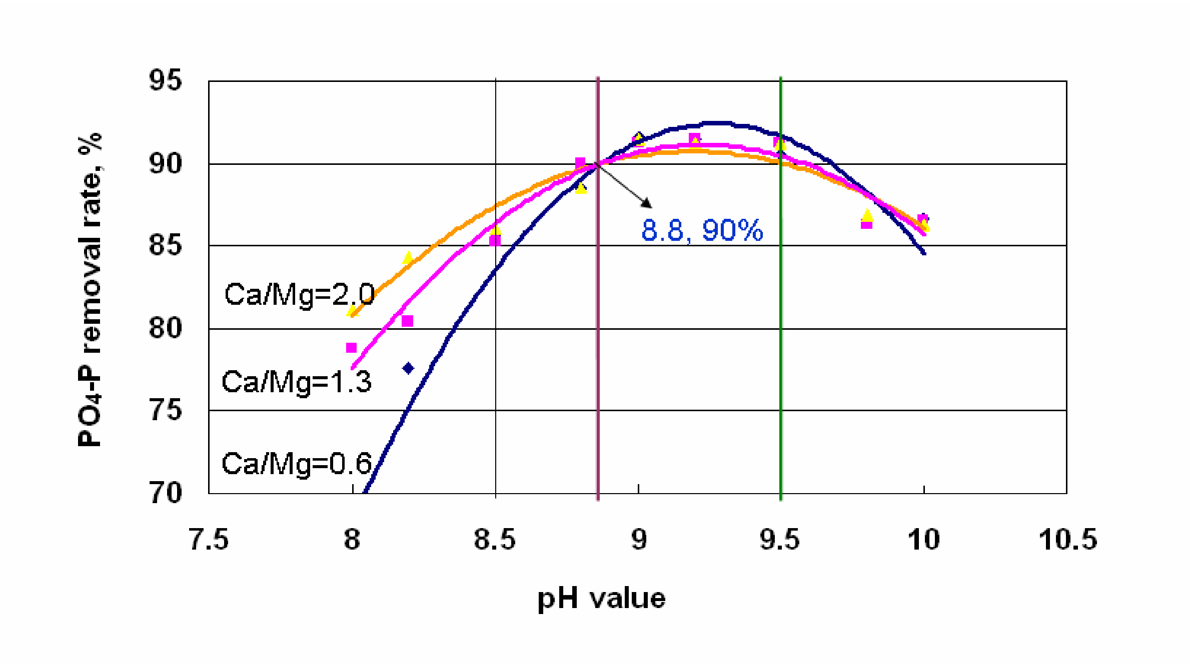

Fig. 7.6: The effect of Ca/Mg molar ratio on $PO_4$-P removal rate

## 7.4 Study of the effect of MgO supplementation

The addition of MgO was able not only to supply $Mg^{2+}$ source, but also to increase the pH value of the solution. As demonstrated above, the pH value in homogeneous raw and digested manure can be raised to over 8.5 by adding MgO. The experiments covered in this section will investigated the effect of the addition of MgO on the reactant concentrations for P-precipitation Excessive MgO (2g) was added to each homogeneous manure sample solution (2.5 liters), and the samples were stirred continuously at 20℃. The concentrations of $PO_4$-P, $NH_4$-N, $Mg^{2+}$ and $Ca^{2+}$ were measured initially and after 90 minutes.

### 7.4.1 The effect of MgO addition on pH value

As shown in Fig. 7.7, the pH value significantly increased with the addition of excessive MgO. After 30 minutes, the solution had almost reached equilibrium. The equilibrium pH value for both raw and digested manure is over 8.5. After 30 minutes, the pH value remained virtually constant. The pH values measured at the end of the 90-minute test period were 8.67 and 8.79 respectively.

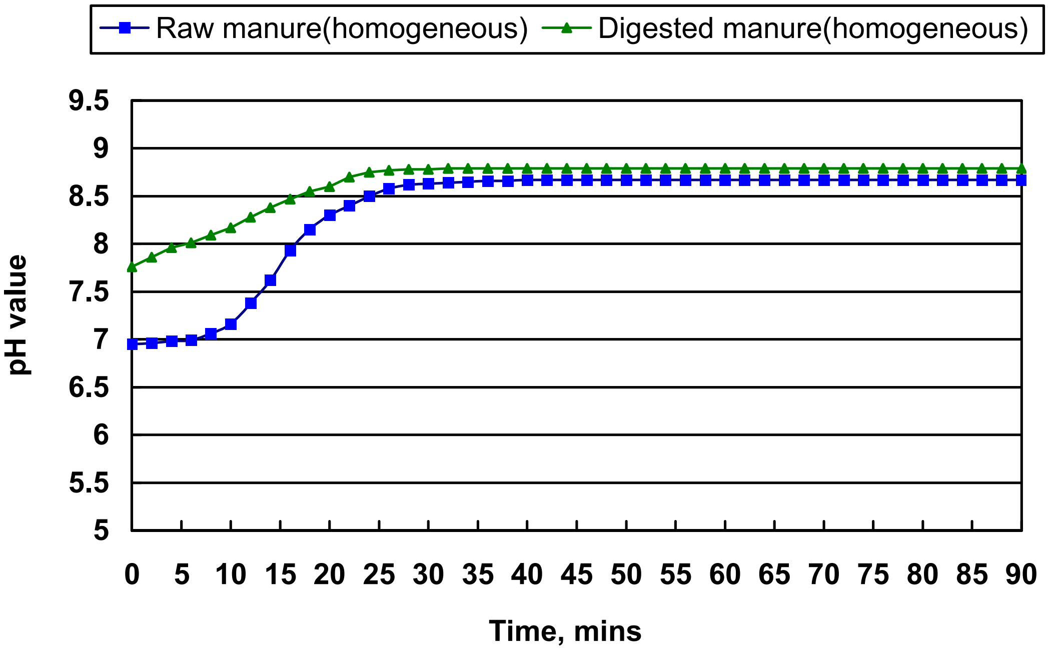

Fig. 7.7: The change of pH value in homogeneous raw and digested manure by the addition of MgO

### 7.4.2 P-precipitation in raw pig manure

Fig. 7.8 shows the concentrations of $PO_4$-P, $NH_4$-N, $Mg^{2+}$ and $Ca^{2+}$ after MgO supplementation in raw manure. By comparing the concentrations at 0 and 90 minutes, the variation of each reactant concentration was clearly demonstrated. The concentrations of $PO_4$-P and $Ca^{2+}$ were clearly reduced: $PO_4$-P from 112.6 to 16.2 mg/L, $Ca^{2+}$ from 133.2 to 25.6. As the supplementation of MgO, the $Mg^{2+}$ concentration in the solution remained constant. The concentration of $NH_4$-N decreased from 1,260 to 1080. The reduction of $NH_4$-N is partly due to its reacting with $Mg^{2+}$. Another reason, as stated in 7.2.1, is the formation of $NH_3$ with an increase in pH value.

Within the pH range of 8.5-9.0, $PO_4$-P can react with $Mg^{2+}$ and $Ca^{2+}$ in the solution to form struvite and calcium phosphate compounds. Fig. 7.8 shows that 80% of the $Ca^{2+}$ is removed when MgO is added and the pH values rises.

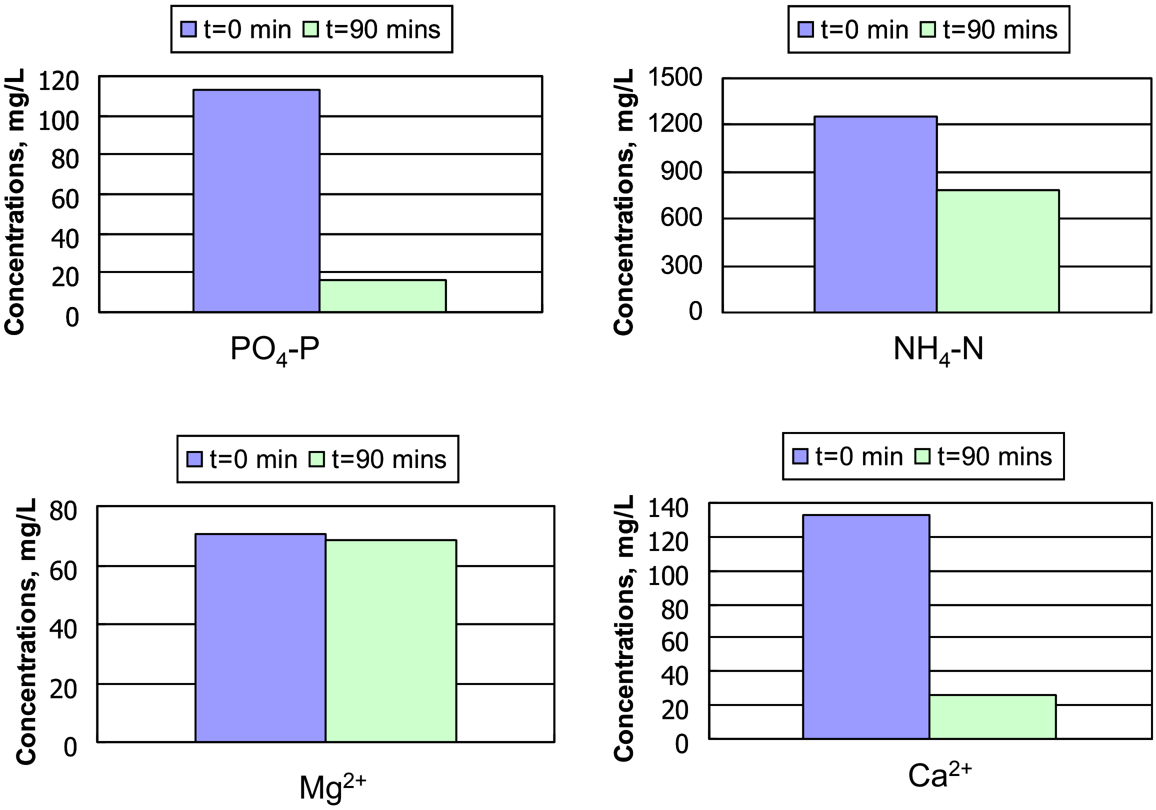

Fig. 7.8: Concentrations of $PO_4$-P, $NH_4$-N, $Mg^{2+}$ and $Ca^{2+}$ in raw pig manure

### 7.4.3 P-precipitation in digested pig manure

Fig. 7.9 shows the concentrations of $PO_4$-P, $NH_4$-N, $Mg^{2+}$ and $Ca^{2+}$ after MgO supplementation in digested manure. The initial concentrations of $PO_4$-P, $Mg^{2+}$ and $Ca^{2+}$ in digested manure were lower than those in raw manure. The concentrations of $PO_4$-P, $NH_4$-N and $Ca^{2+}$ decreased to varying degrees: $PO_4$-P from 48.8 to 18.3, $NH_4$-N from 1,880 to 1220, $Ca^{2+}$ from 132.1 to 37.5. The only exception was $Mg^{2+}$.

In contrast, the results show that the use of MgO as a magnesium source has a better effect in raw than in digested manure (Fig. 7.10). The removal rates of $PO_4$-P, $NH_4$-N and $Ca^{2+}$ in raw manure were all higher than those for digested manure. It can be concluded that, without the addition of NaOH, the pH value of homogeneous raw and digested pig manure can be raised to 8.5 only by means of MgO supplementation. Almost 85% of the $PO_4$-P was precipitated in the raw manure sludge, whilst about 60% was precipitated in the digested manure sludge. The concentration of $Ca^{2+}$ decreased significantly in both raw and digested manure. The removal rates were approx. 80% and 70% respectively. PH enhancement by the addition of MgO is a possible reason for the removal of $Ca^{2+}$ from the solution.

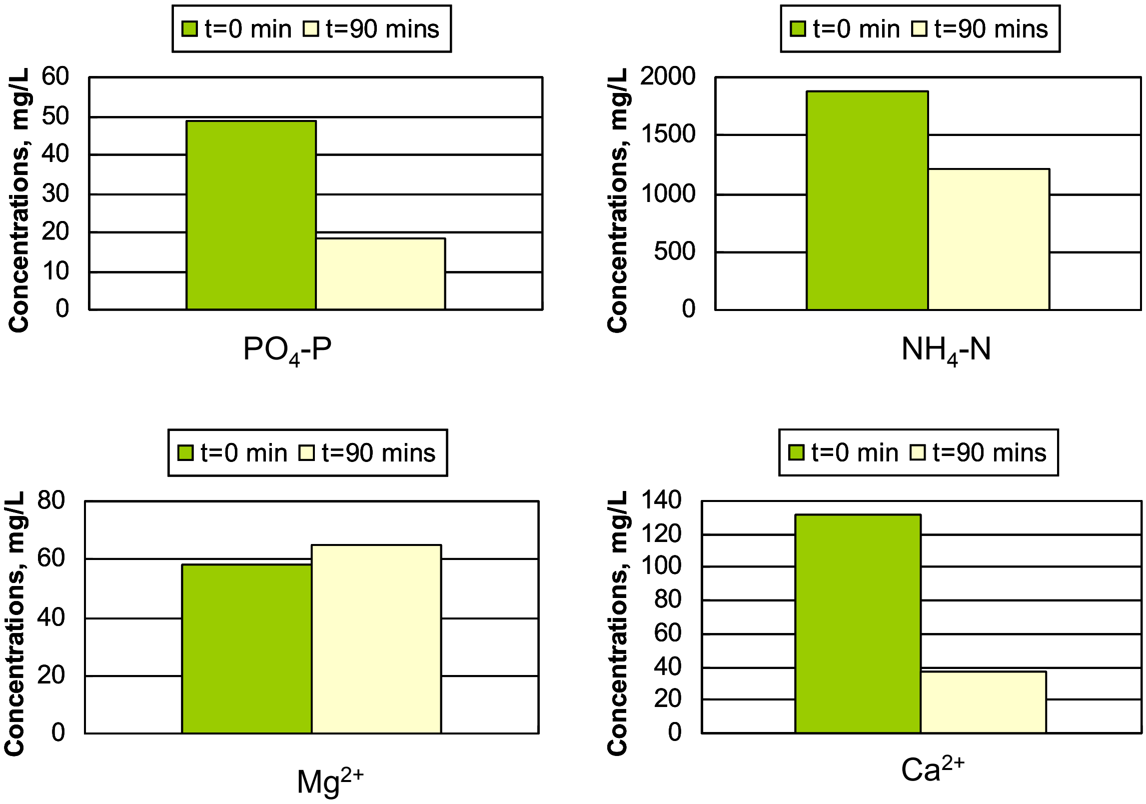

Fig. 7.9: Concentrations of $PO_4$-P, $NH_4$-N, $Mg^{2+}$ and $Ca^{2+}$ in digested pig manure

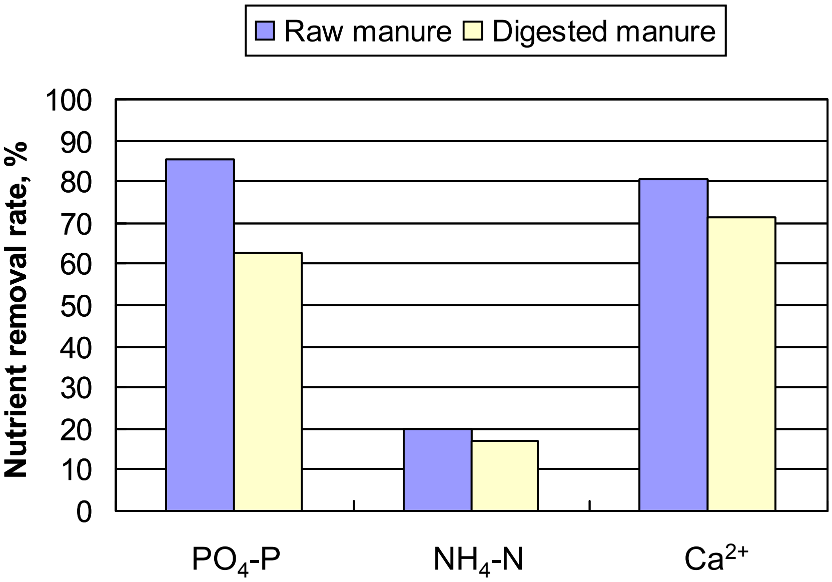

Fig. 7.10: Comparison of $PO_4$-P, $NH_4$-N and $Ca^{2+}$ removal in raw and digested pig manure at 20 ℃ and pH 8.5 by means of MgO supplementation

## 7.5 Study of the equilibrium time of the P-precipitation reaction

The experiments of this section seek to investigate the kinetic characteristics of the P-precipitation reaction. The pH value was adjusted by the addition of NaOH (1N). The initial $Mg^{2+}$/$PO_4$-P molar ratio of the sample solution was adjusted by the addition of $MgCl_2 \cdot 6H_2O$. The residual concentration of $PO_4$-P was measured every ten minutes.

