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PERSPECTIVE METHODS OF SEWAGE SLUDGE UTILISATION FOR ENERGY PRODUCTION

PERSPEKTIVNÍ METODY ENERGETICKÉHO VYUŽITÍ ČISTÍRENSKÝCH KALŮ

DOKTORSKÁ PRÁCE
DOCTORAL THESIS

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Abstract

This thesis on the processing of sewage sludge in waste to energy applications contains a description of sludge material properties (density, specific heat capacity and dynamic viscosity), and is, in its main chapters, devoted to sludge disintegration for improved dewatering and the experimental study of emissions produced in incineration, where the influence of alkali addition was examined. The incineration of dried sludge was done in a fluidized bed reactor and the production of air emissions and distribution of heavy metals was studied. The thermo-chemical disintegration of stabilized sewage sludge, elaborated in the second main chapter, aims at reducing the water content of sludge after dewatering. Experiments conducted in laboratory-scale aimed at identifying a suitable temperature level, required dosage of chemical agent. In the following, a basic economical evaluation is described, where the savings are determined from savings in sludge disposal.

Keywords

sewage sludge, advanced dewatering, sludge incineration, pollutants generation, disintegration of stabilized sludge

Abstrakt

Tato práce o energetickém využití čistírenských kalů obsahuje popis vlastností kalu (hustota, měrná tepelná kapacita a dynamická viskozita). Stěžejní kapitoly jsou věnovány desintegraci kalu pro zvýšení obsahu sušiny po odvodnění a experimentálnímu zkoumání tvorby emisí při spalování kalu, kde byl posuzován vliv přídavku alkálie. Spalování vysušeného kalu proběhlo ve fluidní vrstvě, byla zkoumána produkce škodlivin a distribuce těžkých kovů. Druhá ucelená část práce je věnována termochemické desintegraci stabilizovaného kalu, přičemž byl experimentálně vyhodnocován vliv na obsah vody v odvodněném kalu. Provedené experimenty sloužily k detekci vhodné teploty a dávky chemikálie. Výsledky experimentů byly rovněž podkladem pro ekonomickou bilanci, která je založena na úsporách za likvidaci menšího množství kalu.

Klíčová slova

čistírenský kal, zlepšení odvodnitelnosti, spalování kalu, tvorba polutantů, dezintegrace stabilizovaného kalu

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PROHLÁŠENÍ

Prohlašuji, že jsem disertační práci vypracoval samostatně a že všechny použité literární zdroje jsem správně a úplně citoval.

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Dipl.-Ing.(FH) Thomas Elsäßer

PODĚKOVÁNÍ

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LIST OF ABBREVIATIONS

BAT	Best available technology
BOD_5	Biochemical oxygen demand within 5 days
BOD_u	Ultimate biochemical oxygen demand
BFB	Bubbling fluidized bed
CFB	Circulating fluidized bed
COD	Chemical oxygen demand
COD_{Cr}	Chemical oxygen demand determined by dichromate method
dl-PCB	Dioxin-like polychlorinated biphenyls
DS	Digested sludge
EU 15	European Union including Austria, Belgium, Denmark, Finland, France, Germany, Greece, Ireland, Italy, Luxembourg, the Netherlands, Portugal, Spain, Sweden and the United Kingdom.
exp.	Experiment
HM	Heavy metals
Limest.	Limestone
LOI	Organic fraction or matter determined as loss on ignition
LOQ	Limit of quantification
MPS	Mixed primary sludge
n.d.	Not detected
NKR	Neumann-Kopp rule
PAH	Polyaromatic hydrocarbons
PCB	Polychlorinated biphenyls
PCDD	Polychlorinated dibenzodioxins

PCDF	Polychlorinated dibenzofurans
PE	Population equivalent where 1 PE refers to a BOD_5 load of 60 g of oxygen per day [2]
PE-COD110	Population equivalent where 1 PE refers to a COD load of 110 g of oxygen per day
POP	Persistent organic pollutants
TEF	Toxic equivalence factor for dioxins and furans
TEQ	Toxic equivalent expressed as 2,3,7,8-TCDD
TS	Total solids
USEPA	U.S. Environmental Protection Agency
vol.	Volumetric
waf.	Water and ash free
WWTP	Wastewater treatment plant

LIST OF SYMBOLS

SYMBOL	MEANING	UNIT
$\dot{\gamma}$	Shear rate	[s^{-1}]
η	Dynamic viscosity	[Pa.s]
λ	Stoichiometric air ratio	[-]
τ	Shear stress	[Pa]
τ_y	Yield stress	[Pa]
ω	Mass fraction	[kg/kg]
ω_{vs}	Mass fraction of volatile solids determined as LOI	[kg/kg]
C_{cal}	Calorimeter constant	[J/K]
C_p	Mean heat capacity at constant pressure	[J/K]
C_p^*	Real heat capacity at constant pressure	[J/K]
c_p	Specific heat capacity at constant pressure	[J/(kg K)]
$c_{p,mol}$	Molar heat capacity at constant pressure	[J/(mol K)]
$c_{v,mol}$	Molar heat capacity at constant volume	[J/(mol K)]
E_M	Measured emission concentration	[mg/m_N^3]
E_S	Emission concentration at the standard percentage oxygen concentration	[mg/m_N^3]
f	Conversion factor for converting BOD_5 to BOD_u	[-]
H	Enthalpy	[J]
H_{in}	Enthalpy of sludge at the inlet	[J]
$H_{out, dez}$	Enthalpy of hot sludge at the outlet of disintegration unit	[J]
k	Consistency	[Pa.s]
m	Mass	[kg]
n	Power law coefficient	[-]
O_M	Measured oxygen concentration	[vol.% in dry gas]
O_S	Standard oxygen concentration	[vol.% in dry gas]
OC_C	Specific O_2 consumption for the removal of organic matter contained in wastewater	[g/l]

