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ADVANCED WASTEWATER TREATMENT

Report No 1.

PHOSPHORUS REMOVAL FROM WASTEWATER
A Literature Review

Stanisław Rybicki

Stockholm 1997

Joint Polish - Swedish Reports

E. Płaza, E. Levlin, B. Hultman
(Editors)

Report
Division of Water Resources Engineering
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PREFACE

This report has been realized as a part of the collaboration between the Technical University of Cracow and the Royal Institute of Technology in Stockholm in the area of wastewater treatment. The collaboration is focused on advanced wastewater treatment and will be presented in a report series.

As a part of this co-operation Stanisław Rybicki had the possibility to stay four months in spring 1992 and one month in July 1996 as a guest researcher at the Royal Institute of Technology. During these visits he studied phosphorus removal from wastewater and it resulted in the literature review presented in this report. Moreover, the work presented in this report was partly utilized in the doctorate thesis presented 24 April 1996 in Cracow with the title "Wpływ wstępnego chemicznego strącania na możliwość biologicznego usuwania fosforu w wielofazowych reaktorach osadu czynnego" ('Influence of Primary Chemical Precipitation on Possibility of Biological Phosphorus Removal in Multi-Phase Activated Sludge Reactors').

Financial support has been obtained as fellowship from the Swedish Institute (SI). Bengt Hultman has written some minor parts in the report and acted as a supervisor. Małgorzata Cimochoicz-Rybicka, Erik Levlin, Elżbieta Płaza and Józef Trela have given valuable comments on the manuscript and have helped in the collection of information to the report.

Stockholm in February 1997

Bengt Hultman
Associate professor

ABSTRACT

The purpose of this report is to give an overview of different methods for phosphorus removal from municipal wastewater. Focus is given to chemical precipitation and enhanced biological phosphorus removal although also other methods are discussed, namely, local treatment methods and ecological and natural treatment systems.

The basic removal mechanisms, process schemes and treatment results are described. In the report, a historical background is also given of phosphorus removal methods and trends in research and process design. Important factors for process design is hereby also treatment requirements for other components in the wastewater and interactions with sludge handling. The need for better evaluation methods of different phosphorus removal processes is pointed out.

Phosphorus may become a limiting substance in the future and phosphorus leakage from deposits may be a diffusive phosphorus source. This has led to an increased interest in phosphorus recovery and reuse. Three main routes are briefly discussed: Improvement of the quality of the sludge from the treatment plants, production of different products from the sludge, and source separation of human wastes from grey water.

ABSTRACT (In Polish)

STRESZCZENIE

Niniejszy raport został wykonany w formie przeglądu różnych metod usuwania fosforu ze ścieków miejskich. Szczególną uwagę zwrócono na strącanie chemiczne oraz nadmiarowe usuwanie biologiczne fosforu jakkolwiek zostały opisane także inne procesy technologiczne np. oczyszczanie w systemach lokalnych oraz wykorzystanie systemów naturalnych i ekologicznych.

W raporcie przedstawiono podstawowe mechanizmy, układy technologiczne oraz wyniki oczyszczania. Pokazano rozwój poszczególnych technologii usuwania fosforu w ujęciu historycznym a także przedstawiono bieżące trendy w pracach badawczych oraz w technologiach stosowanych w praktyce. Czynnikiem o szczególnym znaczeniu przy projektowaniu technologii usuwania fosforu są zarówno wymagania w zakresie usuwania innych składników ścieków jak też interakcje pomiędzy oczyszczaniem ścieków a gospodarką osadową. Wykazano konieczność prowadzenia dalszej oceny różnych procesów usuwania fosforu.

Fosfor może stać się w przyszłości substancją limitującą (rozwój) natomiast przecieki fosforu z miejsc składowania mogą stać się rozproszonym źródłem fosforu. Doprowadziło to do zwiększonego zainteresowania odzyskiwaniem i ponownym wykorzystaniem fosforu. Omówiono trzy zasadnicze drogi dalszego rozwoju:

- podniesienie jakości osadu z oczyszczalni ścieków
- wykonywanie różnych produktów z użyciem osadu oraz
- oddzielenie ścieków będących wydaliniami ludzkimi ze strumienia ścieków bytowych.

TABLE OF CONTENTS

PREFACE	i
ABSTRACT	iii
ABSTRACT (IN POLISH)	iv
TABLE OF CONTENTS	v
1. INTRODUCTION	1
1.1. GENERAL	1
1.2. SOURCES OF THE PHOSPHORUS IN MUNICIPAL WASTEWATER	2
1.2.1. <i>Phosphorus sources and its structure in municipal wastewater</i>	2
1.2.2. <i>Basics of phosphorus source control</i>	4
1.3. PHOSPHORUS COMPOUNDS IN AQUEOUS SOLUTIONS	5
1.3.1. <i>General</i>	5
1.3.2. <i>Phosphorus compounds in water environment</i>	5
1.3.3. <i>Hydrolysis of phosphorus compounds</i>	6
2. PHOSPHORUS REMOVAL - PROCESS SCHEMES	9
2.1. GROUPS OF PROCESS SCHEMES.....	9
2.2. CHEMICAL PHOSPHORUS REMOVAL.....	10
2.3. BIOLOGICAL PHOSPHORUS REMOVAL.....	10
3. PHOSPHORUS REMOVAL BY CHEMICAL PRECIPITATION	13
3.1. PROCESS DEVELOPMENT	13
3.2. PRINCIPLES OF THE PROCESS	15
3.2.1. <i>Performance of the process</i>	15
3.2.2. <i>Chemicals applied</i>	17
3.2.3. <i>Chemistry of phosphorus precipitation</i>	18
3.3. PROCESS CONFIGURATION	22
4. BIOLOGICAL PHOSPHORUS REMOVAL	25
4.1. INTRODUCTION AND PRINCIPLES OF THE PROCESS.....	25
4.1.1. <i>Development of technology</i>	25
4.1.2. <i>Microorganisms involved in the process</i>	27
4.1.3. <i>Biochemical background to the process</i>	28
4.2. PROCESS CONFIGURATIONS AND OPERATIONAL RESULTS.....	31
4.2.1. <i>Mainstream processes</i>	31
4.2.2. <i>Alternating processes</i>	38
4.3. SIDESTREAM PROCESS.....	39
4.3.1. <i>General description of the process</i>	39
4.3.2. <i>Application of the process</i>	39
4.4. INTERMITTENT PROCESS	42
5. MAIN FACTORS AFFECTING PERFORMANCE OF BIOLOGICAL PHOSPHORUS REMOVAL	45
5.1. ANAEROBIC CONDITIONS	45
5.2. PHOSPHORUS CONCENTRATION IN A SECONDARY EFFLUENT.....	45
5.3. COMPOSITION OF INCOMING WASTEWATER.....	46
5.4. AVAILABILITY OF EASILY BIODEGRADABLE CARBON SOURCES.....	46
5.5. SOLIDS DETENTION TIME (SDT, SRT)	49
5.6. DISSOLVED OXYGEN CONCENTRATION	49
5.7. TEMPERATURE.....	49
5.8. PHOSTRIP PROCESS	50
6. COMBINED BIOLOGICAL-CHEMICAL PROCESSES	51

7. ALTERNATIVE PROCESSES OF THE PHOSPHORUS REMOVAL.....	53
7.1. INTRODUCTION	53
7.2. TREATMENT WITH THE USE OF ELECTRICITY - THE CASE STUDY.....	53
7.3. ALTERNATIVE PHOSPHORUS REMOVAL TECHNOLOGIES	55
7.3.1. <i>Chemical and physical-chemical methods</i>	55
7.3.2. <i>Biological phosphorus removal methods (at WWTPs)</i>	57
7.3.3. <i>Phosphorus removal in natural systems</i>	58
8. SLUDGE MANAGEMENT	61
8.1. SLUDGE DERIVED FROM CHEMICAL PHOSPHORUS REMOVAL	61
8.1.1. <i>Aluminium salts</i>	61
8.1.2. <i>Iron salts</i>	63
8.2. SLUDGE DERIVED FROM BIOLOGICAL PHOSPHORUS REMOVAL	64
9. RECENT TRENDS IN INVESTIGATIONS ON PHOSPHORUS REMOVAL TECHNOLOGIES.....	69
9.1. INVESTIGATIONS ON MECHANISMS OF PHOSPHORUS REMOVAL	69
9.2. PHOSPHORUS REMOVAL IN NATURAL TREATMENT SYSTEMS	73
9.3. BIOLOGICAL PHOSPHORUS REMOVAL WITH LIMITED AVAILABILITY OF READILY BIODEGRADABLE CARBON SOURCE.....	75
10. FUTURE DIRECTIONS IN PHOSPHORUS REMOVAL MANAGEMENT	77
10.1. INTRODUCTION	77
10.2. PHOSPHORUS IN DETERGENTS AND AS FOOD ADDITIVES.....	77
10.3. SOURCE CONTROL OF PHOSPHORUS	78
10.4. IMPROVED WASTEWATER TREATMENT.....	79
10.5. DIVERSION OF WASTEWATER STREAMS.....	79
10.6. IMPROVED SLUDGE HANDLING MANAGEMENT	80
11. CONCLUSIONS	83
REFERENCES.....	87

PHOSPHORUS REMOVAL FROM WASTEWATER

A Literature Review

1. Introduction

1.1. General

Surface waters contain certain level of phosphorus in various compounds, which is an important constituent of living organisms. In natural conditions the phosphorus concentration in water is balanced i.e. accessible mass of this constituent is close to the requirements of the ecological system. When the input of phosphorus to waters is higher than it can be assimilated by a population of living organisms the problem of excess phosphorus content occurs.

The excess content of phosphorus in receiving waters leads to extensive algae growth (eutrophication). The phenomenon of eutrophication usually decreases the water quality and as a result it may increase significantly the cost of water treatment at treatment plants for surface water. The load of phosphorus discharged to receiving waters comes from various groups of sources of which the main sources are agricultural use of fertilizers, domestic and industrial wastewater, and atmospheric deposition. Reduction of runoff from agricultural usage of land and atmospheric deposition are complex problems better solved by economical and technical means rather than technically. The subject of this presentation is the removal of phosphorus from wastewater because in developed regions the major phosphorus input on receiving waters comes from municipal wastewater.

Numerous compendia, review papers and state-of-arts on phosphorus removal in various aspects have been published in the past (*Nesbitt 1966, Convery 1970, Jenkins et al. 1971, Hultman 1980, Marshal 1990, Sedlak 1991, Randall et al. 1992, Barker & Dold 1996, Ødegaard 1993, Henze et al. 1995*) and on chemical precipitation (*Hahn 1987, Hultman & Balmér 1988, Henze et al. 1995*). Several Nordic dissertations give a good overview on different aspects of phosphorus

removal (*Aspegren 1995, Brattebø 1983, Carlsson 1996, Hanaeus 1991, Hellström 1996, Johansson 1994, Lee 1996, Lie 1996, Nilsson 1990 and Nyberg et al 1994*).

1.2. Sources of the phosphorus in municipal wastewater

1.2.1. Phosphorus sources and its structure in municipal wastewater

Domestic wastewater is the dominating source of phosphorus in municipal discharges in densely populated regions. As presented by *van Starckenburg & Rijs (1988)* in the Netherlands 18 million tons per year of phosphate phosphorus comes from domestic wastewater while only 4.2 million tons per year comes from industrial discharges. This results in a proportion of domestic vs. total of 75%. Similar calculations for Krakow (Poland) showed that as much as 85% of the total phosphorus load comes from domestic sources (*Rybicki 1996*).

The main sources of phosphorus in municipal wastewater appear to be excreta and detergents. *Alexander & Stevens (1976)* measured the total phosphorus content in wastewater collected from a Northern Ireland city and then calculated the total per capita phosphorus value (discharge) as 1.8 g P/cap*d. These authors also surveyed results obtained in various countries and showed that the phosphorus content in excreta and non-detergent household wastes varied between 1.0 and 1.6 g P/cap*d (average approx. 1.4 g P/d*cap).

More complex appears to be the problem of phosphorus coming from detergents because the structure of their use has a tendency to vary in different countries. *Alexander & Stevens* found that the phosphorus input from detergents was between 1.5 and 3.0 g P/cap*d while *Balmér & Hultman (1988)* showed that this value varied within the range of 0.65 - 2.0 g P/cap*d. This difference was probably caused by partial replacement of phosphorus-containing detergents with phosphate-free substitutes in the late 70's. Design manuals from early 80's (*WPCF 1983*) showed as a typical values for domestic wastewater 2.1 to 4.9 g P/cap*day of total P consisting of 0.8 to 1.6 g P/cap*day of organic and 1.3 to 3.3 g P/cap*day of inorganic compounds.

Published data concerning detergents as a phosphorus source tend to decrease with time. In 70's total input of detergents to total load of phosphorus in domestic wastewater was estimated as 1.5 to 3.0 g P/cap*day (Alexander & Stevens 1976). Data from the 80's showed the visible decrease of this unit load down to 0.65 - 1.0 g P/cap*day (Boller 1987, Balmér&Hultman 1988).

The phosphorus concentration in raw municipal wastewater tends to change due to life style (e.g. nutrition), urbanization, industrial development (e.g. washing powders usage). A general increase was observed while the average phosphorus concentrations in raw wastewater varied in the 1940's between 2 to 4 mg P/L. During the following two decades it increased to 10 to 15 mg P/L (Summary report 1982). Then concentrations started to decrease.

Numerous authors use to present table set by Jenkins *et al.* (1971) to show a structure of phosphorus compounds in municipal wastewater. Jenkins & Hermanowicz (1991) completed a revision of this table which showed an influence of changes in phosphorus unit load on the structure of phosphorus compounds. Extraction of these tables are presented below. A comparison of data from 1971 and 1991 shows a decrease of a total phosphorus content in raw wastewater. Most authors agree that orthophosphates are dominating over other phosphorus compounds in domestic (municipal) wastewater:

Table 1.1.		
Phosphorus compound structure in domestic wastewater		
Phosphorus compound group	<i>Jenkins</i> 1971	<i>Jenkins & Hermanowicz</i> 1991
	ppm (mg P/L)	ppm (mg P/L)
Orthophosphates	5	3 - 4
Tripolyphosphates	3	2 - 3
Pyrophosphates	1	(tripoly- and pyro- together)
Organic phosphates	<1	1
Total phosphorus	<10	<7

1.2.2. Basics of phosphorus source control

A “control at source” approach has been successfully applied for phosphorus. Detergents are sources of municipal phosphorus discharge which can be relatively easy controlled and limited. The main user of detergents are households. In the United States in the 1970’s 80.6 % of detergent phosphorus came from household while 17.4% came from commercial/industrial usage (2% unclassified). The main phosphate-containing constituent of washing powder is a sodium tripolyphosphate (STPP) - approx. 90% of phosphate detergent mass in the United States (*Porcella & Bishop 1976*). To eliminate or significantly reduce this source of contamination several STPP substitutes have been proposed e.g. nitriloacetic acid (NTA), zeolites, unsaturated sulphonated organic acids etc. (*Wentzel 1991*).

In Switzerland, a country which had experienced significant problems with eutrophication of lakes, the government decided to first reduce and then prohibit the usage of phosphorus-containing detergents in the 80’s. This resulted in a visible decrease of phosphorus in the effluent of municipal wastewater treatment plants. Phosphorus content measured as P/BOD₅ fraction in primary effluent has been reduced by 30 % using these methods (*Boller 1987*). Parallely several state authorities in the United States issued phosphate bans in 1970’s and 1980’s (*Balmér & Hultman 1988*).

These methods of phosphorus elimination occurred to be not as simple as it had been recognized previously because of :

- the environmental impact of STPP substitutes is not known yet;
- the ecological safety of NTA is still being discussed as this compound cannot be fully removed in biological treatment plants;
- substitutes give decreasing washing performance and may reduce machine and clothing life (*Wentzel 1991*).

Finally the total abandonment of phosphorus-containing detergents may lead to 30-40% reduction of total phosphorus in municipal wastewater, while remaining 60-70% of total phosphorus is to be reduced at the wastewater treatment plants.

Various methods of phosphorus removal are presented in this paper. A focus is given on chemical and biological removal techniques. Newly developed and rarely used

methods are also presented. Those methods of treatment in which phosphorus removal occurs but not as a principal objective are omitted.

1.3. Phosphorus compounds in aqueous solutions

1.3.1. General

Various authors studied the chemistry of phosphorus compounds in aqueous solutions. Most work was done in the 60's and 70's as a theoretical support for chemical precipitation of phosphorus compounds. Despite books and papers focused on phosphorus as a chemical compound (e.g. *Corbridge 1966, 1977, 1995*) some authors focused on the fate of these compounds with a special emphasis on water and wastewater treatment. Fundamental works were done by Stumm & Morgan (*Morgan 1962, Stumm & Morgan 1970, Shen & Morgan 1988*). These works were followed by numerous other papers e.g.: *Snoeyink (1970), Jenkins et al. (1971), Goldsmith & Rubin (1980) and Johnson & Armitrajach (1984)*.

1.3.2. Phosphorus compounds in water environment

As stated above the following groups of phosphorus compounds are of great importance in wastewater:

- organic phosphates (with -P-O-C- bonds), usually constituents of dissolved and suspended compounds of wastewater. Their input to total phosphorus is estimated as approx. 4%, mostly from plasticizers for plastics or pesticides. In a water environment these compounds are degraded chemically and/or biologically to orthophosphates. Forms of compounds: parts of cell walls <phospholipides>, phosphoramides, toxic phosphate esters, phosphor-organic insecticides
- condensed inorganic phosphates (with -P-O-P- bonds), including both chain-bonded polyphosphates and cyclic-bonded metaphosphates. Polyphosphates being basic constituents of detergents and water softeners are the most common inorganic condensed polyphosphates in municipal wastewater

- inorganic orthophosphates PO_4^{3-} ions.

1.3.3. Hydrolysis of phosphorus compounds

Phosphates in raw and domestic wastewater usually occur in dissolved form. Theoretical works on kinetics of reactions of these compounds with water have been conducted since the mid 19th century (*Reynoso 1852*). The issue was also examined by *Jenkins et al. (1971)*, *Stumm & Morgan (1979)* and *Shen & Morgan (1988)*. They confirmed that both phosphoric acid anions and most common polyphosphates dissociate easily in water. *Jenkins et al. (1971)* presented a diagram of changes in molar concentration of P compounds vs. pH for inorganic compounds.