Fig. 7.11 shows $PO_4$-P concentrations in raw manure with reaction times at various pH values. As the initial pH value of homogeneous raw manure is about 7.0, the samples were adjusted to 8, 9 and 10 respectively at beginning of the reaction. The initial concentration of $PO_4$-P in the solution was 113.9 mg/L. The $Mg^{2+}$/$PO_4$-P molar ratios of the samples were all adjusted to 1.3. Fig. 7.12 shows $PO_4$-P concentrations in digested manure with reaction times at various pH values. The initial pH value of each sample was also adjusted at beginning of the reaction to 8, 9 and 10 respectively. The initial concentration of $PO_4$-P in the solution was 55.6 mg/L. The initial $Mg^{2+}$/$PO_4$-P molar ratios of the digested samples were all 1.3.

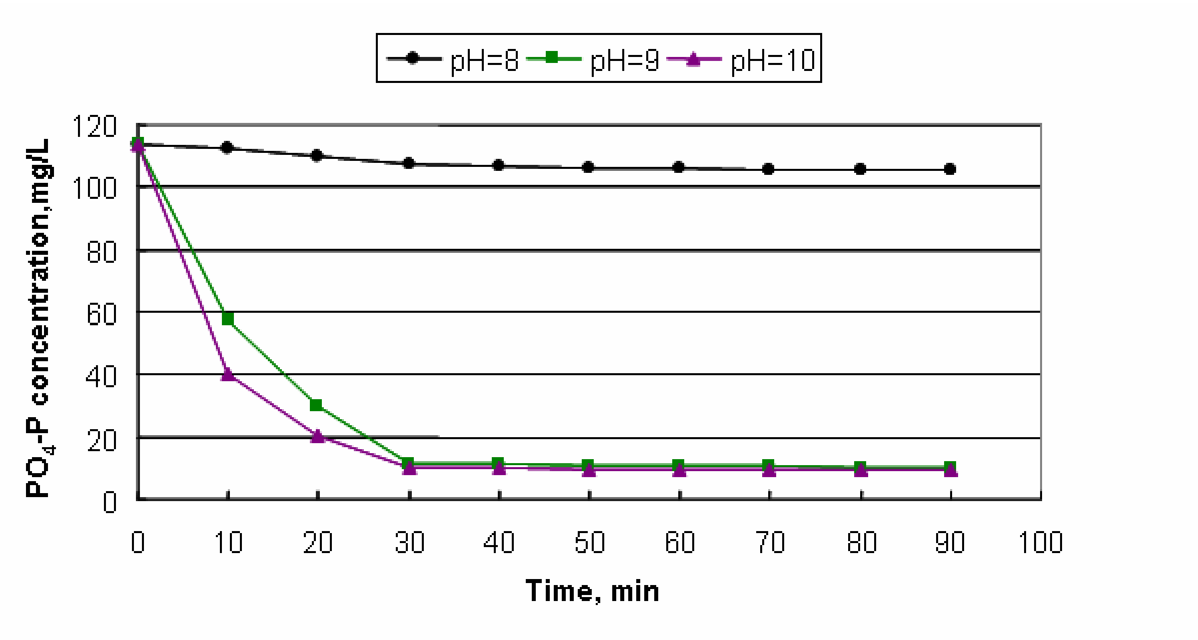

Fig. 7.11: $PO_4$-P concentrations in raw manure at various pH values

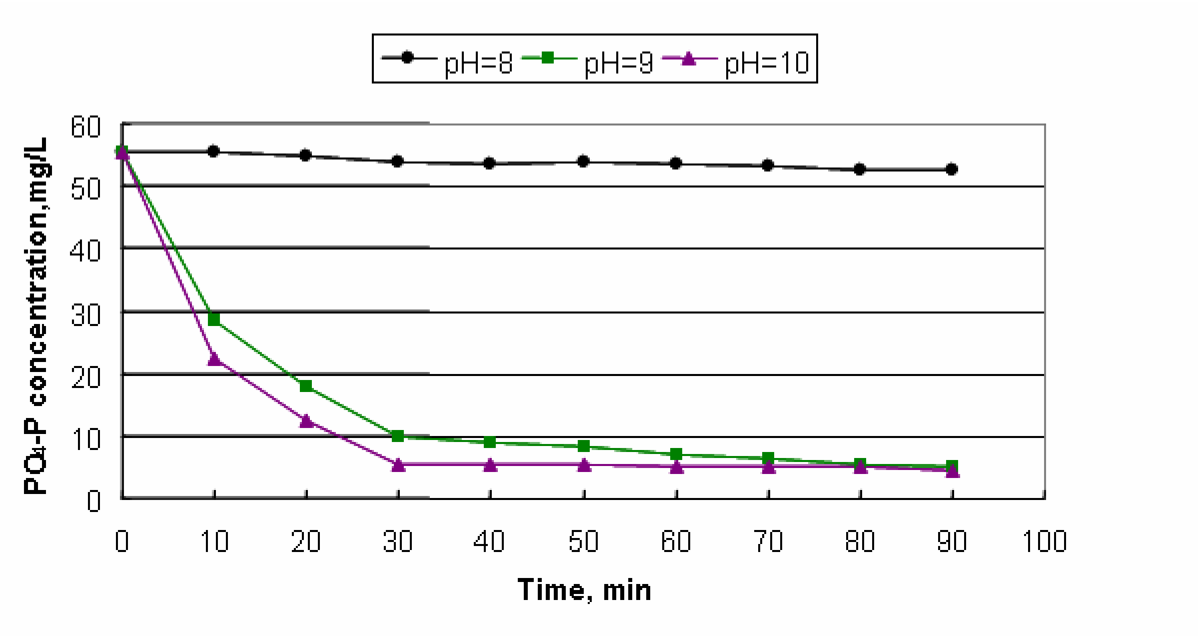

Fig. 7.12: $PO_4$-P concentrations in digested manure at various pH values

As shown in Figs. 7.11 and 7.12, the reaction reached equilibrium after 30 minutes. It can be concluded, therefore, that the pH value has a significant influence on the P-precipitation reaction. The reaction occurs when the pH value is greater than 9.0. As Figs. 7.11 and 7.12 indicate, the curves between pH=9 and pH=10 are similar. In response to the results achieved in 7.2.3, there was almost the same P-removal efficiency at pH values of 9 and 10. Figs. 7.11 and 7.12 also reflect that that the concentration of $PO_4$-P changed slightly at a pH value of 8. With regard to the formation of struvite, Ohlinger et al. (1998) reported that the availability of magnesium, ammonium and phosphate ions in the solution is dependent on the pH of the system. Furthermore, struvite precipitation occurred when the combined concentrations of magnesium, ammonium and phosphate ions exceeded the struvite solubility limit. As a result of the increased pH value, the ion activity product (IAP) exceeded the struvite solubility limit, and thus struvite was produced, leaving fewer phosphate ions in the solution. Considering the cost of chemicals, the ideal pH value for P-precipitation in homogeneous pig manure was set as 9.0. The equilibrium time of the P-precipitation was after 30 minutes.

## 7.6 Study of the effect of initial $PO_4$-P and $Mg^{2+}$ concentrations

The raw manure sample collected in this study contained only a small amount of drinking water. However, some pig farms in China adopt the water-flushing process to clear manure from the piggeries (cf. Chapter four), so the concentration of $PO_4$-P is lower. In this experiment, the pig manure used in Fig. 7.13 was raw pig manure, whilst the $PO_4$-P concentration was 110.2 mg/L. The pig manure used in Fig. 7.14 was diluted, and the initial $PO_4$-P concentration was 55.6. The initial pH values were all adjusted to 9.0. The $Mg^{2+}/PO_4$-P molar ratios were adjusted to 1.0, 1.3 and 1.6 respectively by adding $Na_2HPO_4 \cdot 12H_2O$ and $MgCl_2 \cdot 6H_2O$ according to the mass ratio of the substance. Samples were extracted every ten minutes from the continuously-mixed reactions. Samples were analyzed for soluble phosphorus $PO_4$-P.

Figs. 7.13 and 7.14 show that, at a $Mg^{2+}/PO_4$-P molar ratio of 1.3, the high $PO_4$-P concentration was reduced from 110.2 to 10.9 mg/L, whilst the low $PO_4$-P concentration was reduced from 55.6 to 5.2 mg/L. The $PO_4$-P removal rates were 90.1% and 88.8% respectively. It follows that the equilibrium time of the reaction was 30 minutes. The $PO_4$-P concentration decreased with the increase in the $Mg^{2+}/PO_4$-P molar ratio. However, an excessive $Mg^{2+}$ dosage did not lead to any significant improvement in the efficiency of P-removal. Taking economic factors into consideration, the optimum $Mg^{2+}/PO_4$-P molar ratio is 1.3. In addition, the end phosphate precipitant included struvite and calcium phosphate compounds. However, since the overall aim of this study is to precipitate soluble phosphorus in the sludge rather than to produce pure struvite or calcium phosphate, the phosphorus is recycled from pig manure in the form of mixed phosphate compounds.

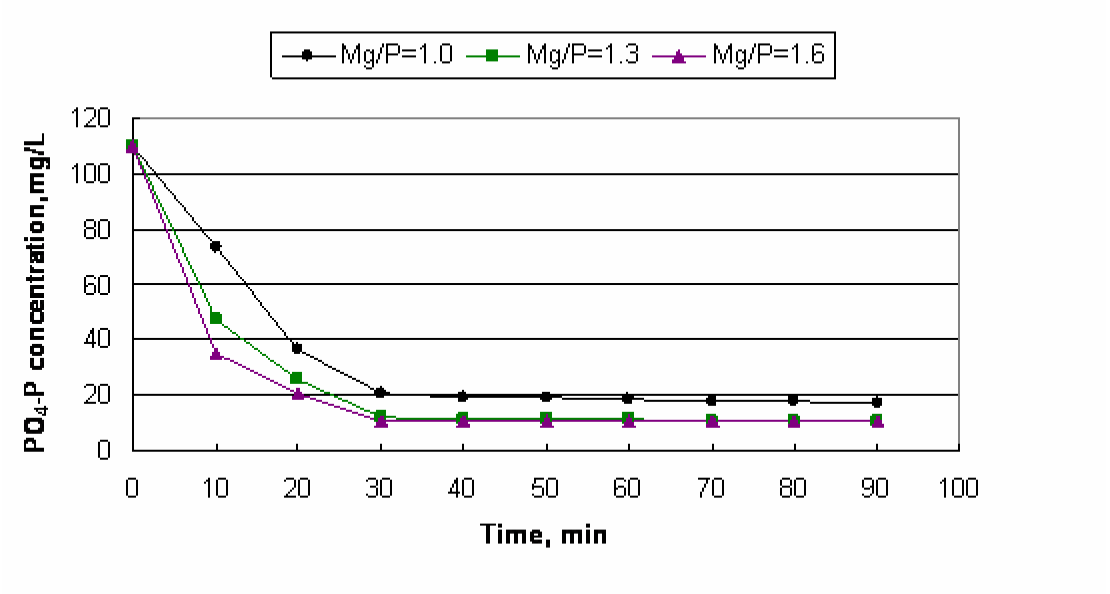

Fig. 7.13: The effect of the $Mg^{2+}/PO_4$-P molar ratio on $PO_4$-P removal from a high concentration of raw pig manure

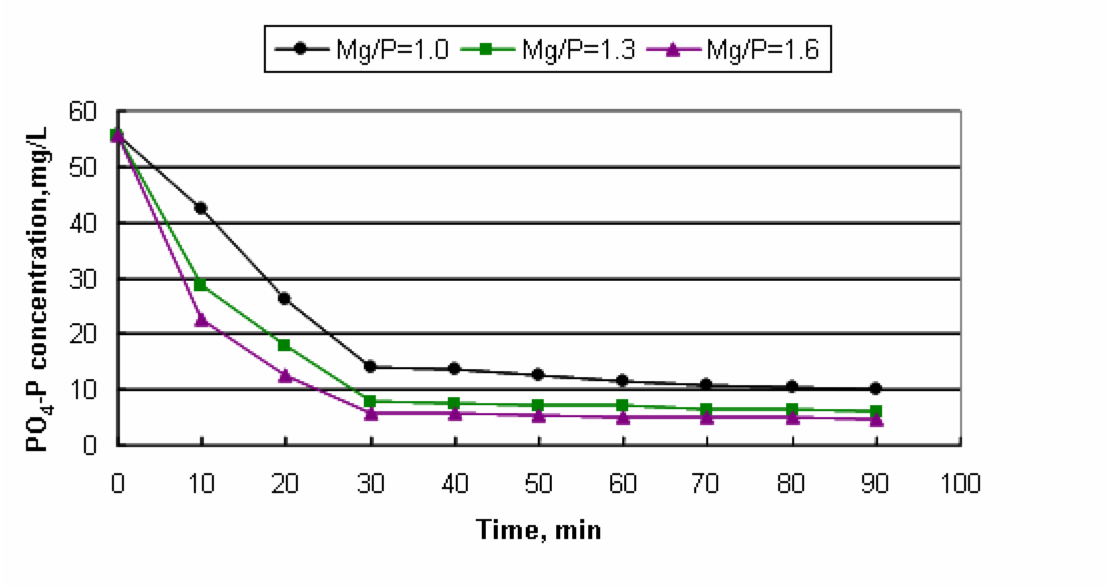

Fig. 7.14: The effect of the $Mg^{2+}/PO_4$-P molar ratio on $PO_4$-P removal from a low concentration of raw pig manure

## 7.7 Chapter summary

In this chapter, the following conclusions have reached on the basis of experimental study and data analysis:

1. The concentrations of $PO_4$-P and $Mg^{2+}$ in digested pig manure were much lower than those in raw pig manure. Solid/liquid separation has little influence

on the change in the concentrations of $PO_4$-P, $Ca^{2+}$ and $Mg^{2+}$. As a result, P-precipitation can be carried out directly in the homogenous manure.

2. pH value is the most important parameter for P-precipitation in pig manure. In the pH range from 8 to 10, over 70% of soluble phosphors can be precipitated. The ideal pH value was determined to be 9.0. When $MgCl_2 \cdot 6H_2O$ was used as a magnesium source, the equilibrium time of the reaction was 30 minutes. The appropriate $Mg^{2+}/PO_4$-P molar ratio was 1.3. Under these conditions, basically 90% of $PO_4$-P can be precipitated in the sludge, whether with raw or digested manure.

3. The coexistence of magnesium and calcium ions in pig manure can result in a competition reaction with soluble phosphorus. The study of the effect of the Ca/Mg molar ratio on P-precipitation showed that, in the pH range of 8 to 8.8, the major P-precipitation reaction is calcium phosphate formation. At a certain pH value within this pH range, increasing the molar ratio of Ca/Mg can help improve the P-removal rate. When the pH value is between 8.8 and 9.5, struvite formation dominates the P-precipitation reaction. Experiments also show that the highest P-removal rate (>90%) is also achieved within the pH range of 8.8-9.5. When the pH is above 9.5, calcium and magnesium ions are more prone to react with other anionic ions instead of with phosphate ions.

