VILNIUS GEDIMINAS TECHNICAL UNIVERSITY

Svetlana OFVERSTROM

RESEARCH AND EVALUATION OF IRON IMPACT ON SLUDGE DIGESTION PROCESS

DOCTORAL DISSERTATION

TECHNOLOGICAL SCIENCES
ENVIRONMENTAL ENGINEERING (04T)

VGTU
LEIDYKLA
Vilnius TECHNIKA 2013

Doctoral dissertation has been prepared at Vilnius Gediminas Technical University in 2008–2013.

Scientific Supervisor

Assoc Prof Dr Regimantas DAUKNYS (Vilnius Gediminas Technical University, Technological sciences, Environmental Engineering – 04T)

VGTU leidyklos TECHNIKA 2207-M mokslo literatūros knyga
http://leidykla.vgtu.lt

ISBN 978-609-457-615-7

svetlana.ofverstrom@vgtu.lt

VILNIAUS GEDIMINO TECHNIKOS UNIVERSITETAS

Svetlana OFVERSTROM

GELEŽIES POVEIKIO DUMBLO PŪDYMO PROCESUI TYRIMAI IR VERTINIMAS

DAKTARO DISERTACIJA

TECHNOLOGIJOS MOKSLAI,
APLINKOS INŽINERIJA (04T)

VGTU LEIDYKLA
Vilnius TECHNIKA 2013

Disertacija rengta 2008–2013 metais Vilniaus Gedimino technikos universitete.

Mokslinis vadovas

doc. dr. Regimantas Dauknys (Vilniaus Gedimino technikos universitetas, technologijos mokslai, aplinkos inžinerija – 04T).

Abstract

The dissertation examines impact of iron salts and ochre (iron sludge from water treatment plant) on digestion of sludge mixture from wastewater treatment plants with biological phosphorus removal process. Research object was anaerobic digestion of sludge mixture with traditional and alternative iron sources added. The aim of work was to examine the potential of ochre as an alternative iron source and to investigate factors governing anaerobic digestion process: methane production rate, hydrogen sulphide removal process and reduction of internal phosphates recycling at wastewater treatment plants with biological treatment plants.

Dissertation consists of introduction, three chapters, general conclusions and recommendations, references and list of author‘s publication on the topic of dissertation.

In introduction main problem is discussed; topicality of work, object of research, aim and objectives of work are formulated, of the work are described; research methodology, scientific novelty of research, practical significance of results and defended propositions are presented. In the end of introduction author’s articles, structure of dissertation and acknowledgements are presented.

In the first chapter literature concerning with the studied topic is analysed. Information about sludge sources, types and characterisation, anaerobic digestion process and previous research on results on impact of aluminium and iron. In the end of chapter conclusions and tasks are reformulated.

Second chapter presence methodologies used for the research. Laboratory and pilot-scale anaerobic reactors and characteristics of sludge and ochre used for the experiments are described.

In third chapter results on impact of iron salts and ochre are presented and discussed, comparison with other researchers obtained results is made. Proposed technological scheme for use of ochre at the wastewater treatment plants with biological phosphorus removal presented and described.

Ten articles have been published on the topic of thesis: two – in scientific journal referred in the other databases, two – in International Conference material, three – in Lithuanian Conference material. 12 presentations were made at the Republic and International Conferences and Seminars.

Reziumė

Disertacijoje nagrinėjama geležies druskų ir geležies paplavų (ochra) iš geriamo vandens paruošimo įrenginių įtaką dumblo pūdymo procesui. Tyrimo objektas – dumblo mišinio pūdymas, į jį įterpiant tradicinį arba alternatyvų geležies šaltinį. Pagrindinis disertacijos tikslas – ištirti geležies paplavų, kaip alternatyvaus geležies šaltinio, panaudojimo galimybes ir nustatyti faktorius, įtakojančius pūdymo proceso kokybę: metano susidarymą, sieros vandenilio pašalinimo procesą ir vidinės fosfatų recirkuliacijos sumažinimą nuotekų valymo įrenginiuose su biologiniu fosforo šalinimu.

Disertaciją sudaro įvadas, trys skyriai, bendrosios išvados ir rekomendacijos, naudotos literatūros ir autoriaus publikacijų disertacijos tema sąrašas.

Įvadiniame skyriuje aptariami tiriamoji problema ir darbo aktualumas, aprašomas tyrimų objektas, formuluojamas darbo tikslas ir uždaviniai, aprašoma tyrimų metodika, darbo mokslinis naujumas, darbo rezultatų praktinė reikšmė, pateikiami ginamieji teiginiai. Įvado pabaigoje pristatomos disertacijos tema autoriaus paskelbtos publikacijos ir pranešimai konferencijose bei disertacijos struktūra, taip pat padėkos.

Pirmasis skyrius skirtas mokslinės literatūros analizei. Pateikiami susidarančio dumblo tipai ir charakteristikos, aprašytas anaerobinio pūdymo procesas, aliuminio ir geležies įtakos dumblo pūdymui moklsininkų rezultatai, aprašytos geležies paplavų charakteristikos ir jų antrinis panaudojimas. Skyriaus pabaigoje formuluojamos išvados ir tikslinami disertacijos uždaviniai.

Antrame skyriuje pateiktos eksperimentams naudojamos tyrimų metodikos. Aprašyta laboratorinė ir pusiau gamybinė įranga, naudojama eksperimentams; dumblo ir geležies paplavų charakteristikos.

Trečiajame skyriuje pateikti ir aptarti geležies druskų ir geležies paplavų anaerobinio pūdymo procesui rezultatai, palyginimas su kitų mokslininikų gautais rezultatais. Aprašyta pasiūlyta geležies paplavų naudojama schema nuotekų valymo įrenginiuose su biologiniu fosforo šalinimu.

Disertacijos tema yra paskelbta 10 mokslinių straipsnių: du – mokslo žurnaluose, įtrauktuose į kitas duomenų bazes, du – konferencijų medžiagoje, referuojamoje ISI Proceedings duomenų bazėje, trys – užsienio tarptautinių konferencijų medžiagose, trys – Lietuvos konferencijos medžiagoje. Disertacijos tema perskaityti dvylika pranešimų respublikinėse ir tarptautinėse mokslinėse konferencijose ir seminaruose.

Notations

Symbols

ALK – alkalinity, mg $CaCO^3$/l;

BA – bicarbonate alkalinity, mg/l;

COD– chemical oxygen demand, mg O_2/l;

FS – fixed solids, % (mg/l);

HRT – hydraulic retention time;

Nm^3– normal cubic meter (gas volume at standard temperature (0ºC) and pressure (1 atm);

OLR – organic loading rate, $kgVS_{in}/m^3/d$;

P_m – actual atmospheric pressure, atm;

$P_{released}$ – released phosphates during sludge mixture digestion process, mg/l;

P_s – standard atmospheric pressure, atm;

Q_{in} – feed sludge flow, l/d (m^3/d);

Q_{out} – digested sludge flow, l/d (m^3/d);

SGP – specific gas production, $Nm^3/kgVS_{in}$;

SRT – solids retention time, d;

T_m – actual temperature, ºC;

T_s– standard atmospheric temperature, ºC;

TS – total solids, % (mg/l);

TS_{dew} – total solids in digested dewatered sludge, % (mg/l);

TS_{in} – total solids in feed sludge, % (mg/l);

TS_{out} – total solids in digested sludge, % (mg/l);

VFA – volatile fatty acids, mg/l;
V_{biogas} – volume, Nm^3;
VS – volatile solids, % (mg/l);
VS_{in} – volatile solids content in feed substrate, % (mg/l);
VS_{dest} – volatile solids destruction efficiency, %;
VS_{out} – volatile solids content in digested sludge, % (mg/l);
X_{STP} – methane content at standard temperature and pressure, ml CH_4/gVS_{in};
X_m – measured methane content, ml CH_4/gVS_{in}.

Abbreviations

Bio-P – biological phosphorus removal;
EBRP – enhanced biological phosphorus removal;
PAOs – polyphosphates accumulating organisms;
PS – primary sludge;
S – soluble;
TKN – total Kjeldahl nitrogen;
WAS – waste activated sludge;
WWTP – wastewater treatment plant;
WTP – water treatment plant.

Chemical compounds

$Al_2(SO_4)_3$ – aliuminium sulphate;
$Al_2(OH)_nCl_{6-n}$ – polyaluminium chloride (PAC);
$Ca_5(PO_4)_3OH$ – hydroxylapatite (HAP);
CH_3OOO - (Hydroxymethyl) dioxidanyl;
CH_4 – methane;
$C_5H_7O_2$ – proteins;
$(C_6H_{10}O_5)_n$ – carbohydrates;
$C_{57}H_{104}O_6$ – fats;
CO – carbon monoxide;
CO_2 – carbon dioxide;
$FeCl_3{\cdot}6H_2O$ – ferric chloride;
Fe_2O_3 – ferric oxide;
$Fe(OH)_3$ – iron hydroxide;
$FePO_4$– iron phosphate;
$Fe(PO_4)_2{\cdot}8H_2O$ – vivianite;

$FeSO_4$ – ferrous sulphate;
Fe_2S_3 – iron sulphide;
$Fe_2(SO_4)_3$ – ferric sulphate;
H_2 – hydrogen gas;
H_2O – water;
H_2PO_4 – dihydrogen phosphate;
HS^- – hydrogen sulphide ion;
H_2S – hydrogen sulphide;
N_2 – nitrogen gas;
$NaSO_4$ – sodium sulphate;
$MgNH_4PO_4 \cdot 6H_2O$ – struvite (MAP);
NH_4^+ – ammonium;
O_2 –oxygen;
PO_4^{3-} – phosphates.

Terminology

Batch I –laboratory test with addition of ochre sediments (18.6 %TS) into feed sludge;

Batch II – batch laboratory test with addition of pressed ochre (40 %TS)into feed sludge;

Control reactor – reactor, receiving undosed sludge (0 Fe^{3+}/l);

Digestion process – anaerobic digestion of sludge mixture under mesophilic conditions;

Inoculum – anaerobic sludge obtained from full-scale digesters;

Ochre – water work sludge precipitated during iron removal from ground water through sand-filtration;

Pilot-scale test – experiment when addition of ochre from Lithuania into feed sludge was implemented;

Sludge mixture –primary and waste activated sludge from biological phosphorus removal process mixture;

Sludge liquor – dewatered sludge filtrate;

Start-up period – digestion period when inoculum was added to digesters and continuous feeding of sludge is applied, biogas production was very unstable;

Steady-state period – digestion period after start-up period when biogas production stabilized.

“Utena” – laboratory semi-continuous experiment with addition of iron chloride and iron sulphate into feed sludge;

“Vilnius” – laboratory semi-continuous experiment with addition of iron chloride into feed sludge.

Content

Introduction

Problem formulation

Stringent requirements on wastewater treatment (nutrient removal) are applied in European Union and worldwide in case to lower eutrophication of water bodies. Biological and (or) chemical processes are used for phosphorus removal from wastewater. Sludge produces during primary and biological wastewater treatment. Sludge handling cost is growing regarding to the strict regulations on wastewater treatment concerting phosphorus removal as well.Increased amounts of sludge generates because of phosphorus removal. Sludge handling cost reaches about 50% of all expenses at wastewater treatment plant. Anaerobic digestion of sludge mixture decreases amounts of sludge due to reduction of organics and produce biogas which can be used at the treatment plant as local energy source. Main problems existing at the wastewater treatment plants with biological phosphorus removal where anaerobic digestion of sludge mixture is implemented are: risk of hydrogen sulphide production in biogas and high concentration of phosphates in digested sludge liquor.

Hydrogen sulphide is toxic for the personal and damages equipment. For the prevention of hydrogen sulphide formation in biogas iron salts are widely used at the treatment plants.

Release of phosphates from polyphosphates accumulating microorganisms cells into digested sludge liquor occurs under anaerobic conditions. Recycled to the beginning of wastewater treatment plant digested sludge liquor can contain up to 600 mgPO_4-P/l phosphates. In case to prevent the overloading of biological phosphorus removal process by released phosphates they should be removed from sludge liquor.

Topicality of work

Huge amounts of ochre (iron sludge) are produced in countries where iron-rich ground water is used as source for the preparation of drinking water. Iron is removed from ground water before supply to customers to meet hygienic norm requirements. At the moment ochre is disposed to landfills and no re-use is implemented. Ochre can be used as the alternative source of iron at the wastewater treatment plant with biological phosphorus removal and anaerobic digestion process applied.

During past years in Lithuania and other countries the main attention has been paid to the recycling of the wastes and investigation of possible local renewable sources. It is necessary to fully investigate use of ochre at the wastewater treatment plant with biological phosphorus removal for the improving of digestion process and prevention of overloading of phosphorus removal process by phosphates in digested sludge liquor.

Research object

Research object was anaerobic digestion of sludge mixture with added traditional and alternative iron sources.

Aim of work

The aim of work was to examine the potential of ochre to be used as alternative iron source and to investigate factors governing anaerobic digestion process quality: methane production, hydrogen sulphide removal process and reduction of internal recycling of phosphates at wastewater treatment plants with biological phosphorus removal.

Tasks of work

Tasks to be solved to achieve the aim of dissertation:

1. To collect, review and analyse operational data of selected existing anaerobic digesters. To compare anaerobic digestion process quality and identify problems regarding use of aluminium and iron salts. To analyse digested sludge mixture samples from wastewater treatment plants with different phosphorus removal (biological and chemical).
2. To determine relationships between iron salt doses and types and anaerobic digestion process quality, this will be qualified by biogas production and phosphates release into digested sludge liquor, by making laboratory experiments.
3. To make anaerobic digestion laboratory experiments with addition of different doses and types of ochre into feed sludge, to evaluate effect of ochre on methane production rate and phosphates precipitation.
4. To make pilot-scale experiments and evaluate ochre ability to reduce hydrogen sulphide production in biogas and phosphates release into digested sludge liquor.
5. To propose technological scheme for possible use of ochre at wastewater treatment plants with biological phosphorus removal.

Methodology of the research

Research has been made in two European countries: Sweden and Lithuania. Used sludge mixture was obtained from wastewater treatment plants (WWTP) with biological phosphorus (Bio-P) removal process located in Lithuania and Sweden; ochre originated from groundwater treatment plants located in Lithuania and Denmark. Laboratory and pilot-scale anaerobic digesters were used for the experiments. Standard and specific methodology was used for the evaluation of anaerobic digestion process quality.

Scientific novelty of the research

Complex evaluation of ochre impact on sludge mixture handling has been made. Technological scheme for possible use of ochre during anaerobic digestion of sludge mixture at the treatment plants with biological phosphorus removal has been proposed.

Practical value of the results

Research results showed that ochre can be used at the wastewater treatment plants with biological phosphorus removal for the improving of anaerobic digestion of sludge mixture process. Proposed doses of ochre can be used for the reduction of hydrogen sulphide formation in biogas and removal of phosphates in digested sludge liquor without inhibition of biogas production and quality.

Defended propositions

1. Addition of ochre into feed sludge mixture before digestion at wastewater treatment plants with biological phosphorus reduce phosphates concentration in digested sludge liquor and prevent hydrogen sulphide formation in biogas.
2. In order to prevent inhibition of anaerobic digestion process ochre dose not higher than 38 $mgTS_{ochre}/gTS_{in}$ should be applied continuously.
3. Reuse of ochre instead of traditional reagents lowers amount of wastes for landfilling and let to recycle them.

Approval of the work results

Author's scientific articles dealing with dissertation object: two in other scientific databases: (Ofverstrom *et al.* 2010, 2012), one in foreign scientific journal (Офверстром and Керинг, 2012), one in conference proceedings referred in ISI proceedings database (Ofverstrom *et al*. 2011), one in Lithuanian International conference proceedings (Tomczak-Wandzel *et al.* 2011), two – in Lithuanian conference proceedings (Ofverstrom *et al.* 2010, Arlauskaitė *et al.* 2012), three – in international conference CD-R proceedings (Ofverstrom *et al.* 2010, Ofverstrom and Dauknys, 2010, Ofverstrom *et al*. 2011).

Author of dissertation has been participating in 10 Republican and International conferences and 2 international seminars with presentations concerning results of dissertation work:

Lithuanian Young scientist conference „Science– Future of Lithuania“, 2010, 2011, 2012, Vilnius, Lithuania (oral and poster presentations);
7th International Conference „ECO-TECH 2010“, 22–24 November, 2010, Kalmar, Sweden (oral presentation);
8th International Conference „Environmental Engineering“, 19–20 May, 2011 Vilnius, Lithuania (co-author);
International Conference of Young Scientist on Energy Issues Cyseni 2011, 26–27 May, 2011, Lithuanian Energy Institute, Kaunas, Lithuania (oral presentation);
IWA 1st Central Asian Regional Young Water Professionals Conference, 22–24 September, Almaty, Kazakhstan (poster presentation);
12th International Conference on Environmental Science and Technology (CEST2011), 8–10 September, 2011, Rhodes, Greece (oral presentation);
Holistic sludge management IWA Specialists Conference, 6–8 May, 2013, Vasteras, Sweden (poster);
13th Nordic Wastewater Conference, NORDIWA 2013, October 8–10, 2013, Malmö, Sweden (co-author);
IWA CIS Young Water Professionals Workshop “Modernisation of wastewater treatment plants” (oral presentation), 1 June, 2010, Moscow, Russia;
International seminar “How to meet the challenges within the wastewater technology“, organized by Swedish Water and Wastewater association and VA-teknik Södra at Lund University, June 12–13, 2012 (invited guest speaker, oral presentation).

The scope of the scientific work

Dissertation consists of an introduction, three chapters, main conclusions, and recommendations. The total amount of dissertation is 96 pages, 23 formulas, 23 figures, and 32 tables. Totally 150 references were used for the preparation of dissertation.

Acknowledgements

The dissertation have been prepared in collaboration between Water management Department at Environmental Engineering Faculty at Vilnius Gediminas Technical University, Lithuania (home university) and Water and Environmental Engineering group at Chemical Department at Lund University, Sweden (host university).

First of all I would like to acknowledge staff at my home university, namely: Head of Water Management Department Assoc Prof Dr M. Rimeika for the support during all years of studies; Assoc Prof Dr R Dauknys is acknowledged for being my supervisor; Assoc. Prof. Dr M. Valentukevičienė and A. Grigaitytė for help with obtaining ochre from Antaviliai WTP, characterization and pictures provided; head of laboratory T. Žemaitis for help with operating laboratory equipment and finally all others for their support.

Secondly, I would like to acknowledge my host university staff. I want to say many thanks toProfDr J.la Cour Jansen for supervising of all experiments made at Lund University, giving useful advices, for his kindness and patience. All Water and Environment Engineering group at my host university, namely: AssocProf DrÅ. Davidsson for being nice companion and co-supervisor during study visit, Assoc. Prof DrK. Jönsson for being very nice to me and helping with evaluation of results, S. Haghihatafshar and H. Kjerstadius for helping with operating of pilot-scale digesters, G. Persson for helping with laboratory analysis. All Chemical Department staff is acknowledgedfor very warm welcome during my stay in Lund.

The Swedish Institute is acknowledged for 8 month study visit grant (Visby grant 00645/2010) to Lund University. Swedish Water Association is acknowledged for financing experiments made in Sweden. Prof Dr A. Žemaitaitis (KTU) for partly financing of experiments made at VGTU. Lithuanian Science Academy is acknowledged for financial support for visits: to Conference (VIZIT-1-KON-036). NSVA (Öresundsverket WWTP), are acknowledged for providing sludge for the experiments and VA SYD (Sjölunda WWTP) for the help with practical problems at the pilot plant. The staff at Utena WWTP, Panevežys WWTP (Lithuania) and Ryaverket WWTP (Sweden), namely Dr G. Vabolienė, R. Vogulis and Dr O. Fredriksson are acknowledged for help with collecting data and samples during case-studies and experiments samples, for their answers to many questions. Assoc Prof Dr H. R. Andersen (DTU) is acknowledged for fruitful discussions at and providing ochre from Marbjerg WTP, Denmark.

And finally, all my three kids, husband, and parents for understanding and support.

1

Anaerobic digestion of sludge review

Chapter one provides reviewed and analysed literature regarding sludge anaerobic digestion. Sewage sludge sources, types and main characteristics are discussed.Mesophilic anaerobic digestion principles, technologies, and parameters affecting process described. Quality and quantity of digestion process end-products is discussed. Results of aluminium and iron salts impacton digestion of sludge are summarized and disscused. Evaluation of waterwork sludgeas possible source of aluminium or iron is made. Research results on reuse of waterworks' sludge are summarised.

Articles published within the chapter (Ofverstrom *et al.* 2011b; Tomczak-Wandzel *et al.* 2011; Офверстром and Керинг, [Ofverstrom and Kering], 2012).

1.1. Sewage sludge sources, types and main characteristics

Depending on wastewater treatment and sludge handling process, different types of sludge produces at wastewater treatment plants (WWTs).Sludge handling and disposal can reach up to 50% of all wastewater treatment plant costs (Appels *et al.* 2008).

When biological or (and) chemical phosphorus removal processes are applied amounts of sludge increase because of phosphorus fixation into sludge (Caravelli *et al*. 2010; García-Delgado *et al*. 2007; De Haas *et al.* 2000; Parsons *et al*. 2009). During enhanced biological phosphorus removal (EBPR) process phosphorus accumulates by polyphosphates-accumulating organisms (PAOs) (Dauknys *et al*. 2009). Insoluble iron or aluminium phosphates precipitate when chemical phosphorus removal is used. This increases sludge production (as solids) compare to biological phosphorus treatment process can be up to 20–30% (Balmér, 1988). Biological phosphorus removal is preferable proces because of promising phosphorus harvesting via struvite (MAP) precipitation. When chemical phosphorus removal is applied, recovery of phosphorus from digested sludge liquor is nearly impossible. Besides this, use of chemicals increases chloride or sulphate concentrations in wastewater (Wu *et al*. 2001).

Sewage sludge types

Primary sludge (PS) is usually gray-green coloured, having strong smell suspension. High amounts of biodegradable organic matter (removed solids, greases, oils) are presented in primary sludge. Primary sludge should be properly thickened prior the digestion process to avoid decrease in biogas production, especially in winter time because of 95–97% content of water (Bolzonella *et al.* 2005). Amount of primary sludge vary from 10 to 70% of waste activated sludge (volume based) depending on the wastewater treatment process. For example, if dosing of iron or aluminium is implemented during primary treatment, then production of secondary sludge reduces.

Waste activated sludge (WAS) is derivered from a biological treatment stage. It is highly concentrated organic material (microbial cell biomass) with 98.8–99.4% of water. When enhanced biological phosphorus removal (EBPR) is used, activated sludge contains high amounts of phosphorus, accumulated by polyphosphates accumulating organisms (PAOs) which are removed withsludge (Andan *et al*. 2003; Takiguchi *et al*. 2004). Magnesium (Mg) is taken up during polyphosphates formation as well (Wild *et al.* 1997; Doyle and Parsons, 2002).

Pretreated sludge is the waste activated sludge affected by different pretreatment methods: mechanical, thermal, chemical, biological etc. for better sludge hydrolysation (Appels *et al.* 2008; Khanal *et al.* 2007; Wei *et al*., 2003; Yoon and Lee, 2005). Pretreatment of sludge leads to increased amounts of nitrogen (mainly in ammonium form) and phosphorus (in phosphates form) released into sludge liquor under anaerobic conditions (Carrère *et al.* 2010; Montusiewicz *et al*. 2010). Müller (2000) reported 10–20% phosphates release from biologically pretreated waste. About 60% release of phosphorus (80% in phosphates form) from waste activated sludge sonicated at 500 kWm^3 for over

1 h was obtained by Wang *et al.* (2010). On the other side, waste activated sludge mechanicalpretreatment (by high pressure homogenizer) decreased daily hydrogen suphide (H_2S) production by 20% compare to untreated sludge (Dhar *et al.* 2011).

Chemical sludge generates during removal of phosphorus by chemical precipitation and contains insoluble aluminium or/and iron phosphates (Andan *et al.* 2003; Oikomidis *et al.* 2010; Yeoman *et al.* 1988). Chemical sludge contains more inert material (including iron phosphates) and less soluble phosphorus than biological sludge (Parsons and Smith, 2008).

Primary and waste activated sludge are usually mixed together before anaerobic digestion in proportions according to the sludge production rates at the wastewater treatment plants.

Sludge characterization

Sludge characteristics strongly depend on incoming wastewater and industrial wastewater influent and the process used at WWTP (Ozkan-Yucel and Gökçay, 2010; Smith and Carliell-Marquet 2008, 2009). Evaluation of sludge is implemented at WWTPsand consists of total solids (TS), volatile solids (VS), pH, volatile fatty acids (VFA), total Kjeldahl Nitrogen (TKN), phosphorus etc. examination (Zaher *et al.* 2009).

Typical characteristics of wastewater sludge are presented in Table 1.1.

Table 1.1. Characteristics of wastewater sludge (Metcalf and Eddy, 1991)

Characteristic	Type of sludge	
	Primary sludge	Activated sludge
Total solids (TS, % (g/l)	2–8 (20–80)	0.83–1.16 (8.3–11.6)
Volatile solids (VS, % of TS (g/l)	60–80	59–88
Total nitrogen, N % of TS	1.5–6.0	2.4–5.0
Total phosphorus (P_2O_5), % of TS	3.5–4.0	2.8.0–11.0
pH	5.0–8.0	6.5–8.0

Sewage sludge is a complex of fractions with different biodegradability characteristics. Characterization of organic components is time concuming process which is not applied at wastewater treatment plants. Some researches reported organic components of sludge. According to Ozkan-Yucel and Gökçay

(2010), total amount of carbohydrates, proteins and lipids (fats) in waste activated sludge is about 80–87% of volatile solids (VS) (based on dry matter content); while in primary sludge organic part vary from 68 to 94% of VS (Pavlostathis and Giraldo-Gomez, 1991) or 58 to 100% of VS according to Tchobanoglous and Burton (1991) found of VS.

Theoretical methane production rate from fats, proteins and carbohydrates is presented in Table 1.2.

Table 1.2. Theoretical methane production for different organic components (Davidsson, 2007)

Component	Formula	Methane production, Nm^3 CH_4/tVS_{in}
Fats	$C_{57}H_{104}O_6$	1014
Proteins	$C_5H_7O_2$	496
Carbohydrates	$(C_6H_{10}O_5)_n$	415

Digestibility of sludge mixture is very hard to predict due to variation in composition of primary sludge; waste activated sludge is more constant (Ozkan-Yucel and Gökçay, 2010; Smith and Carliell-Marquet, 2008, 2009).

If sludge is used for the land application it should be also analysed for the presense of heavy metals. About 50% of heavy metals come into sewage with industrial wastewater (Dewil *et al.* 2006). Commercial chemicals used at the treatment plants contain traces of some metals, mainly Cr, Ni and Zn which contribute to the total amount in sludge and effluent water (Sörme and Lagerkvist, 2002).