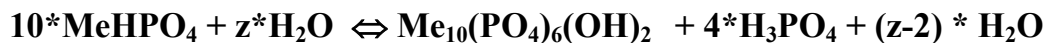
According to these authors a representative constitution (by molar concentration) of municipal wastewater for specific groups of phosphorus compounds is as follows:

◇ total phosphates	$3.0 \cdot 10^{-4}$ mole/L
◇ orthophosphates	$1.5 \cdot 10^{-4}$ mole/L
◇ pyrophosphates	$1.8 \cdot 10^{-4}$ mole/L
◇ tripolyphosphates	$3.8 \cdot 10^{-4}$ mole/L

⇒ Hydrolysis of orthophosphates by *Stumm & Morgan (1970)* and *Shen & Morgan (1988)*: The authors found that phase equilibrium of most inorganic phosphates prefers hydrolytic disproportion of orthophosphates to non-defined complexes whose constituents tend to change depending on pH, temperature and presence of other cations in aqueous solution. An equation of hydrolysis for orthophosphate of a bivalent (e.g. calcium hydroxyapatite) metal is exemplified below:



and



⇒ Hydrolysis of low-weight polyphosphates according to *Stumm & Morgan (1979)* and *Shen & Morgan (1988)* shows that bonds type P-O-P are broken and this

process does not cause cyclic metaphosphates while in highly diluted water solutions, during most of the process, first order reactions takes place on conditions of constant pH. At higher concentrations some authors, *Griffith & Baxton (1967)*, and *Stumm & Morgan (1970)* have suggested that hydrolysis performs in another way - for example by division of tetrakisphosphate into two pyrophosphates. *Shen & Morgan (1988)* presented changes in values of reaction constants for a sodium polyphosphate vs. pH value (at constant 333 °K temperature). Hydrolysis constants for octa-, hepta- and hexa- phosphates slowly increase as pH increases from pH 4.0 to pH 7.0-7.4 and then decrease. For penta-, tetra-, tri- and pyrophosphates a value of the constant decreases as the pH value increases. These authors also stated that enzymatic hydrolysis of chain or cyclic phosphates may be up to 10^6 times faster than the same reaction without enzymes present. Many microorganisms are able to convert simple orthophosphate into at least four kinds of polyphosphates which play important roles in the process of phosphorus metabolism in aqueous organisms (algae).

⇒ Hydrolysis of chain high-weight polyphosphates according to *Griffith & Baxton (1967)* and *Stumm & Morgan (1970)* takes part in four stages :

- * hydrolysis inside of a chain to create shorter chain;
 - * disconnection of one end of the chain creating an orthophosphate and a polyphosphate but one P atom shorter;
 - * disconnection of one trimetaphosphate from one of the ends of the chain,
 - * disconnection of one trimetaphosphate from the inside of the chain,
- so three reaction constants are applied in reaction considerations:

k_{it}	-	general constant
k_e	-	phosphate formation constant
k_m	-	trimetaphosphate formation constant

A kinetic equation can be expressed as follows :

$$-dc/dt = k_t * C = (k_e + k_m) * C$$

where C = phosphorus concentration

⇒ hydrolysis of cyclic metaphosphates in general leads to division into tripoly- and tetrapoly- phosphates, polyphosphates coming from large cyclic metaphosphates tend to disconnect into simple lower level orthophosphates. This process is slowest within a pH range from pH 6 to pH 10, i.e. at the natural pH level of municipal wastewater;

⇒ hydrolysis of organic phosphorus compounds is preceded by oxidation or isomerisation of sulfur-containing phosphorus compounds. From this group, frequent in waters, comes sulfur-containing insecticides which are very easily hydrolyzed in base solutions.

2. Phosphorus removal - process schemes

The general purpose of phosphorus removal is to eliminate the excess phosphorus content from wastewater discharged to receiving waters and then to utilize this excluded phosphorus load in the way which is the most proper for the natural phosphorus cycle in nature. This policy should prevent surface waters against eutrophication-related problems.

Between the 1850's and the 1940's the main goals of wastewater treatment were organic matter and suspended solids removal. The nutrient removal occurred unintentionally. Some discussions on prevention against eutrophication of lakes led to early studies on phosphorus removal (*Sawyer 1944, Rudolfs 1947, Lea et al. 1954*).

Phosphorus is present in wastewater usually in soluble form. Only about 15% of total phosphorus contained in settleable particles may be removed by primary sedimentation with no metal salt addition (*Balmér & Hultman 1988*). Due to this fact traditional removal methods are based on the transfer of soluble phosphorus to a solid phase and complemented by solid-liquid separation. The transfer to a solid phase may be performed in the following ways:

- ◆ chemical precipitation and adsorption of phosphorus by trivalent metal salt addition;
- ◆ biological in two general ways :
 - ◇ uptake due to nonexchangeable phosphorus
 - or/and
 - ◇ enhanced uptake by bacteria.
- ◆ ion exchange and adsorption.

2.1. Groups of process schemes

According to the principles of removing phosphorus from wastewater, methods of removal may be divided into three groups:

- chemical

- biological
- combined.

No sharp limits exist between these methods as it was observed that even during biological enhanced phosphorus removal a significant part of the compound was being chemically precipitated by an action of metal ions which were natural constituents of the wastewater.

2.2. Chemical phosphorus removal

Chemical phosphorus removal, called also "removal by a salt addition" (EPA 1987), can be applied as:

- direct precipitation
- pre-precipitation
- simultaneous precipitation
- post - precipitation

Sometimes in one plant metal salts are added in different points resulting in two or more kinds of precipitation at the plant.

2.3. Biological phosphorus removal

Arvin (1984) divided biological phosphorus removal plants into groups, according to their possibility of nitrogen removal. A flow diagram of the plant is as follows:

- plants without a nitrogen removal: recirculation processes
 sidestream processes
- plants with nitrogen removal: recirculation processes
 alternating processes.

Similar systematics was presented by numerous authors as *Boller (1987)* and *Balmér & Hultman (1988)*. Due to the fact that Sequencing Batch Reactors (SBR) techniques have been applied successfully for phosphorus removal (*Manning & Irvine 1985*,

Ketchum et al. 1987, Goronszy & Riegel 1991) the mainstream processes reactors may be divided into two groups:

- * continuous flow reactors (plants)
- * intermittent flow reactors.

Phosphorus removal by chemical precipitation is at present the best known process of those mentioned above and is widely used despite its relatively high costs. During recent years progress has been made to understand the mechanisms of biological phosphorus removal and to develop the design procedures. Lack of proper mathematical models of the process, however, makes application of biological phosphorus removal difficult without primary laboratory investigations.

3. Phosphorus removal by chemical precipitation

3.1. Process development

In the past - until the middle of the 19th Century (*Sidwick & Murray 1976*) the only wastewater handling technologies were discharge to open water through a open gutter or a land disposal. When applied for small communities both technologies were effective but when used to serve large communities they could endanger sanitary safety of citizens.

Well documented is the beginning of modern wastewater management in the United Kingdom (*Sidwick & Murray 1976*). In the 1830's a British Royal Commission was established which emphasized a necessity of integration of sewerage system to avoid water borne epidemic diseases. In 1867 the Sewerage Commission was appointed and suggested continuous land disposal of town sewage to avoid pollution of rivers. The Public Health Act dated 1876 prohibited the passage of sewage into streams ¹. In 1884 the last Sewage Commission was appointed and stated that a certain part of the organic matter should be removed by chemical precipitation. It was obvious at the time that while precipitation was directed towards organic matter removal nutrient removal also occurred unintentionally. What is interesting is both fill-and-draw (an SBR predecessor to some extent) and final filtration with the use of biological filters were applied at that time which technologies described as *New techniques* in chapter 6 of this review.²

Basic chemicals for precipitation were lime alone or lime in conjunction with alum, ferric sulfate, burnt magnesia or animal charcoal, ferric (orig. iron) chloride (*Wardle 1893, Dunbar 1908 <via Report of the Committee...> 1935, Wakeford 1911*)). Precipitation of phosphorus by addition of lime and alum in advanced wastewater treatment technology and different methods to recover aluminium and lime has been described by *Culp and Culp (1971)*. *Kershaw in 1911* mentioned most common precipitants applied in Great Britain including:

¹ It was reported however that it had been very difficult to execute

² Also possibilities of technologies leading to activated sludge technologies and sludge digestion were successfully examined.

- lime
- alumino-ferric
- ferric sulphate
- sulphuric acid
- ferrozone
- lime and ferrous sulphate
- ABC process³
- lime chlorine

Most of these chemicals have been proven to precipitate phosphorus and are in use even today. Until the 1960's chemical addition was used for organic matter (expressed by BOD) and suspended solids removal (*Report of Committee on Sewage Disposal 1935, Streander 1937*).

At that time the role of phosphorus was not fully recognized. Thus in 1918 treatment of sludge by addition of a phosphorus compound (phosphorus acid) was patented (*Report of Committee on Sewage Disposal 1935*).

Since the 1960's major efforts have been made towards phosphorus removal. Initially chemical precipitation technologies were applied in routine operation (*EPA 1967, Convery 1970, Jenkins 1971, Wiechers 1979, Summary Report 1982*). The first application intended for phosphorus removal in routine operational scale took place in Switzerland in the sixties where primary precipitation was applied (*Stumm 1962, Boller 1987, Boller 1993*) and in Scandinavian countries where it was applied in both as primary and simultaneous precipitation (*Balmér & Hultman 1988, Arvin 1983, Antelius 1991*). Final precipitation after a biological treatment stage was reported in 1966 at the Lake Tahoe WWTP (*EPA 1987*)

³ Alumin-ferric + blood + charcoal + clay

3.2. Principles of the process

3.2.1. Performance of the process

In a phosphorus removal process a precipitation process dominates while minor roles are played by coagulation and adsorption. Transformation of phosphorus ions into the solid state takes place in three stages. According to *Shen & Morgan (1988)* and *Stumm & Morgan (1970)* these stages are:

- core formation of a solid matter
- storage of a precipitate and start of crystal growing
- crystal maturation

As was stated in paragraph 2 of this paper orthophosphates are the most common group of phosphorus compounds and theoretical papers mostly focus on these compounds⁴.

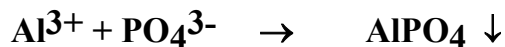
Trivalent metal salts are used for removal of phosphorus from municipal wastewater. The most common are:

- ◆ aluminum sulfate,
- ◆ ferric chloride,
- ◆ ferrous(bivalent) and ferric sulfates.

Lime which previously was one of the main chemicals used for phosphorus removal (*EPA 1976*), now plays only a minor role. This change is due to, a substantial increase in the sludge mass, and problems with maintenance and operation of lime handling and dosage facilities (*Hruschka 1980*).

Precipitants mentioned above: Fe(III), Fe(II), Al(III) and Ca salts form in the presence of aqueous solutions of orthophosphates precipitates. The following equations represent the reactions of precipitation (*Arvin 1983, 1989*):

Aluminum ions combine with phosphate ions as shown by reaction:

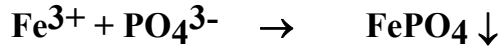


so the weight ratio of the reaction is 0.87 : 1 of Al to P.

⁴ Some works considering other groups showed that condensed phosphates are more difficult to remove than orthophosphates (*Stumm & Morgan 1970, Jenkins et al. 1971*).

On the other side *Jenkins et al. 1971 and Goldsmith & Rubin 1980* stated that polyphosphates can be precipitated with metal ions at Me:P ratio ≈ 1 .

The reaction of ferric ions can be illustrated by:



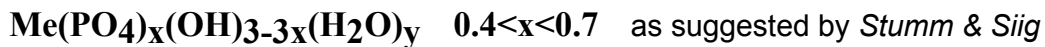
The stoichiometric weight ratio of this reaction is 1.8:1.

There is no specific chemical content structure of a precipitate. Usually the simplified form of FePO_4 or AlPO_4 are used in papers. Empirical tests summarized by (*Sedlak 1991*) allow the assumption that actual content differs from these simplified equations and the following empirical formula is proposed:



According to *Jenkins&Hermanowicz via Sedlak (1991)* the value for a stoichiometric coefficient differs depending on the metal salt. For aluminum salts $r(\text{Al}^{3+}) = 0.8$ while $r(\text{Fe}^{3+}) = 1.6$. Possible diversions from these values are explained by some authors by the effect of ion adsorption on the surface of a precipitated phase.

Another proposal for the real conditions of precipitation of municipal wastewater was presented by *Boller (1987)*: iron and aluminum salts are transformed to basic metal-hydroxy-phosphate complexes of the form presented below:



or



Real structure and solubility of these compounds are not known but their stoichiometry indicates that to achieve a low level of dissolved phosphorus compounds, the metal ions should be present in excess relative to phosphorus ion concentration. *EPA Design Manual (1976)* suggests that 20% excess of aluminum ions (by weight) is necessary if 80% reduction of phosphorus is desired while 100% excess is recommended for 95% P removal.

3.2.2. Chemicals applied

For routine use the following chemicals are widely applied:

Lime

⇒ lime $\langle \text{CaO}, \text{Ca(OH)}_2 \rangle$: recently more common due to low cost and low problems with sludge dewatering (EPA 1976); plays minor role as a auxiliary chemical for pH adjustment often replaced by relatively less expensive alum- and iron-salts;

Iron salts

⇒ ferric chloride $\langle \text{FeCl}_3 \rangle$: usually produced by oxidation of ferrous oxide with the use of hydrochloric acid supplied as a liquid;

⇒ ferric sulfate $\langle \text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O} \rangle$ supplied as a bulk or liquid, produced by oxidation of copperas (ferrous sulfate) or illmenite⁵

⇒ another iron salt widely used for precipitation of phosphorus is a ferrous sulfate $\langle \text{FeSO}_4 \cdot 7\text{H}_2\text{O} \rangle$, usually known as copperas. It is a cheap by-product in the steel industry which can be successfully applied in simultaneous precipitation processes.

Aluminum salts

⇒ widely used mostly for water treatment purpose is alum i.e. aluminum sulfate $\langle \text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O} \rangle$; Farrell et al (1968) has studied the recovery of aluminium from sludge with precipitated aluminium phosphate by use of the addition of lime or a combined process with the addition of lime and sodium hydroxide in order to reduce the high cost of using aluminium salt. A waste material formed by leaching bauxite during production of aluminium, red mud, can together with sulphuric acid be manufactured into a precipitation agent for phosphorus removal (Shanon & Verghese 1976).

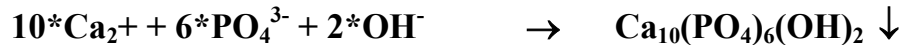
⁵ In-site technology of tri-valent iron salt production was formerly applied at wastewater treatment plants. This was oxidation of a copperas (ferrous sulphate) with the use of a hydrochloric acid. Mixture of ferric sulphate and ferric chloride may be applied as a precipitant.

3.2.3. Chemistry of phosphorus precipitation

3.2.3.1. Precipitation with lime

An application of lime was described in detail by *Jenkins et (1971)* and by *EPA (1967)*. A lime <calcium hydroxide $\text{Ca}(\text{OH})_2$ > has relatively low purchase costs but its disadvantages are low solubility in water (1.65 g/L at 20 ° C) which is 220 lower than alum's and 550 lower than ferric chloride's solubility. *Kurbiel & Rybicki (1989)* described an application of this chemical for pH adjustment during chemical precipitation with ferrous sulfate. Lime is also applied in sidestream technologies described later in this report.

A simplified reaction of precipitation of phosphates with lime is expressed as:



Fergusson & McCarthy (1970) explained that both the creation of crystals and wastewater content are of great influence on calcium phosphate formation. They also stated that it was found the presence of H^+ , HCO_3^- , Mg^{2+} and F^- ions may impact the solid phase content of precipitated phosphates. At pH values typical for municipal wastewater i.e. pH 7.5 - pH 8.5 the dominating precipitate is calcium phosphate (hydroxyapatite). This information was also presented by *Jenkins et al. (1971)*. Presence of magnesium ions may lead to precipitation of beta-tricalciumphosphate instead of an apatite and magnesium-calcium phosphate instead of calcium carbonate. It may also cause an increase of phosphate solubility in wastewater at pH 9.0.

3.2.3.2. Precipitation with iron salts

Two unit processes should be considered while discussing precipitation with lime:

- hydrolysis of iron compounds
- precipitation of phosphorus compounds.

A hydrolysis of trivalent iron compounds (ferric) was described by *Stumm (1962)*, *Stumm & Morgan (1970)*, *Snoeyink (1970)*, *Snoeyink & Jenkins (1980)*, *Fergusson & McCarthy (1970)* and *Johnson & Armitrajach (1984)*.

In general simple compounds such as Fe^{3+} never occur in water under natural conditions. These ions are present in complexes as $\text{Fe}(\text{H}_2\text{O})_6^{3+}$. Addition of trivalent iron salts to water in concentrations lower than the limit of solubility causes formation of soluble hydroxymetal complexes. *Snoeyink & Jenkins (1980)* stated that hydroxy-complexes and products of trivalent iron ions play important roles in the solubility of these ions. These authors calculated equilibria equations for specific trivalent iron compounds. Finally they presented equilibria diagrams showing that at pH values typical for municipal wastewater the solubility of $\text{Fe}(\text{OH})_3$ is low and reaches its minimum (i.e. 10^{-6} mole/L) at pH 8.0.