4. Results show that the use of MgO as a magnesium source in raw manure for P-precipitation has a greater P-removal efficiency. The pH value of the homogeneous manure can be raised to 8.5 without additional alkaline addition. Almost 85% of $PO_4$-P was precipitated in raw manure sludge. Under the same reaction conditions, however, the $PO_4$-P removal rate in digested manure was only about 60%.

# 8 Solutions for the further treatment and the optimal P- recovery process

## 8.1 Solid/liquid separation and sedimentation

The main options for removing solid from the liquid include screening, centrifuging and sedimentation. Sieves and centrifuge are common mechanical separation facilities. Sieves are usually used in removing large particles. Centrifuges are much more effective in removal of fine solids, but they are limited by the high operation cost. Therefore, sedimentation seems to be the optimal solution for the solid/liquid separation of swine manure. A sedimentation system not only requires a low capital investment, but it is also simple and can act as a temporary storage of manure.

To improve natural sedimentation, especially for removal of fine particles, chemical flocculants should be added in order to alter the physical state of dissolved and suspended solids (Tchobanoglous and Burton, 1991). When the particles are to be aggregated or flocculated, solution stability is broken, and then the separation will be done. Chemical flocculants mostly used in wastewater treatment include aluminum salts, ferrous ($Fe^{2+}$) and ferric ($Fe^{3+}$) salts, as well as polymers in conjunction with iron salts.

In this study, a cheaper ferrous chloride solution (30 % $FeCl_2$, industrial pure) was adopted as flocculants. $FeCl_2$ can not only remove suspended solids but also the residual phosphorus from the liquid part. The effect of $FeCl_2$ on removal of phosphors is shown in Figure 8.1. Manure samples used in this study were digested manure after P-precipitation with a TS value of 4.5%. As presented in chapter 7, after P-precipitation there were still a small amount of phosphorus can not be precipitated in the solid. Figure 8.1 showed that after 4 hours of sedimentation, the removal rate of soluble P by ferrous chloride was 85.7%, while by natural sedimentation only 30.6% soluble phosphorus can be further removed from the liquid part of the treated swine manure. The removal of TP on the other hand was 93.6% by flocculants addition and 43.9% by unaided natural sedimentation.

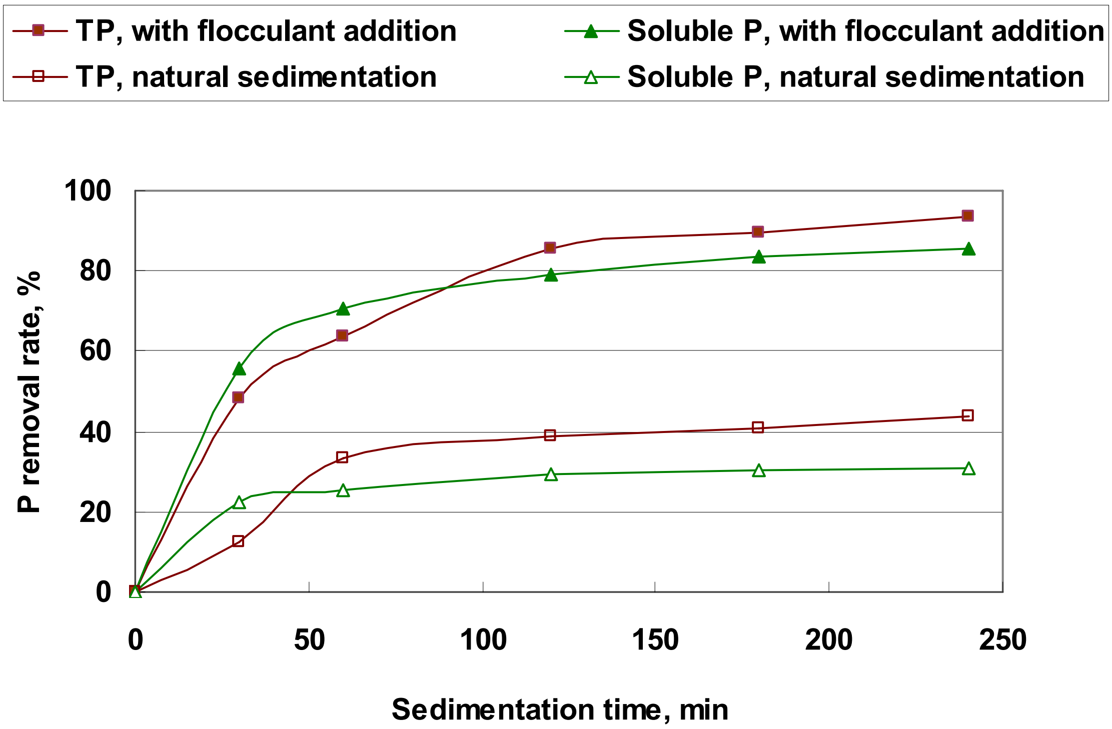

Fig. 8.1: Effect of flocculants addition on removal of phosphorus from treated pig manure

Considering the variation of water content, which may be produced by different manure clearing processes (such as water flushing), an experiment was conducted to determine the effect of solid levels on sedimentation. Total solids (TS) levels of 0.5, 1.5, 2.5, 3.5, and 4.5% were adjusted by addition of tap water. Curve was drawn as shown in Figure 8.2. After 4h of quiescent sedimentation, TS removal were achieved by the aid of flocculants (30% $FeCl_2$) at the rates of 46.1%, 86.1%, 80.3%, 76.9% and 51.8% for TS levels of 0.5%, 1.5%, 2.5%, 3.5% and 4.5%, respectively. These data suggest that both too high and too low levels of TS content in the manure result in a reduced removal of suspended solid by sedimentation. Manure samples with solids level in the middle (1.5%, 2.5% and 3.5%) had better removal efficiency. The figure also reflects that except for TS of 0.5%, the sedimentation process seems in general can be complete within one hour of detention time and only a marginal improvement was achieved afterwards.

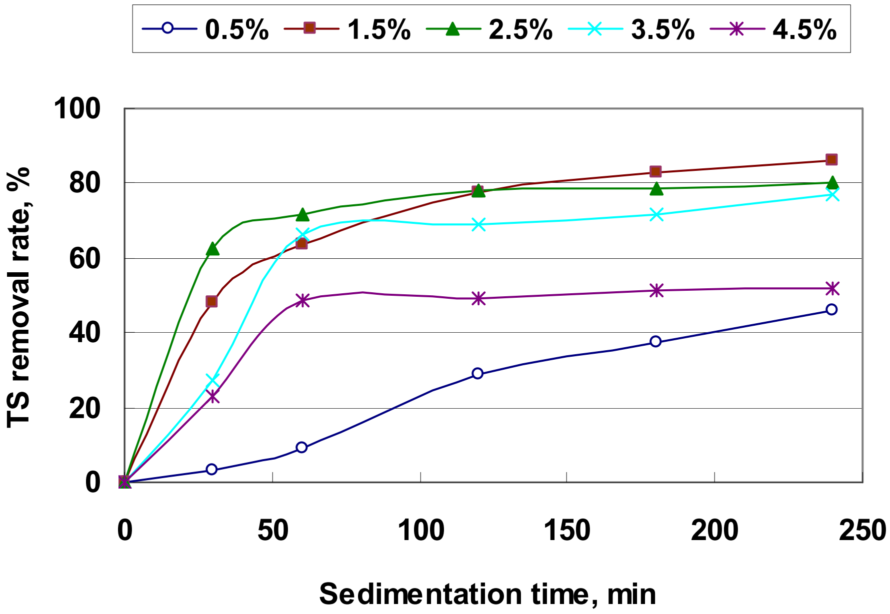

Fig. 8.2: Effect of solid concentration on sedimentation of swine manure

## 8.2 Mass balance analysis

Phosphorus balance analysis is shown in Table 8.1. The average concentration of SP and TP in the liquid part of the original raw swine manure were 113.8 and 130.6 mg/L separately. After anaerobic digestion, SP and TP concentration dropped to 59.6 and 83.9 mg/L. Forced P-precipitation made 90.3% of SP removed from the anaerobic effluent, however, the most part of TP remained in the homogeneous liquid phase. With the aid of flocculants, 95.7% of TP was in the end precipitated in the manure solid. In order to avoid the production of large amount of sludge and to save expense, the last treatment step can also be replaced by some natural treatment methods.

Tab. 8.1: Phosphorus balance analysis

| | Soluble P (SP) (mg/L) | TP in the liquid phase (mg/L) | Percentage of SP precipitated from the liquid phase | Percentage of TP precipitated from the liquid phase |
|---|---|---|---|---|
| Raw swine manure | 113.8 | 130.6 | - | - |
| After AD | 59.6 | 83.9 | - | - |
| After P-precipitation | 5.8 | 56.5 | 90.3% | 32.7% |
| After flocculants addition | 0.83 | 3.61 | 98.7% | 95.7% |

After sedimentation, the end product of P precipitated manure sludge was dried and prepared for sludge analysis. The comparison of metallic elements concentration between raw manure and the end product is shown in Table 8.2. The contents of calcium and magnesium in the end product sludge were all increased compared to the untreated raw manure. Because of the usage of ferrous chloride, the percentage of iron was also increased.

Tab. 8.2: Content of metallic elements in manure sludge that necessary for plant growth

| | K | Ca | Mg | Fe | Zn | Cu |
|---|---|---|---|---|---|---|
| Raw manure | 5.94% | 2.68% | 0.37% | 0.23% | N.A* | N.A* |
| End product | 4.12% | 3.55% | 1.16% | 3.15% | 0.41% | 0.16% |

* Not analysis

Fig. 8.3: Picture of the precipitated manure sludge compound

## 8.3 The optimal P-recovery process recommendation

In subject to the possibility of P-recovery technology in application in China, the following three aspects have been taken into the consideration of this study.

1. Technological applicable
2. Economical acceptable
3. The government's high attention to phosphorus crisis and the support of anaerobic digestion technology.

Taking in account of the above factors, the optimal P-recovery process for manure treatment in intensive swine farms is shown in Figure 8.4.

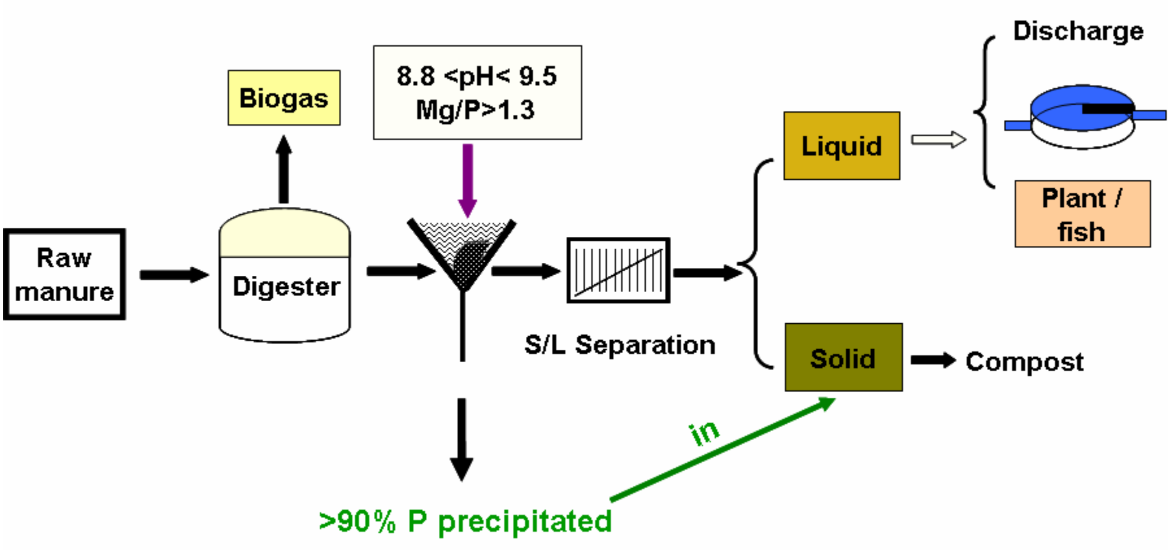

Fig. 8.4: A suggested swine manure treatment process for P-recovery combined with anaerobic digestion

The suggested process includes four parts, which are anaerobic digestion, forced P-precipitation, solid-liquid separation and post treatment. The front three parts have been discussed in this study. According to the post treatment, the solid part should best to be composted and used as fertilizer, because it contains rich nutrients and metallic elements. The liquid part could possibly to be treated with traditional sewage treatment method or to be discharged into fishery pond or used for plant application.

# 9 Conclusions

## (1) Problem

Phosphorus (P) is a key irreplaceable nutrient element in all life forms. Almost all phosphorus used by society is mined from non-renewable phosphate rock. Approximately 80% of global phosphate rock consumption is used for fertilizer production. However, as a finite resource, the world phosphate reserve could be exhausted within the next 100-250 years. The phosphate resource in China is also limited. The exploitable deposits could be exhausted within 70 years.

The discharge of untreated nutrient-rich wastewater may lead to the eutrophication of the receiving water. Phosphorus could be recovered from waste streams such as municipal wastewater, sewage sludge and animal manure, in the form of struvite and calcium phosphate compounds. Struvite is chemically known as magnesium ammonium phosphate and can be used as a slow-release fertilizer.

Investigations show that the largest recoverable phosphate resource in China is found in animal manure. It was estimated that the potential phosphate resource in intensive-scale animal plants accounts for 47% of the total consumption of phosphate rock of the country each year. Pig manure contains phosphorus and nitrogen in high concentration. Intensive pig-raising and poor manure management result in environmental pollution and excessive nutrient loading on nearby farmland. A method of concentrating the high content of nutrients in the solid is therefore worthwhile for utilization and transportation elsewhere.

## (2) Objectives of this study

The objective of this study is to investigate forced struvite precipitation in pig manure combined with anaerobic digestion; when biogas is generated, an enriched P-containing digested manure sludge can be obtained.

## (3) Methods

First of all, a pilot anaerobic digestion system was established. Two anaerobic reactors with different sludge retention times (R1=15 days; R2=25 days) were operated over the same period of time for comparison. The performance of the two anaerobic reactors was evaluated in terms of biogas yield, methane production and organic matter reduction.

In order to evaluate the suitable position for P-precipitation, the chemical composition of raw and digested pig manure was analyzed. Possible locations for P-precipitation include: P-precipitation in raw manure; P-precipitation during anaerobic digestion; P-precipitation after anaerobic digestion

P-precipitation experiments were conducted in a batch system. Solid magnesium oxide (MgO) and magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$) were used as the magnesium source for forced struvite precipitation. The conditions for phosphorus precipitation, including pH value, molar ratio and equilibrium time etc., were studied.

## (4) Results

### 1. The performance of anaerobic digestion operation

Anaerobic digestion experiments indicated that Reactor R2 (SRT=25 days) operated more steadily and had better performance levels than Reactor R1 (SRT=15 days). The average biogas yield of R2 was 0.4 $m^3$/kg $COD_{added}$. The mean methane yield value was 60.6%. The mean VS reduction rate was 57.2%. The effluent from R2 was selected as sample manure for P-precipitation experiments.

### 2. The effect of anaerobic digestion on the chemical characteristics of pig manure

Total concentrations of phosphorus (TP) and kjeldahl nitrogen (TKN) remained basically constant before and after anaerobic digestion. However, the composition of nitrogen and phosphorus in digested manure was quite different; 37.7% of phosphorus existed as $PO_4$-P in the raw pig manure, whilst 20.8% of $PO_4$-P was present in the digested pig manure. $NH_4$-N accounted for 50.4% of the total TKN in raw pig manure, while most of the TKN in digested manure (79.3%) was composed of $NH_4$-N.