1.2. Anaerobic digestion process and technologies

Mesophilic anaerobic digestion is widely applied sludge handling process (Gracia *et al.* 2009; Tavares *et al.* 2002) due to the optimization of WWTP costs regarding to reduction of the solids' mass in sludge and use of end-product of digestion – biogas as energy source (Appels *et al.* 2008, Bouallagui *et al.* 2010; Jenicek *et al.* 2012; Marsili-Libelli and Beni, 1996; Takiguchi *et al.* 2004).

During anaerobic digestion process, organic material existing in sludge is converted into biogas by anaerobic organisms. Whole process consists of four phases (Fig. 1.1).

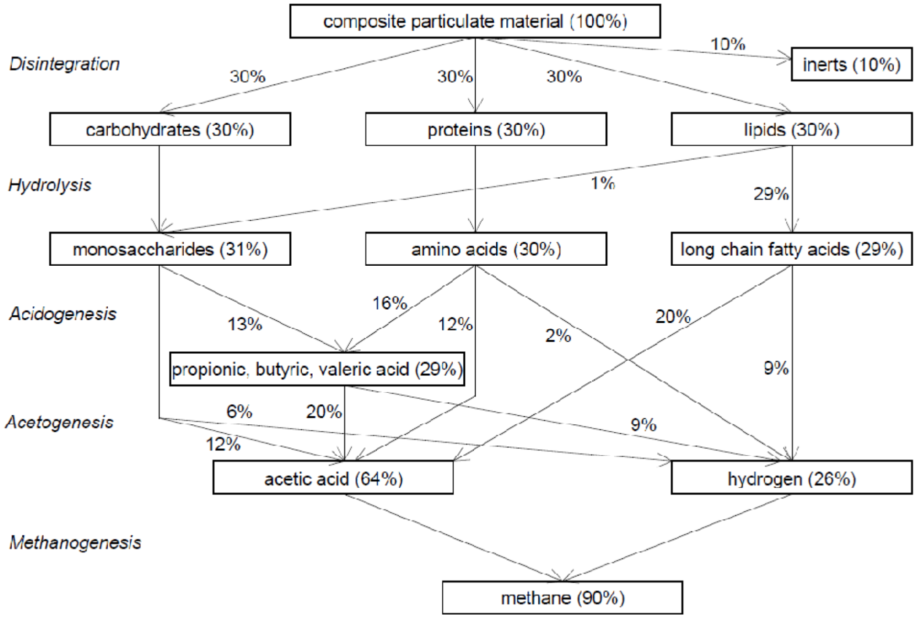

Fig. 1.1. Methane production during anaerobic digestion process
(from Batstone *et al.* 2002)

Hydrolysis is slow process and often the rate-limiting step in anaerobic digestion. During hydrolysis particulate and soluble polymers (carbohydrates, proteins, and carbohydrates) are converted into soluble products (amino acids, monosaccharides and long chain fatty acids) by enzymes. Digestion of waste activated sludge requires longer time because of this first phase of anaerobic digestion (Seng *et al.* 2010).

Acidogenesis (i.e. fermentation) is the second and fastest step in anaerobic digestion when hydrolysis end-products are degraded into several compounds: mainly volatile fatty acids (acetate, propionate, butyrate), also alcohols, formate, hydrogen and carbon dioxide. Presence of hydrogen in biogas shows increase of propionic and butyric acids (Marsili-Libelli and Beni, 1996).

Acetogenesis is the process when obligate hydrogen-producing acetogens degrade long chain and volatile fatty acids and productions of acetate, hydrogen and carbon dioxide occurs.

Methanogenesis is the final slowest phase in anaerobic digestion process when methane is produced. Methanogens consume acetic acid (methanogenic acetoclastic bacteria) or hydrogen and carbon dioxide (hydrogenotrophic methanogens) and produce methane. About 70% of methane is produced by acetoclastic methanogens (equation 1.1) and the rest (about 30%) by hydrogenotrophic methanogens (equation 1.2) (Marsili-Libelli and Beni, 1996).

$$CH_3COO \rightarrow CH_4 + CO_2, \quad (1.1)$$

$$CO_2 + H_2 \rightarrow CH_4 + H_2O. \quad (1.2)$$

Anaerobic digestion is a very complex biological process, where hundreds of microbial populations and substrates are involved (Donoso-Bravo *et al.* 2011). Methanogenesis kinetics is lower than acidogenesis and any disturbance can have negatively effect process stability. Besides this, methanogens are very sensitive to environmental conditions.

Anaerobic digesters design parameters and factors, affecting process efficiency

High-rate digesters are metallic or concrete cylindrical form tanks (6–40 m of diameter) with heating and complete mixing of sludge (Appels *et al.* 2008). High-rate digesters are widely applied at the wastewater treatment plants for the digestion of sludge.

Fig 1.2 presents high-rate mesophilic digesters at Ryaverket WWTP, Gothenborg (Sweden).

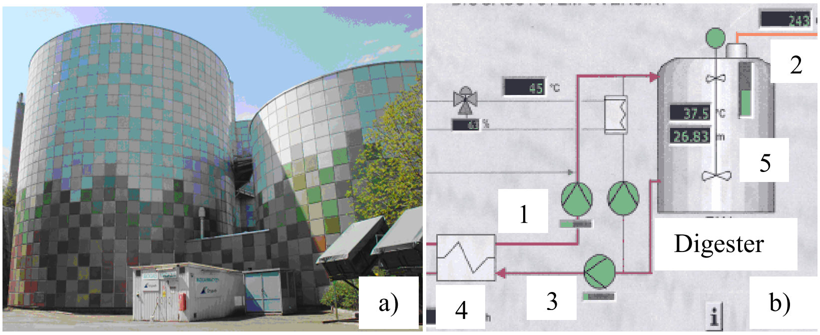

Fig. 1.2. High-rate mesophilic digesters at Ryaverket WWTP: a)picture of digesters; b) technological scheme: 1 – thickened sludge mixture; 2 –biogas outlet; 3 – digested sludge to the dewatering; 4 – heat exchanger; 5 – mixing.

During 2009–2013 amount of anaerobic sludge digesters in Lithuania increased from 3 to >10 because of the implementation of National Sustainable Development Strategy, National Energy Strategy and Renewable Energy strategy goals to stimulate heat production renewable energy sources for local heat and electricity production. Nowadays, most of wastewater treatment plants have anaerobic digestion of sludge and use produced biogas for the local energy needs.

Digesters can be operated in mesophilic (30–38 °C) or termophilic (50–57 °C) temperatures. Biochemical reactions rates increases in termophilic conditions but termophilic bacteria is more sensitive than mesophilic to the temperature fluctuations. Also, mesophilic anaerobic digestion is more popular because of lower energy demand for heating of digesters.

Different factors are affecting anaerobic digestion process efficiency: mixing, temperature (T), solids retention time (SRT), hydraulic retention time (HRT), organic loading rate (OLR), volatile fatty acids (VFA), alkalinity (ALK), VFA/ALK ratio, pH, toxicity, etc.

High-rate mesophilic operational parameters and conditions are presented in Table 1.3.

Table 1.3. Operational conditions of high-rate mesophilic digesters (Appels *et al.* 2008)

Parameter	Optimal	Limits
OLR, kgVS/m^3/d	1.6–4.8	ND
SRT, d	10–20	ND
T, °C	30–38	20–40
VFA, mg/l as acetic acid	50–500	50–2000
ALK, mg/l as $CaCO_3$	1500–3000	1000–5000
VFA/ALK	0.1–0.3	ND
pH	6.8–7.2	6.6–7.6

Proper mixingof active biomass and feed sludge prevents formation of scum layers and provides good temperature distribution in digester (Appels *et al.* 2008).

Organic loading rate (OLR) shows how much organic material as volatile solids (VS_{in}) is pumped into the reactor per day. Continuous organic loading rate should be provided for the prevention of system overloading.

Solids retention time (SRT) is an average time when bacteria (solids) are in the anaerobic digester. Hydraulic retention time (HRT) shows time that the sludge is in the anaerobic digester. HRT values affect the rate and extent of methane production. If no recycle is implemented, HRT is equal to SRT.

Temperature in digesters should be stable because of the sensitivity of microorganisms (especially methanogens) to the temperature fluctuations (Appels *et al.* 2008).

Volatile fatty acids (VFA) are by-product of acid-forming bacteria. As higher amount of volatile solids is presented in feed sludge as higher amount of volatile acids is produced in digester. Primary sludge usually contains high concentration of volatile solids (Pastor *et al.* 2008). Slow feed of sludge with high VS concentration should be provided due to the direct dependence of VS amount on VFA production. If acetogens and methanogens are unable to metabolise the volatile fatty acids (VFA) produced by the acidogenic bacteria fast enough, excess VFAs are produced, which leads to drop of alkalinity and pH (Reed *et al.* 2011). For successful digestion process good conditions for the equilibrium between consumed and concumed VFA should be provided (Stein and Malone, 1980).

Alkalinity (ALK) shows digester stability. Decrease of alkalinity below the operating level indicates pending failure. Any chemicals selected for the adjustments of alkalinity should be added slowly to digester to avoid excess alkalinity andprevent any inhibition impact on bacteria. Methanogens require bicarbonate alkalinity (BA), chemicals that release bicarbonate alkalinity directly are preferred.

pH – is usually the last indicator of digester failure. pH values should be from 6.8 to 7.2; pH levels in the range of 6.4 to 7.4 are tolerable (Stein and Mallone, 1980).

Efficiency of digestion process can also be affected with toxic substances – chemical compounds presented in wastewater stream and removed together with primary sludge (Chen *et al.* 2008). Depending on the concentration toxic substrances can improve or inhibit process (Appels *et al.* 2008) (Table 1.4).

Table 1.4.Toxic compounds and their concentrations (Appels *et al.* 2008)

Compounds	Unit	Stimulating concentration	Moderately inhibitory	Toxic concentration
Ammonium (NH_4^+)	mg/l	50–200	1500–3000*	>3000
Magnesium ($Mg^{2+)}$	mg/l	75–150	1000–1500	3000
Sodium (Na^+)	mg/l	100–350	3500–5500	8000
Calcium ($Ca^{2+)}$	mg/l	100–200	2500–4000	8000
Sulphide (S^{2-})	mg/l	ND	50–100	200–400
Chloride (Cl^-)	mg/l	ND	6000	

*inhibitory at higher pH values (>7.4–7.6); ND – no data

Toxicity can be acute or chronic. Acute toxicity is the rapid appearance of high concentrations of toxic substances which leads to the failure of digestion process due to the inhibition of methane bacteria. Chronic toxicity is usually tolerated by methane bacteria after acclimation period. Indicators of toxicity (inhibition) are: decrease in methane production, alkalinity and pH; and the increase in volatile fatty acid concentration. Anaerobic digestion has limited application in industrial sludge treatment because of high potential of toxic compounds presence in industrial wastes (Tomei *et al.* 2009).

In industrials wastewater streams amounts of sulphate can be from 2 up to 50 g/l: up to 2 g/l of sulphate in the paper industry, from 2.5 to 9 g/l in molasses-based fermentation industries (e.g., alcohol, citric acid, and monosodium glutamate production) and up to 50 g/l in oil refineries.

Pretreatment of sludge can also affect digestion process. Release of ammonia in toxic concentrations (over 3 mg/l) during digestion of waste activated sludge pre-treated by thermal hydrolysis has been reported by Carrère *et al.*(2010).

Heavy metals (cadmium (Cd), copper (Cu), cobalt (Co), nickel (Ni), lead (Pb) and zinc (Zn)) mainy presented in industrial wastewater can be also toxic for the methanogens.

Evaluation of digestion process efficiency

Evaluation of digestion process efficiency is usually made by the estimating of the anaerobic digestion end-products: biogas, digested sludge and sludge liquor (Jenicek *et al.* 2013). Schematic view of biogas production end-products and recirculation of waste streams is presented in Fig. 1.3.

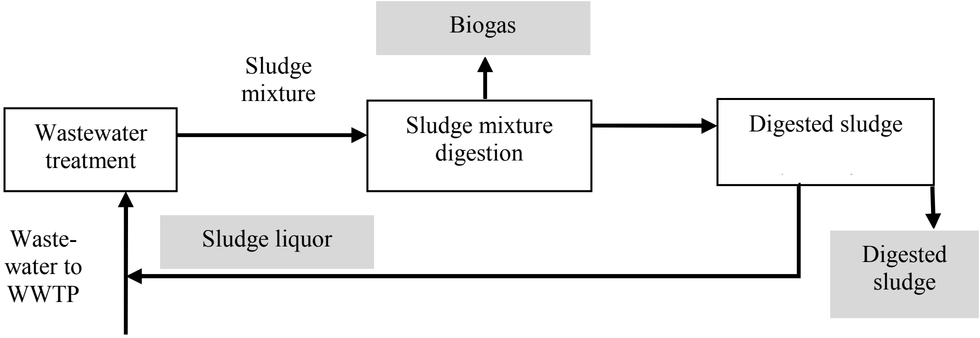

Fig. 1.3. Recirculation of wastes at WWTP
(grey colour – end-products of anaerobic digestion process).

Biogasis end-product produced during the degradation of organics under anaerobic conditions. Biogas is the mixture of gases and typically contains about 55–70% of methane (CH_4), 30–40% of carbon dioxide (CO_2), water vapour, traces of nitrogen N_2 (<1%), hydrogen sulphide H_2S (10–2000 ppm or higher), ammonia (NH_3), small amounts of carbon oxide (CO), and oxygen (O_2) (Appels *et al.* 2008).
Biogas is renewable and environmental friendly fuel which can be used at the wastewater treatment plants for the heating needs or for the production of electricity. Local use of biogas produced contributes to the European Union aim to share energy from renewable sources up 20% of total energy consumed in 2020 (Holm-Nielsen *et al.* 2009; Mottet *et al.* 2010).

Biogas production rate is usually evaluated by calculating the specific biogas (or methane) production.

Specific biogas production (SGP) m^3per kg of volatile solids fed (VS_{in}) is calculated by equation 1.3:

$$SGP = V_{biogas}/VS_{in,}\ Nm^3/kgVS_{in}, \qquad (1.3)$$

where V_{biogas} – is the produced volume of biogas or methane (Nm^3); VS_{in} – the mass of volatile solids in feed substrate (kgVS).

Bouallagui *et al.* (2010) has been studying biogas production from sludge mixture using different ratios of primary and secondary sludge (volume base). He found out that specific biogas production from the sludge mixture depends of primary and waste activated sludge proportion and can be from 0.38 to 0.60 $m^3/kgVS_{in}$. The results of his research are presented in Table 1.5.

Table 1.5. Specific biogas production from sludge mixture (Bouallagui *et al.* 2010)

Sludge mixture	Proportion (volume based)	SGP, $m^3/kgVS_{in}$	SGP, $m^3/kgVS_{dest}$	CH_4, %
Primary and waste activated (PS:WAS)	90:10	0.57	0.80	62
	80:20	0.60	0.83	64
	50:50	0.57	0.81	65
	30:70	0.49	0.78	64
	20:80	0.38	0.74	64

Specific biogas production can be expressed in m^3 per kg of volatile solids destroyed ($m^3/kgVS_{dest}$) as well. Bolzonnella *et al.* (2005) determined decrease in the specific gas production (SGP) ($m^3/kgVS_{in}$) by 25% while SRT of activated sludge process increased from 10 to 20 days (aged sludge).

As it was mentioned above, biogas consists mainly of methane, carbon dioxide and other gases. The major component is methane (CH_4) – poorly soluble in water and inert under anaerobic conditions non-toxic gas. Methane is most valuable component of biogas and can be used as a fuel for heating requirements at the WWTP (Vilniškis *et al.* 2011).

Carbon dioxide (CO_2) formats in acidogenesis and methanogenesis stage of anaerobic digestion. If percent of carbon dioxide (CO_2) is above 35% biogas will not burn. Presence of high amount of carbon dioxide in biogas produced is reflective to the alkalinity requirements in digesters.

Hydrogen sulphide (H_2S) is toxic gas which is dangerous for the personal of WWTP. When concentration of H_2S in biogas produced increases above 500 ppm risk of respiratory and central nervous system paralysis occurs (Smet *et al.* 1998). Hydrogen sulphide is also corrosive for the equipment (Dhar *et al.* 2011) and should be physically or chemically removed from biogas. Removal of hydrogen sulphide by activated carbon, addition of iron salts or using oxidants is very expensive (Ahammad *et al.* 2008; Lens *et al.* 1998). When iron (Fe^{3+}) is used for the removal of hydrogen sulphide, it reacts with hydrogen sulphide and forms elemental sulphur, iron and hydrogen according to equation 1.4 (Wei and Osseo-Asare, 1996):

$$2Fe^{3+} + HS^{-} \rightarrow 2Fe^{2+} + S^{0} + H^{+}. \quad (1.4)$$

Precipitation of dissolved hydrogen sulphide with iron (Fe^{2+}) occurs by equation 1.5 (Khanal, 2008):

$$Fe^{2+} + HS^{-} \rightarrow FeS^{-} + H^{+}. \quad (1.5)$$

As can be seen, one mole of Fe^{3+} removes 1.5 moles of sulphide, either as ferrous sulphide or elemental sulphur. Continuous precipitation of ferrous sulphide leads to the increased total solids (TS) content in the reactor. Strasser *et al.*(1995) noted that major part of metals in digested sludge occurs in the form of sulphides.

Results of chemical adsorption of H_2S in chemical adsorption reactor obtained by Chung *et al.* (2006) showed effective removal of very high H_2S concentrations in a short time: 95% removal efficiency of H_2S have been obtained when concentration of Fe^{3+} was 6.8 gFe^{3+}/l for 500 ppm and 9.0 gFe^{3+}/l for 1500 ppm of inlet H_2S concentration.

The second main end-product of the sludge anaerobic digestion process is digested sludge. Digested sludge is dark coloured suspension, which usually containing large quantities of gas bubbles. If sludge has strong smell it means problems in digestion process.

Novak *et al.* (2007) suggested that organics bound with metals presented in feed sludge differently degrades during anaerobic digestion. He found out that iron bound organics degrades under anaerobic conditions, while fractions associated with divalent cations (Ca^{2+} and Mg^{2+}) are degrading only aerobically. Aluminium bound fraction generally resists to any biological degradation. All this factors affect an odour generation from anaerobic sludge. Only part of volatile solids presented in feed sludge is destructed and converted into biogas during digestion process. The efficiency of volatile solids destruction (VS_{dest}) is calculated by the following formula (equation 1.6):

$$VS_{dest}=((VS_{in}-VS_{out})/(VS_{in}-(VS_{in}\cdot VS_{out}))\cdot 100\ \%, \qquad (1.6)$$

where VS_{in} – volatile solids content in feed sludge, %;VS_{out} – volatile solids content in digested sludge, %.

Boulugulli *et al.* (2010) made research on sludge mixture digestion and reported volatile solids destruction efficiencies from 51% to 72% depending PS and WAS ratio: higher primary sludge percent added results better volatile solids destruction. When waste activated sludge is digested separately, volatile solids destruction efficiency seeks only30–45% (Gavala *et al.* 2003). Sludge mixture is preferable to digest because of high concentration of easy degradable organics in primary sludge.

Digested sludge liquor – is the filtrate produced during dewatering of the digested sludge. Direct recycling to the beginning of treatment process is usually implemented at wastewater treatment plants. Digested sludge liqours from biological nutrientsremoval processes often contain high concentrations of magnesium (Mg^{2+}), calcium (Ca^{2+}); ammonia (NH_4^+) and high alkalinity (Battistoni *et al.* 2000). Up to 80–90% of phosphorus removed together with waste activated sludge from EBPR process can be released during anaerobic digestion due to polyphosphates degradation and re-introduced to the beginning of the process (Andan *et al.* 2003, Dueñas *et al.* 2003; Stabnikov *et al.* 2004).

Researchers obtained very different concentrations of phosphates in digested sludge liquor depending on feed sludge origin. Battistoni *et al.* (2000) reported 60–100 mg PO_4-P /l, while Marti *et al.* (2008) obtained 152±56 mg PO_4-P/l during digestion of mixture of pre-fermented primary sludge and waste activated sludge from EBPR process.

Even higher concentrations (up to 600 mg/l of PO_4-P) have been reported by Barat *et al.* (2009). When release of phosphates into sludge liquor is obtained precipitation of phosphates should be applied (Jardin and Pöpel, 1996; Pitman, 1999; Münch and Barr, 2001; Wu *et al.* 2001).

Different suggestions on decreasing of phosphates release into sludge liquor were reporeted by researches. Pastor *et al.* (2008) found out that mixed thickening of primary and EBPR sludge reduces phosphorus release in digester: polyphosphates (Poly-P) hydrolysis begins in the thickener. Pitman (1999) recommended separate digestion of primary and BNR sludge. Previously, Wild *et al.* (1996) reported reduction of phosphates up to 50% in digested sludge liquor when waste activated sludge from EBPR process was digested together with primary sludge because of low phosphorus and high calcium content in it.

Reported amount of magnesium released during polyphosphate hydrolysis was about 0.25 g of magnesium per gram of phosphorus (Wild *et al.* 1997, Doyle and Parsons, 2002). Increasing levels of soluble magnesium raises the potential for struvite (crystalline solid precipitates) or MAP formation (Ohlinger *et al.* 1998; Le Corre *et al.* 2007; Parsons *et al.* 2009). Struvite forms according to the equation 1.7. Molar ratio of Mg:NH_4:PO_4 should be1:1:1 (El Diwani *et al.* 2007):

$$Mg^{2+} + NH^{4+} + HPO_4^{2-} + 6H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O + 2H^+\uparrow \qquad (1.7)$$

The other possible precipitate is hydroxylapatite (HAP) ($Ca_5(PO_4)_3OH$) which forms at high Ca:Mg ratios and inhibits struvite precipitation. According to Le Corre *et al.* (2007) for the effective struvite formation Ca:Mg molar ratio should be below 1. To avoid precipitation of phosphates with calcium, pH should be kept below 7 (Tykesson and la Cour Jansen, 2005).

When metal salts are used at the treatment plant then phosphorus can precipitate as metal phosphates (Uysal *et al.* 2010). Using of ferrous salts ((Fe^{2+}) can cause precipitation of vivianite ($Fe(PO_4)_2 \cdot 8H_2O$) (at high temperatures, for example in heat exchangers). Frossard *et al.* (1997) reported formation of vivianite, a non-soluble ferrous phosphate after dosing of iron sulphate (Fe_2SO_4). Previously, formation of vivianite was obtained during direct addition of $FeCl_2$ into feed sludge at the real WWTP (Dezham *et al.* 1988). Addition of iron should be balanced due to possible formation of vivianite.

Accumulation of insoluble precipitates which reduces diameters of pipes has been reported by many researchers in different countries: USA, UK, Italy (Neethling and Benisch, 2004; Ohlinger *et al.* 1998, Williams *et al.* 1999).

Nowadays, there are two mainly published opinions concerning solving of precipitation problems under anaerobic conditions: mitigation or harvesting of struvite. Addition of iron chloride is one of main methods recommended for the prediction of struvite formation by WEF (1991).

Mamais *et al.* (1994) presented results on addition of iron salts into digester for the prevention of struvite formation during digestion of sludge mixture at the wastewater treatment plant in San-Francisco (USA). The minimal dose of iron chloride was 100 kg/$FeCl^3$/ton total solids (TS) of feed sludge.

In recent years, significant increase in interest on harvesting of struvite for the recovery of phosphorus can be seen. Phosphorus is the one of most valuable nutrients presented in sludge because of limited reserves of phosphorus rocks (Uludag-Demirer and Othman, 2009). Evaluation of controlled struvite precipitation process has been made by number of researchers (Le Corre *et al.* 2007, Pastor and Smith, 2008, Marti *et al.* 2008). At the biological phosphorus removal plants controlled struvite precipitation can be applied for the harvesting of phosphorus though struvite or calcium phosphates; when chemical phosphorus removal is applied recovery of phosphorus is nearly impossible (Battistoni *et al.* 2002).

1.3. The impact of aluminium and iron on anaerobic digestion process

Aluminium and an iron based chemicals are widely used at wastewater treatment plants for different purposes. At WWTPs with chemical phosphorus removal aluminium and iron salts are used for chemical phosphorus precipitation, and at WWTP with biological phosphorus removal iron salts are used for prediction of hydrogen sulphide production in biogas, mitigation of struvite formation and improvement of sludge settling, thickening and dewatering properties (Mamais *et al.* 1994; Philips *et al.* 2003).

Mainly used aluminium and iron salts are: aluminium sulphate ($Al_2(SO_4)_3$), polyaluminum chloride (PAC) ($Al_2(OH)_nCl_{6-n}$), iron chloride ($FeCl_3$or $FeCl_2$), and iron sulphate ($Fe_2(SO_4)_3$ or $FeSO_4$) (Dueñas *et al.* 2003; Fytianos *et al.* 1998).

Suschka *et al.* (2001) reviewed typical reactions of phosphates precipitation by ferric and ferrous iron salts (equations 1.8–1.10):

$$FeCl_3+PO_4^{3-}\rightarrow FePO_4\downarrow+3Cl^-, \qquad (1.8)$$

$$3FeCl_2+2PO_4^{3-}\rightarrow Fe_3(PO4)_2\downarrow+6Cl^-, \qquad (1.9)$$

$$3FeSO_4+2PO_4^{3-}\rightarrow Fe_3(PO_4)_2\downarrow+3SO_4^{2-}. \qquad (1.10)$$

Ferric (Fe^{3+}) salts result higher phosphorus removal than ferrous (Fe^{2+}) salts (Gutierrez *et al.* 2010; Philips *et al.* 2003). The molar ratio of ferric iron to phosphates is 1:1 while ferrous iron to phosphates is 3:2 (Suschka *et al.* 2001). Mixing in iron addition point should be provided (Parsons and Smith, 2008). Ferric (Fe^{3+}) iron reacts with soluble phosphates and form ferric phosphate (insoluble salt) according to equation 1.11 (Parsons and Smith, 2008):

$$Fe^{3+}+PO_4^{3-} \rightarrow FePO_{4(s)}. \qquad (1.11)$$

Philips *et al.* (2003) reported inhibition by dosing of ferrous or ferric iron salts into activated sludge. Drop of pH have been obtained because of formation of iron hydroxides after addition of ferric salt. Waste activated sludge with formed insoluble iron or aluminium phosphates is removed directly to the anaerobic digestion process where is mixed with the primary sludge.

At the WWTPs with biological phopshorus removal chemicals are used for the prediction of hydrogen sulphide production. Novak *et al.* (2010) reported that iron based chemicals can benefit reduction of hydrogen sulphide (H_2S) at the wastewater treatment plants with low iron content, and in opposite, aluminium salts addition can cause the increase in H_2S production in biogas.Addition of aluminium sulphate for chemical removal of phosphates can cause hydrogen sulphide production in biogas.