Hydrolysis of bivalent (ferrous) compounds was examined by *Stumm (1962)*, *Stumm & Morgan (1970)*, *Snoeyink (1970)* and *Snoeyink & Jenkins (1980)*. These authors found that in neutral or basic water with a high concentration of ferrous compounds there may occur precipitation of ferrous hydroxide ($\text{Fe}(\text{OH})_2$). Equilibria diagrams prepared for the hydrolysis of Fe^{2+} compounds leads to the conclusion that ferrous hydroxide reaches its lowest solubility at pH 12. This pH value is not typical of municipal wastewater. At typical pH values of pH 7.0 the dominating forms of ferrous compounds would be ions of Fe^{2+} . To obtain insoluble $\text{Fe}(\text{OH})_2$ in treated wastewater it is necessary to adjust the pH to 9.0⁶. Another factor makes theoretical description of this process difficult to be done precisely. It is possible for ferrous (Fe^{2+}) ions to form ferric (Fe^{3+}). This problem was mentioned by *Stumm (1962)* and *Jenkins et al. (1970)*. The rate of oxidation at pH 5.5 is described by an equation:

$$- \frac{d[\text{Fe}^{2+}]}{dt} = K * [\text{Fe}^{2+}] * [\text{OH}^-] * p\text{O}_2$$

where: K - rate constant
 $[\text{Fe}^{2+}]$ - molar concentration of ferrous ions
 $[\text{OH}^-]$ - molar concentration of hydroxy ions
 $p\text{O}_2$ - partial pressure of oxygen

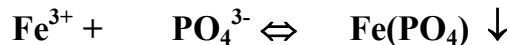
This equation shows the rate of oxidation depends mainly on pH of the environment.

Precipitation of phosphorus compounds by ferric and ferrous salts This problem was described widely at first by *Stumm (1962)*, *Stumm & Morgan (1970)*,

⁶ At pH 9.0 solubility of $\text{Fe}(\text{OH})_2$ is approx $2 \cdot 10^{-5}$ mole/L.

Snoeyink (1970) and *Jenkins et al. (1971)*. All authors consider that it is difficult to describe this process as both ferric and ferrous ions may create stable compounds with phosphorus at pH values and concentration levels typical for municipal wastewater. Comparing it to precipitation with alum, *Stumm (1962, 1979)* found the solubility of FePO₄ is 10 times higher than that of AlPO₄. Minimum solubility of FePO₄ occurs at pH 5. Ferric ions create strong complexes with pyro- and tripoli-phosphates. In a process of phosphorus precipitation in raw wastewater these complexes can be absorbed at ferric hydroxyphosphates surfaces. Competition between hydroxy ions and phosphates for ferric ions when ferric salt ions are added causes a situation where the actual dose of ferric salts is higher than calculated by stoichiometric equations. Another factor increasing ferric salt consumption is the use of some part of these ions for destabilization of colloids.

Reactions in hydrolysis and precipitation of phosphorus compounds (as represented by phosphates) reacting with trivalent iron salts can be summarized as in following equation:



Molar Fe:P ratio is equal to 1:1 so weight ratio Fe³⁺ : P = 1.8:1. In actual practice the weight ratio applied is actually from (3 - 5):1.

Chemical equations for precipitation with bivalent iron salts are usually simplified to⁷:



Molar Fe:P ratio is equal to 1.5:1 therefore weight ratio Fe²⁺ : P = 3.6:1. In actual practice the weight ratio applied is actually from (3 - 5):1.

For simultaneous precipitation, i.e. when parallel with precipitation oxidation of bivalent to trivalent iron takes place, the summarized reaction for ferrous ions may be expressed as follows:

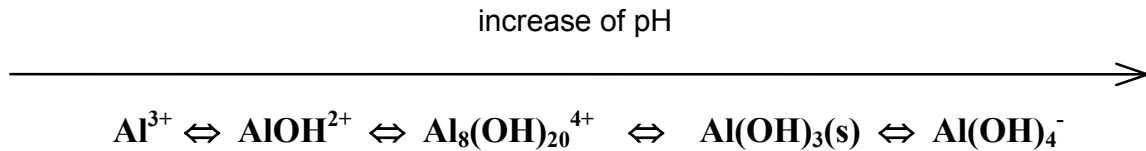


⁷ Assuming that a reaction of ferrous ions with phosphates before oxidation can be generalized by a following equation : $3 * \text{Fe}^{2+} + 2 * \text{PO}_4^{3-} \Leftrightarrow \text{Fe}_3(\text{PO}_4)_2 \downarrow$

According to this equation the Fe:P ratio equals to 1:1 while the weight ratio is 1.8:1.

3.2.3.3. Precipitation of phosphorus with aluminum sulfate

A precipitation of phosphorus compounds by aluminum sulfate is described by numerous authors including *Stumm & Morgan (1970)*, *Jenkins et al. (1971)*, *Goldsmith & Rubin (1980)*, *Johnson & Armitrajah (1994)*, *Sedlak (1991)* and *Boller (1993)*. Much like the iron salts previously described the process consists of hydrolysis and precipitation. Existence of specific aluminum compounds may be generalized depending on pH. With increase of pH it will change as follows:



Within pH ranges typical for municipal wastewater aluminum ions create soluble hydroxy complexes and low soluble $\text{Al}(\text{OH})_3$. Equilibrium equations for aluminum were presented by listed author similarly to those for iron salts. An assumption was made that AlPO_4 is the only compound of precipitated phosphates. According to these equations the lowest solubility of aluminum phosphate⁸ is achieved at pH 5.5. Stoichiometric Al : P ratio is 1 : 1 (by moles).

In real terms necessary alum dose varies from calculated values.

Necessary alum dose may increase compared with calculated values due to the following factors:

- + According to *Jenkins et al (1971)* some of the added Al ions react with phosphate ions while others react with hydroxy ions. It is therefore necessary to add Al salts in quantities larger than molar ratio Al:P = 1:1. By this author minimum real ratio is (5 to 3): 1,
- + In functional terms alum also reacts with other constituents of wastewater as well as serving to coagulate micropollutants and colloids present in wastewater,

⁸ this solubility is approx. 0.09 mg/L i.e. 10^{-6} mole/L

Decrease of an alum dose might be caused by :

- sorption of phosphates on surfaces of aluminum hydroxides,
- precipitation of phosphorus compounds by metal ions present in municipal wastewater (described later).

3.3. *Process configuration*

Chemical precipitation process configuration is divided by groups according to dosage point and way of reaction. Basic process configurations are as following:

Direct Precipitation - involves no further biological treatment.

Process in which the precipitant is applied before the primary settling tank. This concept is usually applied when the receiver can adopt relatively high concentrations of carbonaceous matter and nitrogen compounds but because of the risk of eutrophication highly effective phosphorus removal is necessary (e.g. plants discharging their effluent to the sea). *Boller (1987)* suggests all of the mentioned chemicals except Fe^{2+} salts can be used for this process.

Several wastewater treatment plants based on this technique are operating in Norway with the largest Oslo plant having a capacity of $3 \text{ m}^3/\text{s}$. In the year 1977 138 of 760 Swedish treatment plants used this method and had 0.70 g P/m^3 average effluent concentration.

Pre-precipitation - process preceding further biological treatment. Its scheme consists of the addition of salts followed by rapid mixing, flocculation, and (primary) sedimentation. Anionic polymers are sometimes added before flocculation to enhance solids separation. Strong base is also added between addition of ferrous iron and a polymer to counteract the depression of pH. Pre-precipitation is widely used in northern countries.

In 1983 28% of 370 wastewater treatment plants in Norway applied this process (*Boller 1987*). 21 of 102 (i.e. 20%) of the biggest treatment plants in Norway, as reported by *Ødegaard (1988)*, used chemicals during the pre-precipitation step. Results of *EPA (1987)* research in the Great Lakes Area showed that 38% of plants

in this region used pre-precipitation. Operational results of this method showed an average of 90% removal of total phosphorus along with approximately 80% removal of BOD₅ and suspended solids can be obtained. For the 90% of wastewater treatment plants reviewed by *Ødegaard (1988)* the phosphorus concentration after pre-precipitation was below 1.0 g P/m³. *Rebhun et al. (1978)* reported reduction of phosphorus from 28.0 to 0.8 g PO₄/m³. *Mäkelä (1985)* achieved 80% of P removal using pre-precipitation and achieved a final concentration of phosphorus as low as 0.2 g P/m³. Careful operation can lead to final concentrations as low as 0.1 g P/m³.

Simultaneous Precipitation - precipitating salts are added to the inlet of the aeration basin or directly to the basin.

This alternative has a good flexibility with respect to chemical addition. This allows the choice of the proper dosage point to create best available conditions for coagulation and flocculation. The dosage point has a tendency to vary depending on the choice of chemicals, velocity gradients in the basin, and wastewater characteristics. The disadvantage of this method is that velocity gradients and turbulence levels are far from ideal conditions for rapid mixing and flocculation processes. This method is widely used in Switzerland (94% of plants in 1983), Finland (73% in 1980) and Germany (49% in 1980). An *EPA (1987)* review of different types of activated sludge plants with simultaneous precipitation applied showed that in all but one case (of 14) the effluent concentration was below 1.0 g P/m³, with a best achieved result of 0.29 g P/m³. Metal ion to phosphate weight ratio varied between 0.42 to 4.05.

In most countries the easy use of ferrous sulfate was credited as a great advantage. *Seyfried et al (1988)*, however, showed the application of a ferrous sulfate is an inhibiting factor to *Nitrosomonas* bacteria. This is a disadvantage of this method for those plants where nitrogen removal is to be achieved. Application of FeSO₄ with doses over 20 g Fe/m³ resulted in a slowing down of nitrification by 20 %. Alum, on the other hand, did not create any problems while ferric and ferrous chlorides caused activation of *Nitrosomonas*. For higher efficiency phosphorus removal this process may be accomplished by final precipitation (*Kurbiel et al. 1995*).

Post precipitation - chemicals are dosed after the secondary clarification to the inflow of tertiary flocculation and sedimentation facilities.

In this process trivalent metal salts are often applied by polymer addition. The required ratio of metal ion to phosphorus tends to be higher than at other dosing points. The author's own investigations showed that to decrease the concentration from 3.0 g P/m³ to below 0.1 g P/m³ the Fe³⁺ : P weight ratio had to be 4.8. Post precipitation is the most common phosphorus removal process in Sweden and was applied in 1980 at 87% of the treatment plants. The average concentration achieved in the effluent was 0.53 g P/m³. *Ødegaard (1988)* reported that in 1985 30% of Norway's largest treatment plants used this method with 93 % average removal of phosphorus down to 0.5 g P/m³.

Another method of final ("polishing") treatment is filtration which can decrease phosphorus concentration to levels below 0.2 g P/m³.

The method which combines coagulation and filtration is called *contact filtration* and has become more popular in recent years. This method is mainly used as the second of two phosphorus removal steps following pre-, simultaneous or post- precipitation as well as biological phosphorus removal. When the P-content after the first step precipitation is between 0.8 and 1.2 g P/m³ contact filtration can reduce it further to 0.1-0.2 g P/m³ with a relatively low salt dose.

Boller (1984) reduced by this way total phosphorus of 69% down to 0.28 g P/m³ with Fe³⁺ dose = 2.0 g/m³ and without polymer addition. Continuous sand filters (*Larsson 1985*) allow the reduction of phosphorus values down to below 0.3 g P/m³ with significant reduction of BOD at the same time.

Methods presented above may be combined into two-step precipitation. In Norway in 1985 half of the wastewater treatment plants applied primary precipitation followed by post precipitation with 91.6% phosphorus removal. Hultman and Nordström found 1978 (*Balmér & Hultman 1988*) that two-point precipitation is advantageous if low effluent total phosphorus concentration is required.

4. Biological phosphorus removal

4.1. Introduction and principles of the process

4.1.1. Development of technology

Early surveys on biological phosphorus removal on activated sludge plants took place in the 1940's by Sawyer (1944) and Rudolfs (Balmér & Hultman 1988) and in 1955 by Greenburg et al. (EPA 1987). These authors as well as Marais et al. (1983) state that the evolution of biological phosphorus removal started with Levin & Shapiro (1965) who reported on extensive investigations into phosphorus uptake and release. They named the observed high phosphorus removal a "luxury uptake". They also observed in further investigations that uptake and release of phosphorus are reversible processes; an observation of great importance for the development of the process. During further works Shapiro observed high phosphorus uptake at the Baltimore treatment plant followed by its release to the bottom of secondary clarifiers. He proposed to expose return sludge to such conditions prior to return to the aeration basin in order to strip out phosphorus. This was a predecessor to the Phostrip process (to be described later).

Contrary to this method Vacker et al. (1967) stated that a "luxury uptake" of phosphorus is possible without the process of phosphate stripping. At the initial stages of development of biological phosphorus removal some researchers credited a phosphate removal in activated sludge systems to chemical precipitation and adsorption on to the biological sludge (Menar & Jenkins 1969, Menar & Jenkins 1970, Wiechers & van Vuuren 1979, Simpkins 1979).

Menar & Jenkins (1970) presented an involvement of the precipitation mechanism in an enhanced phosphorus removal as proven. At the same time other authors were rather skeptical about biological phosphorus removal. Convery (1970) recommended to avoid design WWTPs based on phosphorus removal by luxury uptake and/or physical phenomena methods⁹. Since Fuchs & Chen's (1975) observation that phosphate accumulation mostly in form of polyphosphates by activated sludge micro-

⁹ Calling them "biological" - inverted commas by Convery.

organisms (*Acinetobacter*) it has been obvious that this might be a prospective technology.

For years many investigators reported the "luxury uptake" effect. It was, however, questioned if all cases were results of a biological and not a chemical process. Phosphorus removal in a biological treatment plant can also be credited to chemical precipitation of phosphate by cations present in wastewater. Presence of some metal cations, mainly calcium but also magnesium, iron, aluminium and zinc, may lead to precipitate of up to 6 g P/m³ which suggests natural chemical precipitation plays an important role in total phosphorus removal. Small amounts of soluble phosphate may also be removed by adsorption to clay particles and other minerals (e.g. washed with storm urban water) (*Arvin 1985*).

De Haas & Greben (1991) studied biological phosphorus removal plant and found that chemical precipitation makes an important contribution to P removal because of the occurrence of natural precipitants. At the plant not dosed with chemicals 14 g P/g VSS was formed by natural precipitation. The problem of an "luxury uptake" was also studied by *Bergman (1970)*.

Initial studies led to a general observation that in activated sludge plug-flow chambers with local decrease of a dissolved oxygen level content of a phosphorus in excess sludge was higher than in conventional sludge and varied between 5 - 7% of VSS. *Barnard (1975)* recognized a link between phosphate release under anaerobic conditions and phosphate uptake under aerobic conditions. He also stated a biological phosphorus removal plant should operate at low solids retention time. Process configuration of a multistage biological reactor for biological phosphorus and nitrogen removal was developed by retrofitting a nitrification-denitrification reactor for the phosphorus removal conditions. The main innovation was a creation of anaerobic conditions to perform the phosphorus release process. Further experience in biological phosphorus removal showed the great necessity for anaerob conditions as a prerequisite for phosphorus removal¹⁰.

¹⁰ The anaerobic conditions refers to those conditions where both oxygen and nitrates are excluded. *Barnard 1982,1983*).

Marais et al. (1983) reviewed observations on biological phosphorus removal and named main conditions to be fulfilled for biological phosphorus removal:

- ◆ anaerobic (i.e. oxygen and nitrate free) zone must be included;
- ◆ phosphorus uptake takes place if phosphorus release had been obtained and oxygen and nitrate is present; a sequence of anaerobic-aerobic conditions is essential;
- ◆ to obtain phosphorus removal it is necessary to supply an anaerobic zone with a high amount of readily biodegradable carbon sources,
- ◆ bacteria cells are growing while passing through aerobic stage after the anaerobic zone.

The authors emphasized that to obtain phosphorus removal not only must appropriate organisms be present but specific conditions have to be met.

4.1.2. Microorganisms involved in the process

Fuch & Chen (1975) reported the role of an *Acinetobacter* species in a biologically enhanced phosphorus removal process.

Some aqueous microorganisms can store an excess amount of phosphorus compounds within an intracellular material. Most important are *Acinetobacter* species (*Sedlak 1991*); Gram-negative short bacteria of 1.5 µm length existing in pairs, short chains, and clusters. *Cloete et al (1988)*, *Beacham (1990)* and *Beacham et al. (1992)* found that bacteria of this group play a major role in enhanced phosphorus removal. Other bacteria species which can store excess amounts of phosphorus are *Arthrobacter globiformis* and *Klebsiella pneumoniae*. Other bacteria are also involved in this process including: *Pseudomonas* taking part in phosphorus uptake and *Aeromonas* responsible for primary fermentation and synthesis of SCFA¹¹.

Investigations done by *Cloete et al (1988)*, *Beacham (1990)* and *Beacham et al. (1992)* on the structure of these bacteria showed that of the many *Acinetobacter* species three of those most frequently encountered are *5.-A.junii* (30% of species), *7.-*

¹¹ SCFA = Short Chainy Fatty Acids - in some papers this term is representing sources of easibiodegradable carbon

A.johnsonii (20%) and *8/9 A.lwoffii* (30%). These authors also found slight differences between bacterial structure in anaerobic, anoxic and aerobic zones. *Mino (1984)* analyzed changes in phosphorus compounds along aerobic and anaerobic zones and found visible changes of concentration in biomass between zones only in cases of low-weight polyphosphates while concentrations of remaining phosphorus compounds¹² were stable or only changed slightly. It showed the major role played by polyphosphate in intracellular storage of phosphorus compounds.

4.1.3. Biochemical background to the process

In parallel with solving technical problems investigations on biochemical models were also conducted. *Nicholls & Osborn (1979)* suggested polyphosphates stored energy to sustain the organisms during the anaerobic stressed state and to build a reservoir of PHB (beta-polyhydroxybutyrate). *Marais et al. (1983)* proposed a basic biological model and described the advantage of usage (consumption) of polyphosphate reserves as a supply of energy for the portioning of readily biodegradable carbon source with the exclusive use of *Acinetobacter*. This model was supplemented by *Siebritz et al.(1983)* where a prerequisite for biological phosphorus removal was presented. The minimum concentration of readily biodegradable carbon supply was estimated as 25 g COD/m³. This work made a provision for Phoredox and UCT models development. Investigations on biochemical changes in an activated sludge at the Phoredox system led to the conclusion that PHB is involved in the supply of ATP and the result is reduction of power and carbon skeletons for various synthetic pathways. This phenomenon took place mainly under anaerobic conditions. It was also found that acetate stimulated PHB formation to a much greater extent than glucose (*Potgeier & Evans, 1983*).