The pH value of pig manure rose by 0.88 units after anaerobic digestion. $PO_4$-P was reduced by 45% during anaerobic digestion. The average molar ratios of Mg/P and Ca/P achieved were 1.3 and 1.7. It was found that solid/liquid separation has little influence on the change in the molar ratios.

### 3. Position for forced P-precipitation

The experiment showed that P-precipitation should be conducted in homogeneous digested pig manure. This is not only because a part of the soluble phosphorus would be reduced during the anaerobic digestion, but also because the molar ratios of reactant ions such as Mg/P and Ca/P in the digested pig manure are close to the theoretical value of P when precipitated as struvite and calcium phosphate.

4. Ideal conditions for P-precipitation

Both $MgCl_2 \cdot 6H_2O$ and MgO were adopted as a magnesium source. MgO is suitable for supplementation in raw manure. Without the addition of other alkali, the pH value rose to 8.5. Nearly 85% of soluble phosphorus ($PO_4$-P) could be removed from liquid portion.

$MgCl_2 \cdot 6H_2O$ has good solubility. When $MgCl_2 \cdot 6H_2O$ was used at a pH value of 9.0, the equilibrium time required was 30 minutes. The appropriate $Mg^{2+}$/$PO_4$-P molar ratio was 1.3. Under these conditions, whether with raw or digested manure, 90% of $PO_4$-P could be removed.

The ideal pH range for P-precipitation is between 8.0 and 9.5. In the pH range of 8.8-9.5, struvite precipitation dominates the precipitation reaction. The existence of calcium ions results in competitive reaction with magnesium ions. In the pH range of 8.0-8.8, calcium phosphate was apt to form.

5. End product analysis

More than 90% of the soluble phosphorus could be removed from the liquid portion of pig manure through forced P-precipitation. With the aid of flocculants, 95.7% of the total phosphorus could be precipitated in the final manure solid.

Forced P-precipitation combined with anaerobic digestion is suitable for application in China. The cost of this process is much less than P-recovery in pure struvite or calcium phosphate. However, the end product cannot compare in quality or price to currently-available chemical fertilizers.

# 10 References

## A

Aage, H. K., Andersen, B. L.,Blom, A. and Jensen, I. (1997). The Solubility of Struvite. Journal of Radioanalytical and Nuclear Chemistry, Vol. 223 (1-2), 213-215.

Abbona, F. and Madsen, H.L. (1986). The initial phases of calcium and magnesium phosphates precipitated from solutions of high to medium concentrations. J. Cryst. Growth, 74, 581–590.

Ali. Md. Imtiaj and Schneider P.A. (2005). Crystallization of struvite from metastable region with different types of seed crystal. J. Non-Equilib. Thermodyn, Vol. 30, 95 – 111.

## B

Battistoni, P., Paven, P.; Cecchi, F. and Meta-Halvarez, J. (1998). Phosphate removal in anaerobic supernatants: modeling and performance of a fluidized bed reactor. Water Sci. Technol., 38 (1), 275–283.

Battistoni, P., Pavan, P., Prisciandaro, M. and Cecchi, F. (2000). Struvite Crystallization: A Feasible and Reliable Way to Fix Phosphorus in Anaerobic Supematants. Water Res., *34* (11), 3033-3041.

Battistoni P., De Angelis A., Prisciandaro M., Boccadoro R. and Bolzonella D. (2002). P removal from anaerobic supernatants by struvite crystallization: long term validation and process modeling. Water Res., 36, 1927–1938.

Beal, L. J., Burns, R. T. and Stalder, K. J. (1999). Effect of anaerobic digestion on struvite production for nutrient removal from swine waste prior to land application. Presented at the 1999 ASAE International Meeting in Toronto, Canada, Paper No. 994042.

Booram, C. V., Smith, R. J., and Hazen, T. E. (1975). Crystalline phosphate precipitation from anaerobic animal waste treatment lagoon liquors. ASAE Trans, 18, 340–343.

Borgerding, J. (1972). Phosphate Deposits in Digestion Systems. *J.-Water Pollut Control Fed.,* 44, 813–819.

Brett, S., Guy, J., Morse, G. K. and Lester, J. N. (1997). Phosphorus removal and recovery technologies, London: Selper Publication

Buchanan, J. R., Mote, C. R. and Robinson, R. B. (1994). Struvite Control by Chemical Treatment. *Trans. Am. Soc. Agric. Eng.,* 37, 1301.

Burns J.R. and Finlayson B. (1982). Solubility of magnesium ammonium phosphate hexahydrate at various temperatures. J Urol, 128, 426–428.

Burns, R. T., Moody, L. B., Walker, F. R. and Raman, D. R. (2001). Laboratory and in-situ reductions of soluble phosphorus in liquid swine waste slurries, Environmental Technology, 22, 1273–1278.

Burns, R.T., Moody and L.B., (2002) Phosphorus recovery from animal manures using optimized struvite precipitation. Proceedings of Coagulants and Flocculants: Global market and technical opportunities for water treatment chemicals, May 22–24, Illinois, Chicago

Burns R.T., Moody L.B., Celen I. and J.R. Buchanan (2003). Optimization of phosphorus precipitation from swine manure slurries to enhance recovery. Water Science and Technology, 48(1), 139–146.

## C

CEEP (1998). International conference on Recovery of phosphates for recycling from sewage and animal wastes. 6th-7th May, Warwick University, UK

CEEP (2001). Conference Summary Second International Conference on the recovery of phosphorus from sewage and animal wastes. Noordwijkerhout, Netherlands, March 12-14; European Centre of Enterprises with Public Participation and of Enterprises of General Econ*omic Interest: Brussels,* Belgium, http://www.nhm.ac.uk/mineralogy/P-recovery

Çelen I., Buchanan J. R., Burns R.T., Robinson R. B. and Raj Raman D. (2007). Using a chemical equilibrium model to predict amendments required to precipitate phosphorus as struvite in liquid swine manure. Water Res., Vol. 41 (8), 1689-1696.

Chimenos J M, Fernández I., Villalba G., Segarra M., Urruticoechea A., Artaza B. and Espiell F. (2003). Removal of ammonium and phosphates from wastewater resulting from the process of cochineal extraction using MgO-containing by-product. Water Res., 37, 1601—1607.

China statistical year book (2006). National Bureau of Statistics of China, Beijing: China Statistics Press

China Animal Husbandry Yearbook (2004). Beijing: China Agricultural Press

Chynoweth D.PL, Wilkie A.C., Owens J.M. (1998). Anaerobic processing og piggery wastes: a review. ASAE Annual International Meeting

Cornel. P. and Schaum. C. (2005). Von der Phosphorelmination zur Phosphorrueckgewinnung, 75. Darmstaedter Seminar Abwassertechnik, Darmstadt,13-38.

## D

de-Bashan, L.E. and Bashan, Y. (2004). Recent advances in removing phosphorus from wastewater and its future use as fertilizer (1997–2003). Water Res., 38, 4222–4246.

De Rooij, J.F., Heughebaert, J.C. and Nancollas, G.H. (1984). A pH study of calcium phosphate seeded precipitation. J. Colloid Interf. Sci., 100 (2), 350–358.

DIN EN 1189 D 11 (1996). Bestimmung von Phosphor-Phostometrisches Verfahren mittels Ammoniummolybdat

Dong H., Zhu Z., Shang B., Kang G., Zhu H. and Xin H. (2007). Greenhouse gas emissions from swine barns of various production stages in suburban Beijing, China. Atmospheric Environment, 41, 2391–2399.

Doyle, J.D. and Parsons, S.A., (2002). Struvite formation, control and recovery. Water Res., 36, 3925–3940.

Driver J., Lijmbach D. and Steen I. (1999). Why recover phosphorus for recycling, and how? Environ Technl., 20, 651-662.

## F

FAO (2002) FAOSTAT On-line Statistical Service, http://www.fao.org

Fujimoto, N., Mizuochi, T. and Togami, Y. (1991). Phosphorus fixation in the sludge treatment system of a biological phosphorus removal process, Wat. Sci. Tech., 23, 635–640.

## G

Gaterell, M.R., Gay, R., Wilson, R., Gochin, R.J. and Lester, J.N. (2000). An economic and environmental evaluation of the opportunities for substituting phosphorus recovered from wastewater treatment works in existing UK fertilizer markets. Environ. Technol., 21, 1067-1084.

Gerber P., Chilond P., Franceschini G. and Menzi H. (2005). Geographical determinants and environmental implications of livestock production intensification in Asia, Bioresource Technology, 96 (2), 263–276.

Ghosh G.K., Mohan K.S. and Sarkar A.K. (1996). Characterisation of soil fertilizer P reaction products and their evaluation as sources of P for gram (Cirer arietinum L.). Nutr Cycling Agroecosyst, 46, 71-79.

Graveland A., Dijk J.C., Moel P.J. and Oomen J.H.C.M. (1983). Development in Water Softening by Means of Pellet Reactors. J. Am. Water Works Assoc., 75 (12), 619-625.

Grimm, E., Döhler, H., Fritzsche, S., Schwab, M., Jäger, P., Siegel, F., Witzel, E., de Baey-Ernsten, H., Hackeschmidt, A. and Achilles, W. (2002). Beste verfügbare Technik in der Intensivtierhaltung (Schweine- und Geflügelhaltung), Umweltbundesamt. Nr. 75/2002

## H

Hawkes (1980). Factors affecting net energy production from mesophilic anaerobic digestion. In: Anaerobic Digestion (eds. D.A. Stratford, B.I. Wheatley and D.E. Hughes), 131-150.

Helfferich F. (1995). Ion exchange, Dover publications Inc. New York, USA.

Hobson, P.N., Bousefield S. and Summers R. (1974). Anaerobic digestion of organic matter. CRC Critical Reviews in Environmental Control, 4,132-191.

Hong. J. (2005). Anaerobic Biotreatment of Animal Manure- A review of current knowledge and direction for future research. J. Lives. Hous. & Env., 11(2), 97-102.

House, W. A. (1999) The Physico-Chemical Conditions for the Precipitation of Phosphate with Calcium, *Environ. Technol.,* 20 (7), 727-733.

## J

Jardin, N. (1995). Untersuchungen zum Einfluss der erhöhten biologischen Phosphorelimination auf die Phosphordynamik bei der Schlammbehandlung, Dissertation TU Darmstadt 1995, Schriftenreihe WAR 87.

Jiang B.F., Lu R.K. and Li C.K. (1990). A review of the studies on phosphate rock for agricultural use in China. *Fertilizer Research,* 26, 11-20.

Joko, I. (1984). Phosphorus removal from wastewater by the crystallization method, Water Sci. Technol., 17, 121-132.

## K

Karakashev, D., Batstone, D.J. and Angelidaki, I. (2005). Influence of Environmental Conditions on Methanogenic Compositions in Anaerobic Biogas Reactors. Applied and Environmental Microbiology, Jan 2005, 331-338.

Kofina A.N. and Koutsou kos P.G. (2005) Spontaneous precipitation of struvite from synthetic wastewater solution. Crystal growth & design, Vol. 5(2), 489-496.

Koutsoukos P.G., Amjad Z., Tomson M.B. and Nancollas G.H. (1980). Crystallization of calcium phosphates; a constant composition study, Journal of the American Chemical Society, 102 (5), 1553–1557.

Koutsoukos, P.G. and Nancollas, G.H. (1981). Crystal growth of calcium phosphates-epitaxial considerations, Journal of Crystal Growth, 53 (1), 10–19.

Kuma M., Badruzzaman M., Adham S. and Oppenheimer J. (2007). Beneficial phosphate recovery from reverse osmosis (RO) concentrate of an integrated membrane system using polymeric ligand exchanger (PLE). Water Res., Volume 41 (10), 2211-2219.

Kumashiro, K., Isiwatari, H. and Nawamura, Y. (2001). A pilot study on using seawater as magnesium source for struvite precipitation. In: Proceedings of the 2nd International Conference on Phosphorus Recovery for Recycling from Sewage and Animal Wastes, Noordwijkerhout, Holland, March 12–14.

Kuo, S., Huang, B. and Bembenek, R. (2005). Effects of long-term phosphorus fertilization and winter cover cropping on soil phosphorus transformations in less weathered soil. Biol. Fertil. Soils, 41, 116–123.

## L

Le Corre, K. S, Valsami-Jones. E., Hobbsc, P. and Parsons S.A. (2005). Impact of calcium on struvitecrystal size, shapeand purity. Journal of Crystal Growth, 283, 514 – 522.

Lee S. I., Weon S. Y., Lee C. W. and Koopman B. (2003). Removal of nitrogen and phosphate from wastewater by addition of bittern, Chemosphere. 51 (4), 265—271.

Lee, J.J., Choi, C.U., Lee, M.J., Chung, I.H. and Kim, D.S. (2004). A study of NH3-N and P refixation by struvite formation in hybrid anaerobic reactor. Water Science and Technology, 49, 207 – 214.

Lens P., Zeeman G. and Lettinga G. (2001). Decentralised sanitation and reuse: Concepts, systems and implementation, IWA Publishing. London. 8.

Lens P., Hamelers B., Hoitink H. and Bidlingmaier W. (2004). Resource recovery and reuse in organic solid waste management. IWA publishing, UK

Lester J. N. and Birkett J.W. (1999). Microbiology and chemistry for environmental scientists and engineers. 2nd edition. E&FN Spon, London. 97-98.

Liao, C.M., Maekawa T., and Feng X.D. (1995). Nitrogen and phosphorus removal for swine wastewater by ammonium crystallization and intermittent aeration process. Journal of Environmental Science and Health, B30 (5), 733-758.

Liberti, L., Limoni N., Lopez A., Passino R. and Boari G. (1986). The 10 $m^3$ h-1 RIM-NUT demonstration plant at West Bari for removing and recovering nitrogen and phosphorus from wastewater. Water Res., 20(6), 735-739.

Liberti, L., Petruzzelli, D. and De Florio, L. (2001). RIM-NUT Ion Exchange Plus Struvite Precipitation Process. *Environ. Technol.,* 22, 1313.

Lin W. F. (2005). The status and utilization of phosphate rock of china and its effects on competitiveness of Chinese phosphorus industry. Master thesis. Beijing: Agriculture University

Lind, B.B., Ban, Z. and Byden, S. (2000). Nutrient recovery from human urine by struvite crystallization with ammonia adsorption on zeolite and wollastonite. Bioresour. Technol., 73(2), 169–174.

Liu Y., Mol APJ and Chen J.N. (2004). Material flow and ecological restructuring in China: the case of phosphorus. Journal of Industrial Ecology, 8(3),103–120.

Liu Y., Chen J.N., Mol, A.P.J. and Ayres, R.U. (2007). Comparative analysis of phosphorus use within national and local economies in China. Resources Conservation and Recycling, 51(2), 454-474.

Liu Y.H. (2005). Phosphorus resource at home & abroad, and the current situation of their exploitation & utilization. Phosphate & compound Fertilizer, 20(5), 1-5, 10.

Lowenthal, R.E., Korumuller, U.R.C. and van Heerden, E.P. (1994). Struvite precipitation in anaerobic treatment systems, Proceedings, 7th International Symposium on Anaerobic Digestion, Cape Town, S.A.

# M

Mamais, D., Pitt, P. A., Cheng, Y. W., Loiacono, J. and Jenkins, D. (1994). Determination of Ferric Chloride Dose to Control Struvite Precipitation in Anaerobic Sludge Digesters. Water Environ. Res., 66 (7), 912-918.

Manahan Stanley E. (2005). Manahan. Environmental chemistry. 8th ed. CRC Press, Washinton, D.C. United States of America. 15

Mathew, M. and Schroeder, L. W. (1979). Crystal structure of a struvite analogue, $MgKPO_4{\cdot}6H_2O$. Acta Cryst. B35, 11-13.