A number of researchers have been investigated the impact of aluminium and iron on sludge anaerobic digestion. First article obtained on this topic was dated by 1931 year. Some researchers reported specific iron requirements for the methanogens growth (Hoban and van den Berg, 1979; Jackson-Moss and Duncan, 1990).

Dentel and Gossett (1982) reported that bioavailability of several biomolecules (including proteins) for the methanogens reduced after addition of both aluminium and iron salts. Rabinowitz and Marais (1980) concluded that all added iron can be adsorbed or precipitated into biomass. Carter and McKinney (1973) suggested that when too much iron is added, iron form precipitates rapidly and coats the particles such as bacteria and block available soluble nutrients.

According to Hoban and van der Berg (1979) iron precipitation rate relates to the amount of carbon dioxide in reactors. Mainly iron precipitates as carbonate, but some iron can form phosphates and sulphides.

Jack *et al.* (1976) studied digestion of primary sludge dosed with iron using laboratory scale semi-continuous digesters and found out that sludge with added iron required longer degrading.

Short inhibitory affect (during first 2–4 days) on methanogens activity had addition of iron salt ($FeCl_2$) (20 mM of Fe^{2+}/l) into feed primary sludge, later microorganismsadaptation to higher iron concentrations (Hoban and van den Berg, 1979).

Negative aluminium impact on sludge digestion process has been reported by number of researchers. Addition of aluminium into feed sludge caused accumulation of volatile fatty acids (VFA) (Cabirol *et al.*, 2003; Emig, 1979; Jackson-Moss and Duncan, 1991). Aluminium sulphate ($Al_2(SO_4)_3$) at concentration of 1.000 mgAl^{3+}/l showed impaired activity of methanogens and acetogens; accumulation of propionic acid during digestion of enhanced primary treatment sludge; low conversion rate of the organic matter to methane was obtained (Cabirol *et al.* 2002). An increase of VFA concentration, decrease in bicarbonate alkalinity (BA) and drop of pH below optimal was reported during digestion of sludge mixture with 2500 mg/l concentration of aluminium ($Al(OH)_3$) by Jackson-Moss and Duncan (1991). Previously, Emig (1979) reported impared primary sludge digestion in full-scale digesters because of overdose of aluminium at even lower concentrations (400 mg/l).

Decrease in methane production during laboratory batch and semi-continuos digestion of primary sludge with both aluminium and iron salts added has been reported by Dentel and Gosset (1982). It was suggested by authors, that coagulation process resulted in less available for the methanogens organics. Lower biogas production (about 20% compare to biogas production from the control reactor) from both Al and Fe dosed primary sludge was obtained during semi-continuous laboratory experiment made by Yeoman *et al.* (1990).

Efficiency of digestion process of waste activated sludge was impared because of addition of iron or both iron and aluminium into feed sludge. Decrease in production of methane (in some experiments up to 32%) compare to biogas production from the control reactor, receiving sludge without addition of any reagents have been reported by number of researchers.

Addition of iron resulted in decrease of volume of biogas produced (Johnson *et al.* 2003). Smith and Carliell-Marquet (2008, 2009) obtained reduction of biogas and methane production by 12–20% and 10–22% relatively. At the same moment removal of phosphates from the sludge liquor was up to 99.5%.

Addition of both aluminium and iron to the waste activated sludge during anaerobic digestion batch test showed reduce of available organics and dectease of methane production compare to the methane production from the control reactors (Kindzierski and Hrudey, 1986).

There was difficult to compare results obtained in studied literature regarding impact of aluminium and iron on anaerobic digestion of sludge due to different sludge types and experimental design used for the research. Selected iron and aluminium doses and addition methods varied a lot. Only few articles regarding the results of impact of aluminium and iron on anaerobic digestion of sludge mixture were obtained. According to Novak *et al.* (2007) with increase of iron in feed sludge mixture destruction of the volatile solids during anaerobic digestion process also increases which results increased organic sulphur odours from the dewatered cake. Dosing of ferric salts for the precipitation of phosphates during anaerobic digestion can produce large quantities of sludge and has poor molar removal of phosphate per mole of iron added (Doyle *et al.* 2003; Fytianos *et al.* 1998).

Mamais *et al.* (1994) suggested that addition of iron chloride lowers the alkalinity in digesters because of precipitation of iron carbonates ($FeCO_{3(s)}$) (equation 1.12):

$$FeCl_3+CO_3^{2-}\leftrightarrow FeCO_{3(s)}+3Cl^-. \qquad (1.12)$$

Summarised results, reported by Jackson-Moss and Duncan (1991); Mamais *et al*. (1994), and Novak *et al*. (2010) are presented in Table 1.6.

Table 1.6. The effect of iron and aluminium on anaerobic digestion of sludge mixture

Type of test	Chemical dose	Effect	Reference
Batch and lab-scale	2500 $mgAl^{3+}/l$	Negative. Increase in the VFA concentration and a decrease in the bicarbonate alkalinity and decrease of pH below optimal.	Jackson-Moss *and* Duncan (1991)
Batch test	Fe and Al	Both. Fe and Al can decrease the available phosphorus and that may decrease VS destruction and reduce the concentration of organic sulphur compounds by binding protein.	Novak *and* Park (2010)
Batch test, Lab-scale test	$FeCl_3$	Positive. $FeCl_3$ prevented struvite formation, no effect on anaerobic digestion process.	Mamais *et al.* (1994)

As could be seen, results show variation in opinions on impact of iron and aliuminium on anaerobic digestion process.

Literature study showed lack of information about the impact of iron on anaerobic digestion of sludge mixture. Since iron based chemicals are widely used at the treatment plants complex evaluation of iron impact on anaerobic digestion process efficiency should be made.

1.4. Waterworks sludge as alternative source of iron

Water treatment works sludge is inevitable by-product of water treatment processes which classified as non-hazardous waste (code number 190902) in the European list of wastes (Babatunde and Zhao, 2007). Before supply to customers water should be treated to meet hygienic norms. Amount of water treatment plant sludge generated during treatment of source water will increase because of stingent drinking water standarts and increase of population (Ippolito *et al.* 2011). Depending on technology used for the preparation of drinking water sludge can be classified to the coagulant sludge and ochre (groundwater iron sludge).

Coagulant sludge produces during coagulation/flocculation processes for the removal of suspended solids from source water. Aluminium or iron based salts are used as coagulants (Basibuyuk *et al.* 2002; Albrektienė *et al.* 2011). Ferric salts are preferable because of rapid flock growth and better settling characteristics (Waite, 2002). Several experiments were made to examine possible re-use of coagulant waterworks' sludge. Razali *et al.* (2007) found good potential of dewatered aluminium based sludge from water treatment plant to be used as raw material for the phosphorus removal from wastewater.

Combined treatment of sludge from water treatment plants (WTP) and wastewater treatment plants have been proposed by Miyanoshita *et al.* (2009). Experiments with re-use of ochre in cement industry have been made by Husillos Rodríguez *et al.* (2010). The main problem in prediction of possible coagulant waterworks sludge reuse is variation in elemental composition even from the same source (Babatunde and Zhao, 2007).

Another type of waterworks sludge is ochre which produces during biological removal of iron. Iron should be removed from ground water before supply to customers because of unpleasant taste, colour and corrosion of water supply pipes (Mettler *et al.* 2001). Rosborg, (2009) has been reporting that using of water with high content of iron (over 1 mg/l) can be risky for health. In Russia research showed correlation between consuming of water with high concentration of iron and skin deceases. In Lithuania high iron and manganese concentrations can be associated with toxicity on embryos and fetus (Grazuleviciene *et al.* 2009).

Even higher concentrations of iron (1–23 mg/l with 6 mg/l as average) in Finnish ground water were reported by Carlson and Schwertmann (1987). In Ukraine iron concentrations in groundwater where found from 0.4 to 5.45 mg/l (Мамченко *et al.* 2009). In Lithuania too high concentrations of iron were obtained in 87% of all investigated ground water resources (3.2 Mln. m^3) (Diliūnas *et al*. 2006).

According to EU Council Directive 98/83/EB „On the Quality of Water Intended for Human Consumption" and Lithuanian Hygiene Standard HN 24:2003 total iron concentration should be 200 µg/l. World Health Organization (WHO) recommended iron concentration in drinking water is 300 µg/l. Shvartsev (2008) summarized quality of groundwater from selected European and outside of Europe countries.

Too high concentration can be found in many groundwater sources (see Table 1.7).

Table 1.7. Iron concentration in groundwater sources of selected countries (from Shvartsev, 2008)

Europeanc ountry	Iron, µg/l	Number of analyses	Other countries	Iron, µg/l	Number of analyses
Lithuania	**1125**	362	Northern Nigeria	**650**	46
Belarus	**941**	216	North-eastern US	**390**	28
Sweden	**826**	25	Russia (Siberian Platform)	**380**	415
Poland	**770**	40	Alaska	**340**	22
France	**469**	92	Southern US	185	92
Czech Republic	**396**	418	Guinea	90	44
Finland	150	7506	Brasil	88	42
Norway	18.6	1604	Kazakhstan	-	1035
EU Standard	200		WHO recommended concentration	300	

Iron is removed from groundwater by sand filtration, when Fe^{2+} is oxidized to Fe^{3+}, creating a brown-coloured ochre on the filter media surface. This excessive sludge, containing iron bacteria as well as the precipitated iron is removed by backwashing (Katsoyiannis and Zouboulis 2006; Mettler *et al.* 2001, Straub *et al.* 2001). Carlson and Schwertmann (1987) have been reported total iron oxide content of the concentrated precipitates between 26 and 43% Fe. Similar content (36.5–42.3%) of iron in ochre deposits were presented in Moelants *et al.* (2011) research.

Žáček (2000) proposed formula for the calculation of the iron content in ochre produced during removal of iron from ground water:

$$p_{Fe}=100q_{Fe}/(q_{su}+1.43q_{Fe}+1.58q_{Mn}+m_{CaCO3}),\ \%, \qquad (1.13)$$

where p_{Fe} – content of Fe in the ochre (weight %); qFe – weight concentration of Fe in water, mg/l; q_{Mn} – weight concentration of Mn in water, mg/l; q_{su} – is the concentration of particles suspended in water (mg/l); m_{CaCO3} – is the weight of calcium carbonate deposites from 1 liter of water.

Characterization of selected chemical compounds in ochre has been made by Усова *et al.* (2011). Resuts presented in Table 1.8 showed that ochre deposites obtained from Tomsk WTP (Russia), where filtration of groundwater without using reagents is applied, contained about 42–44 % of iron oxide (Fe_2O_3).

Table 1.8. Content of analysed selected chemical compounds in ochre (Усова et al. 2011)

WTP	Mass, %				
	Fe_2O_3	SiO_2	Al_2O_3	CaO	MgO
Tomsk, Russia	42.45	5.48	1.02	4.20	2.0

Mettler *et al.* 2001 characterized ochre and found out that iron precipitates as crystalline Fe-oxide, mainly goethite (FeOOH). Семакина *et al.* (2013) suggested that ochre is similar to natural mineral and can be recycled. According to Лукашевич *et al.* (2008) ochre mainly consists of iron oxide-hydroxide (FeOOH), the rest is iron hydroxide $Fe(OH)_3$ and iron oxide (Fe_2O_3). When iron in water is presented in ferrous form (Fe^{2+}) ochre formates according to equations 1.14-1.16 (Усова *et al.* 2011):

$$Fe(HCO_3)_2 \rightarrow Fe(OH)_2 + 2CO_2, \quad (1.14)$$

$$4Fe(OH)_2 + 2H_2O + O_2 \rightarrow 4Fe(OH)_3, \quad (1.15)$$

$$Fe(OH)_3 \rightarrow FeOOH + H_2. \quad (1.16)$$

Ochre usually contains over 70% of water in its structure; free water removal occurs via gravity sedimentation or flotation. Naturally dewatered ochre can contain up to 15% of solids; if ochre is dewatered mechanically, then total solids conent can be up 30% (Georgaki *et al.* 2004).

Nowadays, landfilling or disposing to dumps is typical handling of iron sludge (Husillos Rodríguez *et al.* 2010, Moelants *et al.* 2011, Усова *et al.* 2011). Disposal of waterworks sludge has no specific legislation and is expensive in some countries (Skene *et al.* 1995). If water treatment plant located close to the wastewater treatment plant then ochre can be treated together with wastewater.

At the present time in Lithuania iron is removed in about 70 % of all water supplies. According to “The Environmental Protection Agency (EPA)” official data at the moment ochre deposits in Lithuania are about 6000 t and ochre deposits per year are about 1000 t. For the comparison every year over 600 t of ochre are produced at the water treatment plant in Tomsk town (Russia) and all of this amount is landfilled (Усова *et al.* 2011).

Experiments on re-use of ochre were reported by from Russia, Denmark, Lithuania etc. (Moelants *et al.* 2011; Sharma *et al.* 2013;

Valentukevičienė, 2009; Усова *et al.* 2011). Research on possible re-use of ochre in the production of building materials were made in Russia (Усова *et al.* 2011). According to Kyncl (2008) ochre can be used for reclamation. Moelants *et al.* (2011) evaluated re-use of sand grains with precipitated $Fe(OH)_3$ from drinking water treatment for removal of phosphates in decentralized wastewater treatment systems. Experiments with recover of iron from ochre though acid leaching were made by Tarasova *et al.* (2002).

Researches from Denmark (Sharma *et al.* 2013) made laboratory experiments with addition of ochre (0.16 gdw ochre/gVS and at 0.31 dw ochre/gVS) into sludge mixture fed to digesters. Results showed good precipitation of phosphates, remained phosphate concentration in digested sludge liquor was 5 mgP/l and 0.2 mg/l compare to control 66 mg P/l. Low doses (up to 0.31 g dw ochre/gVS) didn't show any negative effect on biogas production. Addition of higher dosed of ochre (0.63–1.25 gdw ochre/gVS and 6.25–12.5 gdw ochre/gVS) decreased biogas production by 20 and 40-50% relatively.

Possible beneficial re-reuse of ochre can be implementation of ochre at the wastewater treatment plants instead of commercial iron salts for the prediction of hydrogen sulphide formation and precipitation of phosphates during anaerobic digestion of sludge mixture.

1.5. Conclusions and formulation of dissertation tasks

Review and analysis of the literature dealing with dissertation object showed that:

1. Different aluminium and iron salts are widely used at wastewater treatment plants for chemical phosphorus removal. Iron salts in ferric form are preferable reagents.
2. At the wastewater treatment plants with biological phosphorus removal process addition of iron salts into feed sludge is implemented for the reduction of hydrogen sulphide in biogas produced.
3. Case studies needed for the evaluation of impact of iron and aluminium on anaerobic digestion process at full-scale digesters.
4. According to the literature studied, iron chloride has double-effect on anaerobic digestion process efficiency: reduction of hydrogen sulphide production and struvite compounds formation.

5. There is lack of information on impact of iron chloride on sludge mixture digestion process. Complex evaluation of iron chloride impact on anaerobic digestion process efficiency is required.
6. Some investigations of possible re-use of ochre were made. But there is still lack of information on impact of ochre on anaerobic digestion process. Laboratory and pilot-scale analysis required to discover effect of ochre on anaerobic digestion process.
7. Finally, technology for practical use of ochre at the biological phosphorus removal with anaerobic digestion of sludge mixture should be proposed.

2

Research methodology on iron impact on sludge digestion process

Chapter 2 provides information of research methodology and experimental design of the experiments. Totally one case study and five experiments were made in two European countries: Lithuania and Sweden during 2009–2012 years. Total duration of all studies and experiments was about 20 month. Origin and characteristics of inoculums, sludge and ochre used for the experiments are described in details. Iron salts and ochre selected for addition to reactors are presented. Pictures and technological schemes of laboratory batch, semi-continuous and pilot-scale equipment are presented and described. Analytical methods used for the characterization of substrates and ochre are presented. Statistical methods used for the evaluation of obtained results are described.

Articles published within the chapter (Ofverstrom *et al.*, 2010a; Ofverstrom *et al.*, 2010b; Ofverstrom *et al.*, 2010c; Ofverstrom, *et al.* 2011; Ofverstrom *et al.* 2012; Arlauskaitė *et al.* 2012). Master theses conducted within dissertation: Sapkaitė, 2011; Arlauskaitė, 2012; Katinauskas, 2013.

2.1. Case study on iron impact on sludge digestion process at wastewater treatment plants

The objective of case study was evaluation of any problems existing at the wastewater treatment plants (WWTPs) regarding to use of iron or aluminium based chemicals. Besides this, results of case study have been used for the designing ot the laboratory semi-continuos and pilot-scale experiment.

Selected wastewater treatment plants had some similarities and differences. All WWTPs had phosphorus removal process and mesophilic high-rate anaerobic digesters but varied in sizes and phosphorus removal process applied (chemical or biological). Operational data of 2008 year was collected during visiting of wastewater treatment plants. The main information about selected WWTPs and chemicals used at the is presented in Table 2.1.

Table 2.1. Information about selected wastewater treatment plants

Name of WWTP, town, country	P.E.	Industry influent	P- removal process	Sludge digested	Chemicals, used at WWTP	
					P-removal	H_2S prevention
Utena (Utena, Lithuania)	33000	Yes, 60% of inflow	Biological	Primary	$AlSO_4$*	$Fe_2(SO_4)_3$
Panevežys (Panevėžys, (Lithuania)	113650	No	Biological	Primary	–	$FeCl_3$
Öresunds-verket (Helsingborg, Sweden)	120000	No	Biological	Mixture	–	$FeCl_3$
Ryaverket, (Gothenborg, Sweden)	630000	Wide range of industry	Chemical	Mixture	$FeSO_4$, PAC**	–

*ifbiological removal of phosphorus is not enough to achieve norms;
**during rainfalls.

Case study has been made in 2009 year in two European countries: Lithuania and Sweden In both countries phosphates discharge limit is regulated by Urban Wastewater Treatment Directive (91/27/EEC). For the complex evaluation of the impact of iron on anaerobic digestion process wastewater treatment plants with different iron and aluminium based reagents and anaerobic digestion processes were selected.

In Lithuania phosphorus is mainly removed by biological process and in Sweden both biological and chemical phosphorus removal schemes are applied. In Sweden anaerobic digestion of sewage sludge is developed process and applied to treat about 2/3 of produced sewage sludge (Davidsson and la Cour Jansen, 2006). Part of domestic energy supply is based on renewable energy sources. In 2009, when case study have been made, in Lithuania only three wastewater treatment plants had anaerobic digestion of sludge: two of them were selected for the evaluation.

At the WWTP with chemical phosphorus removal (Ryaverket) hydrogen sulphide was not produced. At the wastewater treatment plants with primary sludge digestion (Utena and Panevėžys WWTP) and plant with enhanced biological sludge removal (Öresundsverket WWTP) hydrogen sulphide concentration in biogas exceeded safety norms and chemical addition of iron base chemicals was implemented.

For example, concentration of hydrogen sulphide in biogas at Utena WWTP during 2005–2006 years was from 800–2700 ppm with average 1597±800 ppm. Addition of iron sulphate was implemented in September, 2006. Nowadays, hydrogen sulphide concentration is about 319±80 ppm which is below the safety for humans' norm – 500 ppm, presented in studied literature (Smet *et al.* 1998).

At the same time at Utena WWTP formation of precipitates in pipelines from the sludge holding tank to the centrifuges occurres (see Fig. 2.1).

Fig. 2.1. Precipitates, formated at Utena wastewater treatment plant

Accumulation of precipitants reduces diameter of pipes and require repair works every three month. Precipitates were taken to Lund University laboratory

(Sweden) for the characterization. Precipitant were smashed before the analysing by X-ray diffraction test (XRD).

The second part of the experiment was examination of digested sludge samples obtained from biological and chemical removal of phosphorus plants (Öresundsverket and Ryaverket WWTP). Samples were analysed for the total phosphorus (TP), iron (Fe), aluminium (Al), calcium (Ca), and magnesium (Mg) by inductively coupled plasma mass spectrometry (ICP-SM) method. Prior detection of metals sludge samples were digested according to Standard Methods (APHA, 2000).

2.2. Research methodology of iron salts impact on sludge digestion process

Two experiments were carried out at Water Management Chemical laboratory at Vilnius Gediminas Technical University, Lithuania. Total duration of the experiments was 8 month (February-June, 2010) and (October-December, 2011) for experiments with sludge mixture obtained from Vilnius WWTP ("Vilnius") and Utena WWTP ("Utena") relatively.

"Vilnius" experiment was designed for the evaluation of impact of two different doses of iron chloride on digestion of sludge mixture obtained from Vilnius WWTP. During "Utena" experiment impact of iron chloride ($FeCl_3$) and iron sulphate ($Fe_2(SO_4)_3$ at same doses on anaerobic digestion of sludge mixture has been investigated.

Equipment used for the experiments

Two laboratory-scale semi-continuous high-rate anaerobic digesters (W8, Armfield, United Kingdom) were used for the both "Vilnius" and "Utena" experiments.

The same equipment has been previously used for the research experiments and described in details by Menert *et al.* (2001), Blonskaya and Zub, (2009). Cylindrical shape reactors each of 4.8 l were working in parallel. Anaerobic digestion was carried-out under mesophilic conditions (35 °C). Electric heating mat wrapped around the external wall let to keep the selected temperature which has been measured electronically by internal probe added into digesters.

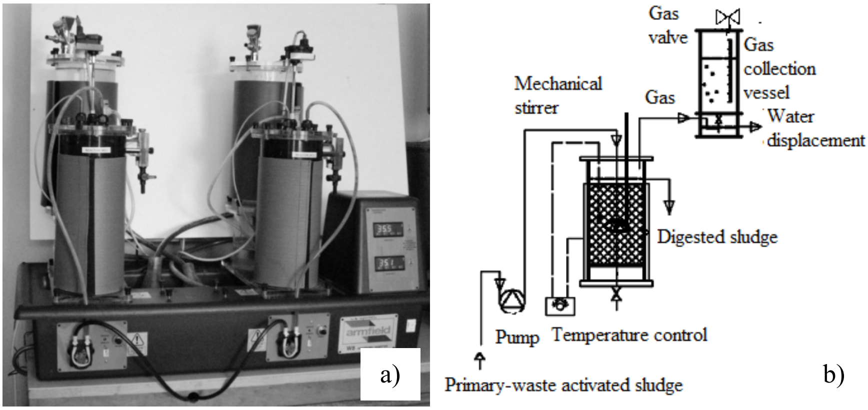

Fig. 2.2. a) Laboratory-scale digesters; b) technological scheme

Both reactors (see Fig. 2.2) were modified at the laboratory by inserting internal mechanical stirrer for the continuous mixing. The gas off-take from each reactor was taken into a volumetrically calibrated collector vessel (3.3 l) operating by liquid displacement. Biogas production has been recorded daily. Gas/water valve was installed to each gas collector vessel for filling of water and for biogas composition measurements.

According to the selected solids retention time (SRT) of 20 days sludge mixture flow rates to the reactors were set and controlled by calibrated peristaltic pumps. Feed sludge has been pumped daily from the bowl with constant mixing by magnetic stirrer.

Sludge and inoculum

Inoculums for both experiments have been collected from the Utena WWTP full-scale high-rate mesophilic digesters. Main characteristics of the treatment plant are presented in Chapter 2.1. During “start-up” period of the experiment laboratory reactors were filled with inoculums and daily feeding of prepared sludge mixture has been applied. The “start-up” period was excluded from the evaluation of results due to instability of the process.

Sludge for both experiments was collected every 5th day and then refrigerated at +4°C. Selected storage period and conditions was chosen to avoid changes in sludge characteristics. Longer storage time can reduce biogas production due to the breakdown of readily degradable organics (Gosset and Belser, 1982). Primary and secondary sludge were stored separately. Sludge mixture was prepared at the laboratory prior each feeding of the reactors. The average characteristics of the feed sludge mixture are given in Table 2.2.

Table 2.2. Average characteristics of prepared sludge mixture used for the "Vilnius" and "Utena" experiments

WWTP, country	Characteristics of sludge mixture				
	Total sludge			Sludge liquor	
	TS, %	VS, %	pH	PO_4-P, mg/l	Fe^{3+}, mg/l
Vilnius WWTP, Lithuania	2.0±0.4	1.4±0.2	6.02±0.1	55±24	1.1±0.05
Utena WWTP, Lithuania	2.8±0.3*	2.1±0.2 *	6.5±0.1	102±21	4.5±0.1

*prior thickening up to 4% at laboratory.

For "Vilnius" experiment sludge has been collected from Vilnius WWTP where biological phosphorus removal process is implemented. Primary sludge (PS) was taken from the primary sludge pumping station before thickening and waste activated sludge was collected from the distribution chamber of secondary sedimentation tank. Sludge mixture has been prepared according to primary and waste activated sludge daily production rates at WWTP and was 1:2 (primary to waste activated sludge) by volume.

Operational parameters of laboratory digesters were selected according to the results obtained from case study and presented in Table 2.3.

Table 2.3. Operational conditions of laboratory digesters

Parameter	"Vilnius"	"Utena"
Ratio PS:WAS (volume based)	1:2	1:2
Q_{in}, l/d	0.24	0.24
OLR, $kgVS_{in}/m^3/d$	0.76±0.22	1.22±0.16
SRT, d	20	20
T, °C	35±1	35±1

For "Utena" experiment sludge has been collected from Utena WWTP. Both primary and waste-activated sludge were taken prior the thickening and then thickened at the laboratory with flocculants used at the wastewater treatment plant up to 4% of TS. Organic loading rate (OLR) was higher during Utena experiment (1.22±0.16 kg $VS_{in}/m^3/d$) than Vilnius experiment (0.76±0.22) because feed sludge mixture was thickening up to 4% during Utena experiment.

Evaluation of results has been started during “Steady-state” (or “Control”) period when addition of iron salts was not implemented.

Doses of iron salts selected

Two mainly used iron salts in ferric form were selected for the Vilnius and Utena experiment: iron chloride in iron chloride hexahydrate form ($FeCl_3 \cdot 6H_2O$) and iron sulphate ($Fe_2(SO_4)_3$ were selected for the experiment (see Table 2.4).

Table 2.4.Selected iron salts

Iron salt	Molar mass	Iron form	Iron content
$FeCl_3 \cdot 6H_2O$	270.3g/mol	Fe^{3+}	20.7%
$Fe_2(SO_4)_3$	399.9 g/mol	Fe^{3+}	27.9%

For the evaluation of any inhibition effect of iron on sludge mixture digestion process iron chloride concentrations for“Vilnius” experiment were selected according to the results obtained by case study. Amounts of iron in digested sludge samples at the wastewater treatment plant with chemical phosphorus removal process (Ryaverket WWTP) in 2008 year were 52–81 mgFe/gTS. Doses, selected for the experiment, were 50 and 100 mgFe/gTS of sludge. The average concentration of TS in sludge mixture was 16.8 gTS/l.