Mino et al. (1984) developed a method called STS for the fractionation of intracellular phosphorus. It was concluded low-molecular polyphosphates function as the energy pool for the uptake of organic substrates under the anaerobic conditions. High-molecular polyphosphates work as the phosphorus source for the microbial growth under the anaerobic conditions.

¹² i.e. nucleic acids, metal phosphates, lipides and proteins

A biochemical model for enhanced phosphorus removal was developed by *Wentzel (1985, 1990)* and *Comeau et al (1986, 1987)*. *Wentzel et al. (1985)* proposed a kinetic model for biological phosphorus release based on readily biodegradable COD concentrations in the influent, the non-polyphosphate heterotrophic mass, the anaerobic mass fraction and the reactor flow regime. The mathematical model describing the kinetics of phosphorus uptake has not been fully developed yet.

General conclusions from the efforts on kinetic model creation were the following :

- ◆ in the anaerobic reactor, readily biodegradable carbon source from the influent is converted into SCFA form by the non-polyP heterotrophs;
- ◆ in the anaerobic reactor the lower fatty acids are sequestered by the polyphosphate organisms, energy for this process is obtained from hydrolysis of polyP chains accumulated in this organisms.
- ◆ the rate of sequestration is faster than rate of conversion, so the conversion is the limiting rate for sequestration and hence for the phosphorus release.
- ◆ fraction of the total sludge in the anaerobic reactor is an important parameter in assessing phosphorus release behavior
- ◆ the linear relationship between the mass of phosphorus release in the anaerobic reactor and the mass of phosphorus uptake in anoxic/aerobic stage of the process.

Comeau et al. (1986, 1987) proposed a model describing the metabolism of bio-P bacteria under aerated and non-aerated conditions. Their assumptions were made on the concept the mechanism of phosphorus uptake and release can be explained by the regulation of the pH gradient across the inner bacterial membrane and of the internal energy level (ATP/ADP ratio). It was shown bio-P bacteria when subjected to anaerobic conditions could consume their polyphosphate reserve to produce energy for the storage and transport of simple carbon substrates such as acetate. Unused phosphate molecules would then be released. Under aerobic conditions energy produced from the consumption of carbon (stored or external) will create high energy levels and result in the growth and accumulation of phosphate by bio-P bacteria.

After series of batch experiments *Comeau et al. (1986, 1987)* finally suggested bacteria responsible for biological phosphorus removal (bio-P bacteria) should possess the ability of accumulation of two types of reserve polymers: polyphosphates

and carbon reserves such as PHB. Polyphosphate degradation and phosphate release, when simple carbon sources such as acetate had been applied, were correlated with the accumulation of carbon storage compounds (PHB).

Comeau et al. (1986, 1987) also stated biological phosphorus removal process seemed to be essential for the maximization of anaerobic carbon storage. Subsequent aerobic phosphate uptake would be maximized as a result of large carbon reserves in bio-P bacteria. To obtain these conditions two requirements have to be fulfilled :

- ◇ high level of simple carbon substrates should be added to anaerobic zone;
- ◇ the addition of electron acceptors (nitrate , oxygen) to the anaerobic zone should be minimized.

The importance of minimization of both oxygen and nitrate presence in the anaerobic zone was also concluded by *Gerber et al. (1987)*. They found increasing nitrate concentration led to significant reduction of phosphorus release during the anaerobic stage, as well as it diminished an uptake under aeration.

The model was further developed by *Comeau and by Wentzel et al. (1987)* and *Mino (1987)*. Both of those models have two things in common:

- stimulation of biological (excess) phosphorus removal requires anaerobic/aerobic sequencing;
- short chainy fatty acids play a central role in the anaerobic phase.

The general difference between those models is the Comeau/Wentzel model hypothesizes the reducing equivalents (NADH_2) are supplied by operation of the TCA cycle under anaerobic conditions. In the adopted Mino model production of required NADH_2 is explained by the considerations in which the Euther-Doudorff pathway has been found as an alternative to the Emden-Meyerhof-Panas pathway with consumption of a carbohydrate under anaerobic conditions.

Ohtake et al. (1985) conducted studies on uptake and release of phosphate by pure culture of *Acinetobacter* which was generally found the main bio-P bacteria. They stated that pure culture of this bacteria could accumulate polyphosphates in an amount of 0.9 - 1.9% of dry cell weight during the logarithmic scale of growth while the release of phosphate had linear characteristics with time during a transfer from

aerobic to anaerobic conditions. The release rate was measured as $5.9-14-7 \cdot 10^3$ mmol P/g dry cells/h.

The kinetics of the phosphorus release and uptake were also studied by *Suzuki & Cho-Hee-Yon (1989)*. They propose first order kinetics mathematical model for both release and uptake, a decision based on the distinctive release step under anaerobic conditions into two phases. They also presented an evaluation of kinetic constants for a proposed model calculated for specific conditions. These biological and kinetic models have been a great step forward in explaining the biological phosphorus removal process. There is, however, still no proper mathematical model to design and operate the process in full scale.

4.2. Process configurations and operational results

As was previously mentioned process schemes can be divided into mainstream and sidestream and continuous and intermittent flow.

4.2.1. Mainstream processes

4.2.1.1. General description

In these processes phosphorus is being removed together with surplus sludge. It is required the surplus sludge contains approx. 7% of P (normal phosphorus content is approx. 2%). The key position for the process is a fermentation anaerobic reactor with retention time of about 1 to 2 h. Sludge in mainstream processes is recycled from a final sedimentation tank to the head of an anaerobic zone or through anoxic to anaerobic. Those processes are usually divided into two groups : recirculation and alternating (*Arvin 1985*). The recirculation processes are most frequently applied.

Barnard (1975) first achieved phosphorus removal in a four stage anoxic-aerobic-anoxic-aerobic reactor originally designed for nitrogen removal (*Simpkins 1979, Wiechers & van Stuuren 1979*). At the pilot plant in Daasport (South Africa) *Barnard* performed tests with different retention times in basins and found the best configurations to be 3h, 7h, 3h and 1h respectively. Sludge from the secondary clarifier and the mixed liquor from first aerobic basin were recirculated to the first

anoxic step. Significant phosphorus removal was achieved but its effluent concentration varied between 1 and 4 g P/m³ and was very sensitive to changing maintenance conditions. This process received the trademark of Bardenpho™. It was stated the biological phosphorus removal was induced by exposition of organisms' mass to a stress in anaerobic state. It was, therefore, suggested to create this state by including an anaerobic reactor ahead of the primary anoxic reactor in the four stage Bardenpho process. The role of this reactor is to receive the influent flow as well as the sludge recycled from the secondary clarifier. This configuration is known in South Africa and in Europe as the Phoredox™ process. A stock-taking of German WWTP (Scheer, 1996) showed that the Phoredox process was used in 31% of the plants with enhanced phosphorus removal. In German speaking areas 125 sewage treatment plants were operated with enhanced biological phosphorus removal and 240 were planned or under construction in 1994.

A first stage with a retention time (HRT) of 1-2 h prevents anaerobic conditions for a phosphorus release, next step - first anoxic with a HRT of 2-4 h is to conduct a pre-denitrification. A third stage with a HRT of 4-12 h is designed for nitrification. About 70 percent of the nitrate nitrogen produced in the system is removed in this stage. A fourth stage with a HRT of 2-4 h provides conditions for additional denitrification by a mixed liquor endogenous respiration. A relatively small final aerobic stage (HRT 0.5-1.0 h) provides reaeration of mixed liquor to prevent against anaerobic conditions in a clarifier which may cause phosphorus release there. Basic conditions of operation for this process are as follows : F/M ratio 0.1-0.3 kg TBOD/kg MLVSS d ; SDT 10 -30 days; MLSS 2000 -4000 g/m³.

This method is widely applied, mostly in countries of mild to warm climate. Different activated sludge systems may be applied to perform this process. For example, EIMCO(1987) - the company which markets the Bardenpho systems in the United States, suggests the "Carrousel™" type oxidation ditch as the anoxic - aerobic part of the reactor. Basic operational parameters of selected Bardenpho and Phoredox process wastewater treatment plants are presented in Table 2 below.

Tab.2.							
parameters of selected Bardenpho and Phoredox process wastewater treatment plants.							
Plant	Daspoort	Goudkoppies	Johannesburg	Marienfelde	Palmetto	Orange Count	Kelowna
System	<u>Bardenpho</u>	<u>Phoredox</u>	<u>Phoredox</u>	<u>Phoredox</u> §	<u>Mod Bard</u>	<u>Mod Bard</u>	<u>Mod Bard</u>
Flow m ³ /d	100	50 000	73 000	24 000	4 900	12 500	22 700
<u>Influent parmeters</u>	-	-	-	-	-	-	-
BOD g O ₂ /m ³	300*	220	580*	251	158	167	-
TSS g/m ³	-	200	190	133	135	149	-
Tot P g P/m ³	9-12	5.9	8.5	10	-	-	4.5
PO ₄ P g P/m ³	5-8	2.5	4.6	-	6.5	8.2	3.8
<u>Effluent parameters</u>	-	-	-	-	-	-	-
BOD g O ₂ /m ³	35*	8	49*	9	2	1.5	-
TSS g/m ³	-	9	13	9	2	1.8	-
TotP g P/m ³	1-4	2.1	6.3	1.37	-	-	0.8
PO ₄ P g P/m ³	-	1.9	5.5	0.84	0.6	0.7	0.77
P: BOD	-	0.02	0.004	0.04	0.04**	0.045**	0.03
<u>Process parameters</u>	-	-	-	-	-	-	-
F/M g BOD/ MLVSS d	0.30*	-	-	0.28	0.23	-	-
MLSS g/m ³	max 6000	2600	-	3400	3500	-	3000
MLVSS g/m ³	-	2000	-	-	-	-	-
SDT days	18-25	19	-	3.6	14-20	-	30-40
HRT hours	16	-	-	8.1	11.6	15	21
SVI ml/g	150	230	-	160	-	-	-
Reference	<i>Barnard 1976</i>	<i>Pitman 1983</i>	<i>Pitman 1983</i>	<i>Boll 1989</i>	<i>Morales 1991</i>	<i>Morales 1991</i>	<i>EPA 1987</i>

* - data refer to COD

** - data refer to PO₄-P

§ - plant layout similar to Phoredox

Tab.3.				
Basic parameters of selected A2/O and VIP process wastewater treatment plants.				
Plant	Largo	York River	York River	Lamberts Point
System	<u>A2/O</u>	<u>A2/O</u>	<u>VIP</u>	<u>VIP</u>
Flow m ³ /d	37 500	22.3	27 500	3.0
<u>Influent parameters</u>	-	-	-	-
BOD g O ₂ /m ³	193	229*	180	111
TSS g/m ³	227	112	190	110
Tot P g P/m ³	-	12.5	-	-
PO4 P g P/m ³	9.5	-	9.2	5.3
<u>Effluent parameters</u>	-	-	-	-
BOD g O ₂ /m ³	5	-	10	4
TSS g/m ³	4	6.1	7	8
TotP g P/m ³	-	3.2	-	-
PO4-P g P/m ³	2.4	-	1.5	0.79
P: BOD	0.04**	-	0.045	0.042
<u>Process parameters</u>	-	-	-	-
F/M gBOD/ MLVSS d	-	0.65	0.43	0.45
MLSS g/m ³	-	-	-	1576
MLVSS g/m ³	-	-	-	-
SDT days	-	10.3	6.0	-
HRT hours	4.2	2.65	-	6.6
SVI ml/g	-	-	-	114
Reference	<i>Morales 1991</i>	<i>Randall 1990</i>	<i>Morales 1991</i>	<i>Daigger 1988</i>

* - data refer to COD

** - data refer to PO4-P

Table 2. presents basic performance conditions and results for seven selected wastewater treatment plants based on 'early-Barnard' concept. Only one of the described plants achieved average phosphorus concentration in the effluent below 1.0 g P/m^3 (Kelowna 0.8 g P/m^3). At all plants significant variability of phosphorus concentration in the effluent was observed. *Pitman et al. (1983)* reported that at Goudkoppies (South Africa) plant, total phosphorus concentration varied between 0.2 and 1.9 g P/m^3 . *Boll et al. (1989)* obtained a high concentration 4.0 g P/m^3 .

To diminish and to stabilize final effluent concentrations chemicals were dosed at some plants, e.g. alum with a dose of 60 g/m^3 at Palmetto and Orange County (*Morales et al. 1991*). Final filtration as a tertiary treatment was applied at Kelowna (*EPA 1987*) with filtration ratio of $23.4 \text{ m}^3/\text{m}^2\cdot\text{d}$ and in Palmetto at ratio $93.7 \text{ m}^3/\text{m}^2\cdot\text{d}$ (*Morales et al. 1991*).

The Bardenpho and Bardenpho-related processes need proper operation to achieve required effluent standards. A survey made on the performance of eleven multi-stage biological nutrient removal reactors in Johannesburg area showed that only one of the plants being investigated kept effluent phosphorus concentrations at the 1.0 g P/m^3 level while at five of them concentrations of 6.0 g P/m^3 or more were reported (*Paepcke 1983*). Paepcke stated this was due to excessive amounts of oxygen and nitrates in anaerobic zones. Nitrates are believed to be introduced with the return sludge because of incomplete denitrification. Paepcke also suggested in order to avoid a formation of vortices (and as a consequence an aeration) the stirring energy in an anaerobic zone should be limited to below 10 W/m^3 .

Further developments of the Phoredox process done at a temperature of 20° C in South Africa led to the next modification, i.e. a Modified or 3-stage Phoredox system where post-denitrification and reaeration steps were omitted.

The process parameters are similar to those presented for the Phoredox process. A description of such a plant in the Johannesburg area was presented where effluent concentration of phosphorus 2.1 g P/m^3 was achieved (*Pitman 1983*) and in Olifantsfontein where 1.0 g P/m^3 level was reported by *van Huyssten et al. (1990)*. The Olifantsfontein plant achieved these results operating at SDT as low as 6 days. Both plants were operated at MLSS concentration of about 3500 g/m^3 . Further modification of the Phoredox process was done by a group from the University of

Cape Town in South Africa so it has been named the UCT process. The main idea was to return the activated sludge to the anoxic instead of the anaerobic stage to avoid negative affects on the initial phosphorus removal efficiency by nitrate nitrogen entering the anaerobic stage as described above. The anoxic stage of the UCT process is designed and operated to produce relatively low levels of nitrate nitrogen. The mixed liquor recycle from the anoxic stage to the anaerobic stage prevents optimal conditions for a conversion of readily biodegradable COD into fermentation products from occurring.

The relative ratio TKN:COD recommended for this process is 0.08 g N/g COD or more. Experiments with the UCT process exposed another type of problem which could significantly affect the successful operation of the process. If the TKN/COD ratio increases the aerobic-anoxic mixed liquor recycle ratio needs to be reduced to avoid nitrate discharge to the anaerobic reactor. The consequence of such reduction is the increase in actual retention time. In the Modified UCT process the anoxic zone is subdivided into two parts: the first anoxic zone receives sludge recycle while an anoxic-anaerobic mixed liquor recycle is taken from it. The second anoxic part receives aerobic-anoxic mixed liquor recycle. The advantage of this process is that first anoxic part (zone) is designed to reduce only the nitrate nitrogen in the return sludge which prevents against nitrogen intrusion to the anaerobic zone.

Another development within multi-stage processes is the JHB (Johannesburg) process presented by *Pitman (1991)*. In this process the sludge recycled from the clarifier passes through a separate anoxic zone where denitrification by an endogenous respiration occurs. South African experience showed that 10 g N/m³ of nitrate can be removed in this zone. The JHB improvement of adding the anoxic zone prior to the anaerobic one seems to be useful for those cases when the high concentration of dissolved oxygen or/and nitrates from the sludge recycle occurs in the anaerobic zone.

New processes have been developed in the United States. These are the A/O, A2/O and VIP processes. Basic parameters of selected plants using these processes have been shown in Table.3. Flow diagrams of these process are similar to Bardenpho-related processes except each stage is divided into a number of equal size cells of complete mixing. The main difference in process characteristics are: relatively short

design SDT, high organic loading ratios (F/M) - up to 0.7 kg BOD/kg MLVSS d (EPA 1987), (Daigger et al. 1988) and low sludge return ratio 25-60 % (EPA 1987).

The A/O process (trademark comes from Anaerobic/Oxidic sequence) was originally developed for phosphorus removal only so its flow diagram does not include a recycle of a mixed liquor. Organic load is 0.3-0.5 kg BOD/kg MLVSS ; SDT 7-29 days - usually approx. 10 days. Results obtained varied between 0.4 and 1.4 g P/m³ in the effluent (Deakyne 1984, EPA 1987, Morales et al 1991).

The A/O process was later developed for nitrification and denitrification by incorporating an anoxic stage for denitrification between the anaerobic and aerobic stages. This modification has been named A₂/O. Consequently, mixed liquor recycle with ratio 100-200% of plant influent flow has to be added.

The layout of the process is similar to the modified Phoredox in general, but, A₂/O reactor has all its stages divided into complete mixed cells as does A/O. The A₂/O process (trademark by Air Products and Chemicals) was studied by Daigger et al. (1988), Randall et al. (1990) and Morales et al. (1991).

This process provided relatively low phosphorus removal due to the high nitrate recycle to the anaerobic zone (in York River - Randall et al. 1990). The plant at Largo was operated at 30-day discharge limit for phosphate 6.0 g total PO₄/m³, thus fulfilling requirements.

Another mode of operation of high loaded process is the VIP (Virginia Innovative Plant). Its process scheme is similar to the UCT one and division into complete mixed cells is essential (Daigger et al 1988, Morales et al. 1991). It is important to divide each stage into at least two cells (Daigger et al 1991). The mixed liquor recycle ratio is 100-200% of influent flow for both anoxic and nitrified recycles. This type of wastewater treatment plant works at least twice as high F/M ratio than Bardenpho-related plants (0.43 kg BOD/ kg MLVSS d) and showed relatively good operational performance in the phosphorus removal. Randall conducted pilot studies on the VIP process and confirmed its very good operation under summer season conditions (effluent concentration below 0.5 g P/m³). Daigger et al. (1991) stated it is critical for this process to keep the total BOD : total PO₄ ratio over a value of 20:1. These authors found the VIP process a reliable technique of phosphorus removal as well as BOD, suspended solids and nitrogen removal.