Menge. (2003). Duncan Nicholas Lubchenco Menge. Anthropogenic global environmental changes and phosphorus limitation: interactions and implications. Honors thesis, Stanford University, May

Michalowski, T., Pietrzyk, A. (2006). A thermodynamic study of struvite + water system. Talanta, 68, 594 – 601.

Miles, A., Ellis, T.G. (2001). Struvite precipitation potential for nutrient recovery from anerobically treated wastes, Wat. Sci. Tech., 43(11), 259–266.

Mohajit, K., Bhattarai, K., Taignides, E.P., and Yap, B.C. (1989). Struvite deposits in pipes and aerators, Biological Wastes, 30, 133–147.

Momberg, G. A. and Oellerman, R. A. (1992). The removal of phosphate by hydroxyapatite and struvite crystallisation in South Africa, Water Sci. Technol., 26, 987 – 996.

Moreno, E.C. and Varughese, K. (1981). Crystal growth of calcium apatites from dilute solutions, J. Cryst. Growth 53, 20–30.

Moriyama, K., Kojima, T., Minawa, Y. Matsumoto, S. and Nakamachi, K. (2001).

Development of artificial seed crystal for crystallization of calcium phosphate, Environmental Technology, 22, 1245–1252.

Morton S.C. (2003). Phosphorus in the environment and its role in anaerobic iron corrosion, Dissertation of Virginia Polytechnic Institute and State University. November

Mullin J.W. (2001). Crystallization .Butterworth-Heinemann, Boston.

Münch, E., Barr, K. (2001). Controlled struvite crystallisation for removing phosphorus from anaerobic digester sidestreams, Water Research 35 (1), 151-159.

Musvoto, E.V., Wentzel, M.C. and Ekama, G.A. (2000). Integrated chemical–physical processes modelling-II. Simulating aeration treatment of anaerobic digester supernatants, Water Res., 34, 1857–1867.

## N

Nelson, N.O., Mikkelsen, R.L. and Hesterberg, D.L. (2000). Struvite formation to remove phosphorus from anaerobic swine lagoon effluent. Proceedings of the 8th International Symposium on Animal, Agricultural and Food Processing Wastes, October. Des Moines, J.A. Moore (ed.), ASAE Publications. St. Joseph, Michigan 18-26.

Nelson N.O, Mikkelsen R.E, Hesterberg D.L. (2003). Struvite precipitation in anaerobic swine lagoon liquid: effect of pH and Mg:P ratio and determination of rate constant. Bioresource Technology, 89:229–236.

## O

Ohlinger, K.N., Young, T. M., Schroeder, E.D. (1998). Predicting Struvite Formation in Digestion, Water Research, 32 (12), 3607-3614.

Ohlinger K.N, Young TM, Schroeder E.D. (1999). Kinetics effects on preferential struvite accumulation in wastewater. Journal of Environmental Engineering. 125(8), 730-737.

## P

Parsons, S.A., Wall, F., Doyle, J., Oldring, K. and Churchley J. (2001). Assessing the potential for struvite recovery at sewage treatment works. Environmental Technology, 22, 1279–1286.

Petruzzelli D., Dell'Erba A., Liberti L., Notarnicola M. and Sengupta A. K. (2004). A phosphate selective sorbent for the REM NUTs process: field experience at Massafra Wastewater Treatment Plant. Reactive and Functional Polymers, 60, 195–202.

Piekema P.G., Gaastra S.B. (1993). Phosphate recovery by the crystallization process: experience and developments. http://www.nhm.ac.uk/research-curation/projects/phosphate-recovery/Nordwijkerhout/Piekema.pdf

Poliafico M. (2007). Anaerobic digestion: decision support software. Cork institute of technology, Master thesis.

## R

Regy, S., Mangin, D., Klein, J.P., Lieto, J. (2001). Phosphate recovery by struvite precipitation in a stirred reactor. Centre Europeen d’Etudes des Polyphosphates.

Roberts, W.L., Rapp, G.R., Campbell, T.J. (1990) Encyclopedia of minerals, Van Nostrand Reinhold Co., NewYork, U.S.A.

## S

Salutsky, M.L., Duseth, M.G., Ries, K.M. and Shapiero, J.J. (1970). Ultimate disposal of phosphate from wastewater by recovery as fertilizer. Chemical Engineering Progress Symposium Series, 107, 54 – 62.

Salutsky, M.L., Dunseth, M.G., Ries, K.M., Shapiro, J.J. (1972). Ultimate disposal of phosphate from waste water by recovery as fertilizer. Effluent and Water Treatment Journal (October), 509 – 519.

Sarkar, A.K. (1991). Hydration/dehydration characteristics of struvite and dittmarite pertaining to magnesium ammonium phosphate cement systems. J. Mater. Sci., 26: 2514–2518.

Schaum C. (2002). Diskussion der Verfahren zur P-Ruekgewinnung. 66. Darmstaedter Seminar Abwassertechnik, Darmstadt,129-151.

Schuiling, R.D., Andrade, A. (1999). Recovery of struvite from calf manure, J. Environ. Technol., 20, 765–768.

Schulze-Rettmer, R. (1991). The simultaneous chemical precipitation of ammonium and phosphate in the form of magnesium-ammonium-phosphate. Water Sci. Technol., 23, 659-667.

Scope newsletter (1997) Centre Europeen d'Etudes des Polyphosphate, CEFIC Publication, http://www.nkm.ac.uk./mineralogy/phos/index.htm

The State Environmental Protection Administration of China (SEPA) (2002). National Situation Investigation and Pollution Prevention Policy of Concentrated Livestock and Poultry Industries, Beijing: China Environmental Science Press, 35–38.

Shimamura, K.; Homma, Y.; Watanabe, A.; Tanaka, T. (2003). Research on MAP Recovery Conditions Using a Fluidized-Bed Crystallized Phosphorous Removal System. Water Environ. Technol., 1 (1), 73-78.

Shin, H.S., Lee, S.M. (1997). Removal of nutrients in wastewater by using magnesium salts. Environ. Technol., 19: 283–290.

Shu, L., Schneider, P., Jegatheesan, V., Johnson, J. (2006). An economic evaluation of phosphorus recovery as struvite from digester supernatant, Bioresource Technol., 97, 2211–2216.

Song Y.H., Donnert D., Berg U., Weidler P.G., Nueesch R. (2007). Seed selections for crystallization of calcium phosphate for phosphorus recovery. Journal of Environmental Sciences, 19591–595.

Song, Y.H. (2003). Precipitation chemistry of calcium phosphate for phosphorus recovery. Dissertation, Institüt für Siedlungswasserwirtschaft Universität Karlsuhe

Speece, R.E. (1996). Anaerobic biotechnology for industrial wastewaters. Archae Press, Nashville, TN, 392p.

Steve Williams (1998). Adapting strategies for avoiding struvite build-up problems in plants and transforming them into strategies for recovery. INTERNATIONAL CONFERENCE ON PHOSPHORUS RECOVERY FROM SEWAGE AND ANIMAL WASTES, Warwick University, UK. 6th & 7th May

Stevens, M. A. and Schulte, D. D. (1979). Low temperature digestion of swine manure. J. Environmental Enging. Div., ASCE 105, (EE1):33-42.

Stratful, I., Scrimshaw, M.D., Lester, J.N. (2001). Conditions influencing the precipitation of magnesium ammonium phosphate. Water Res., 35, 4191–4199.

Stumm and Morgan. (1970). Aquatic chemistry, New York: Wiley

Suzuki Kazuyoshi, Yasuo Tanaka, Takashi Osada and Waki M. (2002). Removal of phosphate, magnesium and calcium from swine wastewater through crystallization enhanced by aeration. Water Research, 36 (12), 2991–2998.

Suzuki, K., Tanaka, Y., Kuroda, K., Hanajima, D., Fukumoto, Y. (2004). Phosphorous in swine wastewater and its recovery as struvite in Japan. International Conference for Struvite: Its Role in Phosphorus Recovery and Reuse, Cranfield University, UK.

Suzuki, K., Tanaka, Y., Kuroda, K., Hanajima, D., Fukumoto, Y. (2005). Recovery of phosphorous from swine wastewater through crystallization. Bioresource Technology, 96 (14), 1544–1550.

Suzuki, K., Tanaka, Y., Kuroda, K., Hanajima, D., Fukumoto, Y., Yasuda T. and Waki M. (2007). Removal and recovery of phosphorous from swine wastewater by demonstration crystallization reactor and struvite accumulation device. Bioresource Technology, 98 (8), 1573–1578.

## T

Taylor, A.W.; Frazier, A.W.; Gurney, E.L. (1963). Solubility products of magnesium ammonium and magnesium potassium phosphates. J. Chem. Soc., 1580–1584.

Tchobanoglous G. and BURTON F.L. (1991). Wastewater Engineering: Treatment, Disposal and Reuse (3rd edn.) Metcalf and Eddy Inc., McGraw-Hill, New York, USA.

## U

Ueno, Y.; Fujii, M. (2001). Three Years Experience of Operating and Selling Recovered Struvite from Full-Scale Plant. Environ, Technol., 22 (11), 1373-1381.

Uludag-Demirer S, Demirer G N, Chen S. (2005). Ammonia removal from anaerobically digested dairy manure by struvite precipitation. Process Biochemistry, 40, 3667-3674.

Uludag-Demirer S, Demirer G N, Chen S. (2008). Anaerobic digestion of dairy manure with enhanced ammonia removal. Journal of Environmental Management, 86 (1), 193-200

USGS (2007) Phosphate Rock Statistics and Information. Annual Publications, http://minerals.usgs.gov/minerals/pubs/commodity/phosphate_rock/.

## V

Vaclav Smil (2000). Phosphorus in the environment: Natural flows and human interferences. Annu. Rev. Energy Environ., 25, 53-88.

Valsami-Jones (2004). Phosphorus in Environmental Technologies, Principles and Applications, UK:IWA Publishing, London.

van Dijk, J. C., Wilms, D. A. (1991). Water Treatment without Waste Material-Fundamentals and State of the Art of Pellet Softening. J. Water SRT-Aqua, 40 (5), 263-280.

Van Velsen A.F.M. (1981). Anaerobic digestion of piggery waste. Thesis, University of Wageningen, The Netherlands.

Von Horn J. (2007). Untersuchungen zur Rückgewinnung von Phosphat aus Überschussschlamm von Kläranlagen mit vermehrt biologischer Phosphatelimination. Dissertation, Bauhaus-Universitaet Weimar Rhombos-Verlag. Berlin

## W

Wang K.J, Jin D.X, Zho S.X, Cao C.R. (2004). Technology and policy of preventing pollution for livestock and poultry breeding, Beijing: Chemical Industry Press

Webb, K.M. and Ho, G.E. (1992). Struvite ($MgNH_4PO_4 \cdot 6H_2O$) Solubility and its application to a piggery effluent problem. Wat. Sci. Tech., 26, 2229–2232.

Westerman, P.W., Safley L.M., Barker J. C. (1985). Crystalline build-up in swine and poultry recycle flush systems. Agricultural Waste Utilization and Management, Proceedings of the 5th International Symposium on Agricultural Wastes, 613-623.

Westheimer FH. (1987). Why nature chose phosphates. Science, 235:1173–77.

Williams, S. (1999). Struvite Precipitation in the Sludge Stream at Slough Wastewater Treatment Plant and Opportunities for Phosphorus Recovery, Environ. Technol., 20 (7), 743-747.

Wrigley, T.J., Webb, K.M. and Venkitachalm, H. (1992). A laboratory study of struvite precipitation after anaerobic digestion of piggery wastes. Bioresource Technology, 42, 117–121.

# Y

Yi W.G., Lo K.V. (2003). Phosphate Recovery from Greenhouse Wastewater. Journal of environmental sicience and health part B-Pesticides, Food Contaminants, and Agricultural Wastes Vol. B38, No. 4, 501 – 509.

# Z

Zeng L. and Li X.M. (2006). Nutrient removal from anaerobically digested cattle manure by struvite precipitation. J. Environ. Eng. Sci., Vol. 5, 285-294.

Zhang Z.J., Lin R.C. and Jin R.L. (2000). Drainage system, Beijing: China construction industrial press

Zhang W.F. (2005). The status and utilization of phosphate rock of China and its effects on competitiveness of Chinese phosphorus industry. The Agriculture University of China, Master thesis

Zhao, D., Sengupta, A.K., Zhu, Y. (1995). Trace contaminants sorption through polymeric ligand exchange. Ind. Eng. Chem. Res., 34, 2676–2684.

Zhao, D., Sengupta, A.K. (1998). Ultimate removal of phosphate from wastewater using a new class of polymeric ion exchangers. Water Res., 32 (5), 1613–1625.

Zheng, F., Huang, C.H., Norton, L.D. (2004). Effects of near-surface hydraulic gradients on nitrate and phosphorus losses in surface runoff. Journal of Environmental Quality, 33 (6), 2174–2182.

Zhou F. (2005). The study of struvite precipitation from wastewater. Huaqiao University, Master thesis

# Appendix

Figure 6.2: Cumulative gas production and input COD loading rates in R1 and R2

| | Cumulative gas production, $m^3$ | | OLR, kg $COD_{added}/m^3.d$ | |
|---|---|---|---|---|
| | R1 | R2 | R1 | R2 |
| 12.7.06 | 0.0281 | 0.0246 | 0.802 | 0.802 |
| 13.7.06 | 0.0497 | 0.0453 | 0.802 | 0.802 |
| 14.7.06 | 0.0697 | 0.0646 | 0.802 | 0.802 |
| 15.7.06 | 0.0887 | 0.0834 | 0.802 | 0.802 |
| 16.7.06 | 0.107 | 0.1015 | 0.802 | 0.802 |
| 17.7.06 | 0.126 | 0.1194 | 0.802 | 0.802 |
| 18.7.06 | 0.144 | 0.1373 | 0.802 | 0.802 |
| 19.7.06 | 0.1608 | 0.1511 | 0.802 | 0.802 |
| 20.7.06 | 0.1739 | 0.1726 | 0.802 | 0.802 |
| 21.7.06 | 0.1863 | 0.1866 | 0.802 | 0.802 |
| 22.7.06 | 0.1988 | 0.1995 | 0.802 | 0.802 |
| 23.7.06 | 0.2108 | 0.2113 | 0.802 | 0.802 |
| 24.7.06 | 0.2236 | 0.2231 | 0.802 | 0.802 |
| 25.7.06 | 0.2379 | 0.2341 | 0.802 | 0.802 |
| 26.7.06 | 0.2508 | 0.2452 | 0.802 | 0.802 |
| 27.7.06 | 0.2623 | 0.2565 | 0.802 | 0.802 |
| 28.7.06 | 0.2723 | 0.2667 | 0.802 | 0.802 |
| 29.7.06 | 0.2821 | 0.2766 | 0.802 | 0.802 |
| 30.7.06 | 0.2922 | 0.2861 | 0.802 | 0.802 |
| 31.7.06 | 0.3009 | 0.2946 | 0.802 | 0.802 |
| 1.8.06 | 0.3098 | 0.3032 | 0.802 | 0.802 |
| 2.8.06 | 0.3184 | 0.3118 | 0.802 | 0.802 |
| 3.8.06 | 0.3274 | 0.3197 | 0.802 | 0.802 |
| 4.8.06 | 0.3354 | 0.3277 | 0.802 | 0.802 |
| 5.8.06 | 0.3432 | 0.3354 | 0.802 | 0.802 |
| 6.8.06 | 0.3507 | 0.343 | 0.802 | 0.802 |
| 7.8.06 | 0.3581 | 0.35 | 0.802 | 0.802 |
| 8.8.06 | 0.3656 | 0.357 | 0.802 | 0.802 |
| 9.8.06 | 0.3727 | 0.3641 | 0.802 | 0.802 |