Concentrations of salts (gFe^{3+}/l) selected for the experiments are presented in Table 2.5.

Table 2.5. Selected iron chloride concentrations (expressed in Fe^{3+}/l) used during “Vilnius” and “Utena” experiments

<table>
<tr><td colspan="4">“Vilnius” experiment</td></tr>
<tr><td colspan="2">I reactor (R1)</td><td colspan="2">II reactor (R2)</td></tr>
<tr><td>$FeCl_3 \cdot 6H_2O$, g/l</td><td>Fe^{3+}, g/l</td><td>$FeCl_3 \cdot 6H_2O$, g/l</td><td>Fe^{3+}, g/l</td></tr>
<tr><td>4.2</td><td>0.8</td><td>8.4</td><td>1.7</td></tr>
<tr><td colspan="4"><i>“Utena” experiment</i></td></tr>
<tr><td colspan="2">$FeCl_3 \cdot 6H_2O$</td><td colspan="2">$Fe_2(SO_4)_3$</td></tr>
<tr><td>$FeCl_3 \cdot 6H_2O$, g/l</td><td>Fe^{3+}, g/l</td><td>$Fe_2(SO_4)_3$, g/l</td><td>Fe^{3+}, g/l</td></tr>
<tr><td>0.4</td><td>0.1</td><td>0.3</td><td>0.1</td></tr>
</table>

Doses for the “Utena” experiment were selected according to the dosage of $Fe_2(SO_4)_3$ at Utena WWTP – 0.25–0.30 g/l for the prediction of hydrogen sulphide formation in biogas produced.

Analytical methods

Anaerobic digestion process performances were routinely monitored. Evaluation of feed sludge characteristics was made one for each new set of sludge obtained from the wastewater treatment plant. Analyses of digested sludge were performed immediately after sampling of samples.

Total and volatile solids were measured in total sludge according to the Lithuanian Standards: LAND 46:2007 and LST EN 12880:2000 relatively. Alkalinity, volatile fatty acids and phosphates were determinate in sludge liquor. Sludge liquor was obtained after filtering of digested sludge sample through filter with 2–3 µm porous.

Alkalinity (ALK) was analysed according to the Lithuanian Standard LST EN ISO 9963–1:1999, volatile fatty acids (VFA) by titrimetric method, pH was measured with Ino Lab pH 720 pH meter WTW company. pH measurement limits are 2.0–19.999, temperature measurement limits 5.0–105.0. Errors for pH and temperature measurements are 0.005 and 0.001 relatively (when sample temperature 15–35°C).

Phosphates in sludge liquor were analysed using a MERCK Phosphate test kit (Spectroquant), phosphates determination limit 1–30 mg/l, ±0.01 mg/l.

Biogas production was measured by water replacement. During Utena experiment produced biogas composition was measured by INCA T100 equipment. Biogas was analysed for CH_4 (measurement limits 0–100 %), CO_2 (0–100 %) and O_2 (0–25 %) contents.

2.3. Research methodology of ochre impact on sludge digestion process

The objective of the study was evaluation of the effect of different types and concentrations of ochre on anaerobic digestion of sludge mixture. Production of methane, reduction of hydrogen sulphide and prediction of phosphates recirculation were analysed.

All experiments on impact of ochre on anaerobic digestion of sludge mixture were made in Sweden. Laboratory batch experiments were made at Lund University, Chemical Engineering Department laboratory. Totally two batch test experiments have been made in October, 2011 and April-May, 2012. Duration of experiments was about 1 month each. In order to evaluate any inhibitory effect of ochre on methane production and evaluate reduction of dissolved phosphorus through digestion different types and doses of ochre have been selected.

The duration of pilot-scale experiment was February-June, 2012 (4.5 month) and has been made using equipment located at Sjölunda wastewater treatment plant (Malmö, Sweden). Pilot-scale experiment was designed for the evaluation of addition of ochre into feed sludge on rapid reduction of hydrogen sulphide in biogas and for the reduction of phosphates concentration in feed sludge.

Laboratory batch experiments

Batch tests were used for examination of the methane potential according to methodology described in Hansen *et al.* (2004) and Davidsson *et al.* (2008). Batch tests were performed in glass reactors ~2 L (see Fig 2.3a) with a thick rubber septum (chlorobuthyle rubber, Apodan Nordic, Copenhagen, Denmark). The exact volume of each bottle was determined by weighing the water contained into the bottle. Each glass reactors set was made in triplicate. All the reactors were kept under mesophilic conditions (35 °C) in incubator (Fig. 2.3b).

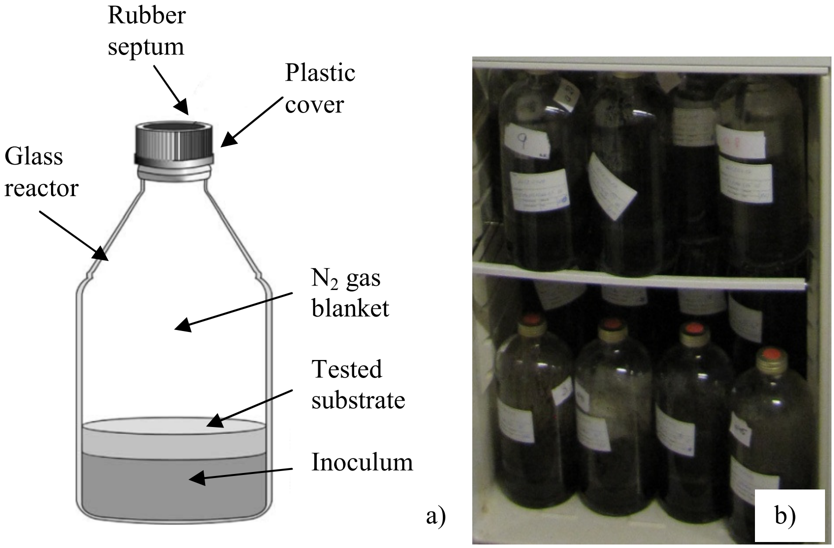

Fig. 2.3. Batch test equipment a) technological scheme; b) reactors placed into incubator.

Total volume of inoculums, sludge and ochre was up to 500 ml with the substrate representing about 45% of the total volatile solids (VS) content. Tested substrate and inoculums were added in the beginning of the test and there was no input and output flow except biogas production. Each bottle was flushed with nitrogen gas (N_2) after filling to ensure the anaerobic conditions in the reactors according to selected methodology. Cellulose powder was used as the reference substrate to test the function of the inoculums. The amount of volatile solids (VS) of cellulose added was similar to the VS of tested substrate according to the methodology described in (Davidsson *et al.* 2008; Hansen *et al.* 2004).

For the evaluation of digestion process efficiency biochemical methane potential test (BMP) was used (Angelidaki and Sanders 2004; Donoso-Bravo *et al.* 2011; Owens and Chynoweth, 1993). BMP test is relatively time-saving test compare to pilot-scale test and widely accepted for the prediction of digestibility of substrate (Lopez and Borzacconi 2010; Noykova *et al.* 2002). In average, BMP experiment takes about 25 days (Leusteur *et al.* 2010).

The BMP value is maximum yield of methane per gram of volatile solid added (VS_{in}).

BMP shows digestion kinetics which could be used for designing and operating anaerobic digesters (Buffiere *et al.* 2006). Also it helps to identify microbial inhibition, overloading, and adaptation (Hansen *et al.* 2004). Methane produced during BMP test had been determined using gas chromatography equipment as is predicted by method (Lesteur *et al.* 2010).

The measurementsof methanewere made in triplicate. For every analytical series, methane standard (30% in nitrogen) was measured and calculated average value has been used as standard. The actual content of methane in the samples was calculated based on this standard. The methane content at standard temperature and pressure (X_{STP}) had been recalculated according to equation 2.1:

$$X_{STP} = X_m \cdot \frac{T_S \cdot P_m}{T_m \cdot P_S}, mlCH_4 / gVS_{in}, \tag{2.1}$$

where T_m – actual temperature, °C; T_S – standard temperature, °C; P_m – actual atmospheric pressure, atm; P_S – standard atmospheric pressure, °C; X_m – measured methane content, $mlCH_4/gVS_{in}$.

The results are given as produced methane per gram VS_{in} at standard conditions (STP: °C, 1 atmosphere versus time).

Based on the volume of the headspace of each reactor and CH_4 content per 0.2 ml of headspace measured directly on the GC, the produced amount of methane was determined.

Typically 80–90% of the methane is produced during 8–10 days from start of experiment (Hansen *et al.* 2004). Biogas had been released by inserting a syringe in the rubber septum during high production period in case to avoid too high pressure in the reactors. Later the gas was released only occasionally. Methane content in reactors was measured and recorded before and after release.

Pilot-scale experiment

Three pilot-scale reactors (20 l of working volume each) located at Sjölunda wastewater treatment plants (Malmö, Sweden) were used for the pilot-scale experiments (Fig. 2.4a). The digestion chamber was surrounded by a water bath to heat up the reactors. Selected mesophilic temperature (35 °C) was regulated by a thermostat connected to a heater. Reactors had mechanical stirrer operated continuously at a constant speed for the mixing of the substrate.

In the beginning of the experiment each reactor was inoculated with anaerobic sludge obtained from the full scale mesophilic digesters located at Öresundsverket WWTP, Sweden. Reactors were fed once per day with 1.33 l of primary and waste activated sludge mixture. Feeding substrate and withdrawal of digested matter were done manually once a day at a certain time (Fig. 2.4b).

Fig. 2.4. a)Pilot-scale digesterslocated at Sjölunda wastewater treatment plants (Malmö, Sweden); b) manual operation of reactors.

Produced biogas was collected in a bell-shape gas collector filled with water. Change in the water level inside the gas bells represented the differential pressure of the produced biogas. Gasometers of this type are used because they are inexpensive, easy in use and do not require much maintenance (Walker *et al.* 2009). Biogas production was corrected for any hydrostatic pressure on the gas.

Fig 2.5 shows technological scheme of the pilot-scale reactors.

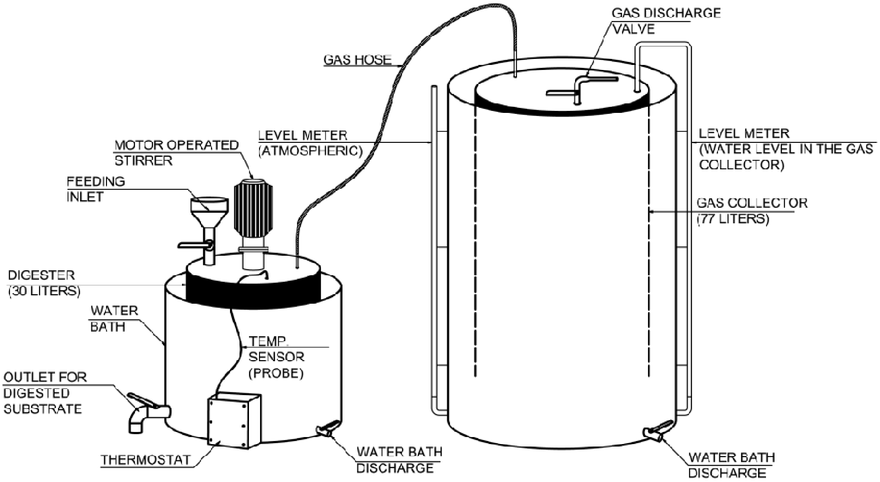

Fig. 2.5. Technological scheme of pilot-scale anaerobic digesters (Haghighatafshar *et al.* 2012).

Operational parameters of pilot-scale digesters are presented in Table 2.6.

Table 2.6. Operational conditions of pilot-scale digesters

Parameter	Units	Value
Working volume, l	l	20
Biogas collection vessel, l	l	77
Ratio PS:WAS (v/v)	v/v	0.35:0.65
Q_{in}, l/d	l/d	1.33
SRT, d	d	15
T,	°C	37±1
OLR,	$kgVS_{in}/m^3/d$	1.42–2.00

The pilot reactors were first operated continuously for 30 days (“Start-up” period) until “Steady state” conditions were obtained and for removal of the remained iron from inoculum. “Start-up” period was excluded from the evaluation due to unstable biogas production.

Sludge and inoculums

Sludge used for the experiments was taken from Öresundsverket WWTP (Helsingborg, Sweden). Enhanced biological phosphorus removal is applied at the treatment plant; hydrolysed primary sludge is used as additional carbon source (Jönsson *et al.* 2008). Sludge from Öresundsverket WWTP has similar to sludge from Lithuanian WWTP with biological phosphorus removal process characteristics.

Two batch tests and one pilot-scale test were performed for the complex evaluation of the effect of ochre on anaerobic digestion of sludge mixture process.

Inoculums for the "Batch I" test and for "start-up" of the pilot digesters were obtained from the Öresundsverket WWTP mesophilic digesters operated in mesophilic regime. Inoculums contained rest of minor dose of iron chloride which was added to the primary sludge before digestion to prevent hydrogen sulphide (H_2S) formation in the biogas. Average characteristics of inoculums and sludge used for both batch and pilot experiments are presented in Tables 2.7, Table 2.8 and Table 2.9.

Table 2.7. Average characteristics of inoculum and sludge used for the Batch I experiment

TS, %	VS, %	PO_4-P, mg/l	Fe (tot), mg/l
Inoculum (Öresundsverket WWTP)			
2.72	1.75	33.8	5.9
Primary sludge (Öresundsverket WWTP)			
2.78	2.35	8.38	5.9
Waste activated sludge (Öresundsverket WWTP)			
2.70	1.90	35.6	2.70

Inoculum used in the "Batch II" test was taken from the pilot-scale digesters after operation for more than 3 solid retention times (SRTs) in order to remove the iron used for hydrogen sulphide control in the full scale installation. In order to readapt the inoculum to 35°C temperature and remove the rest of dissolved methane and ensure degradation of easy degradable organic matter presented in the inoculum, it was stored for three days in the 35°C incubator. For the pilot-scale inoculum was placed directly into digesters.

Table 2.8. Average characteristics of inoculum and sludge used for the Batch II experiment

TS, %	VS, %	PO_4-P, mg/l	Fe (tot), mg/l
Inoculum (Pilot-scale reactors)			
1.65	1.12	337.92	5.5
Primary sludge (Öresundsverket WWTP)			
4.84	2.79	20.0	21.1
Waste activated sludge (Öresundsverket WWTP)			
3.84	2.12	300.0	5.35

Phosphates concentrations in feed waste activated sludge obtained for Batch II and pilot-scale experiments contained about 10 times higher concentration of phosphates compare to waste activated sludge used for Batch I experiment.

Table 2.9. Average characteristics of inoculum and sludge used for the pilot scale experiment

TS, %	VS, %	PO_4-P, mg/l	Fe (tot), mg/l
Inoculum (Öresundsverket WWTP)			
2.75	1.95	98.6	16.3
Primary sludge (Öresundsverket WWTP)			
3.58	2.85	15.0	14.8
Waste activated sludge (Öresundsverket WWTP)			
3.27	2.44	204.0	10.2

Sludge was taken from the ÖresundsverketWWTP every week and stored in a cold room at +4°C. Sludge mixture was prepared in proportions 0.35:0.65 (volume based) primary to waste activated sludge according to the sludge production at theÖresundsverket WWTP. Primary sludge for all experiments was sampled before the addition of iron chloride and manually thickened up to TS concentration 2.78–4.84% at the Lund university laboratory.

Ochre used for the experiments and doses selected

Two types of ochre from Denmark and Lithuania were used for the experiments. In both countries ground water is used as source for the drinking water and contains a lot of iron compounds which has to be removed before supply to customers (Albrektienė *et al*. 2011; Diliūnas *et al*. 2006).

Ochre for the "Batch I" test originated from Marbjerg WTP, (Copenhagen, Denmark). Marbjerg WTP is the one of seven WTPs supplying drinking water to Copenhagen (capacity 4 Mln. m^3/year). Ochresediments were collected from the landfill (~ 1 year of storage) and were manually dewatered at the laboratory up to 18.6% of TS.

For the "Batch II" test fresh pressed ochre was taken from Antaviliai WTP (Vilnius, Lithuania). Antaviliai WTP supplies drinking water for 250,000 people (~41% of Vilnius city inhabitants). Iron content in source water is about 1.1 mg/l and after removal is 0.00 mg/l. Iron is removed using filters with sand media (gravitation open sand filters). Filters are washed and collected water with precipitated iron sludge (ochre) is dewatered and pressed up to 40% of TS. Such type of ochre is easy to transport. Before addition to the pilot-scale digesters ochre was smashed and ground in laboratory. Main characteristics of ochre originated from Marbjerg WTP (Denmark) and Antaviliai WTP (Lithuania) are presented in Table 2.10.

Table 2.10. The main characteristics of ochre used for the experiments

Name of WTP	Type of ochre	Characteristics		
		TS, %	VS, %	Fe^{3+}, % of TS
Marbjerg	Sediments (stored)	18.6	2.87	30
Antaviliai	Pressed cake (fresh)	40.0	ND	35–40

Ochre obtained from the Antaviliai WTP was also analysed by granullametry for 48 elements. Major obtained elements were iron (35.27%), calcium (4.65%), silicon (2.53%), and phosphorus (2.26%).

Iron content was similar to the reported values obtained in the literature. The rest (about 50% of mass) was not analysed. Analyses showed very minor presence of heavy metals in ochre from Antaviliai WTP, most of them where below 0.01%.

Results of Antaviliai WTP ochre analyses are presented in Table 2.11.

Table 2.11. Major elements in ochre from Antaviliai WTP

Element	Name	Concentration, %	Standard deviation
Fe	Iron*	35.27	1.29
Ca	Calcium	4.65	0.12
Si	Silicon	2.53	0.16
P	Phosphorus	2.26	0.04
Mn	Manganese	0.38	0.01
Al	Aluminum	0.28	0.10
S	Sulphur	0.25	0.04
Mg	Magnesium	0.23	0.01
Ti	Titanium	0.14	0.01
Ba	Barium	0.12	0.00
K	Potassium	0.04	0.01
Sr	Strontium	0.03	0.00
Cr	Chromium	0.008	0.00
Pb	Lead	0.003	0.00
Zn	Zinc	0.003	0.00
Cu	Copper	0.002	0.00
Ni	Nickel	0.001	0.00
As	Arsenic	0.001	0.00
Cd	Cadmium	B.D.	0.00

*One gTS of ochre contains approximately 350–400 mgFe^{3+}; BD – below detection limit.

Doses and concentrations of substrates used for both Batch I and Batch II experiments are presented in Table 2.12 and Table 2.13. For the “Batch I” test concentration of ochre from Marbjerg was has been made in wide range: 0; 0.2; 0.4; 0.8; 1.5 and 7.5 gFe^{3+}/l (0–25 gTS$_{ochre}$/l of sludge) for the comprehensive examination and evaluation of impact of ochre on anaerobic digestion process.

Table 2.12. Substrated and ochre doses and concentrations used during Batch I and Batch II experiments

Set	Added inoculum, sludge mixture and ochre			Ochre concentration and doses	
	Inoculum, ml (gVS_{in})	Sludge mixture (gVS_{in})	Ochre, g	gTS_{ochre}/l	Fe^{3+}, g/l
Batch I					
0	300 (5.3)	200 (4.3)	0	0	0
0.2			1.35	0.5	0.2
0.4			3.38	1.25	0.4
0.8			6.80	2.5	0.8
1.5			13.80	5	1.5
7.5			77.59	25	7.5
Batch II					
0	350.0 (3.9)	137.0 (3.5)	0	0	0
0.5			1.58	1.25	0.5
1.0			3.16	2.5	1.0

The dosing of ochre, as solids, in the "Batch II" experiment was set in two levels: 0.5 gFe^{3+}/l and 1.0 gFe^{3+}/l where the lower concentrationof ochre corresponds to a molar ratio of 1:1 mole $Fe:P_{released}$. $P_{released}$ is the release of phosphate into the liquid phase during digestion (about 260 $mgPO_4$-P/l), which was determined by batch digestion of the sludge from Öresundsverket.

Table 2.13. Concentration of ochre in feed sludge during pilot-scale experiment

Dose of ochre			Concentration	
g/d	gTS_{ochre}/d	gTS_{ochre}/gTS_{in}	gTS_{ochre}/l	Fe^{3+}, g/l
40	16	0.75	11.6	4.4
20	8	0.38	5.8	2.2
10	2.9	0.25	2.9	1.1
5	1.4	0.12	1.4	0.6

The high concentration was chosen in order to evaluate any inhibitory effect and the effect of increased concentrationof iron on the phosphate binding capacity.

Dosing of ochre during the Pilot-scale experiment was divided into two small separated experiments: first was designed for the control of hydrogen sulphide in biogas and second for the precipitation of phosphates. Three reactors were working in parallel: one control and two with high and low doses of ochre.

In the first period ochre was added for only three days (49–51 days) at two different levels. The idea was to evaluate the potential to use ochre for rapid reduction of hydrogen sulphide production and to check if very high doses of ochre have any impact on the anaerobic digestion process. In the first experiment concerning hydrogen sulphide reduction via addition of ochre, the concentrations of ochre in feed sludge were 4.4 gFe^{3+}/l and 2.2 gFe^{3+}/l.

In the second period continuous addition of ochre at two levels in two different reactors in addition to one control without addition during 12 days to evaluate the influence on phosphate release.

In the second addition of ochre for phosphates release control (85–96 days of total experiment), concentration of ochre in feed sludge was 1.1 gFe^{3+}/l and 0.56 gFe^{3+}/l respectively (corresponding to a molar ratio of 1.5 and 0.75 $Fe^{3+}/P_{released}$ respectively, where $P_{released}$ was 400 mg/l.

Addition of sodium sulphate

After a long period of operation, the hydrogen sulphide concentration in the biogas was still low probably due to the low content of sulphate in fed sludge. In order to provoke hydrogen sulphide (H_2S) formation because of sulphate reduction conditions (Włodarczyk-Makuła, 2011), sodium sulphate (Na_2SO_4) was added daily into sludge fed to all three reactors, starting on day 28. The dosage of Na_2SO_4 into sludge was increased gradually: 2 gNa_2SO_4/day or for 5 days, 4 gNa_2SO_4/day for the next 10 days, and about 8 gNa_2SO_4/day until the end of the experiment (day 52) (see Table 2.14).

Table 2.14. Sodium sulphatedoses and concentrations in feed sludge used for hydrogen sulphide formation provoking in biogas during pilot-scale experiment

Period of total pilot-scale experiment (days)	Na_2SO_4		Na^+	SO_4^{2-}
	g/d	g/l	g/l	g/l
28–32	2	1.5	0.5	1.0
33–42	4	3.0	1.0	2.0
43–52	8	6.0	1.9	4.1

Sodium concentration inhibition limits reported in the literature are 6–40 g/l (De Baere *et al.* 1984; Omil *et al.* 1995). In opposite, low concentrations of sodium (100–200 mg/l) are beneficial for the growth of the methanogents (McCarty, 1964; Chen *et al.* 2008). Selected sodium sulphate doses from 2 to 8 gNa_2SO_4 resulted sodium concentrations from 0.5 to 1.9 gNa^+/l in feed sludge which was below inhibition and over stimulating levels.

The amount of hydrogen sulphide in the produced biogas started very quickly to increase after addition of Na_2SO_4 into feed sludge. When hydrogen sulphide concentration in biogas exceed 2000 ppm the first experiment with ochre dosing into feed sludge for hydrogen sulphide control started. The experiment ran for 3 days (day 49–51 of total pilot-scale experiment).

After a short rest period for the reactors and removal of remaining ochre from previous experiment (day 53–63) the second part of the experiment started. Reactors were operated without dosing for 20 days (from day 64 until day 84 of total expeiriment) and then operated with relatively lower doses of ochre for phosphates release control until the end of the experiment.

Analytical methods

Total solids (TS) and volatile solids (VS) content were measured according to the Standard Methods (APHA, 2000). Alkalinity was measured according to Swedish standard (ISO 9963–1:1994).

The samples of primary, waste activated and digested sludge from the batch and pilot-scale experiments were analysed using HACH LANGE test tubes: LCK 320 for iron, LCK 049 for the phosphates, calcium and magnesium were analysed with LCK 327. Prepared tubes were analysed with HACH LANGE spectrophotometer (model DR 2800).

Samples were centrifuged for 15 minutes at the speed of 10000 rpm and filtrated through Munktell general purpose filter papers with 6–10 µm pore size before further analysis.

pH of the reactors was measured using a digital pH-meter (pH 3110 SET 2 incl. SenTiz® 41).Volatile fatty acids (VFA) content of samples was analysed with gas- chromatography using Agilent 6850 Series GC System equipped with FID (flame ionization detector) and a column with the dimensions: 25 m x 0.32 µm x 0.5 µm (Fig. 2.6a).

Methane production from the batch experiments was measured with gas chromatograph – Varian 3800 Gas Chromatograph- equipped with TCD (thermal conductivity detector) and a column with the dimensions: 2.0 m x ⅛ inch x 2.0 mm (Fig. 2.6b).

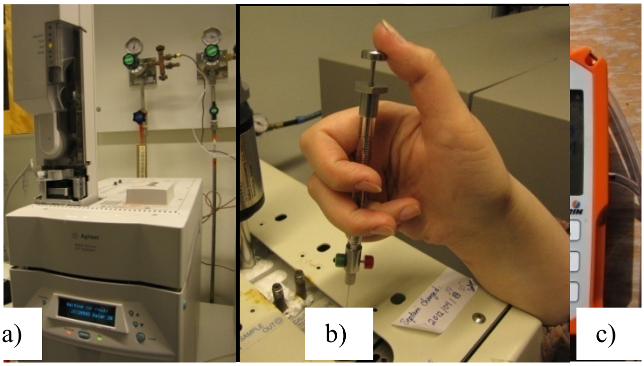

Fig. 2.6. a) gas chromatograph used for VFA measurements; b) gas chromatograph used for methane measurement; c) portable gas-meter.

Composition of produced biogas (methane, carbon dioxide, oxygen and hydrogen sulphide (up to 2000 ppm)) during pilot-scale experiment was measured using portable gas-meter SEWERIN SR2-DO (Fig. 2.6c).

2.4. Statistical evaluation of obtained results

Statistical analyses as sample mean, standard error, median, mode, standard deviation, range, minimum, maximum, sum and confidence level were done using Analysis ToolPak in Microsoft Excel.