In 1990 *Moriyama - Mils et al.* presented a new concept of biological phosphorus and nitrogen removal in a three stage *aerobic-anaerobic-aerobic* low loaded reactor where the first step is nitrification simultaneously with denitrification under oxic conditions. The process was performed at an optimum redox potential level. The plant was operated with a capacity of 1000 m³/d at 15 h HRT at basic parameters as follows: F/M ratio 0.1 -0.16 kg BOD/kg MLVSS d ; MLSS 2800-3200 g/m³; SDT 17-25 d. Phosphorus removal was achieved from 6 g P/m³ down to 0.2-0.6 g P/m³. This system also seems to be very promising, however, its reliability depends very much on redox potential control in the basin and measurement of this parameter still causes some maintenance problems.

In addition to the classifications mentioned above there are plants which originally had been designed as conventional activated sludge plants and later were rebuilt (upgraded) for the biological phosphorus removal. Usually the process layouts being applied on those plants are similar to the A/O process; their anaerobic zone can be either separated from the existing activated sludge tank or built as a new facility. Numerous plants of upgrade activated sludge type exist in the United States (*Tetreault et al. 1987*) .

All systems presented above are of plug-flow or complete-mixed flow schemes. The possibility of biological nutrient removal including biological or chemical phosphorus removal was presented with the Carrousel-2000 circulation system (*Janssen et al. 1996*).¹³

4.2.2 Alternating processes

Alternating techniques were developed in Denmark as reported by *Arvin (1984, 1985)*, *Bundgaard et al. (1989)* and *Bundgaard & Pedersen (1991)*.

The main principle of these processes is phased operations of denitrification and nitrification and is implemented in the same ditch (with no pumping). This is a kind of combination of an idea similar to Sequencing Batch Reactors and recirculation techniques.

¹³ the Carrousel 2000 concept origins from the Passver oxidation ditch

Aeration/anoxic tanks are usually oxidation ditches. For nitrogen removal each tank can be sequentially operated with denitrification under intake of wastewater and agitation or with nitrification by aeration. The wastewater stream is directed to one of the tanks through the anaerobic chamber where incoming wastewater is mixed with recycled sludge from the secondary clarifier to perform phosphorus release and consequently its uptake under aerobic conditions in tanks.

The first Danish wastewater treatment plant using this method was Norre Åby, where the following results were achieved in the effluent : BOD removal from 234 to 8.8 g O₂/m³ and total phosphorus removal from 11.0 to 1.0 g P/m³ (in 90 % of samples; incidental concentrations as high as 3.7 g P/m³ were also observed). To decrease these high phosphorus concentrations further contact filtration by ferric chloride addition was performed. Final concentrations of the total phosphorus were 0.6-1.0 g P/m³. Contact filtration can also be successfully applied as a supplementary treatment for alternating processes (*Christiensen 1991*).

4.3. Sidestream process

4.3.1. General description of the process

As was mentioned in chapter 3.1. the idea of exposing the return sludge to anaerobic conditions prior to return to the aeration basin led to the invention of sidestream processes. In this type of process the phosphorus is extracted from the sludge in the side stream through anaerobic stripping of phosphorus from the sludge to supernatant water or by chemical precipitation. This process combines biological extraction and concentration followed by chemical fixation of phosphorus (*Summary Report 1982*). Wasted sludge directed to the stripper is assumed to contain 3.5% of phosphorus (half of the amount assumed for the mainstream process, *Arvin 1985*).

4.3.2. Application of the process

Phostrip was applied by Shapiro in the 70's in the United States where it became the most popular biological phosphorus removal process that time. The sidestream flow is diverted to the anaerobic phosphorus stripper tank at a ratio approx. 10-30 % of

the influent flow. This tank also plays the role of sludge thickener. Solid detention time in the stripper tank varies between 5 and 20 hours.

Soluble phosphorus is released with the same mechanism as for an anaerobic-aerobic activated sequence in the activated sludge process. Soluble phosphorus is then transferred to the supernatant either by recycling the stripper underflow or by passing an elutriation stream through the stripper. The stripper tank overflow is fed to the chemical treatment tank where phosphorus is precipitated by lime addition. This can be done by the use of a separated reactor-clarifier unit for stripping an overflow or by lime addition to the overflow followed by sedimentation of the precipitate in the primary clarifier.

Deviation from this process was proposed by *Janssen et al. (1989)*. This deviation replaces the precipitation unit with the crystallization of phosphorus compounds in a fluidized bed reactor filled with seed crystals. This reactor has the "Crystalactor" trademark. Testing of this reactor at the Bennekom pilot plant achieved almost 100% removal of phosphorus.

Sidestream processes operate on the basis of the activated sludge units of different kind. Both plug flow (*Tetreault et al. 1986*) and complete mixed units (*Miyamoto-Mills 1983, Peirano et al. 1983*) were reported. Sidestream process based on the contact stabilization process instead of on the conventional activated sludge process was reported by *Arvin (1985)*. This version has not been applied in operational scale.

Typical parameters of an activated sludge are as follows : F/M ratio 0.16-0.5 g BOD/g MLVSS, d., MLSS 1900-4000 g/m³ , HRT 2.5-5 h. For the test with "Crystalactor" a multiphase biological reactor with a load of 0.1 kg BOD/kg MLVSS d was applied.

Phosphorus removal per unit of BOD removal was for the Phostrip process between 0.058 - 0.124 (overall) which was a higher value than for upgraded activated sludge (0.03-0.04 *Tetreault 1986*) or for other biological phosphorus removal processes (0.04 - VIP, 0.03- A2/O, 0.04 - Phoredox).

In summary: sidestream methods are the most effective ones of all biological phosphorus removal techniques. They give a low effluent concentration with good reliability. Some operational data on a Phostrip process application are summarized in table 4.

<p style="text-align: center;">Tab.4. Basic parameters of sidestream processes for phosphorus removal</p>						
Plant	US EPA	Lansdale	Lt Patuxent	CCSD	Reno Sparks	Seneca Falls
System	1987	Phostrip	Phostrip	Phostrip	Phostrip	Phostrip
Flow m ³ /d	DESIGN	8350	40 880	36	152 000	3 400
Activated sludge type-	MANUAL	plug flow	plug flow	complete mix	complete mix	complete mix
Influent parameters						
BOD g O ₂ /m ³	-	41	103	200	-	96
Tot P g P/m ³	-	5.4	6.6	11	6.6	6.8
PO ₄ P g P/m ³	-	-	-	-	-	-
Effluent parameters						
BOD g O ₂ /m ³	-	3	6	-	-	8
Tot P g P/m ³	-	0.8	0.5	1.1	0.5	0.4
PO ₄ P g P/m ³	-	0.7	0.1	-	-	-
P: BOD	-	0.121	0.063	-	-	0.072
Stripper parameters						
Feed as % of flow	20-30	14	34	25	-	10
SDT hours	5-20	20	7	5-20	-	8
Underflow as % of flow	10-20	10	21	16	-	-
Recycle %	-	0	78	-	-	0
Reactor-Clarifier						
Overflow rate m ³ /m ² /d	48	65	34	-	-	-
pH	9-9.5	9.0	9.5-	-	-	7.0
Lime dose g /m ³	100-300	100	100	-	500	100
Reference	EPA 1987	Tetreault 1986	Tetreault 1986	Miyamoto 1983	Peirano 1983	EPA 1987

Recent works on an application of a Phostrip process by *Szpyrkowicz & Zilio-Grandi (1995)*, after two years of plant operation, led to the conclusion that a Phostrip process can be applied as a supporting biological treatment. Under specific conditions in a tourist area this process is applied in high season only. During the rest of the year a local WWTP operates as a conventional biological plant. Seasonal phosphorus removal takes place by directing part of the phosphorus-containing sludge to a Phostrip installation. It proved to be a reliable process during approx. 80% of operational season and phosphorus concentrations in effluent below 1.0 mg/L were achieved.¹⁴

¹⁴ The plant was working at low organic content and at a high presence of nutrients (e.g. TKN/COD = 0.23 and P/COD = 0.017).

4.4. Intermittent process

The Sequencing Batch Reactor (SBR) technique was adopted for biological phosphorus removal in the early 80's when the United States Environmental Protection Agency (EPA) funded a full scale demonstration plant (1330 m³/d capacity) at Culver.

Works focused on the comparison of different periodic process performance characteristics resulted in a new step- "react" (aeration without addition of wastewater) was added to conventional SBR process. *Irvine et al. (1983)* operating at various F/M load of 0.16 to 0.42 kgBOD/kg MLVSS*d established proper operating sequence for this type of plant performing a phosphorus removal:

fill and anaerobic	1.8 h (low loaded)	to 3.0 h (high loaded)
aerobic (react)	1.0 h	to 0.4 h
settle	1.0 h	to 0.7 h
withdraw	0.4 h	to 0.7 h
idle	0.6 h	to 0.0 h

Phosphorus removal was performed in the "classical" anaerobic-aerobic way. Further investigations by *Manning & Irvine (1985)* and *Irvine et al. (1987)* performed on synthetic wastewater led to the conclusion that the best results were obtained where dissolved oxygen and nitrate nitrogen were absent during the first step of operation. This implies complete denitrification during the "fill" period. About 50% of total phosphorus and 90% of nitrogen removal was achieved during those studies. Phosphorus removal by metal salt addition was also tried.

Ketchum et al. (1987) studied phosphorus removal from a biological perspective under the following conditions: MLSS = 1600 g/m³, HRT = 8.6 h. The sequence of operations was FILL w/mix, FILL anoxic, FILL anaerobic. FILL aerobic, REACT, SETTLE, DRAW, IDLE, with retention times 2.30 h/1.0 h/1.0 h/0.0 h/2.0 h/0.75 h/0.75 h/0.8 h, respectively. With this sequence 0.6 g P/m³ of phosphorus concentration in the effluent was achieved. Ketchum showed that it is possible to consistently obtain such effluent quality with this type of process. *Goronszy & Riegel (1991)* obtained similar results operating a three step SBR reactor. In 1994 *Subramanian et al* presented the possibility of achievement of 90% total phosphorus removal at the SBR

reactor. That reactor, however, was operating on high strength¹⁵. *Bortone et al. (1994)* also reported high performance biological P removal in the SBR related reactor¹⁶. Good quality effluent was attained when the reactors were fed with high strength piggery wastewater.

Marklund (1993) presented a Swedish development of SBR technology in practice. Operating on municipal-like wastewater¹⁷ 74% reduction of total and 87% of soluble phosphorus was achieved with following operational schedule:

fill	3.5 h (constant)	
anaerobic(mix)	1.2 h	to 7.5 h
aerobic (react)	1.8 h	to 4.0 h
settle	1.0 h	to 2.0 h
decant	1.0 h	to 2.0 h
idle	0.0 h	to 1.3 h.

Marklund also stated when the temperature of wastewater drops below 5° C higher phosphorus concentration in an effluent might be observed.

This process has one significant disadvantage: it necessitates expensive hardware (pneumatically actuated valves, sensors etc.) to operate properly.

¹⁵ slaughterhouse wastewater had almost 50 mg/L concentration of phosphorus and 600-1500 mg/L soluble COD concentration.

¹⁶ anaerobic-anoxic SBReactor with separated batch biofilm nitrification , same authors tested five step anaerobic-anoxic-oxic SBR with promising results

¹⁷ Influent BOD = 124 mg/L, influent P(total) = 5.97 mg/L

5. Main factors affecting performance of biological phosphorus removal

5.1. Anaerobic conditions

The most important performance factor appears to be the creation of a sequence of anaerobic and aerobic conditions (Barnard 1982, 1983). It was found that fully anaerobic conditions in the first stage of a biological phosphorus removal process were essential for process operation. As has been described above, under anaerobic conditions, activated sludge which has accumulated excess phosphorus has a tendency to release phosphorus into surrounding liquid. This release of about 10-20% of the accumulated P is a prerequisite for further uptake of phosphorus. It is of great importance to create electron acceptors-free (oxygen or nitrate) conditions in an anaerobic reactor (Marais et al. 1983, Toerien et al. 1990). Problems occur in multiphase reactors for integrated nitrogen and phosphorus removal where streams of nitrates may be transported by the sludge return to the anaerobic zone. To protect against this effect the UCT and Modified UCT processes have been developed especially to prevent the uncontrolled discharge of nitrate to the anaerobic stage.

Phosphorus removal capacity per unit MLSS increases with increasing anaerobic retention time with no negative impact on COD and suspended solids removal.

5.2. Phosphorus concentration in a secondary effluent

Both for mainstream and sidestream processes the secondary effluent suspended solids concentration and the phosphorus concentration of those solids are two factors of great importance. Phosphorus content of MLSS on a dry solids basis, of 2.3-5.8 % were reported compared with 1.5-3.0% phosphorus content in conventional activated sludge (Tetreault et al. 1986). To achieve low phosphorus concentration a properly designed secondary clarifier is necessary. Without filtration the effluent suspended phosphorus concentration may be between 0.5-1.0 or even higher. Effluent filtration can reduce this value to 0.1-0.2 g P/m³. For stabilized final concentration below 0.5 g P/m³ an effluent should be filtrated. Lower concentrations

demand final precipitation (*EPA 1987*), however, many authors reported temporary operation of biological phosphorus removal processes, without filtration or final precipitation, where concentrations as low as 0.3-0.5 g P/m³ were achieved in the effluent.

5.3. Composition of incoming wastewater

Organic matter (measured as COD, BOD) and phosphorus loading patterns at full-scale wastewater treatment plants are highly variable. This fact may cause temporary increases in phosphorus concentration in the effluent, especially when depressed daily organic load is accompanied by a higher phosphorus loading rate (*Chiesa et al. 1986*).

Nitrate nitrogen entering the anaerobic zone can significantly reduce the phosphorus removal capability (*Barnard 1975*). It was stated that complete denitrification is essential for phosphorus removal. The value of 0.08 g N/g COD was proposed as a minimum TKN:COD ratio if complete denitrification is to be achieved (*Marais et al. 1983, Tetreault et al. 1986*). *Barnard (1984)*, however, found if a sufficient concentration of volatile fatty acids was present in the effluent the TKN:COD ratio is not so significant.

5.4. Availability of easily biodegradable carbon sources

Earlier in this paper it was shown the phosphorus removal process depends on the availability of easy biodegradable carbon sources (usually fermentation substrate products), which are needed by the phosphorus storing bacteria, relative to the amount of phosphorus that must be removed by the process.

At the initial stage of investigations on phosphorus removal in activated sludge systems *Sawyer (1944)* stated that for biological phosphorus removal in activated sludge systems the BOD:P ratio in wastewater influent to the biological treatment step should exceed 100:1. It seems to be earliest requirement concerning availability of easily biodegradable carbon in wastewater in order to achieve enhanced biological removal.

The amount of the easily biodegradable carbon compounds cannot be measured directly so various authors have proposed different approaches to estimation of the required level of readily biodegradable carbon source in wastewater influent to a biological reactor. Typically some indirect methods were proposed to assess this factor.

Siebritz et al. (1983) stated the minimum concentration of readily biodegradable substrate in the effluent was 25 g COD/m³. At the same time *Ekama et al. (1983)* supposed that for processes with recycle ratio (to the anaerobic reactor) equal 1:1 this concentration is below 50 g COD/m³ and the excess phosphorus removal cannot be achieved.

It was suggested to use routine tests such as volatile fatty acids concentration to assess the availability of easily biodegradable material instead of using the more complex and less reliable techniques of readily biodegradable substrates assessment (*Barnard 1984*).

An influent soluble BOD : soluble P ratio below 12:1 , as was recommended by *Tetrault et al. (1986)*, can hardly be adopted as a standard value because these parameters are very rarely measured. Total BOD : total P ratio has been proposed instead. It has been shown by many authors the minimum value of this ratio is 20 :1. It seems there is no upper limit for this value as excellent removal has been reported even at 74:1 ratio (*Morales et al. 1991*).

The methodology of estimation of readily biodegradable carbon sources concentration has been developed in recent years (*Ekama et al. 1986*). It was observed short chainy fatty acids may not always be a major component of readily biodegradable substrate. It has also been confirmed fermentation products generated via high rate anaerobic digestion of sewage sludge are beneficial to the biological phosphorus removal process. Optimum layout for a nutrient removal plant was proposed (*Nicholls et al. 1985*).

Further studies on biodegradability of residual COD led to the conclusion about 90% of COD which previously had been stated residual (non-biodegradable) ultimately susceptible to biological metabolism. This fact is interesting because it shows with conventional design procedures non-biodegradable COD load in the mixed liquor is

overestimated. This observation is not as important for biological phosphorus removal as for activated sludge process operation (*Gaudy & Bleachly 1985*).

Recently it has been found maximum SCFA generation potential by sludge fermentation is 0.17 g COD/ g influent sludge COD. Increasing fermentation time over a three days period did not result in a significant increase of SCFA yield. Also it was confirmed that non- SCFA soluble COD generated some content of readily biodegradable COD. Observed phosphorus removal was in fact, higher than could be accounted for by SCFA generation alone (*Wentzel, 1991*).

The problem of availability of a biodegradable carbon source is still one of the most important issues of investigation in wastewater treatment.

An innovative technique of supporting biological phosphorus removal was proposed by *Barnard (1984)*. The technique involved a activated sedimentation tank consisting of a simple recycle of primary sedimentation tank or thickener underflow to the influent. Due to the recycle SCFA was simultaneously formed in a sludge blanket. This led to the idea of prefermentation which was developed further by *Barnard (1992)* who presented design guidelines. This possible increase of easily biodegradable carbon content by initial fermentation was also investigated by *GonCalves et al. (1994)* by testing the upflow sludge blanket as a fermentation device. They proved this reactor to be capable of VFA production and clarification of fermented influent. Results obtained showed higher fermentation efficiency than existing processes, but, need to be confirmed in semi-industrial scale. A HYPRO program was directed towards obtaining internal carbon sources from a sludge hydrolysis. Some practical data by *Brinch et al. (1994)* showed the introduction of sludge fermentation/hydrolysis as an additional step may lead to production of direct-degradable organic carbon. It can compensate low C/P and C/N ratios in wastewater entering biological treatment steps. *Charlton (1994)* also reported proper operational results of a biological phosphorus removal with the use of a fermenter prior to the modified UCT process¹⁸ even if applied to weak sewage.