| | | | | |
|---|---|---|---|---|
| 10.8.06 | 0.3801 | 0.371 | 0.802 | 0.802 |
| 11.8.06 | 0.3874 | 0.378 | 0.802 | 0.802 |
| 12.8.06 | 0.3944 | 0.384 | 0.802 | 0.802 |
| 13.8.06 | 0.4024 | 0.391 | 0.802 | 0.802 |
| 14.8.06 | 0.41 | 0.399 | 0.802 | 0.802 |
| 15.8.06 | 0.417 | 0.4058 | 0.802 | 0.802 |
| 16.8.06 | 0.424 | 0.4128 | 0.802 | 0.802 |
| 17.8.06 | 0.431 | 0.4195 | 0.802 | 0.802 |
| 18.8.06 | 0.438 | 0.4262 | 0.802 | 0.802 |
| 19.8.06 | 0.445 | 0.433 | 0.802 | 0.802 |
| 20.8.06 | 0.452 | 0.44 | 0.802 | 0.802 |
| 21.8.06 | 0.458 | 0.446 | 0.802 | 0.802 |
| 22.8.06 | 0.465 | 0.4525 | 0.802 | 0.802 |
| 23.8.06 | 0.471 | 0.4588 | 0.802 | 0.802 |
| 24.8.06 | 0.478 | 0.4654 | 0.802 | 0.802 |
| 25.8.06 | 0.484 | 0.4716 | 0.802 | 0.802 |
| 26.8.06 | 0.49 | 0.4773 | 0.802 | 0.802 |
| 27.8.06 | 0.496 | 0.4829 | 0.802 | 0.802 |
| 28.8.06 | 0.501 | 0.4883 | 0.802 | 0.802 |
| 29.8.06 | 0.507 | 0.4937 | 0.802 | 0.802 |
| 30.8.06 | 0.511 | 0.4984 | 0.802 | 0.802 |
| 31.8.06 | 0.516 | 0.5029 | 0.802 | 0.802 |
| 01.09.06 | 0.52 | 0.5074 | 0.802 | 0.802 |
| 02.09.06 | 0.525 | 0.5117 | 0.802 | 0.802 |
| 03.09.06 | 0.529 | 0.5159 | 0.802 | 0.802 |
| 04.09.06 | 0.533 | 0.5199 | 0.802 | 0.802 |
| 05.09.06 | 0.537 | 0.5237 | 0.802 | 0.802 |
| 06.09.06 | 0.54 | 0.5276 | 0.802 | 0.802 |
| 07.09.06 | 0.544 | 0.5311 | 0.802 | 0.802 |
| 08.09.06 | 0.548 | 0.5346 | 0.802 | 0.802 |
| 09.09.06 | 0.551 | 0.5382 | 0.802 | 0.802 |
| 10.09.06 | 0.555 | 0.5417 | 0.802 | 0.802 |
| 11.09.06 | 0.558 | 0.5453 | 0.802 | 0.802 |
| 12.09.06 | 0.562 | 0.5491 | 0.802 | 0.802 |
| 13.09.06 | 0.566 | 0.5553 | 0.802 | 0.802 |
| 14.09.06 | 0.571 | 0.5623 | 0.863 | 0.863 |

| | | | | |
|---|---|---|---|---|
| 15.09.06 | 0.577 | 0.5695 | 0.863 | 0.863 |
| 16.09.06 | 0.584 | 0.5775 | 0.863 | 0.863 |
| 17.09.06 | 0.591 | 0.5851 | 0.863 | 0.863 |
| 18.09.06 | 0.599 | 0.5932 | 0.863 | 0.863 |
| 19.09.06 | 0.606 | 0.6012 | 0.863 | 0.863 |
| 20.09.06 | 0.614 | 0.6091 | 0.863 | 0.863 |
| 21.09.06 | 0.621 | 0.6166 | 0.863 | 0.863 |
| 22.09.06 | 0.628 | 0.6239 | 0.863 | 0.863 |
| 23.09.06 | 0.635 | 0.6311 | 0.863 | 0.863 |
| 24.09.06 | 0.642 | 0.6381 | 0.863 | 0.863 |
| 25.09.06 | 0.649 | 0.645 | 0.863 | 0.863 |
| 26.09.06 | 0.656 | 0.652 | 0.863 | 0.863 |
| 27.09.06 | 0.662 | 0.659 | 0.863 | 0.863 |
| 28.09.06 | 0.668 | 0.6652 | 0.863 | 0.863 |
| 29.09.06 | 0.675 | 0.6716 | 0.863 | 0.863 |
| 30.09.06 | 0.681 | 0.6778 | 0.863 | 0.863 |
| 1.10.06 | 0.688 | 0.6847 | 0.863 | 0.863 |
| 2.10.06 | 0.694 | 0.6913 | 0.863 | 0.863 |
| 3.10.06 | 0.701 | 0.6977 | 0.863 | 0.863 |
| 4.10.06 | 0.707 | 0.7037 | 0.863 | 0.863 |
| 5.10.06 | 0.713 | 0.7098 | 0.863 | 0.863 |
| 6.10.06 | 0.719 | 0.716 | 0.863 | 0.863 |
| 7.10.06 | 0.725 | 0.7223 | 0.863 | 0.863 |
| 8.10.06 | 0.731 | 0.7286 | 0.863 | 0.863 |
| 9.10.06 | 0.737 | 0.7344 | 0.863 | 0.863 |
| 10.10.06 | 0.743 | 0.7404 | 0.863 | 0.863 |
| 11.10.06 | 0.749 | 0.7464 | 0.863 | 0.863 |
| 12.10.06 | 0.755 | 0.7524 | 0.863 | 0.863 |
| 13.10.06 | 0.761 | 0.7586 | 0.863 | 0.863 |
| 14.10.06 | 0.769 | 0.7666 | 0.863 | 0.863 |
| 15.10.06 | 0.778 | 0.7754 | 0.863 | 0.863 |
| 16.10.06 | 0.79 | 0.7858 | 0.863 | 0.863 |
| 17.10.06 | 0.806 | 0.7985 | 0.863 | 0.863 |
| 18.10.06 | 0.823 | 0.8207 | 0.863 | 0.863 |
| 19.10.06 | 0.841 | 0.8390 | 0.863 | 0.863 |
| 20.10.06 | 0.858 | 0.8354 | 2.18 | 1.3 |

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|---|---|---|---|---|
| 21.10.06 | 0.876 | 0.8481 | 2.18 | 1.3 |
| 22.10.06 | 0.894 | 0.8609 | 2.18 | 1.3 |
| 23.10.06 | 0.913 | 0.8747 | 2.18 | 1.3 |
| 24.10.06 | 0.932 | 0.8883 | 2.18 | 1.3 |
| 25.10.06 | 0.952 | 0.9019 | 2.18 | 1.3 |
| 26.10.06 | 0.972 | 0.9155 | 2.18 | 1.3 |
| 27.10.06 | 0.991 | 0.929 | 2.18 | 1.3 |
| 28.10.06 | 1.011 | 0.9426 | 2.18 | 1.3 |
| 29.10.06 | 1.031 | 0.9566 | 2.18 | 1.3 |
| 30.10.06 | 1.05 | 0.9702 | 2.18 | 1.3 |
| 31.10.06 | 1.07 | 0.984 | 2.18 | 1.3 |
| 1.11.06 | 1.09 | 0.9976 | 2.18 | 1.3 |
| 2.11.06 | 1.109 | 1.0111 | 2.18 | 1.3 |
| 3.11.06 | 1.129 | 1.0243 | 2.18 | 1.3 |
| 4.11.06 | 1.149 | 1.037 | 2.18 | 1.3 |
| 5.11.06 | 1.169 | 1.05 | 2.18 | 1.3 |
| 6.11.06 | 1.189 | 1.063 | 2.18 | 1.3 |
| 7.11.06 | 1.209 | 1.076 | 2.18 | 1.3 |
| 8.11.06 | 1.229 | 1.089 | 2.18 | 1.3 |
| 9.11.06 | 1.249 | 1.101 | 2.18 | 1.3 |
| 10.11.06 | 1.268 | 1.114 | 2.18 | 1.3 |
| 11.11.06 | 1.287 | 1.126 | 2.18 | 1.3 |
| 12.11.06 | 1.306 | 1.139 | 2.18 | 1.3 |
| 13.11.06 | 1.325 | 1.152 | 2.18 | 1.3 |
| 14.11.06 | 1.343 | 1.164 | 2.18 | 1.3 |
| 15.11.06 | 1.362 | 1.176 | 2.18 | 1.3 |
| 16.11.06 | 1.379 | 1.189 | 2.18 | 1.3 |
| 17.11.06 | 1.396 | 1.2 | 2.18 | 1.3 |
| 18.11.06 | 1.413 | 1.212 | 2.18 | 1.3 |
| 19.11.06 | 1.43 | 1.224 | 2.18 | 1.3 |
| 20.11.06 | 1.446 | 1.234 | 2.18 | 1.3 |
| 21.11.06 | 1.462 | 1.245 | 2.18 | 1.3 |
| 22.11.06 | 1.477 | 1.255 | 2.18 | 1.3 |
| 23.11.06 | 1.492 | 1.266 | 2.18 | 1.3 |
| 24.11.06 | 1.506 | 1.276 | 2.18 | 1.3 |
| 25.11.06 | 1.519 | 1.285 | 2.18 | 1.3 |

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|---|---|---|---|---|
| 26.11.06 | 1.531 | 1.295 | 2.18 | 1.3 |
| 27.11.06 | 1.543 | 1.304 | 2.18 | 1.3 |
| 28.11.06 | 1.554 | 1.314 | 2.18 | 1.3 |
| 29.11.06 | 1.565 | 1.323 | 2.18 | 1.3 |
| 30.11.06 | 1.576 | 1.332 | 2.18 | 1.3 |
| 1.12.06 | 1.586 | 1.34 | 2.18 | 1.3 |
| 2.12.06 | 1.596 | 1.349 | 2.18 | 1.3 |
| 3.12.06 | 1.607 | 1.357 | 2.18 | 1.3 |
| 4.12.06 | 1.617 | 1.366 | 2.18 | 1.3 |
| 5.12.06 | 1.627 | 1.374 | 2.18 | 1.3 |
| 6.12.06 | 1.636 | 1.382 | 2.18 | 1.3 |
| 7.12.06 | 1.646 | 1.39 | 2.18 | 1.3 |
| 8.12.06 | 1.655 | 1.398 | 2.18 | 1.3 |
| 9.12.06 | 1.665 | 1.406 | 2.18 | 1.3 |
| 10.12.06 | 1.675 | 1.413 | 2.18 | 1.3 |
| 11.12.06 | 1.684 | 1.42 | 2.18 | 1.3 |
| 12.12.06 | 1.694 | 1.427 | 2.18 | 1.3 |
| 13.12.06 | 1.704 | 1.434 | 2.18 | 1.3 |
| 14.12.06 | 1.713 | 1.44 | 2.18 | 1.3 |
| 15.12.06 | 1.723 | 1.447 | 2.18 | 1.3 |
| 16.12.06 | 1.732 | 1.454 | 2.18 | 1.3 |
| 17.12.06 | 1.741 | 1.46 | 2.18 | 1.3 |
| 18.12.06 | 1.75 | 1.4662 | 2.18 | 1.3 |
| 19.12.06 | 1.759 | 1.472 | 2.18 | 1.3 |
| 20.12.06 | 1.768 | 1.478 | 2.18 | 1.3 |
| 21.12.06 | 1.778 | 1.4844 | 1.48 | 0.89 |
| 22.12.06 | 1.789 | 1.491 | 1.48 | 0.89 |
| 23.12.06 | 1.8 | 1.4974 | 1.48 | 0.89 |
| 24.12.06 | 1.812 | 1.5036 | 1.48 | 0.89 |
| 25.12.06 | 1.823 | 1.51 | 1.48 | 0.89 |
| 26.12.06 | 1.835 | 1.5166 | 1.48 | 0.89 |
| 27.12.06 | 1.846 | 1.523 | 1.48 | 0.89 |
| 28.12.06 | 1.858 | 1.5297 | 1.48 | 0.89 |
| 29.12.06 | 1.87 | 1.5366 | 1.48 | 0.89 |
| 30.12.06 | 1.882 | 1.5439 | 1.48 | 0.89 |
| 31.12.06 | 1.894 | 1.551 | 1.48 | 0.89 |

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|---|---|---|---|---|
| 1.1.07 | 1.906 | 1.5579 | 1.48 | 0.89 |
| 2.1.07 | 1.918 | 1.5644 | 1.48 | 0.89 |
| 3.1.07 | 1.929 | 1.571 | 1.48 | 0.89 |
| 4.1.07 | 1.941 | 1.5774 | 1.48 | 0.89 |
| 5.1.07 | 1.952 | 1.5837 | 1.48 | 0.89 |
| 6.1.07 | 1.964 | 1.59 | 1.48 | 0.89 |
| 7.1.07 | 1.975 | 1.5964 | 1.48 | 0.89 |
| 8.1.07 | 1.986 | 1.6027 | 1.48 | 0.89 |
| 9.1.07 | 1.997 | 1.6088 | 1.48 | 0.89 |
| 10.1.07 | 2.008 | 1.6146 | 1.48 | 0.89 |
| 11.1.07 | 2.019 | 1.6203 | 1.48 | 0.89 |
| 12.1.07 | 2.029 | 1.6258 | 1.48 | 0.89 |
| 13.1.07 | 2.04 | 1.6314 | 1.48 | 0.89 |
| 14.1.07 | 2.05 | 1.6367 | 1.48 | 0.89 |
| 15.1.07 | 2.06 | 1.6422 | 1.48 | 0.89 |
| 16.1.07 | 2.07 | 1.6477 | 1.48 | 0.89 |
| 17.1.07 | 2.081 | 1.653 | 1.48 | 0.89 |
| 18.1.07 | 2.091 | 1.6581 | 1.48 | 0.89 |
| 19.1.07 | 2.101 | 1.6633 | 1.48 | 0.89 |
| 20.1.07 | 2.112 | 1.6683 | 1.48 | 0.89 |
| 21.1.07 | 2.122 | 1.6735 | 1.48 | 0.89 |
| 22.1.07 | 2.132 | 1.6785 | 1.48 | 0.89 |
| 23.1.07 | 2.142 | 1.6837 | 1.48 | 0.89 |
| 24.1.07 | 2.152 | 1.6888 | 1.48 | 0.89 |
| 25.1.07 | 2.162 | 1.6938 | 1.48 | 0.89 |
| 26.1.07 | 2.173 | 1.6991 | 1.48 | 0.89 |
| 27.1.07 | 2.183 | 1.7042 | 1.48 | 0.89 |
| 28.1.07 | 2.193 | 1.7093 | 1.48 | 0.89 |
| 29.1.07 | 2.203 | 1.7145 | 1.48 | 0.89 |
| 30.1.07 | 2.213 | 1.7195 | 1.48 | 0.89 |
| 31.1.07 | 2.223 | 1.7246 | 1.48 | 0.89 |