Mean (AVERAGE) is the sum of all samples divided by the number of values:

$$\overline{\mathrm{x}} = \frac{\sum_{1}^{\mathrm{n}} \mathrm{x}_{\mathrm{i}}}{\mathrm{n}} . \qquad (2.2)$$

wherex$_{av}$ –average value (the mean) of the range; x_i– i-value; n – number of values. Standard Error estimates standard deviation of many measurements of a mean ofn samples. It is estimated by the standard deviation of one measurement of the mean divided by the square root of n:

$$\frac{s}{\sqrt{n}} = \sqrt{\frac{\sum_{1}^{n} \left(x_i - x_{av}\right)^2}{n(n-1)}} . \qquad (2.3)$$

Standard Deviation – is a measure of how widely values are dispersed from the average value (the mean).

$$s = \sqrt{\frac{\sum (x_i - x_{av})^2}{n-1}}. \tag{2.4}$$

Sample variance(VAR) is the square of the standard deviation:

$$s^2 = \frac{\sum_1^n (x_i - x_{av})^2}{n-1}. \tag{2.5}$$

Sum (SUM) is calculated sum of all values:

$$\sum_1^n \mathrm{x_i} \tag{2.6}$$

Confidence Level (chosen 95%) (α = 0.05), then the probability is 95%.

The Confidence Level = $\frac{\mathrm{ts}}{\sqrt{\mathrm{n}}}$, where t is Student’s t.

Correlation analysis between two or more examinated values have been made by thethe Analysis ToolPak in Microsoft Excel as well. The correlation coefficiencyis a measure of the extent to which two measurement variables "vary together".Correlation provides an output table (correlation matrix) where the value of CORREL (or PEARSON) applied to each possible pair of measurement variables is presented.The value of any correlation coefficient must be between -1 and +1 inclusive.

If large values of one variable tend to be associated with large values of the other (positive correlation), whether small values of one variable tend to be associated with large values of the other (negative correlation), or whether values of both variables tend to be unrelated (correlation near 0 (zero)).

Regression relationships between two variables (X and Y) have been used for the graphical evaluation of the results. Coefficient of correlation r was used for the determination of the relationship between two or more variables and lies between –1 and +1. Coefficient of determination is computed as the square of the coefficient of correlation (i.e. R^2). If the coefficient of correlation has been computed to be $R^2 = 0.9777$, $R = 0.95589$. Then we can claim that 95.6% of the variability of Y is explained by the variability of X; and, 4.4 percent of the variability of Y is unexplained.

2.5. Second chapter conclusions

1. For the evaluation of the impact of chemicals on digestion process case studies were made. Operational data of the existing digesters was treated by described statistical methods; digested sludge samples were analyzed for phosphorus fractions and selected metals content.
2. Design of laboratory experiments of impact of iron salts on anaerobic digestion process included selection of equipment, type and doses of iron salts. Standard methods were used for the evaluation of process results.
3. Laboratory batch experiments were made using specific anaerobic digestion process performance evaluation methodic. Wide range of oche has been selected for the testing.
4. Pilot-scale experiments were designed for the complex evaluation of impact of ochre on anaerobic digestion.
5. Statistical evaluation of obtained results has been made by Analysis ToolPak in Microsoft Excel.

3

Results and discussion on iron impacton sludge digestion

Chapter 3 contains main results on the impact of iron salts and ochre on anaerobic digestion process. Treated operational data of existing digesters and digested sludge quality is discussed; results on laboratory investigations of impact of iron salts and ochre on anaerobic digestion process are presented and discussed.

Articles published within the chapter (Ofverstrom *et al*. 2010a; Ofverstrom *et al*. 2010b; Ofverstrom *et al*. 2010c; Ofverstrom, *et al*. 2011; Ofverstrom, *et al*. 2012; Arlauskaitė *et al*. 2012).

3.1. Results of case studies on impact of iron use at wastewater treatment plants

Operational data collected at the selected wastewater treatment plants was statistically treated. Results were used for the designing of the laboratory semi-continuos and pilot-scale experiements.

Table 3.1. Main operational parameters of selected anaerobic digesters (case study)

Parameter	Utena WWTP	Panevezys WWTP	Ryaverket WWTP
V, m^3x amount	1000x2	1600x2	11400x2
Q_{in}, m^3/d	111 (81–130)	145 (120–168)	1091 (642–1539)
T, °C	35.0	37.5	37.5
SRT, d	16 (12– 20)	22 (17–27)	21 (20–24)
pH	7.4 (7.3–7.5)	7.3 (6.9–7.6)	7.4 (7.3–7.5)
VFA, mg/l as acetic acid	341 (300–360)	414 (300–540)	86 (60–120)
ALK, mg/l as $CaCO_3$	4191 (3750–4600)	3110 (2750–3450)	8034 (5600–10000)
VFA/ALK	0.08 (0.07–0.10)	0.13 (0.07–0.21)	0.01
$TS_{in,}$ %	4.1 (2.6–5.3)	3.7 (2.3–5.2)	4.9 (3.1–7.3)
$VS_{in,}$ g/l	31.6 (23.1–39.5)	ND	29.2 (21.1–49.5)
VS_{out}, g/l	18.5 (14.0–23.3)	ND	15.3 (11.6–21.6)
VS_{dest}, %	39.7 (28.6–50.9)	–	45.1 (16.1–69.9)
SBP, m^3/d	111 (81–130)	2709 (1871–3542)	29475 (15601–43361)
SBP, m^3/m^3VS_{in}		17.7 (13.06–22.58)	26.2 (15.4–37.4)
$CH_{4,}$ %	71 (63–75)	55–65	62–66

ND – no data.

Results presented in Table 3.1 shows that all analysed anaerobic digesters were operated in stable mesophilic temperature – from 35° to 37.5°C. Average solid retention time (SRT) at Utena WWTP and Panevėžys WWTP varried a lot: 12–20 days and 17–27 relatively; SRT at the treatment plants with sludge mixture digestion were 20–23.5 days at Ryaverket WWTP and 20 days at Öresundsverket WWTP.

Volatile fatty acids (VFA) concentrations in all anaerobic digesters were in normal range, a bit higher at the Panevėžys WWTP where iron chloride is used for the prediction of the formation of hydrogen sulphide. Significant increases in volatile fatty acids may take place before pH is changed if digester is heavily buffered (has high alkalinity). The alkalinity (ALK) concentrations in the digesters at Utena and Panevėžys WWTP were also in normal range, but concentration of alkalinity at Ryaverket WWTP was much higher –up to 10000 mg/l, that means that these digesters can absorb much higher swings in organic acids before pH is affected. On the other hand, too high concentrations of alkalinity should be avoided because of good conditions for the precipitates formation.

Ratio of volatile fatty acids to alkalinity (VFA/ALK) is also one of the important parameters of anaerobic digestion efficiency. The ratio of VFA/ALK of both anaerobic digesters for primary sludge (Utena and Panevėžys) was in proper range, from 0.1 to 0.3 (Appels *et al.* 2008). VFA/ALK ratio of Gothenborg AD was very low – only 0.01.

In anaerobic digesters at Panevėžys WWTP pH was up to 7.6, which was a bit higher than normal range (6.8–7.2) but still in proper limits.

The calculated efficiency of volatile solids destruction (VS_{dest}) varied from 28.6 to 50.9% at Utena WWTP and from 16.0 to 69.9% at Ryaverket. The range of efficiency calculated was wider than the usual range mentioned in the literature. The efficiency less than 40% shows low percentage of biodegradable volatile solids.

Biogas from anaerobic digestion at Utena WWTP showed the best result – up to 75% methane (CH_4) in biogas produced. According to the literature primary sludge should give higher amount of biogas because of easily degradable organics. Examination of the methane content of biogas produced from the primary sludge at Utena WWTP and Panevezys WWTP showed that the difference of methane content was about 16% lower possibly due to different iron salts used at the plants or homogenization process of primary sludge at Utena WWTP.

Volume of produced gas was 17.6 m^3/m^3 feed sludge at Utena and 17.7 m^3/m^3 feed sludge at Panevėžys WWTP. At Gothenborg WWTP volume of produced biogas was 27.7 m^3/m^3 feed sludge, which is ~10m^3/m^3 higher than at Lithuanian plants. According to the literature studied biogas production from the primary sludge should be higher than biogas production from the sludge mixture. Probably higher production of biogas was because of digestion of sludge mixture where waste activated sludge contained iron from the chemical precipitation of phosphates

Only at the wastewater treatment plant where iron sulphate is used for the prediction of the hydrogen sulphate (Utena WWTP) precipitates were formed in pipes. Characterization of the precipitates obtained at the Utena WWTP showed that it was struvite.Possible cause of struvite precipitation can be addition of $Fe_2(SO_4)_3$.

Results of analyses of digested sludge mixture samples from wastewater treatment plants with chemical phosphorus removal (Ryaverket WWTP) and biological phosphorus removal (Öresundsverket WWTP) are presented in Fig. 3.1.

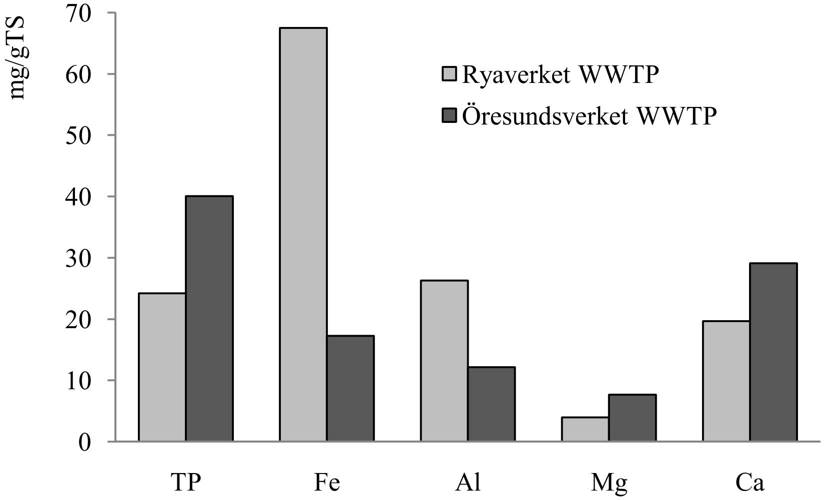

Fig. 3.1. Total phosphorus and metal content in digested sludge samples obtained from Ryaverket WWTP and Öresundsverket WWTP (case study experiment)

As can be seen from Fig. 3.1 iron content high (67.5 mg/gTS) at Ryaverket WWTP where chemical phosphorus removal is applied compare iron content in digested sludge from Öresundsverket WWTP where iron chloride is used for hydrogen sulphide formation prediction.

Phosphorus content in digested sludge from WWTP with biological phosphorus removal is 40.1 mg/gTS which is 60% higher than at the WWTP with chemical phosphorus removal. At Ryaverket WWTP where polyaluminium chloride (PAC) is used during rainfalls concentration of aluminium (Al) content is 52% higher than at Öresundsverket WWT.

Magnesium content is below 10 mg/gTS at both WWTP and calcium is a bit higher at the treatment plant with the biological phosphorus removal process.

3.2. Impact of iron salts on anaerobic digestion process results and discussion

Analysesof digestion process efficiency via evaluation of quality and quantity of end-products (biogas, digested sludge and digested sludge liquor) have been evaluated.

Impact of iron salts on biogas production rate and quality

During Vilnius experimentaverage biogas production from the control reactors (without addition of iron salts)was 0.30 $m^3/kgVS_{in}$. Feeding of sludge mixture with added iron chloride in concentrations of 0.8 $gFe^{3+}/l$and 1.7 g Fe^{3+}/l showed immediate drop in biogas production during first three days of addition. Amount of biogas was 0.18 and 0.11 $m^3/kgVS_{in}$ relatively (Fig. 3.2).

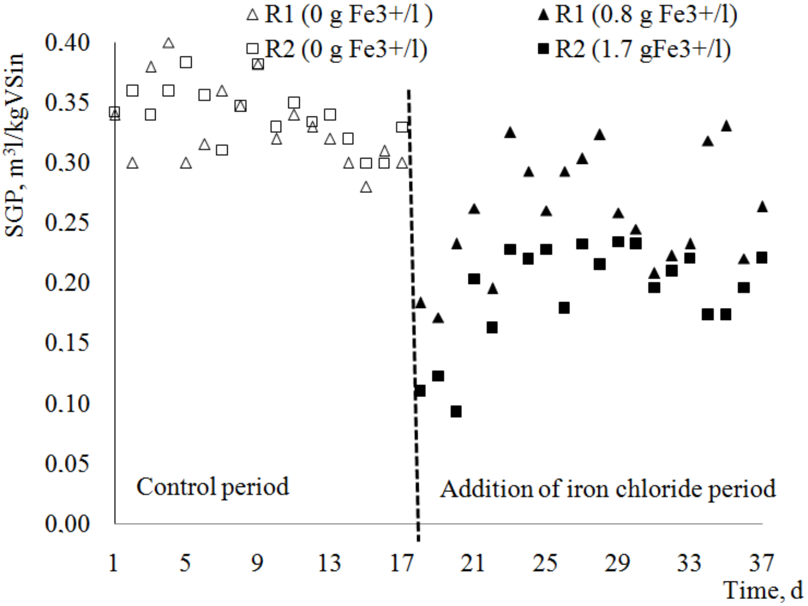

Fig. 3.2. Specific biogas production ($m^3/kg\ VS_{in}$) during control and addition of iron chloride periods (Vilnius experiment)

Obtained results correlates with results obtained by Hoban and van den Berg, (1979) and Philips *et al.* (2003) when methanogens were inhibited during first 2–4 days after addition of iron into feed sludge.

After this period slow increase in biogas production showed adaptation of methanogens to iron dosed sludge. Average biogas production from reactor with low concentration of iron in feed sludge during the experiment was 0.26±0.07 $m^3/kgVS_{in}$ which was 21% lower than before addition of iron dosed sludge.

Biogas production from reactor with iron chloride in 1.7 gFe^{3+}/l concentration was 0.19±0.04$m^3/kgVS_{in}$or 44% lower compare to the average production of biogas from the same reactor during control period (0.34±0.04 $m^3/kgVS_{in}$). Probably, methanogens activity was inhibited after addition of iron chloride into feed sludge. High iron doses cam inhibite biogas production (Chen *et al.* 2008). The other reduction of biogas reason can be that biovailability of nutrients reduced after addition of high doses of iron (Dentel and Gossett, 1982). Results on anaerobic digestion process are presented in Table 3.2.

Table 3.2. Main characteristics of the anaerobic digestion process

Parameter		I reactor		II reactor	
		0 gFe^{3+}/d	0.8 g Fe^{3+}/l	0 gFe^{3+}/l	1.7 gFe^{3+}/l
SGP, m^3/VS_{in}	Min	0.28	0.20	0.30	0.16
	Max	0.40	0.30	0.38	0.23
	average	0.33	0.26	0.34	0.19
	St dev	0.03	0.03	0.02	0.02
ALK, mg/l	Min	1600	900	1600	250
	Max	1850	1000	1850	450
	average	1714	963	1714	367
	St dev	85	48	85	104
VFA, mg/l	Min	60	60	60	120
	Max	360	300	360	180
	average	213	135	213	140
	St dev	116	114	116	35
pH	Min	6.80	6.48	6.80	6.31
	Max	7.00	6.72	7.00	6.37
	average	6.90	6.58	6.90	6.34
	St dev	0.06	0.10	0.06	0.03

All digestion stability parameters were affected by the addition of iron chloride into feed sludge. During control period when feed sludge was without any added iron chloride measured alkalinity was 1714±85 mg/l which is optimal for the mesophilic digesters (Appels *et al*. 2008). Drop in alkalinity was obtained immediately after receiving sludge with iron chloride added: 963±48 and 367±104 mg/l in reactors receiving sludge of iron chlroride in concentrations 0.8 gFe^{3+}/l and 1.7 gFe^{3+}/l relatively. Alkalinity in digester with 1.7 gFe^{3+}/lconcentration showed failure of the process. Mamais *et al.* (1994) suggested that addition of iron chloride lowers alkalinity because of precipitation of iron carbonate ($FeCO_{3(s)}$) (equation 3.1):

$$FeCl^3 + CO_3^{2-} \leftrightarrow FeCO_{3(s)} + 3Cl^-. \tag{3.1}$$

pH was also affected after feeding of sludge with iron chloride. During control period (without addition of iron chloride) pH was in optimal range (from 6.8 to 7.2). Immediate drop in pH was obtained when addition of iron chloride started (Fig. 3.3).

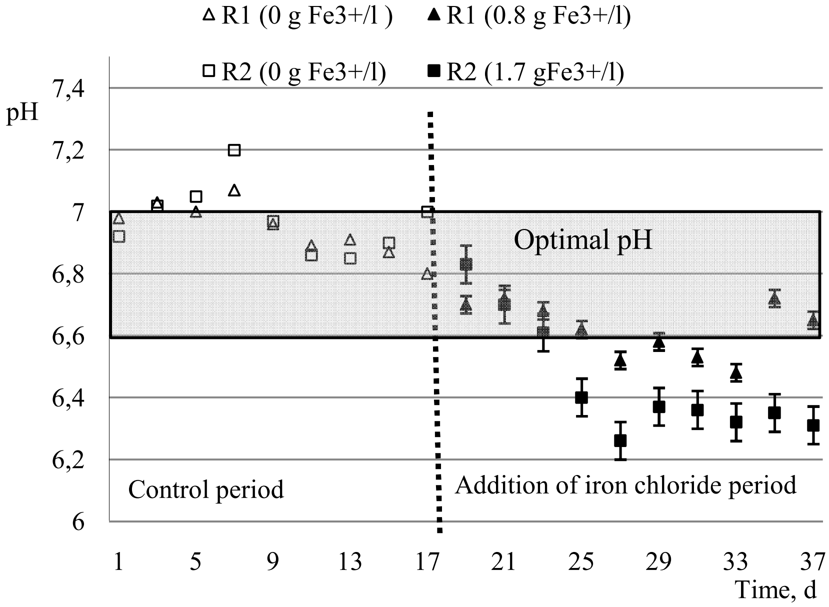

Fig. 3.3. pH changes during control and adittion of iron chloride into feed sludge periods (Vilnius experiment). R1 – reactor; R2 – reactor.

Experiments made with dosing of iron chloride showed that overdose of iron chloride cause negative impact of digestion process.

Main anaerobic digestion efficiency parameters (alkalinity, volatile fatty acids and pH) were affected after receiving of sludge with iron. Overdose of iron chloride should be avoided due to lower biogas production and failure of the process.

Resuts of the laboratory experiment ("Utena") with sludge from Utena WWTP and two mainly used at iron salts (iron chloride and iron sulphate) for hydrogen sulphide formation in biogas prediction dosed into feed sludge are presented in Table 3.3.

Table 3.3. Main characteristics of anaerobic digestion process parameters obtained during "Utena" experiment

Characteristics		0 gFe^{3+}/l	0.1 gFe^{3+}/l	
			Iron sulphate	Iron chloride
SGP, m^3/kgVS$_{in}$	Min	0.16	0.18	0.25
	Max	0.34	0.24	0.31
	average	0.24	0.21	0.28
	Stdev	0.05	0.16	0.02
% CH$_4$	Average	62.7	65.0	63.4
SGP, m^{3}CH$_4$/kgVS$_{in}$	average	0.15	0.14	0.18
ALK	limits	1800–2200	2600–2700	2050–2200
VFA	limits	240–360	180–480	240–360
pH	limits	7.16–7.17	7.24–7.28	7.16–7.20

If compare results obtained during "Vilnius" and "Utena" laboratory semi-continuous experiments, biogas production from the control reactor receiving sludge without any addition of iron salts, showed lower average biogas production during "Utena"experiment. Biogas production from control reactors during "Vilnius" experiment was 0.33±0.03 and 0.34±0.02m^3/kgVS$_{in}$ and only 0.24±0.05 m^3/kgVS$_{in}$ during "Utena" experiment. In reactor receiving sludge mixture with iron chloride added in concentrations of 0.1 g Fe^{3+}/l the average biogas production was 0.28±0.02 m^3/kgVS$_{in}$which means about 16 % increase in biogas production compare to control reactor.

In opposite, feeding of sludge with 0.1 $mgFe^{3+}/l$ concentration of iron sulphate salt decreased biogas production about 14 % compares to biogas production from control reactor and was 0.21±0.01 $m^3/kgVS_{in}$.

Feeding of sludge with added iron chloride in concentrations 0.1 gFe^{3+}/l increased pH and alkalinity in the reactor compare to control and reactor receiving sludge with iron sulphate. That suits with case study results were pH in the reactors at Panevėžys WWTP was higher than normal range. Low concentrations of iron chloride (0.1 gFe^{3+}/l) increased biogas production compare to reactors without iron or with iron sulphate added and showed more stable biogas production process. Without overdose iron chloride has positive impact on biogas production rate.

Digested sludge liquor quality

During Vilnius experiment phosphates concentration in feed sludge mixture liquor was 40.5±16.1 $mgPO_4$-P/l. Under anaerobic conditions in reactors release of phosphates was obtained. A concentration of phosphates in digested sludge liquor increased in about 29% compare to the phosphates in feed sludge and was 59.0±10.5 $mgPO_4$-P/l (Fig. 3.4).

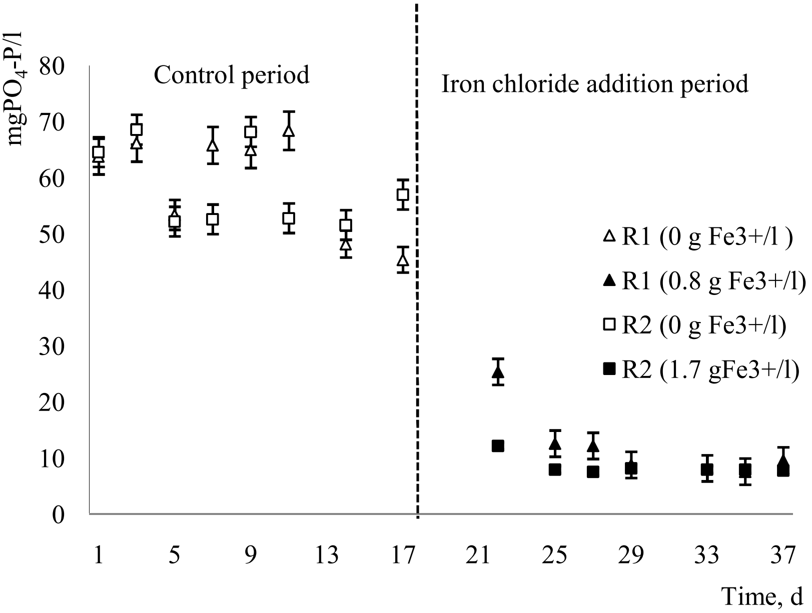

Fig. 3.4. Changes of phosphates concentration in digested sludge liquor (Vilnius experiment)

Precipitation of phosphates in digested sludge liquor was obtained directly after addition of iron chloride into feed sludge. Increase of phosphates in digested sludge liquor increased because of anaerobic conditions in digester. Under described conditions phosphates were released from the polyphosphates acculumating microorganisms' (PAOs) cells into sludge liquor.

Concentration of phosphates in digested sludge liquor was 8.6±0.9 and 9.2±2.0 mg PO_4-P/l for 0.8 and 1.7 gFe^{3+}/l relatively. Both concentrations of iron in feed sludge showed similar considerable precipitation of phosphates efficiency – about 80%.

Taking into account very similar remained concentration of phoshpates, it could be noted that addition of 0.8 gFe^{3+}/l iron chloride concentration into feed sludge is enough to obtain 8–9 $mgPO_4$-P/l of phosphates in digested sludge liquor. Addition of iron chloride into feed sludge showed good results on precipitation of phosphates and remained concentration of phosphates was similar to typical concentration in wastewater stream to wastewater treatment plant.In order to evaluate relationship between several independent parameters, statistical evaluation of the obtained results dependence of phosphates concentration in digested sludge liquor on iron chloride concentration and pH was observed (Table 3.4).

Table 3.4. Statistical evaluation of dependence of phosphate concentration in sludge liquor on pH and iron concentration

Parameters	PO_4-P, mg/l	gFe^{3+}/l	pH
R1 (iron chloride in 0 and 0.8 gFe^{3+}/l concentrations)			
PO_4-P, mg/l	1		
gFe^{3+}/l	-0,95528	1	
pH	0,924094	-0,89236	1
R2(iron chloride in 0 and 1.7 gFe^{3+}/l concentrations)			
PO_4-P, mg/l	1		
gFe^{3+}/l	-0,97886	1	
pH	0,943432	-0,86706	1

Result showed stong dependence of phosphates concentration in digested sludge liquor, iron chloride concentration in feed sludge and pH in each reactor (R1 and R2) separately. All obtained correlation coefficients were over 0.8 which means strong correlation between evaluated parameters.

There was positive linear correlation between phosphates concentration in digested sludge liquor and pH in both reactors. Higher amount of phosphates was obtained when pH in digesters was also high. Negative strong correlation was found between iron concentration in feed sludge and phosphate concentration in digested sludge liquor and iron concentration in feed sludge and pH in reactors. Addition of iron chloride into feed sludge decreased the pH in digesters and concentration of phosphates in digested sludge liquor.

Phosphate concentration in feed sludge liquor during Utena experiment was from 80 to 100 mg PO_4-P/l about 40% higher compare to phosphates concentration in feed sludge liquor during Vilnius experiment. Increasing of phosphates under anaerobic conditions due to the solubilisation of phosphates was also obtained during “Utena” experiment.

Average amount of phosphates in digested sludge liquor was 130 mg PO_4-P/l (35% higher than in feed sludge). Addition of iron chloride and iron sulphate into feed sludge in concentrations of 0.1 g Fe^{3+}/l had tendency to precipitate very low part of released phosphates.

Molar mass of iron to phosphorus Fe:P was lower than 1 which is necessary for the formation of iron chlorides of iron sulphides (Gutierrez *et al.* 2010; Philips *et al.* 2003).

Digested sludge samples obtained from the digesters during Utena experiments were also analysed for the total phosphorus, iron and magnesiumin mg/gTS (Fig. 3.5).

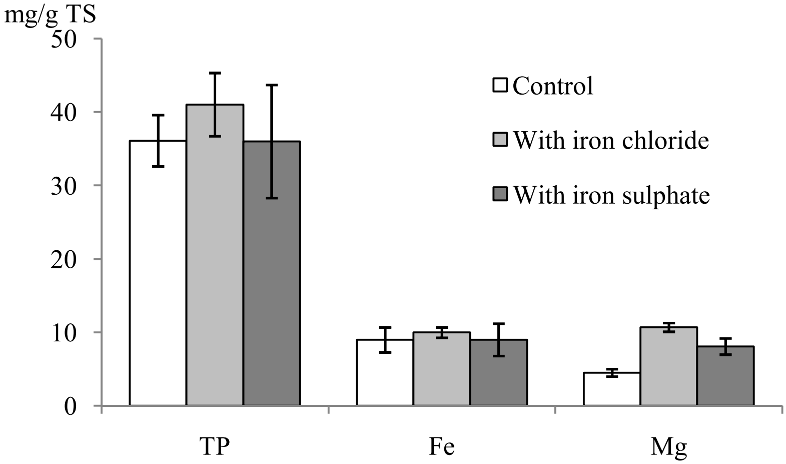

Fig. 3.5. Total phosphorus (TP), iron (Fe) and magnesium (Mg) content in digested sludge samples from control and reactors with iron chloride and iron sulphate (Utena experiment)

Total phosphorus amount in all tested samples was about 40 mg/g, which is similar amount of phosphorus in digested sludge from biological phosphorus removal plant. Iron content was below 10 mg/g, which was twice lower than at the WWTP with biological phosphorus removal. Amount of magnesium was two times lower in control reactor probably because of sedimentation of precipitants in digesters. If compare with digested sludge results obtained during case study, amount of magnesium was similar to magnesium amount obtained during case studies.