Recent works on this problem are presented in the review on chapter 9.

¹⁸ Concentration of total phosphorus was lower than 0.7 mg/L in 50% of samples and 0.9 mg/L in 85% of samples

5.5. Solids detention time (SDT, SRT)

Many authors (e.g. *Ekama et al. 1983, EPA 1987*) showed operation at longer SDT can cause a decrease of efficiency of phosphorus removal per unit of BOD removed. A system should, therefore, not be operated with SDT values excessive of those required for overall treatment needs.

5.6. Dissolved oxygen concentration

Biological phosphorus removal can be affected in biological nutrient removal systems unless the dissolved oxygen concentration in the phosphorus uptake zone remains between 1.5 and 3.0 g/m³. It should be neither higher (as affecting anaerobic processes in first zone) nor lower (as limiting nitrification, poor settleability).

5.7. Temperature

Wastewater temperature's influence on biological phosphorus removal was widely discussed. One should remember the biological phosphorus removal processes were developed originally in countries of mild to warm climates. Phostrip, Bardenpho-related and A/O processes were also applied at lower temperature. *Vassos et al. (1987)* reported the operation of this process in Kelowna, Canada in mild-cold climate, with performance of phosphorus removal, however, the process efficiency in temperature below 15°C dropped from 90% to 60 %. *Peirano (1983)* observed no significant decrease of the Phostrip process efficiency at low temperature. The specific phosphorus release rate dropped from 3.15 g/m³-h/g VSS at 30°C to 0.63 g/m³-h/g VSS at temperature 10°C.

Increase in the volume of Bardenpho-type reactors operating at lower temperature is necessary mostly because of nitrogen removal *parameters (Burdick 1982)*. Full scale operation of an A/O system demonstrated no process influence by low temperature. This result is credited by *Groenstijn et al. (1985)* to a population shift to more slow growing psychrophilic bacteria with high cell yield.

5.8. Phostrip process

Phostrip process performance influencing factors are mainly, stripper SDT, elutriation rate and elutriation source. Optimum SDT was tested by *the US EPA (1987)*. As an elutriant source the chemical system overflow is recommended because of its low phosphorus content.

6. Combined biological-chemical processes

The most common combined i.e. biological/chemical processes of nutrient removal are those in which the phosphorus removal is done by simultaneous precipitation while the nitrification/denitrification takes place in the same basin, but, techniques designed especially for combined phosphorus removal have also been developed.

As was mentioned in chapter 3.1, natural chemical precipitation plays some role in biological phosphorus removal (*Arvin 1985, de Haas & Greben 1991*). There are also processes in which biological and chemical phosphorus removal are combined intentionally.

Bundgaard & Tholander (1978) tested biological nitrification and denitrification with chemical phosphorus removal by simultaneous precipitation with ferrous salts. They operated a Bio-Denitro oxidation ditch at the following conditions: F/M ratio 0.1 g BOD/ g MLVSS d, MLSS = 4100g/m³, SDT = 12 days. They achieved an effluent concentration of 0.8 g P/m³ in the effluent but did not observe parallel biological and chemical phosphorus removal.

Arvin (1983) surveyed phosphate removal by biologically mediated chemical precipitation. He stated two biological mechanism, normal phosphorus assimilation and polyphosphate accumulation. Two chemical mechanisms, bulk- and biofilm- precipitation, are responsible for enhanced phosphorus removal in biological treatment plants.

Ketchum et al. (1987) tested chemical addition to the SBR operating in biological phosphorus removal mode. They found alum dosing near the end of the "react" phase maximized any biological phosphorus removal.

Lötter (1990) conducted investigations at a treatment plant where operational problems with primary sedimentation forced users to dose chemicals. It was observed the crucial point of the whole process is the estimation of the chemical dosage being required to precipitate only those part of phosphates which cannot be removed biologically. It was concluded iron salts are inhibitors for the polyphosphate storage process. Permanent concentration below 1.0 g P/m³, however, was

achieved. It was also found that any addition of iron salts should be done prior to primary fermentation.

Studies on the Bardenpho type plant with and without addition of chemicals showed that not only a natural precipitation in the activated sludge played an important role in biological phosphorus removal, but, also salt addition to the feed of the Bardenpho plant may result in 30-50 % removal of phosphorus (*de Haas & Greben 1991*). Dosage of a ferric sulfate to the anaerobic zone assures 1.0 g P/m^3 in the effluent even after an elapse of a nominal sludge age.

To control and optimize the process performance a statistically adequate multivariate time series model was proposed (*Adeyemi et al. 1979*). Its application may lead to 60 % reduction in variability of effluent phosphorus concentration compared with a classical feedforward-feedback control.

7. Alternative processes of the phosphorus removal

7.1. Introduction

As presented in Chapter 3 most treatment technologies have their roots in 19th Century inventions. Examples of chemical precipitation, activated sludge process and sludge digestion were presented.

Some other technologies which are at present often reported as 'brand new' come from old but forgotten ideas. Chlorination or natural treatment technologies may be the best examples. It was obvious from the time of their first application these methods were not intended for a phosphorus removal even though this process took place. A historical background of precipitation technologies was presented previously. Some technologies to be presented as recently proposed derive much from these old concepts.

A good example is treatment by gas chlorination. Patented in the United States in the year 1893 by the 1930's several cases of successful operation were reported¹⁹.

Another example appears to be an electrolytical treatment. Some technologies which recently became more popular but were invented some time ago are: land application (*Nesbitt 1966, Sidwick & Murray 1976*), ion exchange (*Nesbitt 1966*) or use of algal cultures (*Nesbitt 1966*).

Alternative technologies presented below should, therefore, be called 'recently proposed' rather than 'new'.

7.2. Treatment with the use of electricity - the case study

The use of electricity directly for treatment of wastewater seems to be a good example of the cyclical development of treatment technologies.

The first use of electricity for wastewater treatment was patented in England in the year 1856²⁰, but no success in routine operation was reported (*Creighton & Franklin*

¹⁹ with lime, also other chemicals were tested for the pH - adjustment.

²⁰ patent pending No 1499 : "disinfection and deodorization by electric or galvanic agency"

1919). Development of the direct use of electricity for treatment proceeded in the 19th Century. In 1889 Webster (also in England) applied electrical related treatment. It was, in fact, chemical precipitation by iron compounds (oxides) formed on electrodes. Plant operations showed satisfactory results. Later came the 'Landreth Direct Oxidation Process which was electrolytic precipitation combined with lime precipitation (*Creighton & Franklin 1919*). This process was presented as economically feasible.

Sixteen years later the Report of *Committee on Sewage Disposal (1935)* summarized full-scale application of the Landreth Process as not very successful. Most operators reported no visible advantage was observed over lime-only use. Consequently the idea was suspended for some time.

In the 1950's Föyn initiated works on electrolytic treatment of municipal sewage which was mixed with seawater. His tests were one of first investigations which addressed nutrient removal. During long-term operation he obtained reliable phosphorus removal which reduced its content in treated wastewater down to 1.0 mg P/L (*Föyn 1964*).

Miller & Knipe (1965) conducted studies on the feasibility of using electrolytic processes to treat municipal wastewater with no addition of salty water. These authors proved the method is reliable but is not economically feasible for wastewater reclamation.

Marson (1967) presented results of a full-scale operation of an electrolytic treatment of wastewater with a special emphasis on phosphorus removal. The method was similar to those presented by Föyn in that wastewater was mixed with seawater prior to electrolytic treatment.

Further development was reported by *Onsott et al. (1973)* who proved electroprecipitation can result in over 80% efficiency of the phosphate removal²¹.

In the beginning of the 1990's electrolytic phosphorus removal has been proposed yet again (see below).

²¹ the same authors presented a lanthanum precipitation technology as a reliable treatment process;

7.3. Alternative phosphorus removal technologies

Apart from the chemical and biological processes being systematized above, each year several purely new or 'renewed' alternative methods of phosphorus removal are proposed.

7.3.1. Chemical and physical-chemical methods

In 1966 *Nesbitt* completed a state-of-the-art phosphorus removal report which included ion exchange process as an efficient process. This author, however, warned its application depended on access to macroporus resins to absorb organic matter and the potential for application of cheap regeneration chemicals. A demonstration ion exchange process for removal and recovery of ammonium phosphate from sewage has been built in Italy (*Liberti 1982, Liberti et al. 1985*). Economical comparison with conventional treatment shows the capital costs are of the same magnitude while running costs may be low depending on revenue from sale of recovered fertilizer.

A quartz sand which has previously been used for treatment of groundwater containing high iron and manganese concentrations can be used as filter material in a filter for elimination of phosphorus from wastewater (*Wegner et al. 1989*). This sand is a waste material in many water treatment plants and a laboratory test proved that it has high hydraulic conductivity as well as high phosphorus sorption capacity.

Tests made on phosphorus removal by a crystallization process were presented, in which seeded supersaturated hydroxyapatite solutions are applied. Experiments on phosphate rock as a seed crystal (*Joko 1984*) showed in long-term operation effluent concentration never exceeded 1.0 g P/m³. *Kaneko et al.* presented results of laboratory-scale and pilot-scale tests on application of a crystallization method; they achieved phosphorus concentration in an effluent lower than 0.5 mg P/L. Full scale tests conducted by *Eggers et al. (1991)* on 'a new process' showed not only the possibility of reliable removal of phosphorus but also presented the possibility of a phosphorus recovery from wastewater in reusable form. *Janssen et al. (1991)* tested

the combination of biological phosphorus removal and the Crystallactor in order to obtain below 0.1 mg P/L in an effluent.

Kaneko & Nakajima (1988) found an **activated magnesia clinker** to be the most effective chemical for this process. Pumice stone, zirconium hydroxide and conventional seed crystals of a phosphate rock and a bone charcoal were also tested.

During the process of **fixation from wastewater with half burned dolomite**, the phosphorus can be removed with a capacity of 10 mg PO₄-P/g solids (*Roques et al. 1991*).

In the 1970's **magnetic separation of phosphorus** was examined by *De Latour (1973)* who found it an effective method if applied after alum or iron salts addition. Further investigations proved this method is a reliable auxiliary for chemical coagulation of phosphorus (*De Latour 1975*). The concept of a magnetic separation system for the phosphorus removal was proposed as 'new' by *van Velsen et al. (1991)* and said to be very promising as the effluent values, 0.1 - 0.5 g P/m³, can be achieved at costs comparable with other processes. Great advantages of this process are: high elimination performance, compact process and low power input.

Gangoli & Thodos (1973) tested **adsorption of phosphorus** with the use of fly ash, F1 alumina and an AHB alumina. They concluded the adsorptive capacity for phosphates was greatest when adsorbents were used without any treatment.

Removal of phosphorus by adsorption on aluminium oxide has been studied in laboratory scale by *Donnert et al. (1978)*. The aluminium oxide was regenerated by sodium hydroxide and the phosphate was precipitated from the sodium hydroxide with calcium oxide. The transfer mechanism of the adsorption process has been studied by *Brattebø (1983)*. The adsorption capacity of the activated alumina is strongly pH-dependent and fairly constant when related to the available surface area. Thus, the size of the alumina particles is the most important parameter. The phosphorus in a water stream can be reduced with 80% in a filter by adsorption on amorphous iron oxide (*Wiess et al. 1992*).

Activated fly ash is a waste product which can be used for phosphorus removal (*Clark & Othmer*). Fly ash is produced at burners. In boiler plants, for example, fly ash is a fluffy material with large external and internal surfaces for adsorption and is

activated by treatment with acid to remove lime and other occupants of the active sites for adsorption.

Gleisberg (1982) found activated carbon had no effect on the phosphorus precipitation process and recommended activated carbon be used in combination with precipitation agents for phosphorus removal.

Another concept was phosphorus removal by orthophosphate nucleation (*Zoltek 1974*). Use of phosphate rock in a packed column system seemed to be an applicable technology as a 'polishing' process after a lime treatment.

Phosphorus removal together with chlorination by electrolysis allow a achievement of almost 100% phosphorus removal (*Groterud & Smoczyński 1991*)²².

7.3.2. Biological phosphorus removal methods (at WWTPs)

Some observations on **phosphorus removal in a fluidized bed reactor** were published by *Rovatti et al. (1995)*. Observations were made on a bench scale FBBR reactor operating successfully in an SBR mode. During use of a fluidized bed a thin biofilm with high surface/volume ratio has been obtained, operational results including over 50% efficiency of a phosphorus removal was found by authors as *satisfactory*.

Another attempt towards phosphorus removal in a fluidized bed was presented by *Seckler et al. (1996)*. These authors recognized physical processes incorporated into this technology with a special emphasis on primary nucleation and molecular growth, which seem to be responsible for conversion of phosphate from liquid to solid state. The second part of their work was optimization of the process. This led to the conclusion the most important mechanism for the phosphate removal in a fluidized bed was an aggregation of primarily formed particles with the grains constituting the bed. Thus, optimization may be reached by selecting proper media i.e. sand grains of small sizes, proper operational parameters i.e. low superficial velocity, and also by spreading a base addition over two locations. The highest phosphate removal

²² see paragraph 7.2. of this paper

efficiency was 80%. This work contains limited practical information, however, and is best used as a basis for further development of this technology.

Dichtl et al. (1994) tested and evaluated various wastewater treatment plant configurations for biological nutrient removal in an attempt to integrate **trickling filters** into phosphorus removal technology. They found, however, it is better to convert a concrete structure into an SBR-reactor.²³

Bringmann & Kühn (1975) studied the use of filters for biological phosphorus elimination. The elimination was done by micro-organism oxidising ferrous ions to ferric iron added as 1.36 mole ferrous chloride per mole phosphate. With four filters they achieved a 99,93% elimination of phosphate, compared to 87% elimination in the first filter. Phosphorus may also be removed by microorganisms due to assimilation by addition of an organic carbon source before, for instance, a trickling or deep-bed filter (*Bringmann 1973, Jonsson et al. 1996*).

7.3.3. Phosphorus removal in natural systems

Doran and Boyle (1979) proposed **phosphorus removal by activated algae**. They obtained almost 95% of phosphorus removal down to 0.2 g P/m³ when they exposed an open culture of algae to artificial wastewater. Related investigations were performed by *Wong et al. (1995)* to reclaim nutrient-polluted river water with the use of **microalgae**²⁴. *Lessard et al. (1994)* performed some batch-reactor tests on nutrient removal using cyanobacteria (*Phormidium bohneri*). They found nitrogen removal with this bacteria more promising than with phosphorus²⁵. Approx. 1.0 mg P/L concentration in the effluent was obtained

Tam et al. (1994) tested immobilized **Chloral vulgarize** for domestic wastewater treatment. They proved this organism may be used for phosphorus removal while obtaining over 70% removal efficiency. It required, however, 7 days of contact time. A combination of algae and pond treatment was presented by *Craggs et al. (1995)*.

²³ So it is rather not an application of trickling filter *per se*

²⁴ It is not real wastewater treatment but includes some general observation useful for wetlands.

²⁵ Only 1% of the biomass dry weight is phosphorus while up to 15% is nitrogen.

They tested marine microalgal species, *Phaetodactylum tricornutum*, to remove ammonium and phosphorus from wastewater. Results showed over 70% phosphorus removal by one of the species (B2) and showed potential for practical application in larger scale ponds.

Water hyacinths might also be applied to achieve over 90% nitrogen and phosphorus removal (*Stewart 1986* according to *Balmér & Hultman 1988*).

Wastewater treatment in ponds has increased in popularity but in northern areas their biological phosphorus removal capabilities tend to decrease. Attempts were, therefore, made to upgrade existing stabilization ponds by the addition of chemical precipitants. Removal of phosphorus down to 0.5 g P/m³ using lime and 0.11 g P/m³ using iron salts (Fe³⁺) was achieved (*Hanaeus 1991*). *Nurdogan & Oswald (1995)* tested high rate ponding (HRP) processes. They described both ways of phosphorus removal in ponds: by algal uptake and by chemical precipitation²⁶. They applied HRP as a tertiary stage with over 90% total P removal.

Wetlands, artificial and natural, can be successfully applied (usually as a tertiary treatment following biological phosphorus removal). Land disposal, lagooning and sedimentation ponds are examples of natural systems for sewage treatment (*O'Connel & Farnsworth Gray, 1944*).

Artificial wetlands are adequate to final treat ("polish") the wastewater without the addition of chemicals. In the Netherlands wetlands have been applied for polishing the effluent from trickling filters. The effluent phosphorus concentration of 1.7 g P/m³ has been obtained without addition of chemicals (*Butijn & Greiner 1985*). *Adcock et al. (1995)* surveyed constructed clay-based wetlands and tested the fate of nutrients in them. The authors showed plants and sediments are major storage components of nutrients in that type of wetland. The possibility of wetland application for sewage treatment was examined by *Hiley (1995)*. He found phosphorus stored by wetland organisms mostly in roots and in dead matter and only 7% of it appears to be removable by harvesting and suggested specialized treatment before or after wetlands for reliable and efficient phosphorus removal.

²⁶ This precipitation takes place due to high pH in ponds and is by some authors called 'autoflocculation'

Some interesting results for the application of **natural wetlands** for lake restoration, rather than for wastewater treatment, were presented by *Yin & Lan (1995)*.

For small communities new technology has been proposed in which **an intensive silviculture** is applied for effluent disposal. This technique allows wastewater treatment with no (zero) effluent. The effluent is totally utilized by multi-clonal poplar forest. This kind of ecologically safe method will be developed in the near future, especially in low density population regions (*Laughton et al. 1990*).

8. Sludge management

Sludge disposal and utilization are important elements in the removal of phosphorus from wastewater. If performed improperly it may cause negative impact on the environment. Specially re-contamination by phosphorus-containing leakages to the waters may harm an environment.

Usually sludge from the wastewater treatment process is thickened, stabilized, conditioned and dewatered. Wastes treated in such a way can be incinerated or disposed. Due to its relatively high phosphorus content processed sludge may be applied in agriculture as a fertilizer. This way of disposal is the most natural method of phosphorus recycling.