Figure 6.3: Daily Specific gas production in R1 and R2 during the operational period

| | Specific gas production, $m^3/d$ | | pH value | |
|---|---|---|---|---|
| | R1 | R2 | R1 | R2 |
| 20.10.06 | 0.447 | 0.531 | 7.42 | 7.48 |
| 21.10.06 | 0.452 | 0.539 | 7.4 | 7.45 |
| 22.10.06 | 0.457 | 0.543 | 7.43 | 7.47 |
| 23.10.06 | 0.483 | 0.586 | 7.42 | 7.49 |
| 24.10.06 | 0.493 | 0.577 | 7.4 | 7.45 |
| 25.10.06 | 0.498 | 0.577 | 7.42 | 7.46 |
| 26.10.06 | 0.501 | 0.577 | 7.41 | 7.43 |
| 27.10.06 | 0.498 | 0.573 | 7.43 | 7.42 |
| 28.10.06 | 0.496 | 0.577 | 7.43 | 7.4 |
| 29.10.06 | 0.503 | 0.594 | 7.41 | 7.42 |
| 30.10.06 | 0.496 | 0.577 | 7.43 | 7.41 |
| 31.10.06 | 0.503 | 0.586 | 7.42 | 7.43 |
| 1.11.06 | 0.501 | 0.577 | 7.42 | 7.43 |
| 2.11.06 | 0.503 | 0.573 | 7.4 | 7.41 |
| 3.11.06 | 0.503 | 0.56 | 7.42 | 7.43 |
| 4.11.06 | 0.513 | 0.552 | 7.43 | 7.42 |
| 5.11.06 | 0.508 | 0.548 | 7.43 | 7.42 |
| 6.11.06 | 0.498 | 0.543 | 7.44 | 7.4 |
| 7.11.06 | 0.503 | 0.548 | 7.46 | 7.42 |
| 8.11.06 | 0.508 | 0.539 | 7.45 | 7.43 |
| 9.11.06 | 0.503 | 0.535 | 7.46 | 7.43 |
| 10.11.06 | 0.496 | 0.535 | 7.45 | 7.44 |
| 11.11.06 | 0.491 | 0.531 | 7.49 | 7.46 |
| 12.11.06 | 0.483 | 0.531 | 7.48 | 7.45 |
| 13.11.06 | 0.473 | 0.539 | 7.47 | 7.46 |
| 14.11.06 | 0.468 | 0.531 | 7.46 | 7.45 |
| 15.11.06 | 0.463 | 0.526 | 7.45 | 7.43 |
| 16.11.06 | 0.452 | 0.518 | 7.43 | 7.44 |
| 17.11.06 | 0.435 | 0.501 | 7.44 | 7.46 |
| 18.11.06 | 0.43 | 0.488 | 7.46 | 7.45 |
| 19.11.06 | 0.422 | 0.492 | 7.45 | 7.46 |
| 20.11.06 | 0.419 | 0.463 | 7.46 | 7.45 |
| 21.11.06 | 0.396 | 0.446 | 7.45 | 7.43 |

| | | | | |
|---|---|---|---|---|
| 22.11.06 | 0.391 | 0.446 | 7.49 | 7.44 |
| 23.11.06 | 0.379 | 0.441 | 7.45 | 7.46 |
| 24.11.06 | 0.343 | 0.424 | 7.46 | 7.45 |
| 25.11.06 | 0.323 | 0.403 | 7.47 | 7.46 |
| 26.11.06 | 0.318 | 0.399 | 7.48 | 7.46 |
| 27.11.06 | 0.297 | 0.407 | 7.45 | 7.45 |
| 28.11.06 | 0.297 | 0.412 | 7.46 | 7.46 |
| 29.11.06 | 0.269 | 0.39 | 7.45 | 7.45 |
| 30.11.06 | 0.267 | 0.365 | 7.49 | 7.46 |
| 1.12.06 | 0.264 | 0.365 | 7.45 | 7.44 |
| 2.12.06 | 0.262 | 0.357 | 7.46 | 7.46 |
| 3.12.06 | 0.264 | 0.361 | 7.43 | 7.46 |
| 4.12.06 | 0.267 | 0.361 | 7.42 | 7.49 |
| 5.12.06 | 0.241 | 0.361 | 7.46 | 7.5 |
| 6.12.06 | 0.239 | 0.34 | 7.45 | 7.5 |
| 7.12.06 | 0.241 | 0.335 | 7.45 | 7.51 |
| 8.12.06 | 0.244 | 0.323 | 7.45 | 7.52 |
| 9.12.06 | 0.252 | 0.327 | 7.48 | 7.51 |
| 10.12.06 | 0.249 | 0.318 | 7.45 | 7.46 |
| 11.12.06 | 0.241 | 0.297 | 7.46 | 7.45 |
| 12.12.06 | 0.244 | 0.293 | 7.45 | 7.46 |
| 13.12.06 | 0.252 | 0.293 | 7.46 | 7.44 |
| 14.12.06 | 0.244 | 0.28 | 7.45 | 7.46 |
| 15.12.06 | 0.241 | 0.284 | 7.46 | 7.48 |
| 16.12.06 | 0.241 | 0.28 | 7.44 | 7.45 |
| 17.12.06 | 0.229 | 0.267 | 7.46 | 7.46 |
| 18.12.06 | 0.229 | 0.263 | 7.46 | 7.45 |
| 19.12.06 | 0.226 | 0.255 | 7.48 | 7.46 |
| 20.12.06 | 0.226 | 0.25 | 7.46 | 7.46 |
| 21.12.06 | 0.229 | 0.257 | 7.48 | 7.48 |
| 22.12.06 | 0.286 | 0.338 | 7.53 | 7.56 |
| 23.12.06 | 0.31 | 0.348 | 7.52 | 7.55 |
| 24.12.06 | 0.302 | 0.345 | 7.55 | 7.53 |
| 25.12.06 | 0.313 | 0.343 | 7.56 | 7.55 |
| 26.12.06 | 0.313 | 0.344 | 7.55 | 7.55 |
| 27.12.06 | 0.308 | 0.344 | 7.53 | 7.56 |

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|---|---|---|---|---|
| 28.12.06 | 0.319 | 0.347 | 7.55 | 7.55 |
| 29.12.06 | 0.324 | 0.356 | 7.56 | 7.53 |
| 30.12.06 | 0.332 | 0.359 | 7.55 | 7.54 |
| 31.12.06 | 0.324 | 0.352 | 7.53 | 7.55 |
| 1.1.07 | 0.319 | 0.349 | 7.54 | 7.56 |
| 2.1.07 | 0.31 | 0.349 | 7.55 | 7.53 |
| 3.1.07 | 0.313 | 0.343 | 7.56 | 7.55 |
| 4.1.07 | 0.31 | 0.344 | 7.55 | 7.55 |
| 5.1.07 | 0.302 | 0.348 | 7.55 | 7.56 |
| 6.1.07 | 0.31 | 0.344 | 7.53 | 7.55 |
| 7.1.07 | 0.305 | 0.339 | 7.54 | 7.55 |
| 8.1.07 | 0.31 | 0.339 | 7.55 | 7.55 |
| 9.1.07 | 0.297 | 0.33 | 7.56 | 7.56 |
| 10.1.07 | 0.292 | 0.327 | 7.55 | 7.55 |
| 11.1.07 | 0.286 | 0.322 | 7.55 | 7.49 |
| 12.1.07 | 0.283 | 0.323 | 7.59 | 7.5 |
| 13.1.07 | 0.283 | 0.328 | 7.55 | 7.55 |
| 14.1.07 | 0.278 | 0.322 | 7.53 | 7.51 |
| 15.1.07 | 0.281 | 0.315 | 7.5 | 7.51 |
| 16.1.07 | 0.275 | 0.314 | 7.5 | 7.51 |
| 17.1.07 | 0.278 | 0.316 | 7.48 | 7.51 |
| 18.1.07 | 0.275 | 0.315 | 7.54 | 7.49 |
| 19.1.07 | 0.275 | 0.314 | 7.55 | 7.48 |
| 20.1.07 | 0.278 | 0.315 | 7.56 | 7.47 |
| 21.1.07 | 0.275 | 0.312 | 7.57 | 7.5 |
| 22.1.07 | 0.273 | 0.313 | 7.56 | 7.52 |
| 23.1.07 | 0.27 | 0.312 | 7.55 | 7.53 |
| 24.1.07 | 0.275 | 0.314 | 7.53 | 7.53 |
| 25.1.07 | 0.275 | 0.311 | 7.53 | 7.52 |
| 26.1.07 | 0.278 | 0.312 | 7.55 | 7.52 |
| 27.1.07 | 0.273 | 0.311 | 7.57 | 7.53 |
| 28.1.07 | 0.27 | 0.312 | 7.56 | 7.53 |
| 29.1.07 | 0.27 | 0.313 | 7.55 | 7.53 |
| 30.1.07 | 0.273 | 0.315 | 7.56 | 7.5 |
| 31.1.07 | 0.273 | 0.315 | 7.56 | 7.55 |

Figure 6.4: Percentage of methane and carbon dioxide in the biogas during the operational period

| | Content of $CH_4$, % | | Content of $CO_2$, % | |
|---|---|---|---|---|
| | R1 | R2 | R1 | R2 |
| 20.10.06 | 55.7 | 55.3 | 34.5 | 34.6 |
| 21.10.06 | 56.5 | 55.8 | 30.2 | 30.7 |
| 22.10.06 | 50.1 | 52.2 | 34.9 | 32.3 |
| 23.10.06 | 50 | 53.8 | 33.2 | 31 |
| 24.10.06 | 47.9 | 55.4 | 32 | 28.7 |
| 25.10.06 | 51.8 | 57.6 | 31 | 29.5 |
| 26.10.06 | 52.4 | 58.8 | 29.3 | 27.5 |
| 27.10.06 | 51.8 | 58.6 | 29.2 | 27.3 |
| 28.10.06 | 53.7 | 59.7 | 28.5 | 27.2 |
| 29.10.06 | 51.5 | 59.7 | 27.8 | 24.3 |
| 30.10.06 | 53.2 | 60 | 28.2 | 25.5 |
| 31.10.06 | 52.4 | 59.9 | 28.2 | 25.5 |
| 1.11.06 | 52 | 61.4 | 28.4 | 24.4 |
| 2.11.06 | 54.7 | 59.9 | 28.2 | 25.4 |
| 3.11.06 | 53.2 | 61.4 | 28.8 | 25.2 |
| 4.11.06 | 52 | 60.7 | 28.7 | 25.3 |
| 5.11.06 | 51.2 | 59.9 | 28.6 | 25.1 |
| 6.11.06 | 52.9 | 61.4 | 29.2 | 25.7 |
| 7.11.06 | 51.5 | 59.9 | 29.9 | 26.7 |
| 8.11.06 | 50.5 | 60.6 | 29.8 | 25.7 |
| 9.11.06 | 50.4 | 58.9 | 29.7 | 26.4 |
| 10.11.06 | 53 | 60.1 | 29.2 | 26.8 |
| 11.11.06 | 52 | 60 | 29 | 25.7 |
| 12.11.06 | 51 | 61.6 | 30.1 | 22.6 |
| 13.11.06 | 50.9 | 58.3 | 30.2 | 27.1 |
| 14.11.06 | 50.1 | 58.8 | 28.9 | 25.9 |
| 15.11.06 | 51.3 | 61.5 | 27.7 | 23.7 |
| 16.11.06 | 51.5 | 60.6 | 30.3 | 27 |
| 17.11.06 | 58.3 | 53 | 27.2 | 30.4 |
| 18.11.06 | 49.9 | 62.1 | 29.2 | 25 |
| 19.11.06 | 51.3 | 61.1 | 29.7 | 26 |
| 20.11.06 | 51.8 | 62 | 29.5 | 25.9 |
| 21.11.06 | 62.8 | 66.4 | 31.2 | 29.4 |

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|---|---|---|---|---|
| 22.11.06 | 62.1 | 66.2 | 31.1 | 29.1 |
| 23.11.06 | 62.5 | 65.2 | 31 | 29.6 |
| 24.11.06 | 63.4 | 65.6 | 30.1 | 28.3 |
| 25.11.06 | 62.1 | 66 | 31.1 | 29.1 |
| 26.11.06 | 63.5 | 63.2 | 31 | 29.6 |
| 27.11.06 | 63.2 | 64.8 | 31.4 | 29.9 |
| 28.11.06 | 62.7 | 66.1 | 30.9 | 29.3 |
| 29.11.06 | 63.4 | 64.8 | 31.1 | 30.2 |
| 30.11.06 | 63.5 | 66.5 | 30.6 | 28.8 |
| 1.12.06 | 66.2 | 66.8 | 30.9 | 29.7 |
| 2.12.06 | 62.7 | 65.1 | 32.3 | 29.6 |
| 3.12.06 | 61.8 | 64.4 | 33.7 | 30.3 |
| 4.12.06 | 60.1 | 62.2 | 33.6 | 33 |
| 5.12.06 | 61.4 | 64.8 | 32.3 | 29.8 |
| 6.12.06 | 63.2 | 64.5 | 32.4 | 30.5 |
| 7.12.06 | 62.2 | 63.8 | 32 | 30 |
| 8.12.06 | 60.1 | 62.2 | 33.6 | 33 |
| 9.12.06 | 61.4 | 64.8 | 32.3 | 29.8 |
| 10.12.06 | 62.7 | 65.1 | 32.3 | 29.6 |
| 11.12.06 | 61.8 | 64.4 | 33.7 | 30.3 |
| 12.12.06 | 60.1 | 62.2 | 33.6 | 33 |
| 13.12.06 | 60.1 | 62.2 | 33.6 | 33 |
| 14.12.06 | 61.4 | 64.8 | 32.3 | 29.8 |
| 15.12.06 | 62.7 | 65.1 | 32.3 | 29.6 |
| 16.12.06 | 62.2 | 63.8 | 32 | 30 |
| 17.12.06 | 60.1 | 62.2 | 33.6 | 33 |
| 18.12.06 | 61.4 | 64.8 | 32.3 | 29.8 |
| 19.12.06 | 60.1 | 62.2 | 34.9 | 32.3 |
| 20.12.06 | 60 | 63.8 | 33.2 | 31 |
| 21.12.06 | 56.9 | 60.4 | 32 | 28.7 |
| 22.12.06 | 49.9 | 57.8 | 29.2 | 26.5 |
| 23.12.06 | 46.2 | 55.8 | 28.2 | 25.5 |
| 24.12.06 | 50.6 | 56.5 | 29.4 | 27.3 |
| 25.12.06 | 49.9 | 57.8 | 29.2 | 26.5 |
| 26.12.06 | 46.2 | 55.8 | 28.2 | 25.5 |
| 27.12.06 | 47.5 | 56 | 28.6 | 26 |

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|---|---|---|---|---|
| 28.12.06 | 47.3 | 56.5 | 29.7 | 26.7 |
| 29.12.06 | 45.7 | 53.9 | 30.6 | 28.3 |
| 30.12.06 | 52.9 | 54.7 | 32.3 | 30.6 |
| 31.12.06 | 51.6 | 52.9 | 30.5 | 28.9 |
| 1.1.07 | 51.4 | 55.7 | 29.6 | 27.3 |
| 2.1.07 | 50.6 | 56.5 | 29.4 | 27.3 |
| 3.1.07 | 49.9 | 57.8 | 29.2 | 26.5 |
| 4.1.07 | 48.9 | 52.2 | 30.5 | 25.9 |
| 5.1.07 | 50 | 55.7 | 29.6 | 27.3 |
| 6.1.07 | 50 | 56.5 | 29.4 | 27.3 |
| 7.1.07 | 49.9 | 55.4 | 32 | 28.7 |
| 8.1.07 | 51.8 | 57.6 | 31 | 29.5 |
| 9.1.07 | 52.4 | 58.8 | 29.3 | 27.5 |
| 10.1.07 | 51.8 | 58.6 | 29.2 | 27.3 |
| 11.1.07 | 53.7 | 59.7 | 28.5 | 27.2 |
| 12.1.07 | 51.5 | 59.7 | 27.8 | 24.3 |
| 13.1.07 | 53.2 | 60 | 28.2 | 25.5 |
| 14.1.07 | 54.4 | 59.9 | 28.2 | 25.5 |
| 15.1.07 | 63.4 | 65.6 | 30.1 | 28.3 |
| 16.1.07 | 62.1 | 66 | 31.1 | 29.1 |
| 17.1.07 | 63.5 | 63.2 | 31 | 29.6 |
| 18.1.07 | 63.2 | 64.8 | 31.4 | 29.9 |
| 19.1.07 | 62.7 | 66.1 | 30.9 | 29.3 |
| 20.1.07 | 63.4 | 64.8 | 31.1 | 30.2 |
| 21.1.07 | 63.5 | 66.5 | 30.6 | 28.8 |
| 22.1.07 | 60.4 | 58.9 | 29.7 | 26.4 |
| 23.1.07 | 60 | 60.1 | 29.2 | 26.8 |
| 24.1.07 | 60.5 | 60.6 | 29.8 | 25.7 |
| 25.1.07 | 60.4 | 58.9 | 29.7 | 26.4 |
| 26.1.07 | 63 | 60.1 | 29.2 | 26.8 |
| 27.1.07 | 62 | 60 | 29 | 25.7 |
| 28.1.07 | 61 | 61.6 | 30.1 | 22.6 |
| 29.1.07 | 60.9 | 58.3 | 30.2 | 27.1 |
| 30.1.07 | 60.1 | 58.8 | 28.9 | 25.9 |
| 31.1.07 | 61 | 61.6 | 30.1 | 22.6 |