3.3. Results on impact of ochre on anaerobic sludge digestion

Evaluation of impact of ochre dosing into feed sludge on anaerobic digestion of sludge mixture have been made by evaluating of methane production during laboratory batch experiments and amounts of methane and hydrogen sulphide produced during pilot-scale experiments; digested sludge liquor in feed and digesteds sludge was analysed during laboratory and pilot-scale experiments as well.

Biogas production and quality

During Batch I and Batch II tests only methane production has been measured. Accumulated methane production from the reference substrate (cellulose) was similar in both Batch experiments – 316 $NmlCH_4/gVS_{in}$ and 317 $NmlCH_4/gVS_{in}$ for Batch I and Batch II respectlively which showed good inoculum was selected for the experiments.

Most of the methane produced during the first week of the both experiments. That was expected according to the specific methodology bescribed in Hansen *et al.* (2004) and Davidsson *et al.* (2008).

Fig. 3.6 shows obtained methane potentials from the sets with different concentrations of ochre sediments originated from the Marbjerg WTP, Denmark. As described in methodology part, each reactors contained inoculum, taken from full-scale reactors.

Methane potential determined from inoculum (97±3 $NmlCH_4/gVS_{in}$) was withdrawn from the total methane produced in each reactor (data is not presented).

The changes in methane production from reactors with different concentrations of ochre in sludge (0.2; 0.4; 0.8; 1.5 and 7.5 g Fe^{3+}/l) and from control reactor without addition of any ochre (0 gFe^{3+}/l) are shown as a function of experiment run time (days).

Total methane production from the reactor with 0 gFe^{3+}/l was from 343±12 NmlCH$_4$/gVS$_{in}$. As can be seen in Fig. 3.6, in reactors with 0.8 gFe^{3+}/l some kind of inhibition or leakeage happened (methane production line goes not similar to others).

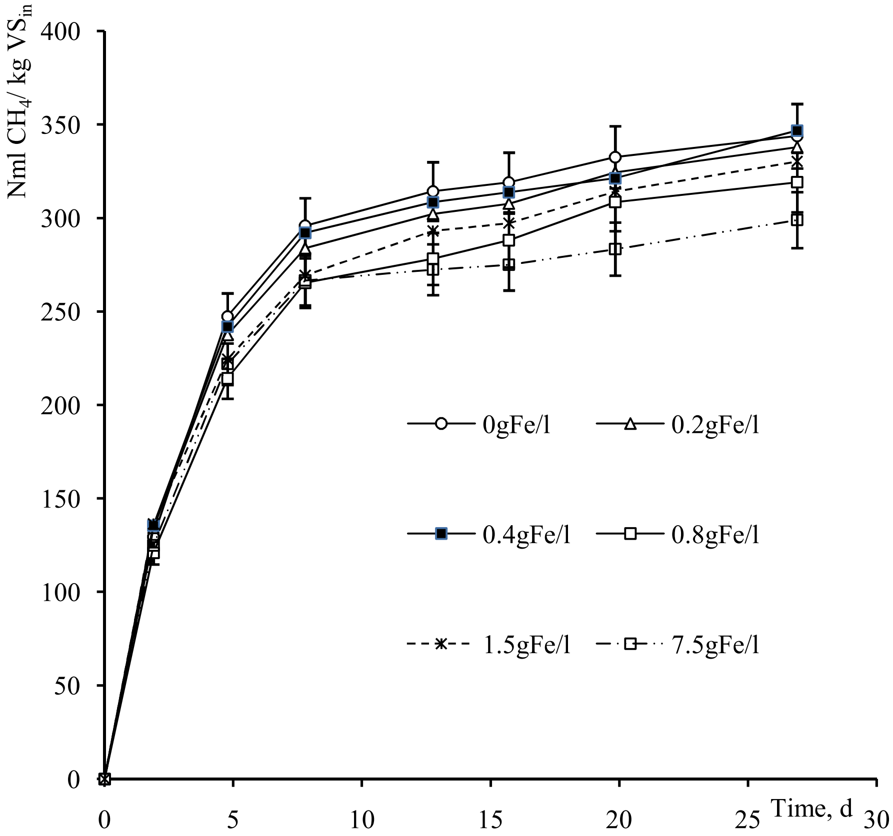

Fig. 3.6. Methane production during the Batch I test period.
Each point shows mean of triplicates with standard deviation

Total methane potential obtained from the reactor with 0.8 gFe^{3+}/l concentration of ochre was 319±18 NmlCH$_4$/gVS$_{in}$ or 8% lower compare to control reactor with 0 gFe^{3+}/l. Lower methane production was also obtained from the reactors with the highest concentration of ochre (7.5 gFe^{3+}/l).

Produced methane amount was 13 % lower compare to methane production from reactor with 0 gFe^{3+}/l ochre concentration. Table 3.5 shows production of methane from the reactors with different ochre concentrations during Batch I experiment.

Table 3.5. Methane production from the reactors with different concentrations of ochre (Batch I experiment)

Parameter		Concentration of ochre in g Fe^{3+}/l					
		0	0.2	0.4	0.8	1.5	7.5
SGP, l/g VS_{in}	Min	356	292	341	302	314	279
	Max	332	339	351	337	344	312
	average	344	322	347	319	330	299
	St dev	12	26	5	18	15	17

Fig. 3.7 presents results on methane production from Batch II experiment made with pressed ochre (about 40% TS) obtained from Antraviliai WTP (Lithuania).

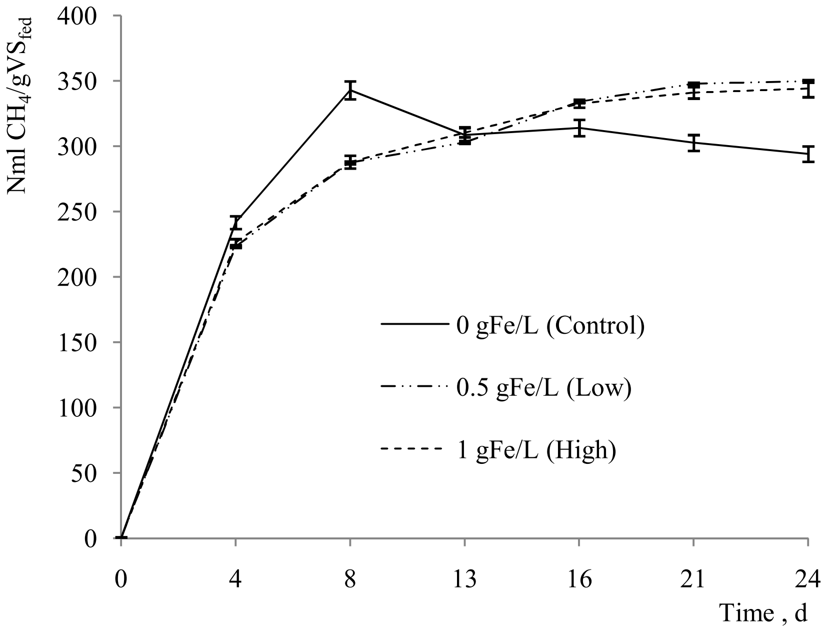

Fig. 3.7. Methane production from reactors with 0; 0,5 and 1.0 gFe^{3+}/l concentrations of ochre $NmlCH_4/gVS_{in.}$ Each point shows mean of triplicates with standard deviation

During first week of the experiment methane production from the reactors with 0 gFe^{3+}/l concentration of ochre reached 327 $NmCH_4/gVS_{in}$ and then decreased down to 304±10 $NmCH_4/gVS_{in}$. That probably happened because of inhibition of the process or leaking from the control reactors.

Reactors with 0.5 and 1.0 gFe^{3+}/l concentration of ochre behaved similarly. Most of methane was produced during the first week of the experiment. Methane production was about 10% higher in the both sets of reactors with ochre compare to the control reactors and reached 344±9 and 339±6 $NmlCH_4/gVS_{in}$.

Accumulated methane from all tested reactors with 0; 0.5 and 1.0 gFe^{3+}/l concentration of ochre is presented in Table 3.6.

Table 3.6. Methane production from reactors with different concentrations of ochre (Batch II experiment)

Parameter		Concentration of ochre in g Fe^{3+}/l		
		0	0.5	1.0
SGP, $mlCH_4/gVS_{in}$	Min	294	334	332
	Max	314	349	344
	average	303	344	339
	St dev	10	9	6

Organic loading rate during all pilot-scale experiment was from 1.42 to 2.0 $kgVS_{in}/m^3/d$. Relationships between organic loading rate and methane production during control and addition of sodium sulphate periods have been checked statistically. Evaluated data showed very low correlation between daily methane production and organic loading rate. Observed correlation factors were below 0.6 in all three reactors.

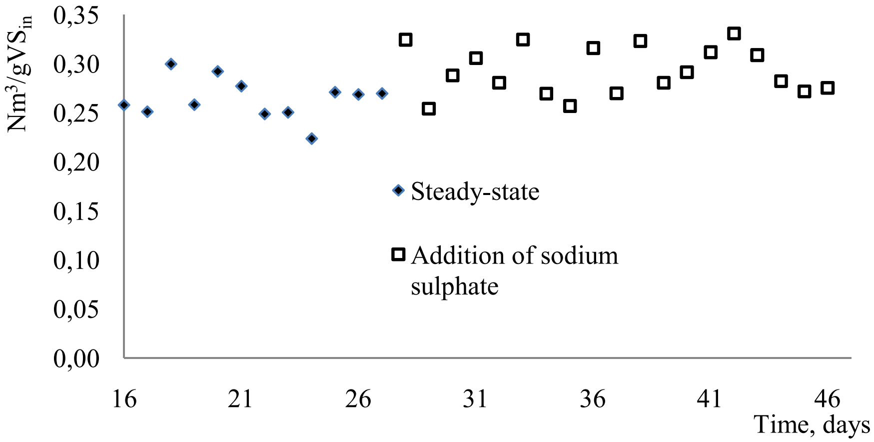

Fig. 3.8. Methane production rates during steady-state and addition of sodium sulphate periods (pilot-scale experiment)

Fig 3.8 shows results obtained during pilot-scale experiment control period (from 16 day of total experiment) and methane production rate when sodium sulphate was dosed. Methane production rate during control period was about 0.31±0.07 $m^3CH_4/kgVS_{in}$.After addition of sodium sulphate average methane production was similar to control period – 0.31±0.07 $m^3CH_4/kg\ VS_{in}$. Addition of sodium sulphate in selected doses (from 2 to 8 gNa_2SO_4/d did not inhibit anaerobic digestion of sludge process (Table 3.7).

Table 3.7. Methane production from digested feed sludge during steady-state conditions and addition of sodium sulphate conditions (pilot-scale experiment)

Parameter		Steady state (control period)	Sodium sulphate addition
SGP, $m^3CH_4/kgVS_{in}$	average	0.31	0.31
	Stdev	0.07	0.07
	Min	0.24	0.25
	Max	0.08	0.07

After continuous addition of sodium sulphate (Na_2SO_4) equally to all reactors (to provoke H_2S formation) the concentration increased very rapidly up to >2000 ppm before ochre was added (period from day 28–53). Figure 3.9 shows the development of hydrogen sulphide during the experimental period.

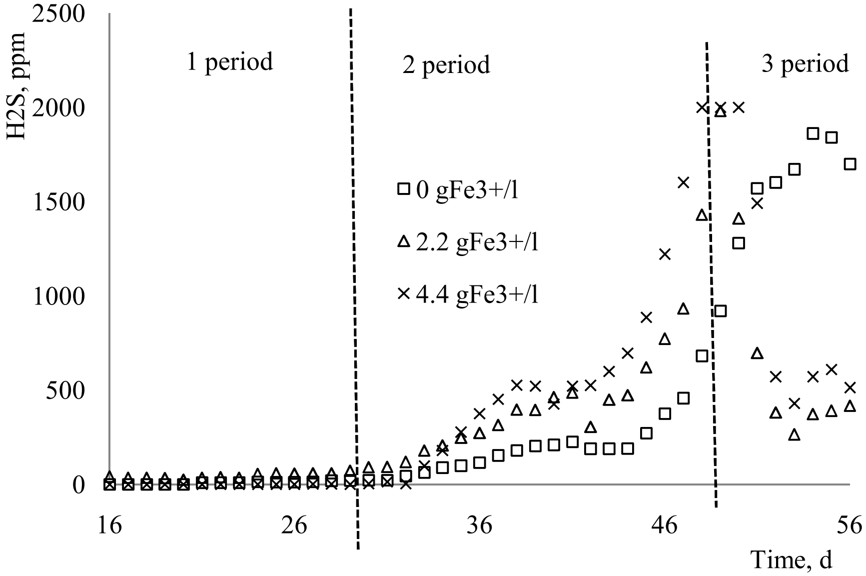

Fig. 3.9. Hydrogen sulphide production changes: 1 – steady-state period; 2 – addition of sodium sulphate period; 3 – addition of ochre period.

Cirne *et al.* (2008) and Lens *et al.* (1998) reported that H_2S production leads to the reduction of the methane production due to competition of sulphate-reducing bacteria (SRB) and methanogens for the available organic compounds and hydrogen. Results on methane production obtained during control and additions of sodium sulphate periods showed similar methane production before and after addition of sodium sulphate into feed sludge.

During first experiment dosing of ochre into feed sludge 38 $mgTS_{ochre}/gTS_{in}$ and 75 $mgTS_{ochre}/gTS_{in}$ was impelemented for 3 days (day 49–51 of total experiment), concentrations of ochre in feed sludge were 2.2 and 4.4 gFe^{3+}/l relatively. Drop in hydrogen sulphide production in biogas (from >2000 ppm to 570 ppm) have been obtained in both reactors, receiving feed sludge with 4.4 gFe^{3+}/l and 2.2 gFe^{3+}/l concentrations of ochre, while the control reactor (without ochre addition into feed sludge) still produced biogas with high H_2S-content (up to 2000 ppm).

It should be also noted that sulphide concentrations below 1000 ppm in biogas are recommended in order to guarantee the safe use of gas heater and combined heat and power production (CHP) (Appels *et al.* 2008; Dhar *et al.* 2011; Pol *et al.* 1998).

In digesters under anaerobic conditions, sulphide reacts with metals in solution to form precipitates which are highly insoluble. Chemical reactions describing the precipitation of hydrogen sulphide by iron sponge ochre are follows (equation 3.1) (Abatzoglou and Boivin, 2009):

$$Fe_2O_3 + 2H_2S \rightarrow Fe_2S_3 + 3H_2O. \qquad (3.2)$$

Feeding of sludge mixture with 4.4 gFe^{3+}/l (75 $mgTS_{ochre}/gTS_{in}$) had negative affect on anaerobic digestion process. Measurements of volatile fatty acids (VFA) showed that acetate level increased from ~50 mg/l (as COD) before addition of ochre to levels up 1700 mg/l. This indicated that the digester receiving iron with 4.4 gFe^{3+}/l concentration was inhibiting the acetate utilising microorganisms. Hoban and van den Berg (1979) found that iron inhibit acetic acid conversion during first 2–4 days of addition of high doses of iron.

Because of increased volatile fatty acids in digesters reactors were let to recover up to 63 day of the total experiment and then operated without addition of any ochre and sodium sulphate into feed sludge.

Digested sludge liquor quality

Evaluation of digested sludge liquor quality showed relationship of ochre concentration on phosphates precipitation rate. It should be noted that inoculum obtained for batch experiments influenced obtained results: inoculum used for Batch I experiment had remained concentration of iron chloride used at the Öresundsverket wastewater treatment plant for the prediction of hydrogen sulphate (H_2S) production in biogas.

Fig. 3.10 grafically presents relantionship between ochre concentrations in reactors and released into digested sludge liquor phosphates, calcium and magnesium concentrations (Batch I experiment). Released cations (Ca^{2+} and Mg^{2+}) are good coagulants (Seida and Nakano, 2002).

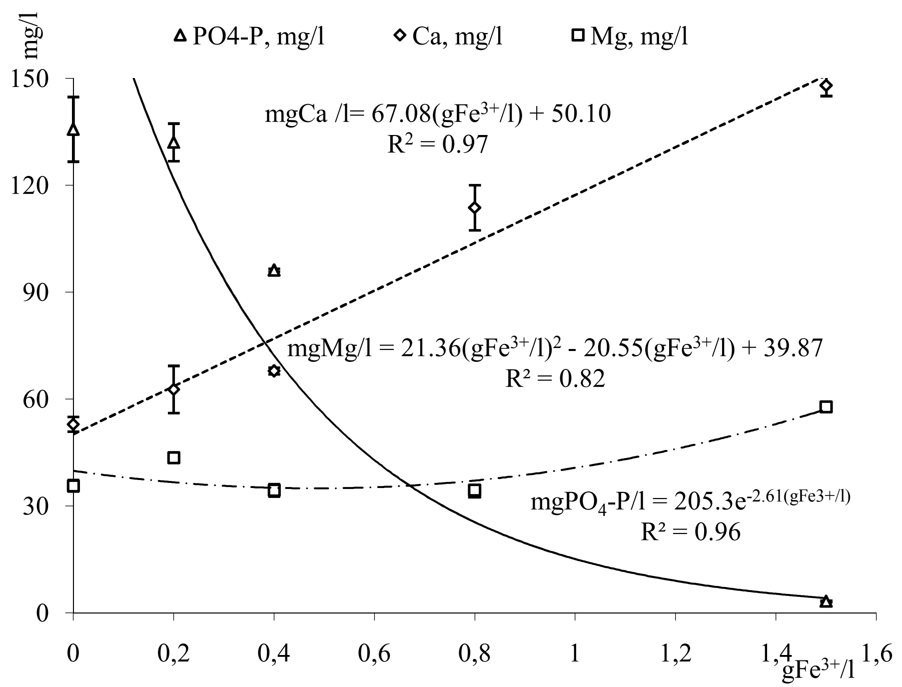

Fig. 3.10. Relationship between ochre concentration in reactors and phosphates, calcium and magnesium concentrations in digested sludge liquor (Batch I experiment)

That was similar to remained phosphates concentration in digested sludge liquor from the reactor with 1.5 gFe^{3+}/l of ochre. Strong exponential correlation R^2=0.96 was found between two tested values: concentration of ochre in feed sludge and precipitation of phosphates in digested sludge liquor. Strong linear correlation between ochre concentration in reactors and calcium concentration in digested sludge liquor have been obtained (R^2=0.97). Addition of ochre stimulated release of calcium in reactors: in reactors with 1.5 gFe^{3+}/l was 2.8 times higher (148.0±3.0 mgCa/l) than in control reactor without addition of ochre (52.9±2.1 mgCa/l (see Fig. 3.10). High concentration of calcium can lead to the precipitation of insoluble hydroxylapatite (HAP) ($Ca_5(PO_4)_3OH$). According to Tykesson and la Cour Jansen (2005), precipitation of calcium with phosphates can occur when pH is over 7. Because of very low concentration of phosphates in digested sludge liquor, precipitation of calcium phosphates and hydroxylapatite will not form.

Concentration of magnesium in reactors with 0–0.8 gFe^{3+}/l was very similar – about 40 mgMg/l, and in digested sludge liquor from reactor with 1.5 gFe^{3+}/l showed 62% higher concentration of magnesium (57.8 mgMg/l).There was not enough of phosphates to form hydroxylapatite or struvite precipitates.

Relationship between concentration of ochre in reactors and phosphates and calcium concentration in digested sludge liquor during Batch II experiment is presented in Fig 3.11.

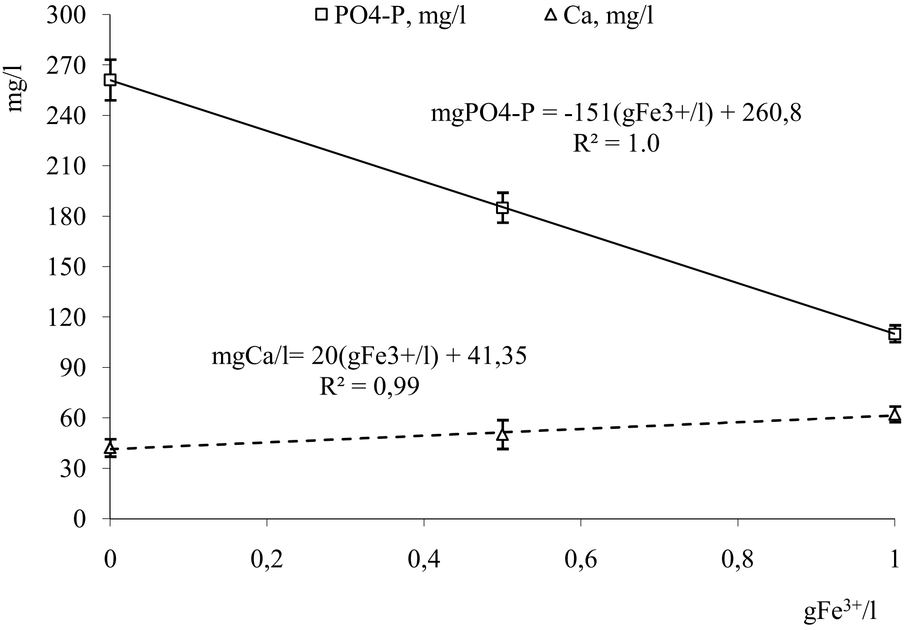

Fig. 3.11. Relationship between ochre concentration in reactors and phosphates and calcium in digested sludge liquor (Batch II experiment)

Strong linear correlation (R^2=1.0) was obtained between ochre dose and remained phosphate concentration in reactors. Inreactors with 0.5 gFe^{3+}/l and 1.0 gFe^{3+}/l concentration of ochre reduction of phosphates by 29 and 57% relatively was obtained.

Additions of ochre into digesters lead to release of calcium into digested sludge liquor. Strong linear relationship was obtained between ochre concentration and concentration of calcium in digested sludge liquor. In reactors with 0.5 and 1.0 gFe^{3+}/l ochre concentration release of calcium by 19 and 48% was obtained.

During 3-days addition of ochre into feed sludge for reduction of hydrogen sulphide production (49–51 days of total pilot-scale experiment) analyses of sludge liquor showed precipitation of phosphates (Fig 3.12) in reactors receiving feed sludge with ochre.

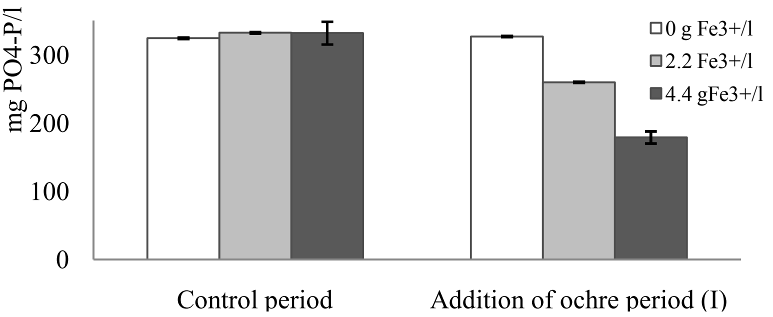

Fig. 3.12. Phosphate concentration (mgPO_4-P/l in anaerobic sludge liquor before and after addition of ochre

According to Suchka *et al.* (2001) first iron reacts with sulphides presented in liquid and only after precipitation of iron sulphides, precipitation of iron phosphates occurs.

As can be seen, average concentration of phosphates in digested sludge liquor from the reactor receiving sluge without any ochre added was 327 mgPO_4-P/l, and in reactors with ochre in concentrations of 2.2 gFe^{3+}/l and 4.4 gFe^{3+}/l phosphates released into digested sludge liquor were 260 mgPO_4-P/l and 179 mgPO_4-P/l relatively. This means reduction of phosphates by 25 and 45% after addition of sludge with 2.2 gFe^{3+}/l and 4.4 gFe^{3+}/l concentrations of ochre relatively. Statistical evaluation of the results also showed strong correlation between dosing of ochre and phosphates precipitation.

Because of high concentration of volatile fatty acids in one of reactor obtained after addition of the sludge with 4.4 gFe^{3+}/l ochre concentration it was decided to stop dosing of ochre as well as feeding of sludge from day 53 to let the reactors recover.

After a short recovery period, the reactors where fed with sludge for 20 days (days 64–84) to get rid of the effect from the ochre dosing (H_2S-experiment).

When analysis of sludge liquor showed phosphates concentration up to 400 mgPO_4-P/l in all three reactors and acetate level decreased dosing of ochre (day 85–100) resulted in lowered phosphate concentrations in the sludge liquor compared to the control (without ochre dosing).

Within a few days the phosphate concentration levelled out around 150 $mgPO_4$-P/l in the reactor dosed with 1.1 gFe^{3+}/l (1.5 mole Fe^{3+}/mole $P_{released}$ or 25 $mgTS_{ochre}/gTS_{in}$), which can be compared with a level around 300 mg/l for 0.56 gFe^{3+}/d (0.75 mole Fe^{3+}/mole $P_{released}$ or 0.12 gTS_{ochre}/gTS_{in}) and around 450 mg/l for the control (Fig 3.13).

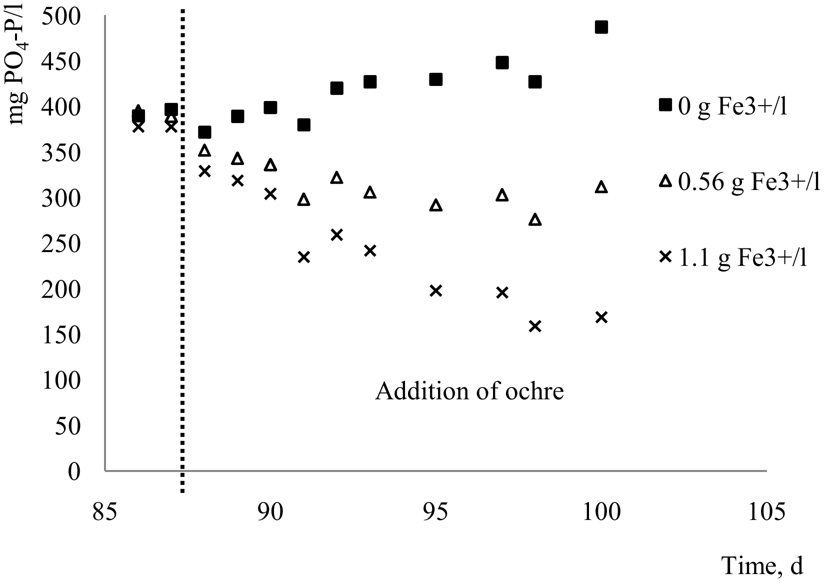

Fig. 3.13. Concentration of phosphates (mg PO_4-P/l in digested sludge liquorin reactors receiving feed sludge with 0, 0.56 and 1.1 gFe^{3}+/l concentrations of ochre (pilot-scale experiment)

Statistical evaluation of obtained results showed strong correlations between phosphate concentration in digested sludge liquor and ochre concentration in feed sludge.