In following chapter basics of sludge treatment and disposal are summarized.

8.1. Sludge derived from chemical phosphorus removal

8.1.1. Aluminium salts

Sludge characteristics depend on numerous factors such as wastewater composition, chemical dosage and point of its application, mode of combination of various sludges (primary, secondary or tertiary), retention time in clarifiers, etc. In general, two rules usually apply:

- aluminum salts addition will result in an increase in sludge volume and mass,
- addition of chemicals to the sludge impacts its dewatering and thickening characteristics.

Broad experience with this kind of sludge shows it is difficult to generalize the methodology of its thickening and dewatering so the choice of sludge handling must be based on case-by-case studies (*EPA 1987*) .

Sludge thickening

- ◆ gravity thickening is rarely applied for this kind of sludge. Addition of polymer to the influent to the gravity thickener usually improves solids capture.
- ◆ flotation thickening is not being applied for primary or combined primary-secondary sludges. This technique is useful for waste activated sludge, and typically applied design loadings range from 2.4 - 4.0 kg/m²/hour without polymer or twice as high with polymer addition.

Sludge stabilization

aerobic stabilization - this method is applied by a quarter of phosphorus removing plant in the United States, generally without major problem with stabilization of chemical sludge (*US EPA 1987*).

Some problems were reported with the release of phosphorus from the solid to the liquid phase during anoxic storage of digested primary sludge (increase of orthophosphate phosphorus concentration in the liquid from 5-10 to 25-50 g P/m³). No such increase has been reported for mixed primary and secondary sludge.

anaerobic digestion - existing data indicate different results of this process mainly because of the impact of alum addition on the digestion process and the resulting increase in energy requirements (*Grigoropoulos et al. 1971*). Tests showed a decrease in anaerobic digestibility caused by alum presence in sludge (*Dentel & Gossett 1982, Seyfried et al. 1988*).

Conditioning

- ◆ chemical conditioning can be applied but chemical dosage tends to be higher than for non-chemical sludges;
- ◆ thermal conditioning seems to be a less applicable process because sludges from chemical phosphorus removal have an inverse impact on this conditioning process and usually require higher conditioning temperatures (over 200°C *EPA, 1987*),
- ◆ freezing of this kind of sludge shows good results and may be applicable in cold climates (*Farell et al. 1970, Cornier et al. 1983*).

Before the choice of the method of conditioning is made pilot studies are recommended to establish sludge parameters, estimate type and dose of conditioner, and assess mixing conditions (*Eden, 1983*).

Dewatering

is usually performed in drying beds, vacuum filters or centrifuges. Individual pilot studies, however, are recommended for each case. The new techniques of pressure filtration or the belt filter press have been implemented more often in recent years. Their advantages are low moisture in the produced sludge cake and lower operation costs.

Agricultural disposal

Tests on the potential impacts of this kind of sludge on crop and soil showed increasing metal content in the soil. Addition of aluminum for phosphorus removal has been found to not affect the agricultural value of resulting sludge as compared without chemical sludge. Due to the risk of soil contamination by heavy metals the agricultural application of this kind of sludge must be preceded by individual studies for each case.

8.1.2. Iron salts

Disposal of this kind of sludge is based on procedures similar to those presented for aluminum salts.

Thickening

- ◆ gravity thickening - both positive and negative impacts on thickener performance have been reported; if no other data is available thickeners are designed on the basis of maximum overflow rate which is equal to:

* 1.0 -1.2 m³/m² hour for primary sludges

* 0.16-0.32 m³/m² hour for combined (mixed) sludges

- ◆ flotation thickening - mostly applied to waste activated sludges with typical design overflow rates:
 - * 29-117 m³/m² s for non chemical activated sludge
 - * 58-88 m³/m² s for iron-activated sludge.

Stabilization

- ◇ aerobic digestion - a quarter of the phosphorus removal plants in the United States use this method of stabilization while reporting few problems due to increased volumes of sludge exceeding the design capacity of the digesters. Further studies showed this process is similar to the one described for aluminum salts.
- ◇ anaerobic digestion - the most common sludge stabilization process, especially for large plants. The negative impacts, if reported, were similar to those presented for an aluminum process, i.e. increased requirements for sludge mixing, lower digestibility and poor solid liquid separation (*Dentel & Gossett 1982, Seyfried et al. 1988*).

Conditioning and dewatering

- operational aspects observed were mostly the same as for aluminum salts (*EPA 1987*).

8.2. Sludge derived from biological phosphorus removal.

Sludge from biological phosphorus removal usually forms light, but cohesive and settleable flocs with a sludge volume index of 150 ml/g or lower. In systems designed for nitrogen and phosphorus removal a sludge bulking effect has been reported. (*Barnard 1975, Deakyne et al. 1984, Daigger et al 1985, Pitman 1991*)

The sludges exhibit characteristics similar to conventional biological sludges. Resulting waste activated sludge, however, tends to have twice the phosphorus concentrations than conventional sludges. To avoid re-solubilization of phosphorus

when sludge is exposed to anaerobic conditions it is recommended that waste coming from "pure" biological removal systems should be kept in aerobic conditions.

Problems of phosphate release were studied by *Jardin & Pöpel (1994)* who concluded most of the phosphorus is stored in sludge mass in the form of polyphosphate. They also showed approx. 20% of phosphorus in the digester is precipitated in the form of a struvite²⁷. The principal challenge in designing sludge handling facilities is to minimise the mass of nitrogen and phosphorus being recycled to the plant in the sludge handling return streams (*Rabinowits & Barnard 1994*). Separate thickening of primary and waste activated sludge is thereby recommended. The dissolution during anaerobic digestion of precipitated phosphate has been studied by *Mosebach (1975)*. Dissolution is mainly dependent on the molar proportion between phosphate and iron and increases at decreased molar proportion. At high dissolution a large part of the phosphate is recycled to the plant. The dissolved phosphate can be used for precipitation of ammonium from the recycled water, thus improving the denitrification by decreasing the amount of recycled nitrogen (*Bundesamt für Umwelt, Wald und Landschaft, Bern 1993*).

Waste sludges from biological phosphorus removal plants tend to be unstable and cause technical and aesthetic (odor) problems. Sometimes additional precipitation of sludges is necessary. Recently presented investigations have been directed towards fixation of phosphorus compounds and estimation of requirements to obtain chemically and microbiologically stable sludges (*Jardin & Pöpel 1993*).

Hing et al (1992) summarized sludge disposal technologies currently practiced. These authors presented technical solutions of sludge disposal (e.g. digestion, dewatering, drying) while also emphasizing the real applicability of treated sludge in the life cycle. Worldwide sludge management practices described how approaches to sludge application differs in various countries. In general four basic disposal ideas are most common: agriculture use, landfill disposal, incineration and dumping into sea. Of European countries surveyed West Germany and England are larger users in agriculture, West Germany and France dispose large quantities into landfills and incinerate sludges while England disposes the largest (in Europe) amount of sludges

²⁷ struvite is a popular name of a magnesium ammonium phosphate

into the sea²⁸. The important role of public acceptance for sludge use in natural systems has also been presented by the authors.

Specific problems of sludge handling at a biological nutrient removal plant were also presented by *Randall et al (1992)* which included some case studies with a biomass balance for US WWTPs.

Thickening

To minimize the risk of phosphorus release (as it has been mentioned above) the use of dissolved air flotation thickening is usually recommended. Gravity thickening of this waste activated sludge, however, has been successfully tested at some plants (*Pitman 1991*).

Stabilization

Aerobic stabilization is usually applied, but phosphorus release may also be possible during anaerobic digestion due to destruction and lysing of biological solids (*EPA 1987*)

Conditioning and dewatering

These sludges are supposed to have the same conditioning requirements and dewatering characteristics as those from conventional activated sludge systems (*Randall et al. 1992*).

Agricultural disposal

Sludges from biological phosphorus removal systems can be disposed of as sludges from conventional biological systems. The most natural way of sludge disposal seems to be agricultural application. For this usage, however, sludge quality must meet the strongest standards. The advantage of this application is high fertilizer value of sludges from wastewater treatment e.g. it is estimated that sewage sludge can cover over 5 % of phosphate fertilizer needs in the United Kingdom (*Matthews 1983*). Other methods of disposal are either costly (incineration) or ecologically unsafe (ocean dumping, landfilling or lagooning). The amount of sludge applied in agriculture varies in different countries. In the 1980's 24% of annual sludge

²⁸ all these data refer sludge in general not the sludge from a phosphorus removal only

production in the United States was agriculturally disposed. This amount was for the United Kingdom 44% and for South Africa 89%.

The general practice is to dispose of only those kinds of sludge which do not contain an excess of heavy metals and which are bacteriologically safe. British quality guidelines provide limiting values for addition of different metals and for their maximum concentration in arable soil. Guidelines prepared by South African Health authorities give detailed restrictions for agricultural application of sewage sludge:

- ⇒ primary sludge: only supplementary addition in making compost is permitted;
- ⇒ secondary sludge: permitted for crops not eaten raw by humans, forbidden on lawns, sport fields, forage for animals and on low growing vegetables;
- ⇒ matured secondary sludge (composted, pasteurised): use on vegetables permitted only if pathogen free, forbidden as top dressing;
- ⇒ advanced treated sludge (irradiation, high temperature): use unrestricted (*Oberholster 1983*);

Surveys in the United Kingdom (*Matthews 1983, Lue-Hing et al. 1992*) showed most of the sludge is applied on arable land and grazing land while a relatively low amount is applied in horticulture. Sewage sludge is applied on land in liquid or semi-dry form. This creates some aesthetic problems. To avoid them various methods of sludge final treatment have been tested. Composting has been found to be a very attractive system of management. Composted sludge is a healthy, safe, easy to use and valuable fertilizer with a broad range of applications. Sewage sludge for composting is generally dewatered to approx. 30 % solids. In order to meet biological criteria for aerobic composting a bulking material is added. Sludges usually are low in volatile solids so a bulking agent is added to provide available carbon. It may be woodchip, rice hulls, brush chips, grass clippings or even shredded rubber tires. Sludge is mixed, aerated and then screened. Financial analysis proved it to be a cost-effective process.

9. Recent trends in investigations on phosphorus removal technologies.

Phosphorus removal technology is still under development. Despite works on mathematical models of these processes (which are not a subject of this review) large effort is made on optimization of dosage of chemicals, external and/or internal carbon sources, anaerobic/aerobic conditions sequences, also brand new concepts of phosphorus removal are presented every year.

Some authors focus on upgrading existing plants to meet new phosphorus-in-effluent standards (*EPA 1987, Barnard 1984, Randall et al. 1992*). Some interesting full-scale results of upgrading were presented by *Buß et al. (1994)*.

Recent investigations into the field of phosphorus removal show the following topics to be important:

- investigations on mechanisms of biological phosphorus removal.
- possibility of nutrient (including phosphorus) removal in natural systems.
- biological phosphorus removal with limited availability of easily biodegradable carbon source.

9.1. Investigations on mechanisms of phosphorus removal

Barker & Dold (1996) presented a review paper on denitrification behavior in biological phosphorus removal systems summarizing some works cited in this paper. In general they confirmed a role of amount and type of readily biodegradable material in the feed on an anaerobic uptake. They also confirmed a possible negative impact of nitrate on enhanced phosphorus removal. They questioned, however, if nitrate can serve as electron acceptor for direct utilization of SCFAs.

Randall et al. (1994) tested the influence of fermentation on biological phosphorus removal with a special emphasis on microbial population dynamics. They showed the entire process depended on results of pre-fermentation products. The same tests proved an anaerobic phase of a sequencing batch reactor (SBR) did not act as a fermentation zone for glucose. After comparing glucose-population and starch-

population behavior in the SBR they stated glucose population yielded significantly greater phosphorus removals than the starch population.

Satoh et al (1994) conducted laboratory scale bench tests on activated sludge with no phosphate accumulation. It was observed sludge can absorb acetate and propionate under anaerobic conditions. Further studies showed these bacteria did not obtain energy via hydrolysis of polyphosphate²⁹. It proved there is a considerable risk of competition between these groups of bacteria which may lead to a break-down of enhanced biological phosphorus removal.

Removal of phosphorus as magnesium ammonium phosphate has been discussed from many aspects. Magnesium ammonium phosphate is known to cause severe disturbances such as clogging of pipes, pumps etc (*Rabinowitz & Barnard 1994*). Precipitation of magnesium ammonium phosphate may be seen as a possibility to recover phosphorus and ammonium (*Kuttig 1991 and Stefanowicz et al. 1992*). Studies have also been made to evaluate the possibilities of adding phosphorus to a wastewater stream to recover magnesium ammonium phosphate as a product (*Schultze-Reimer & Yawari 1988*).

A genetic approach was presented by *Ohtake et al. (1994)*. Testing an *Escherichia coli* species they found a possibility for improvement of intra-cellular storage of phosphorus by modifying a genetic regulation of some genes encoding polyphosphate kinase, acetate kinase, and phosphate inducible transport systems. This method achieved 16% phosphorus dry weight content in combinant biomass, thus, showing genetic engineering to be a way of future development.

Tests on physiological characteristics of phosphate removing bacteria were done by *Ubukata (1994)*. It was found during induction of excess phosphorus removal a presence of organic substrates in the aerobic incubation severely suppressed the uptake of phosphate. This confirmed, from the physiological point of view, no substrate in aerobic phase is necessary for the confirmation procedure of phosphate removing bacteria.

²⁹ They obtained energy under anaerobic conditions by converting glycose to PHA via Acetyl-CoA and propionyl-CoA

Some further steps on *Acinetobacter* species' role have since been done. *Muyina & Cloete (1995)* investigated *Acinetobacter* cell while immobilized in a mixed liquor. These conditions did not affect the viability of cells. They found neither *A.calcoaceticus* nor *A.johnsonii* growing cells took up phosphate while immobilized.

A relationship between biomass and phosphate uptake by *A.junii* was presented by *Momba & Cloete (1996)*. The main aim of their work was to clearly define a role of *Acinetobacter* organisms in excess phosphate removal. The authors stated removal of phosphate by *A.junii* had been associated with the initial biomass cell concentration and growth stage. At a high initial cell concentration these bacteria removed phosphates during the entire growth phase while at low initial concentration they adversely affected the process. *Fleit (1995)* performed research on biochemical mechanisms of intracellular pH regulation under an enhanced phosphorus removal process. He stated the major biochemical signal to induce P release and intracellular PHA synthesis under anaerobic conditions is the pH_i decrease caused by SCVFA sequestration. Furthermore the author gave some detailed additional information on intracellular mechanisms which support biochemical models as presented in chapter 4 of this review.

Interaction between biological and physico-chemical mechanisms was studied by *Witt et al. (1994)*. They conducted batch experiments showing magnesium participates in biological removal mechanisms (counter-ion of polyphosphates). Biologically mediated P-precipitation should be concerned while taking bio-P removal into consideration and the amount of phosphate phosphorus bound physico-chemically cannot be neglected. Despite physico-chemical observation the author also stated biodegradable COD availability is of great importance.

In the border area between biological and chemical experimentation *Roske & Schonborn (1994)* made bench scale tests on biological phosphorus removal at a WWTP with chemical phosphorus precipitation in a mechanical treatment stage. They found a low dose (3 mg Fe/l) of chemical addition did not adversely impact biologically enhanced phosphorus removal while a higher dose did. Their conclusions match those presented by *Rybicki (1996)*: to some value primary precipitation may not adversely affect a biological phosphorus removal processes. *Bliss et al. (1994)* tested simultaneous biological nitrification and chemical phosphorus removal

and obtained, as a result of this combination, low ammonia nitrogen and phosphorus concentration in the effluent³⁰.

Kuba et al. (1994) performed tests on nitrate impact on phosphorus release (which was discussed previously in chapter 7 of this review). Their conclusions generally supported the *Mino* biochemical model as to DPB metabolism. They proved nitrates do not block phosphorus release in the DPB and reduction of phosphorus release by nitrates occurs due, in fact, to HAC utilization for the ATP formation in the TCA cycle and the oxidation of NADH₂/FADH₂ with nitrate.

Mino et al. (1994) stated the system usually applied for oxidation-reduction balance in the cells enables the anaerobic uptake of organic substrates. It is, therefore, essential for the microorganisms survival in anaerobic-aerobic processes.

Kuba et al. (1996) tested a 'two-sludge' idea. Knowing denitrifying dephosphatation enables phosphorus removal and nitrogen removal with minimum usage of COD, minimum oxygen consumption, and minimum excess sludge production, they tested anaerobic-anoxic SBR coupled to a nitrification SBR. They stated the 'two-sludge' system lead to an optimal process design of denitrifying dephosphatation. They also confirmed the necessity of external COD addition in case of a too low COD/N ratio.

Matsuo (1994) examined the effect of the anaerobic solids retention time in biological P removal on a continuous flow treatment system. It was shown, in a system operating at a short anaerobic SRT, phosphorus removal declined due to non-phosphate microbe growth. Extending a SRT resulted in improvement of the phosphorus removal.

Maurer & Gujer (1995) proposed their own new method of monitoring a microbial phosphorus release with the use of electric conductivity. They found this method very useful for P release measurement for non-aerated batch experiments and for SBR reactors. This method may be helpful in the further operation of bio-P technologies.

Some interesting results of experiments were released in Sweden recently.

Aspegren (1995) tested biological phosphorus removal in a highly loaded activated sludge process and obtained results of around 0.5 mg P/L in the effluent. His work

³⁰ below 1 mg ammonia N/L and below 1 mg P/L

also covered immobilization of phosphorus in sludges and showed almost 1/3 of the phosphorus immobilized in the sludge was released during anaerobic digestion. Related works on the circulation of phosphorus in a biological phosphorus removal system was presented by a team with the same author (*Nyberg et al. 1994*). More of these works are presented in point 9.3. below.