Figure 6.5: VS reduction rate of R1 and R2 during the operational period

| | VS reduction, % | |
|---|---|---|
| | R1 | R2 |
| 20.10.06 | 55.3 | 55.6 |
| 23.10.06 | 52.2 | 55.2 |
| 27.10.06 | 55.9 | 59 |
| 30.10.06 | 53.7 | 58.2 |
| 3.11.06 | 52.2 | 57.1 |
| 6.11.06 | 53.2 | 59.8 |
| 10.11.06 | 53.6 | 58.1 |
| 13.11.06 | 53.3 | 59.2 |
| 17.11.06 | 53.5 | 58.7 |
| 20.11.06 | 52.9 | 57.3 |
| 24.11.06 | 53.4 | 58.2 |
| 27.11.06 | 53.7 | 59.1 |
| 1.12.06 | 52.9 | 59.3 |
| 4.12.06 | 53.5 | 59.2 |
| 8.12.06 | 53.3 | 58.9 |
| 11.12.06 | 52.6 | 58.6 |
| 15.12.06 | 53.2 | 58.6 |
| 18.12.06 | 52.6 | 58.8 |
| 22.12.06 | 52.3 | 58.2 |
| 25.12.06 | 51.9 | 56.1 |
| 29.12.06 | 50.1 | 55.1 |
| 1.1.07 | 50.7 | 56.2 |
| 5.1.07 | 50.6 | 53.9 |
| 8.1.07 | 50.8 | 55.8 |
| 12.1.07 | 50.9 | 56.1 |
| 15.1.07 | 51.2 | 55.7 |
| 19.1.07 | 51.3 | 55.9 |
| 22.1.07 | 50.6 | 56.1 |
| 26.1.07 | 50.8 | 55.6 |
| 29.1.07 | 50.2 | 56.2 |
| 31.1.07 | 50.8 | 55.6 |

Figure 6.6: $PO_4$-P, $Mg^{2+}$ reduction and the residual Mg/P molar ratio of R1 effluent

| | $PO_4$-P reduction, mmol/L | $Mg^{2+}$ reduction, mmol/L | residual Mg/P molar ratio |
|---|---|---|---|
| 20.10.06 | 1.55 | 0.375 | 1.2 |
| 27.10.06 | 1.60 | 0.28 | 1.2 |
| 3.11.06 | 1.64 | 0.26 | 1.3 |
| 10.11.06 | 1.71 | 0.19 | 1.3 |
| 17.11.06 | 1.77 | 0.28 | 1.3 |
| 24.11.06 | 1.81 | 0.11 | 1.4 |
| 1.12.06 | 1.80 | 0.32 | 1.3 |
| 8.12.06 | 1.75 | 0.16 | 1.4 |
| 15.12.06 | 1.79 | 0.28 | 1.3 |
| 22.12.06 | 0.58 | 0.26 | 1.3 |
| 29.12.06 | 0.55 | 0.43 | 1.2 |
| 5.1.07 | 0.64 | 0.57 | 1.2 |
| 12.1.07 | 0.81 | 0.62 | 1.3 |
| 19.1.07 | 0.89 | 0.65 | 1.4 |
| 26.1.07 | 0.90 | 0.71 | 1.3 |

Figure 6.7: $PO_4$-P, $Mg^{2+}$ reduction and the residual Mg/P molar ratio of R2 effluent

| | $PO_4$-P reduction, mmol/L | $Mg^{2+}$ reduction, mmol/L | residual Mg/P molar ratio |
|---|---|---|---|
| 20.10.06 | 2.04 | 0.48 | 1.4 |
| 27.10.06 | 1.96 | 0.44 | 1.4 |
| 3.11.06 | 1.99 | 0.45 | 1.4 |
| 10.11.06 | 2.03 | 0.52 | 1.4 |
| 17.11.06 | 2.03 | 0.56 | 1.4 |
| 24.11.06 | 2 | 0.6 | 1.3 |
| 1.12.06 | 2 | 0.52 | 1.4 |
| 8.12.06 | 1.98 | 0.58 | 1.3 |
| 15.12.06 | 2.03 | 0.53 | 1.4 |
| 22.12.06 | 0.75 | 0.51 | 1.3 |
| 29.12.06 | 0.82 | 0.59 | 1.3 |
| 5.1.07 | 0.88 | 0.6 | 1.4 |
| 12.1.07 | 0.87 | 0.77 | 1.3 |

| | | | |
|---|---|---|---|
| 19.1.07 | 0.97 | 0.72 | 1.4 |
| 26.1.07 | 0.97 | 0.74 | 1.4 |

Figure 7.1: Removal efficiency of $NH_4$-N in raw and digested swine manure at different pH value

| pH value | Raw manure, % | Digested manure, % |
|---|---|---|
| 8 | 6.2 | 6.3 |
| 9 | 10.1 | 11.2 |
| 10 | 16.3 | 16.5 |
| 11 | 24 | 24.6 |
| 12 | 33.3 | 32.1 |

Figure 7.2: Removal efficiency of $Ca^{2+}$ in raw and digested swine manure at different pH value

| pH value | Raw manure, % | Digested manure, % |
|---|---|---|
| 8 | 76.8 | 76.9 |
| 9 | 82.3 | 81.3 |
| 10 | 86.7 | 87 |
| 11 | 88.5 | 89.3 |
| 12 | 90.3 | 91.2 |

Figure 7.3: Removal efficiency of $Mg^{2+}$ in raw and digested swine manure at different pH value

| pH value | Raw manure, % | Digested manure, % |
|---|---|---|
| 8 | 3.5 | 6.9 |
| 9 | 85.1 | 85.2 |
| 10 | 83.3 | 88.3 |
| 11 | 89 | 90.5 |
| 12 | 91.9 | 92 |

Figure 7.4: Removal efficiency of $PO_4$-P in raw and digested pig manure at different pH value

| pH value | Raw manure, % | Digested manure, % |
|---|---|---|
| 8 | 72.3 | 73.5 |
| 9 | 87.1 | 91.7 |
| 10 | 88.2 | 90.2 |
| 11 | 65.6 | 76.3 |
| 12 | 9.1 | 15.8 |

Figure 7.6: The effect of Ca/Mg molar ratio on $PO_4$-P removal rate

| pH value | Ca/Mg=0.6 | Ca/Mg=1.3 | Ca/Mg=2.0 |
|---|---|---|---|
| 8.0 | 65.6 | 78.8 | 81.2 |
| 8.2 | 77.6 | 80.5 | 84.3 |
| 8.5 | 85.7 | 85.3 | 86.1 |
| 8.8 | 88.6 | 89.9 | 88.6 |
| 9.0 | 91.6 | 91.3 | 91.5 |
| 9.2 | 91.5 | 91.5 | 91.2 |
| 9.5 | 90.5 | 91.3 | 91.2 |
| 9.8 | 86.6 | 86.3 | 86.9 |
| 10.0 | 86.7 | 86.5 | 86.3 |

Figure 7.7: The change of pH value in homogeneous raw and digested manure by the addition of MgO

| Time, minute | Raw manure | Digested manure |
|---|---|---|
| 0 | 6.95 | 7.76 |
| 2 | 6.96 | 7.86 |
| 4 | 6.98 | 7.96 |
| 6 | 6.99 | 8.01 |
| 8 | 7.06 | 8.09 |
| 10 | 7.16 | 8.17 |
| 12 | 7.38 | 8.28 |
| 14 | 7.62 | 8.38 |
| 16 | 7.93 | 8.47 |
| 18 | 8.15 | 8.55 |
| 20 | 8.3 | 8.6 |
| 22 | 8.4 | 8.7 |

| | | |
|---|---|---|
| 24 | 8.5 | 8.75 |
| 26 | 8.58 | 8.77 |
| 28 | 8.62 | 8.78 |
| 30 | 8.63 | 8.78 |
| 32 | 8.64 | 8.79 |
| 34 | 8.65 | 8.79 |
| 36 | 8.66 | 8.79 |
| 38 | 8.66 | 8.79 |
| 40 | 8.67 | 8.79 |
| 42 | 8.67 | 8.79 |
| 44 | 8.67 | 8.79 |
| 46 | 8.67 | 8.79 |
| 48 | 8.67 | 8.79 |
| 50 | 8.67 | 8.79 |
| 52 | 8.67 | 8.79 |
| 54 | 8.67 | 8.79 |
| 56 | 8.67 | 8.79 |
| 58 | 8.67 | 8.79 |
| 60 | 8.67 | 8.79 |
| 62 | 8.67 | 8.79 |
| 64 | 8.67 | 8.79 |
| 66 | 8.67 | 8.79 |
| 68 | 8.67 | 8.79 |
| 70 | 8.67 | 8.79 |
| 72 | 8.67 | 8.79 |
| 74 | 8.67 | 8.79 |
| 76 | 8.67 | 8.79 |
| 78 | 8.67 | 8.79 |
| 80 | 8.67 | 8.79 |
| 82 | 8.67 | 8.79 |
| 84 | 8.67 | 8.79 |
| 86 | 8.67 | 8.79 |
| 88 | 8.67 | 8.79 |
| 90 | 8.67 | 8.79 |

Figure 7.8: Concentrations of $PO_4$-P, $NH_4$-N, $Mg^{2+}$ and $Ca^{2+}$ in raw pig manure

| | $PO_4$-P, mg/L | $NH_4$-N, mg/L | $Mg^{2+}$, mg/L | $Ca^{2+}$, mg/L |
|---|---|---|---|---|
| t=0 minute | 112.6 | 1260 | 70.8 | 133.2 |
| t=90 minutes | 16.2 | 780 | 68.6 | 25.6 |

Figure 7.9: Concentrations of $PO_4$-P, $NH_4$-N, $Mg^{2+}$ and $Ca^{2+}$ in digested pig manure

| | $PO_4$-P, mg/L | $NH_4$-N, mg/L | $Mg^{2+}$, mg/L | $Ca^{2+}$, mg/L |
|---|---|---|---|---|
| t=0 minute | 48.8 | 1880 | 58.3 | 132.1 |
| t=90 minutes | 18.3 | 1220 | 65.2 | 37.5 |

Figure 7.10: Comparison of $PO_4$-P, $NH_4$-N and $Ca^{2+}$ removal in raw and digested pig manure at 20 ℃ and pH 8.5 by means of MgO supplementation

| | $PO_4$-P, % | $NH_4$-N, % | $Ca^{2+}$, % |
|---|---|---|---|
| Raw manure | 48.8 | 1880 | 132.1 |
| Digested manure | 18.3 | 1220 | 37.5 |

Figure 7.11 $PO_4$-P concentrations in raw manure at various pH values

| Time, minute | pH=8 | pH=9 | pH=10 |
|---|---|---|---|
| 0 | 113.9 | 113.9 | 113.9 |
| 10 | 112.2 | 57.6 | 39.9 |
| 20 | 110.1 | 30.2 | 20.6 |
| 30 | 107.3 | 11.6 | 10.3 |
| 40 | 106.5 | 11.5 | 10.1 |
| 50 | 106.1 | 11 | 9.8 |
| 60 | 105.7 | 10.8 | 9.6 |
| 70 | 105.6 | 10.6 | 9.6 |
| 80 | 105.6 | 10.2 | 9.6 |
| 90 | 105.3 | 10.2 | 9.3 |

Figure 7.12 $PO_4$-P concentrations in digested manure at various pH values

| Time, minute | pH=8 | pH=9 | pH=10 |
|---|---|---|---|
| 0 | 55.6 | 55.6 | 55.6 |
| 10 | 55.5 | 28.7 | 22.5 |
| 20 | 55 | 18.1 | 12.6 |
| 30 | 53.9 | 9.8 | 5.6 |
| 40 | 53.6 | 9.1 | 5.6 |
| 50 | 53.8 | 8.3 | 5.3 |
| 60 | 53.5 | 7.2 | 5.2 |
| 70 | 53.2 | 6.5 | 5.2 |
| 80 | 52.7 | 5.6 | 5 |
| 90 | 52.5 | 5.2 | 4.6 |

Figure 7.13 The effect of the $Mg^{2+}/PO_4$-P molar ratio on $PO_4$-P removal from a high concentration of raw pig manure

| Time, minute | Mg/P=1.0 | Mg/P=1.3 | Mg/P=1.6 |
|---|---|---|---|
| 0 | 110.2 | 110.2 | 110.2 |
| 10 | 73.2 | 47.5 | 35.3 |
| 20 | 36.3 | 26.2 | 20.6 |
| 30 | 20.8 | 12 | 11.1 |
| 40 | 19.5 | 11.8 | 10.8 |
| 50 | 19.2 | 11.5 | 10.8 |
| 60 | 18.8 | 11.3 | 10.8 |
| 70 | 18.3 | 11 | 10.6 |
| 80 | 18 | 10.9 | 10.6 |
| 90 | 17.6 | 10.9 | 10.6 |

Figure 7.14 The effect of the $Mg^{2+}/PO_4$-P molar ratio on $PO_4$-P removal from a low concentration of raw pig manure

| Time, minute | Mg/P=1.0 | Mg/P=1.3 | Mg/P=1.6 |
|---|---|---|---|
| 0 | 55.6 | 55.6 | 55.6 |
| 10 | 42.5 | 28.7 | 22.5 |
| 20 | 26.2 | 18.1 | 12.6 |
| 30 | 13.9 | 7.8 | 5.6 |
| 40 | 13.5 | 7.6 | 5.6 |
| 50 | 12.4 | 7.3 | 5.3 |

| | | | |
|---|---|---|---|
| 60 | 11.6 | 7.2 | 5.2 |
| 70 | 10.9 | 6.5 | 5.2 |
| 80 | 10.5 | 6.5 | 5 |
| 90 | 10.1 | 6.2 | 4.6 |

Figure 8.1: Effect of flocculants addition on removal of phosphorus from treated pig manure

| Time, minute | 0 | 30 | 60 | 120 | 180 | 240 |
|---|---|---|---|---|---|---|
| TP, %<br>with flocculant addition | 0 | 48.3 | 63.5 | 85.8 | 89.8 | 93.6 |
| TP, %<br>natural sedimentation | 0 | 55.8 | 70.8 | 78.9 | 83.7 | 85.7 |
| SP, %<br>with flocculant addition | 0 | 12.3 | 33.5 | 38.8 | 40.6 | 43.9 |
| SP, %<br>natural sedimentation | 0 | 22.6 | 25.2 | 29.2 | 30.4 | 30.6 |

Figure 8.2: Effect of solid concentration on sedimentation of swine manure

| Time, minute | TS=0.5% | TS=1.5% | TS=2.5% | TS=3.5% | TS=4.5% |
|---|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 0 | 0 |
| 30 | 3.2 | 48.3 | 62.8 | 27.3 | 22.8 |
| 60 | 9.1 | 63.5 | 71.8 | 66.5 | 48.5 |
| 120 | 28.7 | 77.8 | 77.9 | 68.8 | 49.2 |
| 180 | 37.3 | 82.8 | 78.7 | 71.6 | 51.3 |
| 240 | 46.1 | 86.1 | 80.3 | 76.9 | 51.8 |