3.4 Proposed engineering solutions for use of ochre at Utena wastewater treatment plant

Experiments with alternative iron source (ochre) for improving of anaerobic digestion of sludge mixture process showed good results in hydrogen sulphide prediction and phosphates reduction in digested sludge liquor and can be proposed to be used instead of commercial iron solutions at wastewater treatment plants with biological phosphorus removal process.

Proposed engineering solutions were made for Utena WWTP which is located in Utena town, Lithuania. Wastewater treatment plant has biological phosphorus removal process with additional polishing using aluminium sulphate ($Al_2(SO_4)_3$) if it's needed to achieve limits for phosphorus limits in effluent – 2 mgP/l. About 60% of all wastewater influent are industrial wastewaters (including textile, food and beer producies) containg high concentrations of sulphates.

Nowadays sludge handling process consists of thickened to 4% of TS primary sludge digestion in two mesophilic digesters. The main problem is hydrogen sulphide production in biogas. During 2005–2006 produced biogas contained more than 2000 ppm of hydrogen sulphide. For the reduction of hydrogen sulphide formation addition of iron sulphate ($Fe_2(SO_4)_2$) has been implemented. The other problem is clogging of pipes because of struvite formation. There is no waste activated sludge anaerobic digestion at Utena WWTP. Waste activated sludge is thickened from 99 to 96% TS at the thickeners, and then centrifuged before removal to sludge beds (0,3175 ha and volume – 6000 m^3). Because of all mentioned disadvantages sludge handling system at the wastewater treatment plant needs renovation.

According to the National water supply and wastewater systems renovation and implementation sludge handling system at Utena WWTP should be improved. Proposed technology for sludge handling and improving of digestion process was presented in documents for the renovation by Utena WWTP. Technological scheme has digestion of sludge mixture in mesophilic digesters. Primary sludge was thickened, waste activated sludge thickened and pre-treated by ultrasound (25 kHz) for the improvement of process efficiency.

According to the presented technology solids retention time (SRT) was 20 days which can cause release of phosphates into digested sludge liquor. For the prevention of biological phosphorus removal process overload by extra phosphates released into digested sludge liquor and recycled to the beginning of the wastewater treatment process, additional chemical phosphorus removal by aluminium sulphate was implemented.

Average calculated additional total load of phosphates was 60% more than designed load for the bioological phosphorus removal. For chemical phosphorus removal from digested sludge liqour aluminium sulphate was proposed to add directly to the oxygen chamber of biological reactor.

It could be seen the gap in presented technology. Some factors can negatively affect anaerobic digestion process efficiency if proposed in documents scheme will be implemented at Utena WWTP (Table 3.8).

Table 3.8. Disadvantages of proposed in documents technological scheme for handling of sludge at Utena WWTP

Parameter	Disadvantages
Addition of aluminium sulphate for chemical phosphorus removal	Can provoke hydrogen sulphide production during digestion process. Sulphate reduction bacteria and methanogens compete for available substrate
Pre-treatment of waste activated sludge by ultrasound	Pre-treated sludge release more phosphates and ammonia during anaerobic digestion process
Biogas cleaning from hydrogen sulphide by biological or chemical methods	Expensive method

Based on laboratory and pilot-scale results ochre can be recommended to use at the wastewater treatment plants with biological phosphorus for reduction of recirculation of phosphates and prevention of hydrogen formation in biogas.

Utena WTP is operated by the same JSC Utenos vandenys as Utena WWTP. Water treatment plant is located in about 1 km from wastewater treatment plant. Iron is removed by open filters with sand media when groundwater is aerated and iron is removed. Average daily iron removal from groundwater is about 28 kg Fe/d. Iron is removed by 6 filters with sand media (area of each of 14.72 m^2, capacity 100 m^3/h, filtration rate – 5.66 m/h. Water capacity Utena treatment plant is 12000 m^3/d. Approximately 28.8 kg Fe/d is removed. Nowadays, after washing of filters, water and precipitated iron-rich sludge together with water (ocherous water) is dumped by 300 mm pipe to the sewage line as by-product.

Technological calculations have been made for the proposing of technology for using of ochre at the Utena wastewater treatment plant. Calculations were based on sludge mixture amounts obtained in documents for renovation. Specific biogas production (SGP) 0.60 m^3/kgVS$_{in}$ was based on results obtained by Bouallagui *et al*. (2010). Phosphorus release was based on results obtained from the laboratory analyses made at Vilnius Gediminas Technical University under anaerobic conditions sludge mixture from Utena WWTP release about 130 mg PO_4-P/l. If assume that pre-treated waste activated sludge release more phosphates than biological sludge calculated amount of $P_{released}$ was 150 mgPO_4-P/l (Table 3.9).

Table 3.9. Scenario for biogas production and phosphate release at Utena WWTP

Parameter	Unit	Amount
Feed thickened sludge mixture flow $Q_{in}$to digesters	m^3/d	163
TS_{in} in feed sludge	%	5
VS_{in} in feed sludge	% of TS	77.4
Mass of TS_{in} in feedslude	kg TS_{in}/d	8150
Mass of VS_{in} in feed sludge	kg VS_{in}/d	6307
Mass of FS_{in} in feed sludge	kg FS_{in}/d	1843
Digested sludge flow $Q_{out}$from digesters	m^3/d	163
SGP rate	$m^3/kg\ VS_{in}$	0.60
Biogas flow Q_{biogas}	m^3/d	3785
Mass of VS_{out} in digested sludge	kg VS_{out}/d	2523
Mass of TS_{out} in digested sludge	kgTS_{in}/d	4365
TS_{out} in digested sludge	%	2.7
TS_{dew} in dewatered sludge	%	25
Flow of dewatered sludge Q_{dew}	m^3/d	17.5
Sludge liqourflow Q_{liqour}	m^3/d	145.5
Predicted phosphates concentration in sludge liqour	mg PO4-P/l	150
Mass of phosphorus to be removed	kg P/d	21.8

Amount $Al_2(SO_4)_3$ needed for phosphorus precipitation in digested sludge liquor was also calculated. Calculations were made for 100% removal of phosphates. Aluminium sulphate is provided in solution (24%) where amount of Al^{3+} is 4%. 1.3 kg of Al is required for the precipitation of 1 kg of P. Average price for 1 ton of aluminium sulphate is 400 Lt, then annual cost for the treatment plant would be 103.6 thousands Lt (Table 3.10).

Table 3.10. Aluminium sulphate required for the precipitation of phosphorus in digested sludge liquor at Utena WWTP

Parameter	Unit	Value
Mass of P	kgP/d	21.8
Al:P	mol:mol	1.5:1
Al mass/ P mass	kgAl/kgP	1.30
Aluminium required	kg/d	28.4
$Al_2(SO_4)_2$ solution required	kg solution/d	710
$Al_2(SO_4)_3$solutions required	t/year	259
Cost of $Al_2(SO_4)_3$solution	Lt/t	400
Annual cost for reagents	thousands Lt/year	103.6
Fe:P	mol:mol	1.5:1
Fe mass/P mass	kgFe/kgP	2.7
Ochre required	kgFe/d	58.9
Ochre from Utena WTP	kgFe/d	28.0
Mass of phosphates removed with ochre	kgP/d	10.4
Remained P to be removed with other reagents	kgP/d	11.4
Savings because of use of ochre instead of reagents	thousands Lt/year	49.1

In proposed technology for use of ochre during digestion of sludge mixture after washing of filters at Utena WTP, ocherous water should be collected to the reservoir with constant mixing and the by pressure line should be pumped to mixing reservoir at the Utena WWTP. In reserviour primary sludge and ochre are mixed together and later thickened in thickener. Pre-treated waste activated sludge is mixed with primary sludge and ochre and pumped into digesters.

As was described in documents for renovation of Utena WWTP, old thickeners should be removed. For the implementation of proposed technology, is necessary to order bigger volume thickeners for thickening of both primary sludge and ochre from Utena WTP. After thickening mixture of primary sludge and ochre should be mixed with pretreated waste activated sludge and finally digested by anaerobic digestion where part of phosphates will be precipitated by ochre.

Proposed technology for using of ochre at Utena WWTP is presented in Fig. 3.14.

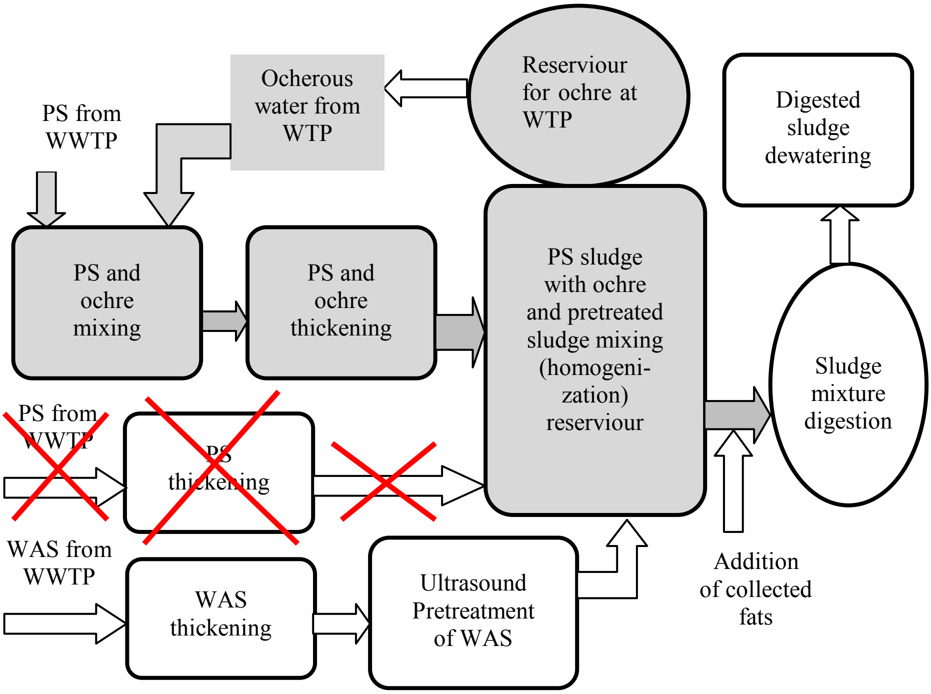

Fig. 3.14. Proposed alternative technology for use of ochre at Utena WWTP: white colour – proposed technological scheme; grey colour – changes according to alternative technology

Partial precipitation may occur during mixing and thickening of primary sludge with ochre. A bit less than half of total amount of phosphates in sludge liquor will be possible to remove by ochre. Then annual cost for the reduction of the remaining part of phosphates by aluminium sulphate will be 1.8 times lower.

Water treatment plants should be interested to recycle wastes. After implementation of proposed technological solutions ochre from WTP will be totally re-used at the WWTP. According to the proposed technology, WWTP will save about 49 thousands Lt. per year for the reduced amount of chemicals.

3.5. Third chapter conclusions

1. At the wastewater plant with chemical phosphorus removal there is no hydrogen sulphate in biogas produced, in opposite, when biological phosphorus removal is applied, amount of hydrogen

sulphate in biogas produced may exceed safety norms. For the prediction of hydrogen sulphide production, iron based salts are used.

2. At the biological phosphorus removal plants with addition of iron chloride prior to digestion process, no precipitants were obtained. Addition of iron sulphate for the prediction of hydrogen sulphate formation resulted in accumulation of struvite in pipes.
3. Results on impact of iron chloride on anaerobic digestion of sludge mixture showed that concentration of iron chloride in 0.8 gFe^{3+}/l and 1.7 gFe^{3+}/l concentrations leads to decrease of biogas production by 26 and 44%.
4. Remained phosphates concentrations in digested sludge liquor receiving feed sludge with iron chloride in 0.8 gFe^{3+}/l and 1.7 gFe^{3+}/l concentrations was 9.2 and 8.6 mg/lor about 80% lower compare to the control period.
5. In reactors with 0.4; 0.8 and 1.5 gFe^{3+}/l of ochre sediments (18% TS) precipitation of phosphates by 29, 75 and 98% in comparison with phosphates from the control reactor (135.7 $mgPO_4$-P/l) was obtained.
6. Accumulated methane in the reactors with 0.5 gFe^{3+}/l and 1 gFe^{3+}/l concentrations of ochre (40% TS) was 10–15% higher than from the control reactor (0 gFe^{3+}/l); reduction of phosphates in digested sludge liquor from reactors with 0.5 and 1.0 gFe^{3+}/l was 29 and 57% compare to phosphates concentration from reactor with 0 gFe^{3+}/l.
7. Dosing of ochre 0.38 gTS_{ochre}/gTS_{in} (2.2 gFe^{3+}/l concentration) into feed sludge during pilot-scale experiment showed drop of H_2S from 2000 ppm down to 570 ppm in biogas produced without any inhibition of digestion process, at the same moment, phosphates concentration decreased by 25%.
8. Addition of 0.12 and 0.25 gTS_{ochre}/gTS_{in} (0.56 and 1.1 gFe^{3+}/l) of ochre resulted precipitation of 33 and 66% phosphates in digested sludge liquor. Phosphates concentration in reactor without addition of ochre was 450 $mgPO_4$-P.
9. Technologicy for ochre use at Utena WWTP was proposed. Addition of ochre from Utena WTP (28 kgFe/d) will lead to reduction of about half of total amount of phosphates in digested sludge liquor.

General conclusions and recommendations

General conclusions

1. Addition of iron chloride into feed sludge in 0.8 and 1.7 gFe^{3+}/l concentrations decreased biogas production 26% and45% relatively compare to biogas production from the reactor with 0 gFe^{3+}/l concentration. Precipitation of phosphates up to 80% in digested sludge liquor from the reactors receiving sludge with iron chloride, compare to control reactor (0 gFe^{3+}/l).
2. Laboratory experiment with addition of ochre into feed sludge showed good results on removal of phosphates. In reactors with added ochre in concentrations of 0.4; 0.8 and 1.5 gFe^{3+}/l precipitation of phosphates in digested sludge liquor was 29, 75 and 98 % relatively, compare to the control reactor with 0 gFe^{3+}/l.
3. Results of laboratory experiments using pressed ochre (40% of TS) in concentrations of 0.5 gFe^{3+}/l and 1 gFe^{3+}/l showed 10–15% higher methane production and 29 and 57% decrease of phosphates

concentration in digested sludge liquor compare to reactor with 0 gFe^{3+}/l.

4. Dosing of ochre into feed sludgede creased hydrogen sulphide formation in biogas. Feeding of sludge with 2.2 and 4.4 gFe^{3+}/l ochre concentrations (or 38 and 75 $mgTS_{ochre}/gTS_{in}$) showed drop in hydrogen sulphide production from > 2000 ppm to 570 ppm.
5. Feeding of sludge with 1.1 gFe^{3+}/l and 0.56 $gFe^{3+/}l$ concentrations of ochre(25 and 12 gTS_{ochre}/gTS_{in}) decreased concentration of phosphatesby 66 and 33% relatively compare to cocnetration of phosphates in digested sludge liquor in control reactor (450 gPO_4-P).
6. Use of ochre (28 kgFe/d)at Utena WWTP according to proposed technological scheme will let to decrease the amount of chemicals used for phosphorus removal in digested sludge liquor. Implementation of proposed technological scheme will let to save about 50 thousands Lt per annual.

Recommendations

1. Ochre can be used for anaerobic digestion process efficiency improvement. Use of ochre is highly recommended at the WWTPs with biological phosphorus removal plants due to precipitation of phosphates in digested sludge liquor. Dosing of ochre will reduce the amount of chemical reagents for removal of phosphates which will lower wastewater treatment price.
2. For the successful implementation, ochre should be dosed continuosly into feed sludge. For this reason, collecting reservoirs with constant mixing should be installed at the water treatment plants. Ochre can be dosed into feed sludge directly or thickened prior the digestion process.

.

References

Adnan, A.; Mavinic, D. S.; Koch, F. A. 2003. Pilot-scale study of phosphorus recovery through struvite crystallization – examining the process feasibility, *J. Environ. Eng. Sci.* 2: 315–324.

Ahammad, S. Z.; Gomes, J.; Sreekrishnan, T. R. 2008. Wastewater treatment for production of H_2S-free biogas, *J. Chem. Technol. Biotechnol.* 83: 1163–1169.

Albrektienė, R.; Rimeika, M.; Jankauskas, J. 2011.Geležies organinio kompleksinio junginio šalinimas iš požeminio vandens naudojant koaguliantus, *Vandens ūkio inžinerija* 38(58): 69–74.

Angelidaki, I.; Sanders, W. 2004. Assessment of the anaerobic biodegradability of macropollutants, *Reviews in Environmental Science and Bio/Technology*, 3(2): 117–129.

Abatzoglou, N.; Boivin, S. 2009. A review of biogas purification processes. *Biofuels, Bioprod. Bioref.* 3:42–71.

Appels, L.; Baeyens, J.; Degrève, J.; Dewil, R. 2008.Principles and potential of the anaerobic digestion of waste-activated sludge, *Progress in Energy and Combustion Science* 34: 755–781.

APHA. 2000. Standard Methods for the Examination of Water and Water Water. 18th ed. Washington DC. USA: *American Public Health Association/American Water Works Association/Water Environment Federation*.

Babatunde, A. O.; Zhao, Y. Q. 2007.Constructive Approaches Toward Water Treatment Works Sludge Management: An International Review of Beneficial Reuses,*Critical Reviews in Environmental Science and Technology* 37: 129–164.

Balmér, P.; Hultman, B.; 1988. Control of phosphorus discharges: present situation and trends, *Hydrobiologia*, 170: 305–319.

Barat, R.; Bouzas, A.; Martí, N., Ferrer, J., Seco, A.2009.Precipitation assessment in wastewater treatment plants operated for biological nutrient removal: A case study in Murcia, Spain, Journal of Environmental Management 90: 850–857.

Basibuyuk, M.; Yilmaz, T.; Kayranli, B.; Yuceer, A.; Forster, C. F. 2002. The Use of Waterworks Sludge for the Treatment of Dye Wastes, *Environmental Technology* 23(3): 345–351.

Batstone, D. J.; Keller, J.; Angelidaki, I.; Kalyuzhnyi, S. V.; Pavlostathis, S. G.; Rozzi, A.; Sanders, W. T. M.; Siegrist, H.; Vavilin, V. A. 2002. *Anaerobic Digestion Model No. 1 (ADM1), IWA Task Group for Mathematical Modelling of Anaerobic Digestion Processes*. London: IWA Publishing.

Battistoni, D.; Pavan, M. P.; Prisciandaro, M.; Cecchi, F. 2000. Struvite crystallization: a feasible and reliable way to fix phosphorus in anaerobic supernatants. *Water Research*, 34 (11): 3033–3041.

Battistoni, D.; De Angelisa, A.; Prisciandaro, M.; Boccadoro, R.; D. Bolzonella, D. 2002. P removal from anaerobic supernatants bystruvite crystallization: long term validation and process modelling, *Water Research* 36: 1927–1938.

Blonskaja, V.; Zub, S. 2009. Possible ways for post-treatment of biologically treated wastewater from yeast factory, *Journal of environmental engineering and landscape management* 17(4): 189–197.

Bolzonella, D.; Pavan, P.; Battistoni, P.; Cecchi, F. 2005. Mesophilic anaerobic digestion of waste activated sludge: influence of the solid retention time in the wastewater treatment process, *Process Biochemistry* 40: 1453–1460.

Bouallagui, H.; Marouani, L.; Hamdi, M. 2010. Performances comparison between laboratory and full-scale anaerobic digesters treating a mixture of primary and waste activated sludge, Resources, *Conservation and Recycling* 55: 29–33.

Buffiere, P; Loisel, D; Bernet, N; Delgenes, J. P. 2006. Towards new indicators for the prediction of solid waste anaerobic digestion properties,*Water Science and Technology* 53:233–41.

Cabirol, N.; Barragán, E. J.; Durán, A.; Noyola, A. 2003. Effect of aluminium and sulphate on anaerobic digestion of sludge from wastewater enhanced primary treatment, *Water Science and Technology*, 48(6): 235–240.

Caravelli, A. H.; Contrerasa, E. M.; Zaritzky, N. E. 2010. Phosphorous removal in batch systems using ferric chloride in the presence of activated sludges, *Journal of Hazardous Materials* 177: 199–208.

Carlson, I.; Schwertmann, U. 1987. Iron and manganese oxides in finish ground water treatment plants, Wat. Res. 21(2): 165–170.

Carlsson, H., Aspegren, H., Lee, N., Hilmer, A., 1997. Calcium phosphate precipitation in biological phosphorus removal systems, *Water Res*. 31, 1047–1055.

Carrère, H.; Dumas, C.; Battimelli, A.; Batstone, D. J.; Delgenès, J. P.; Steyer, J. P.; Ferrer, I. 2010. Pretreatment methods to improve sludge anaerobic degradability: A review,*Journal of Hazardous Materials* 183: 1–15.

Carter, J. L.; McKinney, R. E. 1973. Effects of Iron on Activated Sludge Treatment, *Journal of the Environmental Engineering Division* 99(2): 135–152.

Chen, Y.; Cheng, J. J.; Creamer, K. S. 2008. Inhibition of anaerobic digestion process: A review, *Bioresource Technology* 99: 4044–4064.

Chung, Y.-C.; Ho, K.-L.; Tseng, C.–P. 2006. Theatment of High H_2S Concentrations by Chemical Absorption and Biological Oxidation Process, *Environmental Engineering Science* 23(6): 942–953.

Cirne, D. G.; van der Zee F. P.; Fernandez-Polanco, M.; Fernandez-Polanco, F. 2008. Control of sulphide during anaerobic treatment of S-containing wastewaters by adding limited amounts of oxygen or nitrate, *Rev Environ Sci Biotechnol* 7: 93–105.

Dauknys, R.; Vabolienė, G.; Valentukevičienė, M.; Rimeika, M. 2009. Influence of substrate on biological removal of phosphorus. *Ekologija*, 55(3–4): 220–225.

Davidsson, Å.;la Cour Jansen, J. 2006. Pre-treatment of wastewater sludge before anaerobic digestion – Hygienisation, Ultrasonic treatment and Enzyme dosing, *VATTEN* 62:335–340.

Davidsson,Å. 2007. Increase of biogas production at wastewater treatment plants. Addition of urban organic waste and pre-treatment of sludge: *Doctoral thesis. Lund University. Lund: Media-Tryck. 42 p.*ISBN 978-91-7422-143-5.

Davidsson, Å.; Lovstedt, C.; la Cour Jansen, J.; Gruvberger, C.; Aspegren, H. 2008. Co-digestion of grease trap sludge and sewage sludge, *Waste Management*, 28: 986–992.

De-Bashan, L. E.; Bashan, T. 2004. Recent advances in removing phosphorus from wastewater and its future use as fertilizer (1997–2003),*Water Research* 38: 4222–4246.

De Haas, D. W.; Wentzel, M. C.; Ekama, G. A. 2000.The use of simultaneous chemical precipitation in modified activated sludge systems exhibiting biological excess phosphate removal Part 1: Literature review, *Water SA*26 (4): 439–452.

Dentel, S. K.; Gosset, J. M. 1982. Effect of chemical coagulation on anaerobic digestibility of organic materials, *Water Resources*16: 707–718.

Dewil, R.; Baeyens, J.; Neyens, E. 2006.Reducing the heavy metal content of sewage sludge by advanced sludge treatment methods, *Env Eng Sci*, 23:994–999.

Diliūnas, J.; Jurevičius, A.; Zuzevičius, A. 2006. Formation of iron compounds in the Quaternary groundwater of Lithuania, *Geologija* 55: 67–74.

Dhar, B. R.; Youssef, E.; Nakhla, G.; Ray, M. B. 2011. Pretreatment of municipal waste activated sludge for volatile sulfur compounds control in anaerobic digestion, *Bioresource Technology* 102: 3776–3782.

Donoso-Bravo, A.; Mailier, J.; Martin, C.; Rodrı´guez, J.; Aceves-Lara, C. A.; Wouwer, A. V.2011. Model selection, identification and validation in anaerobic digestion: A review, *Water research* 45: 5347–5364.

Doyle, J. D.; Parsons, S. A. 2002. Struvite formation, control and recovery, *Water Research* 36: 3925–3940.

Doyle, J. D.; Oldring, K.; Churchley, J.; Price, C.; Parsons, S. 2003. Chemical Control of Struvite Precipitation,*Journal of Environmental Engineering* 129(5): 419–427.

Dueñas, J. F.; Alonso, J. R.; Rey, À. F.; Ferrer, A. S. 2003. Characterisation of phosphorous forms in wastewater treatment plants, *Journal of Hazardous Material* B97: 193–205.

El Diwani, G.; El Rafie, S.; El Ibiari, N. N.;El-Aila, H. I. 2007. Recovery of ammonia nitrogen from industrial wastewater treatment as struvite slow releasing fertilizer, *Desalination* 214: 200–214.

European Commission Concil Directive 98/83/EC of 3 November 1998 on the quality of water intented for human consumption 1998/83/31998L0083/1998. Official Journal L'1998 Nr. 330–32, 1998.

European Commission Council Directive 91/271/EEB concerning urban waste water treatment, 21 may, 1991.

Emig, D. 1979. Excessive alum causes indigestion, *Water and Wastes Engineering* April 24–26.

Frossard, E.; Bauer, J. P.; Lothe, F. 1997. Evidence of vivianite in $FeSO_4$-flocculated sludges,*Water Research* 31(10): 2449–2454.

Fytianos, K.; Voudrias, E.; Raikos, N. 1998. Modelling of phosphorus removal from aqueous and wastewater samples using ferric iron, *Environmental Pollution* 101: 123–130.

Gavala, H. N., Yenal, U., Skiadas, I. V.; Westermann, P.; Ahring, B. K. 2003.Mesophilic and thermophilic anaerobic digestion of primary and secondary sludge. Effect of pre-treatment at elevated temperature, *Water Res* 37:4560–4572.

García-Delgado, M.; Rodríguez-Cruz, M. S.; L.F. Lorenzo, L. F.; Arienzo, M.; Sánchez-Martín, M. J. 2007. Seasonal and time variability of heavy metal content andof its chemical forms in sewage sludges from different wastewater treatment plants, *Science of the Total Environment* 382: 82–92.