9.2. Phosphorus removal in natural treatment systems

The concept of phosphorus removal in natural treatment systems comes from most natural way of nutrient handling i.e. to put phosphorus back into the natural life cycle. As stated before this approach also occurred in the past as primary method of wastewater disposal for agricultural use. In the past almost all researchers considered phosphorus a contaminant responsible for water reservoirs' eutrophication. This compound is, however, an important constituent of all living organisms. Its need by agriculture is currently met by the use of artificial (chemical) fertilizers containing phosphorus and nitrogen compounds. Due to similar roles in the food chain both nitrogen and phosphorus are usually considered as one group of wastewater constituents - called 'nutrients'. They differ significantly, however, in that nitrogen resources on the earth are almost endless while mineral phosphorus resources are estimated as equal to 150-200 years consumption. Therefore, more emphasis should be put on the development of phosphorus recovery systems from wastewater such that its fertilizing role might be used in agriculture. Such an approach leads to the idea of recycling nutrients which at present is at the general concept or scientific research stage.

Approaches to this problem may be different, for example:

- separation of wastewater streams and recovery of nutrients from the most concentrated ones, especially in local systems
- recovery of calcium or magnesium phosphate from biological treatment plants,
- recovery by ion exchange;
- recovery of phosphates and coagulants by use of sulfate reducing and sulfide oxidizing bacteria.

It became obvious further development of phosphorus-in-wastewater handling methods should be directed towards its recovery in a cycle as natural as possible.

In contrast to previously discussed phosphorus removal technologies which were intended to be applied on existing and/or designed wastewater treatment plants it is possible to address the problem of a phosphorus removal by a different approach. This is by phosphorus removal in natural systems.

Kruzic (1994, 1995) divided natural treatment system for wastewater into two general categories :

- soil based systems including: subsurface infiltration, soil aquifer treatment, overland flow;
- aquatic systems including ponds, floating aquatic plants and constructed wetlands system.

Some of these natural systems applied for phosphorus removal were presented in the review in chapter 6 concerning new techniques in P removal. General difficulty in their application arises from the fact phosphorus is stored by waterborne organisms or in roots and reeds of plants in wetlands whereby only a small part of it can be removed by harvesting. In general, natural systems are most efficient in phosphorus removal when applied as a tertiary treatment step (i.e. after biological treatment).

Soil based systems were tested by *Turner et al. (1994)* who performed a half-year study on phosphorus removal in artificial wetlands (as a tertiary treatment) which obtained 77% phosphorus removal efficiency in the summer and 52% in the winter. *Suzuki et al. (1992)* made experiments on a sub-surface system obtaining 90% total phosphorus removal with relatively low nitrogen removal. *Guilloteau et al. (1993)* showed a French plant with a rapid infiltration process with over 85% total phosphorus removal efficiency. *Ou et al (1992)* showed a complete design procedure for paddy rice slow-rate land treatment.

For aquatic systems *Gearheart (1993)* checked a nutrient budget for a free-surface wetland (constructed) and evaluated phosphorus removal under different conditions. The author showed wetlands stabilize orthophosphate concentration. Phosphate removal is due to plant uptake so P concentration in the effluent is higher in the fall and early winter than in the rest of the year. *Cripps & Hanaeus (1993)* tested lime addition as a supporting process in phosphorus removal in wetlands. *Green & Upton*

(1994) summarized design procedures, performance, and cost-effectiveness of a reed bed system in secondary treatment used in the United Kingdom. *Jenssen et al* (1993) presented results of operation of submerged flow constructed wetlands in Norway for treatment of the outlet from septic tanks. All these studies show natural treatment systems as a possible way of phosphorus removal. They should, however, be applied as a tertiary treatment. Otherwise additional (chemical) treatment should be applied.

In addition to technological limitations, climatic limitations dictate most of the natural treatment systems are effective only in normal (middle) climate and warm climate *Reed et al. (1988)*. Those which might be widely applied are: ponds, constructed wetlands, and rapid infiltration applied as a tertiary stage. Further investigations should address towards natural systems operation for nutrient removal in mild to cold climates.

9.3. Biological phosphorus removal with limited availability of readily biodegradable carbon source

This problem has been recently studied by different authors. In Sweden *Carlsson (1996)* operated a single sludge system and proved it is possible to achieve 0.5 mg P/L concentration in an effluent. Increase of phosphorus concentration in the effluent was, however, observed in those periods when COD/P and VFA/P ratios decreased. It was stated phosphorus removal is more sensitive to low COD contents than to nitrogen removal.

Lee (1996) tested factors affecting phosphorus removal and found, of various carbon sources, an acetate and methanol to be the most advantageous for nutrient removal³¹. Observing enhanced biological phosphorus removal the same author found a significant difference between operation of this process in various sludge systems. High loaded systems showed worst separation characteristics, especially, in the winter. Limiting factors were examined by *Lie (1996)* who tested the possibility of application of primary sludge fermentation for an increase of easily biodegradable carbon sources. Approximately 20 mg COD in form of volatile fatty acids was

³¹ in this case denitrification was tested

necessary to remove 1 mg of phosphorus. Important tests on biological phosphorus removal combined with biological phosphorus removal were done as a part of the Swedish STAMP research program, including development of mathematical models for biological enhanced phosphorus removal.

10. Future directions in phosphorus removal management

10.1. Introduction

Phosphorus removal in wastewater treatment is today a well-known technology in which two main directions exist: chemical precipitation and enhanced biological removal. This does not mean, however, there is not a great need for improvements in phosphorus removal technologies and management. The principle ways to diminish the phosphorus load on surface waters are reduction or the supply of phosphorus due to:

- (1) Detergents and food additives
- (2) Source control including urine separation toilets and composting toilets
- (3) Improved wastewater treatment
- (4) Diversion of treated and untreated wastewater streams from surface waters from use by irrigation
- (5) Improved sludge handling management including the recovery of phosphorus products

10.2. Phosphorus in detergents and as food additives

When phosphorus compounds were introduced in detergents in the middle of the 1950's there was very little concern for the effects of increased phosphorus and eutrophication in surface waters. It became, however, an increased awareness of the negative effects and different substitutes of phosphorus compounds are available at present as the use of zeolite A in conjunction with polycarboxylic acid (PCA) and nitriloacetic acid (NTA). Today there is a debate on the overall environmental impact of different detergents (*Morse et al. 1993, Wilson & Jones 1995*). Phosphorus compounds are sometimes used as additives in food (as in some soft drinks) and for corrosion protection.

It may be argued phosphorus should not be used in detergents and as additives in foods due to a possible shortage of phosphorus minerals in the future. Considerations of phosphorus as a limiting resource has, for instance, lead to a substantial reduction of the specific amount of phosphorus supplied to municipal wastewater treatment plants in Sweden from about 4 in 1965 to about 2 - 2.5 g P/cap*day³² in 1995 (Hultman, 1980, 1996). Substitutes for phosphorus in different products, which are environmentally safe and consumer friendly, are important for decreasing phosphorus usage.

10.3. Source control of phosphorus

One possible method to increase the recirculation of nutrients from wastewater handling to agriculture is the use of source control, i.e. separate handling of urine and faeces and of gray water. A typical distribution of phosphorus in Swedish domestic wastewater is (SEPA, 1995 and Hellström, 1996): Urine 1.0 g P/cap*d (48%), faeces 0.5 g P/cap*day (24%), and greywater 0.6 g P/cap*day (28%). Corresponding figures for nitrogen are: Urine 11 g N/cap*day (81%), faeces 1.5 g N/cap*day (11%), and greywater 1.0 g N/cap*day (7%).

Systems are available both for separation of urine and faeces from greywater and the separation of urine from faeces by use of urine separation toilets. Different systems with source control of nutrients are at present being investigated and the need for recycling may lead to changes in urban wastewater infrastructure (Jenssen & Etnier, 1996). Henze (1995) considers water savings, sewer network renovation, separation of toilet wastes, solid waste manipulations in the kitchen and the use of phosphate free detergents as the main techniques to be applied in households in order to design the waste composition and to produce a waste, which can be handled in an optimal way with minimal losses of energy, water and material resources.

³² g P/cap*d = gram of phosphorus per person per day

10.4. Improved wastewater treatment

Evaluation methods for wastewater treatment systems are essential in order to consider both cost efficiency (cost in relation to receiving water improvement) and sustainability (consumption of energy and raw materials). Life cycle analysis (LCA) may hereby be an important tool (*Ødegaard, 1995*). By this analysis different alternatives for phosphorus removal may be compared. Based on such an analysis *Ødegaard (1995)* has found treatment methods which maximize biogas production, i.e. use of chemical pre-treatment should be chosen from a sustainability point of view. *Booker et al. (1991)* found the combined use of magnetite and chemical precipitation with ferric or aluminum salts remove most of the organics from sewage. The magnetite is recycled by use of a magnetic separator while the organic material may be treated anaerobically for biogas production. *Charlton (1996)* describes a process which combines biological nutrient removal from wastewater with biogas production from sorted organic waste.

For very stringent treatment requirements it may be necessary to combine two or more treatment steps to remove phosphorus. One possibility is to combine pre-precipitation, simultaneous precipitation, or biological phosphorus with a filtration step. An effluent concentration of phosphorus below 0.1 mg P/L may be obtained if precipitation chemicals are added before the filter. If the filter is used for denitrification the added organic material before the filter will also diminish the effluent phosphorus concentration (*Hultman et al., 1993, Plaza et al., 1995 and Jonsson et al. 1996*). Another process combination is the use of traditional phosphorus removal in a treatment plant with polishing in natural treatment systems by oxidation ponds and wetlands.

10.5. Diversion of wastewater streams

Treated and untreated wastewater may be diverted from a direct discharge to surface waters. One possibility is to use infiltration of wastewater into soil (*Nilsson, 1990*). For countries with water scarcity soil-aquifer treatment can play an important role for groundwater recharge and for wastewater reuse. Another important use of

treated wastewater is irrigation. In this case the water and the nutrients content in the wastewater may be used for agricultural purposes (*Bouwer, 1993*).

10.6. Improved sludge handling management

The value of products in sewage is in general small compared to the sewage handling costs. In *Babitt (1952)* it is stated: "It is true that there are recoverable constituents in sewage, but, like the extraction of gold from seawater, the process of recovery is more costly than the value of the recovered substances. No process of domestic sewage treatment that delivers a sanitary effluent has been devised that has returned a profit. However, since sewage must be treated some of the costs for treatment may be defrayed by the recovery of valuable products. These include liquid for its irrigation value; treatment plant effluent for cooling in steam-power generating plants, and other industrial uses; sludge for its fertilizing value and heat content; grease; grit as a road, walk, and filling material; and combustible gas resulting from sludge digestion."

Early attempts have been reported for the recovery of chemicals and nutrients in sewage treatment. An example is the Guggenheim process, which consisted of (*Gleason & Loonam, 1933*):

- (1) Suspended solids removal by coagulation with ferric salts and lime, with sedimentation of the solids.
- (2) Sludge disposal by filtration and incineration. The iron was recovered as ferric sulphate from the incinerated ash.
- (3) Basic nitrogen compounds were removed from the clarifier supernatant by an exchange reaction with zeolite resin.
- (4) The zeolite was regenerated with a sodium chloride solution, and the basic nitrogen compounds were concentrated with subsequent recovery of ammonia from this solution.

Recovery of nutrients from human wastes follows today three main lines:

- (1) Separate treatment of black water and gray water which gives a possibility to remove more than 80% of the nitrogen and phosphorus from the wastewater (*Jenssen & Etnier 1996*).
- (2) Use of the sludge from wastewater treatment for agricultural purposes has been recognized for a long time (*Niles 1944*). In this case most of the phosphorus may be recovered and about 20% of the nitrogen in the wastewater. Different results are, however, reported on the availability of phosphorus in chemically precipitated sludge (*Bernhardt 1981, de Haan 1981, Gleisberg & Taubel 1979, Larsen 1981, Kuile 1983*). By means of effective control of industrial discharges, public information on handling of wastes, and proper sludge handling methods the sludge quality may be high. However, acceptance from the public, farming organizations, and the food industry are crucial factors for recycling of sludges to agriculture even if authorities consider the sludge to be environmentally safe.
- (3) Solubilisation of parts of the sludge by use of biological, chemical and/or thermal methods in order to release organic material, nitrogen and phosphorus compounds and metals to a concentrated liquid stream. By use of selective methods different products may be recovered from the liquid stream (*Göransson & Karlsson 1994, Dirkzwager et al. 1994*). In this way a phosphorus product may be produced with a high purity.

It may be expected the need to recover and recycle phosphorus from human wastes and wastewater will increase in the future. Phosphorus may be a limiting substance in the future. Another influencing factor is deposits of phosphorus containing sludges may be a source for a diffusive supply of phosphorus to the environment (*Rydin 1996*). These factors may be seen as a basis to better evaluate the possibilities for an efficient recycling of phosphorus in wastewater handling.

11. Conclusions

1. Phosphorus must be removed from wastewater as too high concentration may lead to an eutrophication effect and rapidly deteriorating water quality. Limnologists began to warn about the eutrophication effects of phosphorus compounds at the end of the 1950's due to the increased usage of phosphate containing detergents.

2. Main sources of phosphorus compounds in sewage come from human excreta and detergents. Average amounts of phosphorus from urine and faeces are about 1.0 and 0.5 g P/cap*day, respectively, in Sweden. Due to replacement of phosphates in many detergents with mainly zeolite A in conjunction with polycarboxylic acid and/or nitriloacetic acid the specific per capita load of phosphorus from detergents has declined in many countries, i.e. in Sweden from about 2 g P/cap*day in the middle of the 1960's to about 0.6 g P/cap*day in 1995. A minor part of phosphorus in municipal wastewater is due to food additives, corrosion inhibitors, and industrial sources.

3. Full scale application of chemical precipitation for phosphorus removal started around 1960 and chemical precipitation with the use of aluminum and iron salts and lime was the chosen technology. Chemical precipitation had, however, been widely used earlier in full scale sewage treatment with its purpose to remove suspended solids, reduce the BOD-load on the biological step and to reduce the effects of varying loads to a treatment plant. Much of the present practice in chemical precipitation has its roots in practice from England and Germany 1880-1910 and in the USA in the 1930's.

4. Chemical precipitation is today a well established technology for phosphorus removal from municipal wastewaters. Besides the phosphorus removal, chemical precipitation has many other important effects as previously mentioned. The addition of chemical precipitation agents and removal of produced flocs by sedimentation, flotation and/or filtration is the main process technology. Other technologies such as production of metal ions by electrochemical methods, seeding with magnetite and removal of flocs by magnetic separators or crystallization methods have so far not

come into practice to a significant extent although the methods have certain specific advantages.

5. For larger plants the main alternative for phosphorus removal to chemical precipitation is the use of enhanced biological phosphorus removal. This process technology is about 30 years old with research and development works starting in the USA and South Africa.

6. The theoretical description of the biological phosphorus removal process still needs more research and development. The main conditions for obtaining enhanced biological phosphorus removal are, in general, well-known, but it is still not possible to accurately model the process. Both design and operation must mainly rely on practical experiences. Temperature, presence of readily biodegradable carbon sources and a proper sequence of aerobic and really anaerobic conditions seem to be essential for process performance. Biological phosphorus removal can be applied not only in mild to warm climates where it was developed but also in mild to cold climates if proper operational conditions are fulfilled. Besides biological removal mechanisms, chemical precipitation may play an important role, especially, for municipal wastewaters with a high hardness.

7. Biological phosphorus removal may be designed in several different ways; so it is possible to find a process configuration which fits specific design conditions. Many plants have recently been put into operation or are under construction or planning. In German speaking areas, for instance, 125 sewage treatment plants were operated with enhanced biological phosphorus removal and 240 were planned or under construction in 1994. Biological phosphorus removal allows a total effluent phosphorus concentration below about 1 mg P/L without further treatment steps. In those cases when a more efficient phosphorus removal is necessary biological treatment must be supplemented by precipitation and/or filtration processes.

8. Local treatment and ecotechnical and natural methods have so far only been used at sparsely built-up areas or as polishing steps in countries with moderate or

cold climates. There is, however, an increasing interest to extend the use of these methods.

9. Many combinations with chemical and biological methods are possible for phosphorus removal. The system choice depends on many factors and better evaluation methods are needed. Life cycle analysis (LCA) may be an interesting tool to evaluate the systems with respect to sustainability.

10. Phosphorus recovery and reuse will become a more important issue in the future. Phosphorus from minerals may be a limiting resource in the future and leakage of phosphorus in sludges at deposits may be an important diffusive source of phosphorus to surface and ground waters. Political and public acceptance of eco-cycling, sustainable development and Agenda 21 will intensify these efforts.

11. Main routes for phosphorus recovery and reuse seem to be:

- Improved sludge quality at treatment plants and use of the sludge for agricultural purposes
- Processing of the sludge into separate fractions to obtain different products including a phosphorus containing product with a high purity
- Source separation of human wastes from gray water and/or use of urine separation toilets

12. Efficient industrial control of discharges into the sewer net, development of more environmentally safe consumer products and consumer information may lead to a sludge with a low concentration of harmful contaminants. Phosphorus availability for crops of chemically precipitated sludges needs further evaluation. Acceptance from the public, farmer organizations and the food industry is a crucial factor for potential use of the sludge for agricultural purposes even if the sludge is considered to be environmentally safe by authorities.

13. Sludge may be solubilised by different methods to release phosphorus, nitrogen compounds, organics and metals. The obtained liquid contains a high concentration of the components and by use of selective methods different products may be obtained as a phosphate salt with a high purity. The methodology to produce different products from sludge is still in a developing phase although many ideas have been suggested for quite some time.

14. For Swedish conditions the load of phosphorus and nitrogen is approximately 48% and 81%, respectively, for urine, 24% and 11%, respectively, for faeces, and 28% and 7%, respectively, for gray water. It is, therefore, natural that urine separation toilets or separate handling of black water from greywater increases the possibilities for recovery of phosphorus and nitrogen compounds. Separation of human wastes and, especially, the use of urine separation toilets decrease the risks for contamination of toxic materials. These general ideas of recycling human wastes have been in practice for centuries in, for instance, China, but their application in urban areas in Western Europe is only in a development stage.

15. Although there is still a need for optimization of different methods for phosphorus removal it seems to be more important to evaluate the phosphorus cycle in urban areas and its interactions with rural areas. Such an analysis should include both technical, environmental, hygienic, economical and sociological aspects in order to secure a sustainable wastewater handling system.

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