Georgaki, I.; Dudeney, A. W. L.; Monhemius, A. J. 2004. Characterisation of iron-rich sludge: correlations between reactivity, density and structure, *Minerals Engineering* 17: 305–316.

Grazuleviciene, R.; Nadisauskiene, R.; Buinauskiene, J.; Grazulevicius, T. 2009. Effects of Elevated Levels of Manganese and Iron in Drinking Water on Birth Outcomes, *Polish J. of Environ. Stud.* 18(5): 819–825.

Gutierrez, O.; Park, D.; Sharma, K.; Yuan, Z. 2010. Iron salts dosage for sulfide control in sewers induces chemical phosphorus removal during wastewater treatment,*Water research* 44: 3467–3475.

Hansen, T. L.; Schmidt, J. E.; Angelidaki, I.; Marca, E.; la Cour Jansen, J.; Mosbæk, H.; Christensen, T. H. 2004. Method for determination of methane potentials of solid organic waste, *Waste Management* 24: 393–400.

Haghighatafshar, S.; Kjerstadius, H.; la Cour Jansen, J.; Davidsson, Å. 2012. Management of hydrogen sulfide in anaerobic digestion of enzyme pretreated marine macro-algae, *VATTEN – Journal of Water Management and Research* 68:265–273.

Hoban, D. J.; van den Berg, L. 1979. Effect of Iron on Conversion of Acetic Acid to Methane During Methanogenic Fermentations. *Journal of Applied Bacleriology* 47: 153–159.

Holm-Nielsen, J. B.; Al Seadi, T.; Oleskowicz-Popiel, P. 2009. The future of anaerobic digestion and biogas utilization, *Bioresource Technology* 100: 5478–5484.

Husillos Rodríguez, N.; Martínez Ramírez, S.; Blanco Varela, M.T.; Guillem, M.; Puig, J.; Larrotcha, E.; Flores, J. 2010. Re-use of drinking water treatment plant (DWTP) sludge: Characterization and technological behaviour of cement mortars with atomized sludge additions, *Cement and Concrete Research* 40: 778–786.

Ippolito, J. A.; Barbarick, K. A., Elliott, H. A. 2011. Drinking Water Treatment residuals: A Review of Recent Uses, *Journal of Environmental Quality* 40: 1–12.

Jackson-Moss, C. A.; Duncan, J. R. 1990.The effect of iron on anaerobic digestion, *Biotechnology Letters* 12(2): 149–154.

Jackson-Moss, C. A.; Duncan, J. R. 1991.The effect of aliuminium on anaerobic digestion.*Biotechnology Letters* 13(2): 143–148.

Jardin, N.; Pöpel, H. J. 1996. Behaviour of waste activated sludge from enhanced biological phosphorus removal during sludge treatment, *Water Environment Research* 68(6): 965–973.

Jenicek, P.; Bartacek, J.; Kutil, J.; Zabranska, J.; Dohanyos, M. 2012. Potentials and limits of anaerobic digestion of sewage sludge: Energy self-sufficient municipal wastewater treatment plant?, *Wat. Sci. Tech*. 66: 1277–1281.

Jenicek, P.; Celis, C. A.; Krayzelova, L.; Anferova, N.; Pokorna, D. 2013. Microaeration for improving products of anaerobic sludge digestion, *In Proc. of the 1st IWA Conference Holistic sludge.*

Jönsson, K.; Jönsson, L-E.; la Cour Jansen, J. 2008. Phosphorus removal without chemicals - experiences of bio-P in water- and sludge treatment, *In Proc. of the 10th Nordic /NORDIWA Wastewater Conference, Hamar, Norway, November 2008.*

Katsoyiannis, I. A.; Zouboulis, A. I. 2006.Use of Iron- and Manganese-Oxidizing Bacteria for the Combined Removal of Iron, Manganese and Arsenic from Contaminated Groundwater, *Water Qual. Res. J. Canada* 41(2): 117–129.

Khanal, S. K.; Grewell, D.; Sung, S.; Van Leeuwen, J. H. 2007. Ultrasound applications in wastewater sludge pre-treatment: A Review,*Critical Reviews in Envrironmental Science and Technology* 37: 277–313.

Kindzierski, W. B.; Hrudey, S. E. 1986. Effects of phosphorus removal chemicals upon methane production during anaerobic sludge digestion*, Can. J. Civ. Eng*. 13(1): 33–38.

Kyncl, M. 2008. Opportunities for water treatment sludge re-use, *GeoScience Engineering* 1: 11–22.

Le Corre, K. S.; Valsami-Jones, E.; Hobbs, P.; Jefferson, B.; Parsons, S. A. 2007. Agglomeration of struvite crystals, *Water research* 41: 419–425.

Lens, P. N. L. ; Visser, A.; Janssen, A. J. H.; Hulshoff Pol, L.W.; Lettinga, G. 1998. Biotechnological Treatment of Sulfate-Rich Wastewaters, *Critical Reviews in Environmental Science and Technology* 28(1) 41–88.

Leuster, M.; Bellon-Maurel, V.; Gonzalez, C.; Latrille, E.; Roger, J. M.; Junqua, G.; Steyer, J. P. 2010. Alternative methods for determining anaerobic biodegrability: a review. *Process Biochemistry*, 45: 431–440.

Lopez, I., Borzacconi, L., 2010. Modelling of slaughterhouse solid waste anaerobic digestion: determination of parameters and continuous reactor simulation, *Waste Management* 30: 1813–1821.

Mamais, D.; Pitt, P. A.; Cheng, Y. W. 1994. Determination of Ferric Chloride Dose to Control Struvite Precipitation in Anaerobic Sludge Digesters, *Water Environmental Research* 66(7): 912–918.

Marsili-Libelli, S.; Beni, S. 1996. Shock load modelling in the anaerobic digestion process,*Ecological Modelling* 84: 215–232.

Marti, N.; Bouzas, A.; Seco, A.; Ferrer, J. 2008. Struvite precipitation assessment in anaerobic digestion processes, *Chemical Engineering Journal*, 141: 67–74.

Menert, A.; Liiders, M.; Kurissoo, T.; Vilu, R. 2001. Microcalorimetric monitoring of anaerobic digestion processes,*Journal of Thermal Analysis and Calorimetry* 64: 281–291.

Metcaft and Eddy Inc. 1991. Wastewater engineering: treatment, disposal, reuse. Int. Ed. New York: McGraw-Hill.

Mettler, S.; Abdelmoula, M.; Hoehn, E.; Schoenenberger, R.; Weidler, R.; von Gunten, U. 2001. Characterization of Iron and Manganese Precipitates from an In Situ Ground Water Treatment Plant, *Ground Water*39(6): 921–930.

Miyanoshita, T.; Oda, N.; Hayashi, N.; Fujiwara, M.; Furumai, H. 2009. Economic evaluation of combined treatment for sludge from drinking water and sewage treatment plants in Japan, *Journal of Water Supply: Research & Technology-AQUA*, 58.3: 221–227.

Moelants, N.; Smets, I. Y., Van Impe, J. F. 2011. The potential of an iron rich substrate for phosphorus removal in decentralized wastewater treatment systems, *Separation and Purification Technology* 77: 40–45.

Montusiewicz, A.; Lebiocka, M.; Rozej, A.; Zacharska, E.; Pawłowski, L. 2010. Freezing/thawing effects on anaerobic digestion of mixed sewage sludge, *Bioresource Technology* 101: 3466–3473.

Mottet, A.; Franc¸ E.; Latrille, E.; Steyer, E. P.; Déléris, S.; Vedrenne, F.; Carrère, H. 2010. Estimating anaerobic biodegradability indicators for waste activated sludge, *Chemical Engineering Journal* 160: 488–496.

Münch, E.; Barr, K. 2001. Controlled struvite crystallisation for removing phosphorus from anaerobic digestion sidestreams, *Water Research* 35(1): 151–159.

Neethling, J. B.; Benisch, M. 2004. Struvite control through process and facility design as well as operation strategy, *Water Science and Technology* 49(2): 191–199.

Novak, J. T.; Verma, N.; Muller, C. D. 2007. The role of iron and aluminium in digestion and odor formation, *Water Science and Technology* 56(9): 59–65.

Novak, J. T.; Park, C. M. 2010. The effect of iron and aluminium for phosphorus removal on anaerobic digestion and organic sulfur generation, *Water Science and Technology* 62(2): 419–426.

Noykova, N.; Muller, T. G.; Gyllenberg, M.; Timmer, J., 2002. Quantitative analyses of anaerobic wastewater treatment processes: identifiability and parameter estimation, *Biotechnology and Bioengineering* 78 (1): 89–103.

Ohlinger, K. N.; Young, T. M.; Schroeder, E. D. 1998. Predicting struvite formation in digestion, *Water research* 32(12): 3607–3614.

Oikomidis, I.; Burrows, L. J.; Carliell-Marquet, C. M. 2010. Mode of action of ferric and ferrous iron salts in activated sludge, *J Chem Technol Biotechnol* 85: 1067–1076.

Owens, J.M.; Chynoweth, D. P. 1993. Biochemical methane potential of municipal solid-waste (Msw) components, W*ater Science and Technology* 27 (2): 1–14.

Ozkan-Yucel, U. G.; Gökçay, C. F. 2010. Application of ADM1 model to a full-scale anaerobic digester underdynamic organic loading conditions, *Environmental Technology* 31(6): 633–640.

Parsons S. A.; Smith, J. A. 2008. Phosphorus Removal and Recovery from Municipal Wastewaters, *Elements*, 4: 109–112.

Parsons, S. A.; Corre, K. L.; Jones, E. V.; Hobbs, P. 2009. Phosphorus Recovery from Wastewater by Struvite Crystallization: A Review. *Critical Reviews in Environmental Science and Technology*, 39(6): 433–477.

Pastor, L.; Marti, N.; Bouzas, A.; Seco, A. 2008. Sewage sludge management for phosphorus recovery as struvite in EBPR wastewater treatment plants, *Bioresource Technology*99 : 4817–4824.

Pastor, L.; Mangin, D.; Ferrer, J.; Seco, A. 2010. Struvite formation from supernatants of an anaerobic digestion pilot plant, *Bioresource Technology*, 101: 118–125.

Pavlostathis, S. G. and Giraldo-Gomez, E. 1991.Kinetics of anaerobic treatment: A critical review, *Critical Reviews Environ. Contr.* 21: 411–490.

Philips, S.; Rabaey, K.; Verstraete, W. 2003. Impact of iron salts on activated sludge and interaction with nitrite or nitrate, *Bioresource Technology* 88: 229–239.

Pitman, A. R. 1999. Management of biological nutrient removal plant sludges – change the paradigms?, *Water Resources* 33(5): 1141-1146.

Pol, L. W. H.;.Lens, P. N. L.; Stams, A. J. M.; Lettinga, G. 1998. Anaerobic treatment of sulphate-rich wastewaters, *Biodegradation* 9 (3-4): 213-224.

Rabinowitz, B.; Marais, G. V. R. 1980.Chemical and Biological Phosphorus Removal in the Activated Sludge Process. *Research Report No. W32, Univ. of Cape Town, Dept. of Civil Eng., March 1980*, 88 p.

Razali, M.; Zhao, Y. Q.; Bruen, M. 2007. Effectiveness of a drinking-water treatment sludge in removing different phosphorus species from aqueous solution, *Separation and Purification Technology* 55:300–306.

Reed, J. P.; Devlin, D.; Esteves, S. R. R.; Dinsdale, R.; Guwy, A. J. 2011. Performance parameter prediction for sewage sludge digesters using reflectance FT-NIR *spectroscopy, Water Research 45: 2463–2472.*

Rosborg. 2009. Elevated concentration of iron in drinking water – a potential health risk (Hög koncentration järn i dricksvatten – en potentiell hälsorisk), *The Journal of Water Management and Research (VATTEN)* 65: 125–132.

Seida, Y.; Nakano, Y. 2002.Removal of phosphate by layered double hydroxides containing iron. Water Res,36: 1306–1312.

Seng, B.; Khanal, S. K.; Visvanathan, C. 2010. Anaerobic digestion of waste activated sludge pretreated by a combined ultrasound and chemical process, *Environmental Technology*31 (3): 257–265.

Sharma, A. K.; Thornberg, D.; Andersen, H. R. 2013. Application of waterworks sludge in wastewater treatment plants, *International Journal of Environmental Science and Technology* 10(6): 1157–1166.

Shvartsev, S. L. 2008. Geochemistry of Fresh Groundwater in Main Landscape Zones of the Earth, *Geochemistry International* 46(13): 1285–1398.

Skene, T. M.; Oades, J. M.; Kilmore, G. 1995. Water treatment sludge: a potential plant growth medium, *Soil Use and Management* 11: 29–33.

Smet, E.; Lens, P.; Van Langenhove, H. 1998. Treatment of Waste Gases Contaminated with Odorous Sulfur Compounds, *Critical Reviews in Environmental Science and Technology* 28(1): 89–117.

Smith, J. A.; Carliell-Marquet, C. M. 2008. The digestibility of iron-dosed activated sludge, *Bioresource Technology* 99: 8585–8592.

Smith, J. A.; Carliell-Marquet, C. M. 2009. A novel laboratory method to determine the biogas potential of iron-dosed activated sludge, *Bioresource Technology* 100: 1767–1774.

Sörme, L.; Lagerkvist, R.2002.Sources of heavy metals in urban wastewater in Stockholm, *The Science of the Total Environment* 298: 131–145.

Stabnikov, V. P.; Tay, S. T.-L.; Tay, D.-Kh; Ivanov, V. N. 2004. Effect of Iron Hydroxide on Phosphate Removal during Anaerobic Digestion of Activated Sludge.*Applied Biochemistry and Microbiology*, 40(4): 376–380. *Translated from Prikladnaya Biokhimiya i Mikrobiologiya*, 40(4): 442–447.

Stein, R. M.; Malone, C. D. 1980. Anaerobic digestion of biological sludges, *Environmental Technology*, 1(12): 571–588.

Strasser, H.; Brunner, H.; Schinner, F. 1995. Leaching of iron and toxic heavy metals from anaerobically-digested sewage sludge, *Journal of Industrial Microbiology*14: 281–287.

Straub, K.L.; Benz, M.; Schink, B. 2001. Iron metabolism in anoxic environments at near neutral pH, *FEMS Microbiology Ecology*34: 181–186.

Suschka, J.; Machnicka, A.; Poplawski, S. 2001. Phosphates recovery from iron phosphates sludge,*Environmental Technology* 22: 1295–1301.

Takiguchi, N.; Kishino, M.; Kuroda, A.; Kato, J.; Ohtake, H. 2004. A Laboratory-Scale test of Anaerobic Digestion and Methane Production after Phosphorus Recovery from Waste Activated Sludge, *Journal of Bioscience and Bioengineering* 97(6): 365–368.

Tarasova, I.; Georgaki, I.; Dudeney, A. W.; Monhemius, A. J. 2002. Re-use of iron-rich water treatment sludges. In: Ciccu, R. (Ed.), *Proceedings of the Seventh International Symposium on Environmental Issues and Waste Management in Energy and Mineral Production (SWEMP 2002), Cagliari, October 7–10, 2002. Grafiche Ghiani, Monastir*, 1087–1093.

Tavares, C. R. G.; Benatti, C. T.; Dias Filho, B. P. 2002. Treatment of Sewage Sludge Generated in Municipal Wastewater Treatment Plants, *Applied Biochemistry and Biotechnology* 98–100: 935–945.

Tchobanoglous, G. and Burton, F. L. 1991. Wastewater Engineering, Treatment, Disposal and Reuse, 3rd ed., McGraw-Hill, Singapore.

Tomei, M. C.; Braguglia, C. M.; Cento, G.; Mininni, G. 2009. Modeling of Anaerobic Digestion of Sludge, *Critical Reviews in Environmental Science and Technology* 39:1003–1051.

Tykesson, E.; la Cour Jansen, J. 2005. Evaluation of laboratory tests for enhanced biological phosphorus removal, *VATTEN– Journal of Water Management and Research*61: 43–50.

Uludag-Demirer, S.; Othman, M. 2009. Removal of ammonium and phosphate from the supernatant of anaerobically digested waste activated sludge by chemical precipitation,*Bioresource Technology* 100: 3236–3244.

Uysal, A.; Yilmazel, Y. D.; Demirer, G. N. 2010. The determination of fertilizer quality of the formed struvite from effluent of a sewage sludge anaerobic digester, *Journal of Hazardous Materials* 181: 248–254.

Valentukevičienė, M. 2009. Applying backwash water in order to enhance removal of iron and ammonia from spent filters with fresh filter media, *Environment Protection Engineering* (35):3 135–144.

Vilniškis, R.; Baltrėnas, P.; Vasarevičius, S.; Baltrėnaitė, E. 2011. Research and assessment of biogas evolved during anaerobic digestion on biodegradable agricultural waste, *Ecological chemistry and engineering* 18(4): 409–427.

van Bodegom, P. M.; Scholten J. C. M.; Stams, A. J. M. 2004. Direct inhibition of methanogenesis by ferric iron, *FEMS Microbiology Ecology* 49 (2): 261–268.

Waite, T. D. 2002. Challenges and opportunities in the use of iron in water and wastewater Treatment, *Reviews in Environmental Science and Biotechnology* 1: 9–15.

Walker, M.; Zhang, Y.; Heaven, S.; Banks, C. 2009. Potential errors in the quantitative evaluation of biogas production in anaerobic digestion processes, *Bioresource Technology* 100: 6339–6346.

WEF. 1991. *Design of municipal wastewater treatment plants*, Vol II, Water Environment Federation and American Society of Civil Engineers, Alexandria, Va, 1092–1100.

Wang, X. X.; Qiu, Z. F.; Lu, S. G.; Ying, W.C. 2010. Characteristics of organic, nitrogen and phosphorus species released from ultrasonic treatment of waste activated sludge, *Journal of Hazardous Materials* 176(1–3): 35–40.

Wei, D. W. and Osseo-Asare, K. 1996. Particulate pyrite formation by the Fe^{3+}/HS^- reaction in aqueous solutions: Effects of solution composition, *Colloids and Surfaces a Physicochemical and Engineering Aspects* 118: 51–61.

Wei, Y. S.; Van Houten, R. T.; Borger, A. R.; Eikelboom, D. H.; Fan, Y. B. 2003. Minimization of excess sludge production for biological wastewater treatment, *Water. Res*. 37(18): 4453–4467.

Wild, D.; Kisliakova, A.; Siegrist, H. 1996.P-Fixation by Mg, Ca and Zeolite A during stabilization of excess sludge from enhanced biological P-removal, *Water Science and Technology* 34(1–2): 391–398.

Wild, D.; Kisliakova, A.; Siegrist, H. 1997. Prediction of recycle phosphorus loads from anaerobic digestion, *Water Research* 31: 2300–2308.

Wu, Q.; Bishop, P. L.; Keener, T. C.; Stallard, J.; Stile, L. 2001. Sludge digestion enhancement and nutrient removal from anaerobic supernatant by $Mg(OH)_2$ application,*Water Science and Technology*, 44(1): 161–166.

Yeoman, S.; Stephenson, T.; Lester, J.; Perry, R. 1988. The removal of phosphorus during wastewater treatment: a review, *Environmental Pollution* 49: 183–255.

Yeoman, S.; Lester, J.; Perry, R. 1990. The effects of chemical phosphorus precipitation on anaerobic digestion, *Environmental Technology* 11: 709–720.

Zaher, U.; Buffiere, P.; Steyer, J-P.; Chen, S. 2009a. A Procedure to Estimate Proximate Analysis of Mixed Organic Wastes, *Water Environment Research* 81 (4): 407–415.

Zhang, G. M.; Zhang, P. Y.; Yang, J.M.; Chen.; Y.M. 2007. Ultrasonic reduction of excess sludge from the activated sludge system, *J. Hazard.Mater*. 145 (3): 515–519.

Zhang, L.; De Schryver, P.; De Gusseme, B.; De Muynck, W.; Boon, N.; Verstraete, W. 2008. Chemical and biological technologies for hydrogen sulphide emission control in sewer systems: A review, *Water research* 42: 1–12.

Zhao, H. W.; Viraraghavan, T. 2004.Analysis of the performance of an anaerobic digestion system at the Regina wastewater treatment plant, *Bioresource Technology* 95: 301–307.

Environmental Agency:http://atliekos.gamta.lt/files/Atliekos%202011%20OFICIALI%202012-10-31.xls.

Žáček, L. Chemické a technologické procesy úpravy vody. Brno: NOEL 2000 1999, 228 s. ISBN 80- 86020-22-2. (Chemical and Technological Processes in Water Processing).

Włodarczyk-Makuła, M. 2011.Degradation of PAHs in sewage sludge during fermentation process, *Civil and environmental engineering reports* 6: 137-145.

Лукашевич, О. Д.; Барская, И. В.; Усова Н. Т. 2008. Интенсификация осаждения и утилизации железистых осадков промывных водскорых фильтров [Lukashevich, O. D.; Barskaya, I. V.; Usova N. T. Intensifying of sedimentation and utilization of ocherous sediments fromfast filters], *Вода: технология и экология* [Water: technology and ecology] 2:30–40.

Мамченко, А. В.; Мисочка, И. В.; Дешко, И. И.; Кий, Н. Н.; Герасименко, Н. Г. 2009. Приоритетные направления в технологии очистки подземных вод от железа [Mamchenko, A.V.; Misochka, I. V.; Deshko, I. I.; Kij, N. N.; Gerasimenko, N. G. Priority directions in technologies for iron removal from ground water], *Химия и технология воды [Chemistry and technology of water]* 31 (1): 57–77.

Семакина, О. К.; Игашева, В. П.; Шевченко, А. А. 2013. Получение сорбентов методом экструзии [Semakina, O. K.; Igasheva, V. P.; Shevchenko, A. A. [Semakina, O. K.; Igasheva, V. P.; Shevchenko, A. A. Extrusionmoldingofsorbents], *Известия Томского политехнического университета [Bulletin of Tomsk Polytechnic University]* 322(3): 65–67.

Усова, Н. Т.; Кутугин, В. А.; Лотов, В. А. и др. 2011. Композиционные материалы на основе высокожелезистого шлама водоподготовки, *Известия Томского* *политехнического университета [Usova, N.T.; Kutugin, V.A.; Lotom, V. A. et al.Compositive materials based on water work iron sludge]*, 319 (3): 36–39.

List of author's publications on the topic of the dissertation

In the reviewed scientific journals

Ofverstrom, S.; Sapkaitė, I.; Dauknys, R. 2010a. Cheminio fosforo šalinimo įtaka anaerobiniam dumblo pūdymo procesui, *Mokslas- Lietuvos ateitis – Science – future of Lithuania: Environmental protection engineering* 2 (5): 71–74.ISSN 2029-2341 (Index Copernicus).

Ofverstrom, S.; Dauknys, R.; Sapkaitė, I. 2011a. The effect of iron salt on anaerobic digestion and phosphate release to sludge liquor, *Mokslas– Lietuvos ateitis – Science – future of Lithuania: Environmental protection engineering* 3(5): 123–126.(ICONDA; Gale; Proquest; EBSCOhost; Index Copernicus).

In other editions

Tomczak-Wandzel, R.; Ofverstrom, S.; Dauknys, R.; Mędrzycka, K. 2011. Effect of disintegration pretreatment of sewage sludge for enhanced anaerobic digestion, *8th International Conference „Environmental Engineering", Selected papers (19–20, May 2011, Vilnius, Lithuania)* 2: 679–683, ISSN 2029-7106 (Conferences Proceedings Citation Index).

Ofverstrom, S.; la Cour Jansen, J.; Dauknys, R.2011. Impact of iron salts dosing on anaerobic digestion process and struvite/vivianite formalion: a review, *Proceedings of the 12th International Conference on Environmental Science and Technology (CEST2011) (8–10 September 2011, Rhodes island, Greece)* 1: 1341–1346, ISBN: 978-1-62748-192-2 (Conference Proceedings Citation Index).

Ofverstrom, S. [Офверстром, С.]; Kering, J. [Керинг, Й.]. *2012. Опыт и молодость в решении водных* проблем: обработка осадка сточных вод в Литве – до и после входа в Европейский Союз, Водные ресурсы и водопользование 3(98): 5–9. ISSN *2225–577X.*

Ofverstrom, S.; Sapkaite, I.; Dauknys, R. 2010. An investigation of impact of iron and aluminium addition on the anaerobic digestion process, *Linnaeus ECO-TECH'10 : proceedings of the 7th international conference on natural sciences and technologies for waste and wastewater treatment, remediation, emissions related to climate, environmental and economic effects (November 22–24, Kalmar, Sweden)* 558–563.

Ofverstrom, S.; Sapkaite, I.; Dauknys, R. 2010. Pirminio-perteklinio dumblo mišinio anaerobinio pūdymo tyrimai, *13-osios Lietuvos jaunųjų mokslininkų konferencijos „Mokslas – Lietuvos ateitis“ 2010 m. teminės konferencijos "Pastatų inžinerinės sistemos" (2010 m. balandžio 15–16 d., Vilnius, Lietuva)* straipsnių rinkinys, 72–75, ISBN 9789955285601.

Ofverstrom, S.; Sapkaitė, I.; Dauknys, R.2011. Iron and aluminium as inhibitors of anaerobic digestion of primary-waste activated sludge mixture, *International Conference of young scientists on energy issues (CYSENI 2011) (May 26–27, 2011, Lithuanian Energy Institute, Kaunas, Lithuania) [CD]* 1:6. ISSN 1822-7554.

Arlauskaitė, G.; Katinauskas, D.; Ofverstrom, S.; Dauknys, R.. 2012. Geležies druskų įtaka dumblo pūdymo procesui, *15-osios Lietuvos jaunųjų mokslininkų konferencijos "Mokslas – Lietuvos ateitis" 2012 metų teminės konferencijos "Pastatų inžinerinės sistemos" straipsnių rinkinys (2012 m. balandžio 12–13 d., Vilnius, Lietuva)* 11–15 ISSN 2029-7157.

Svetlana OFVERSTROM

RESEARCH AND EVALUATION OF IRON IMPACT ON SLUDGE DIGESTION PROCESS

Doctoral dissertation

Technological science,
Environmental Engineering (04T)

Svetlana OFVERSTROM

GELEŽIES POVEIKIO DUMBLO PŪDYMO PROCESUI TYRIMAI IR VERTINIMAS

Daktaro disertacija

Technologijos mokslai,
Aplinkos inžinerija (04T)

2013 12 27. 8,75 sp. l. Tiražas 20 egz.
Vilniaus Gedimino technikos universiteto
leidykla „Technika“,
Saulėtekio al. 11, 10223 Vilnius,
http://leidykla.vgtu.lt
Spausdino UAB „Ciklonas“
J. Jasinskio g. 15, 01111 Vilnius