SYMBOL	MEANING	UNIT
OC_N	Specific O_2 consumption of nitrification	[g/l]
OC_D	Specific O_2 consumption of denitrification	[g/l]
OC_{total}	Specific O_2 consumption for the clarification of wastewater	[g/l]
Q	Heat	[kJ]
Q_R	Recovered heat in heat exchanger	[kJ]
Q_H	Required additional heat supplied by heat transfer medium	[kJ]
R	Universal gas constant	[J/(mol K)]
S	Effluent concentration	[mg/l]
S_0	Influent concentration	[mg/l]
T	Temperature	[°C], [K]
U_{mf}	Minimum fluidization velocities of particles	[m/s]
$TS_{lab\text{-}scale}$	Total solid concentration attained in laboratory	[%]
$TS_{op\text{-}scale}$	Total solid concentration attained in operation	[%]
Y_{obs}	Observed yield of produced biomass	[g/g]

1 INTRODUCTION

Sludge is formed as residue from the wastewater treatment process. In terms of the European Union’s environmental legislation, sludges are categorized according to category 19 08 as waste from wastewater treatment plants. For instance, sludge from the treatment of urban wastewater is allocated to the waste code 19 08 05, whereas sludge containing dangerous substances from biological treatment of industrial wastewater is considered as hazardous waste and allocated to 19 08 11.

Due to the physical-chemical processes involved in wastewater treatment, sludge tends to contain a high organic concentration and valuable nutrients such as nitrogen and phosphorus. But also heavy metals and poorly biodegradable trace organic compounds as well as potentially pathogenic organisms (viruses, bacteria etc) [1].

The composition of sludges produced at wastewater treatment plants (WWTP) is influenced by seasonal dependencies, preventing sludge from being credited as a product for the fertilizer industry. Thus, the demands of the agricultural and fertilizer industry for a sludge-based product can only be fulfilled insufficiently.

Due to the implementation of the Urban Wastewater Directive (91/271/EEC) [2] the amount of sludge production in the original 15 European Union’s (EU 15) member states rose from 5.5 million tonnes of dry solids in 1992 to almost 9 million tonnes by the end of 2005.

The main reasons for this increase are:

- an increase in the number of connection rate to public sewer systems.
- an increase in the amount of areas covered.
- enhanced wastewater treatment using phosphorus and nitrate elimination.

Figure 1 shows the development of municipal sewage sludge production for selected EU member states. Currently, the increase in sludge production stagnated and tends to fall slightly in the EU 15 member states as shown in Figure 1. Contrary to the general development in the EU 15 member states, the total amount of dry solids production has increased within the last years in Ireland, Greece and the United Kingdom. The increase in sludge production in Ireland and Greece coincides with the increase in connection rate to municipal wastewater treatment. Thus, the increase in sludge production is a consequence of the lack in connection rate. The sludge production in newly joined member states is expected to rise, as there will be a catching-up process connecting more inhabitants to municipal wastewater treatment.

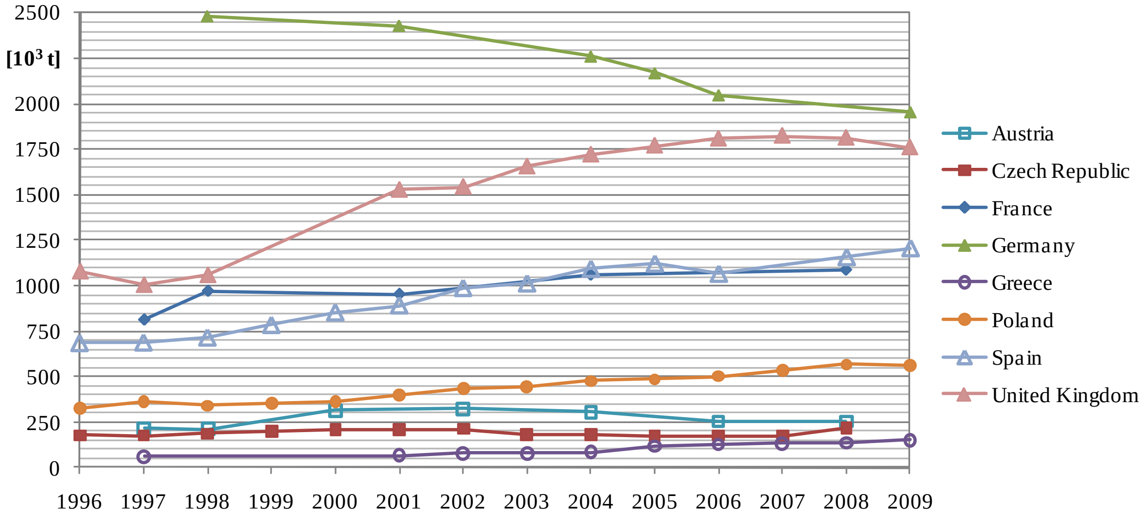


Figure 1 Annual production of sludge solids for selected EU member states [3]

The development of municipal sewage sludge production and connection rate in the Czech Republic is shown in Figure 2. The number of inhabitants connected to municipal wastewater treatment increased by 17 % between 1996 and 2007. The annual production increased from 1996 until 2002 when the production dropped by 14.7 %. Although the connection rate increased by 5 %, production of sludge has been stable since the year 2003.

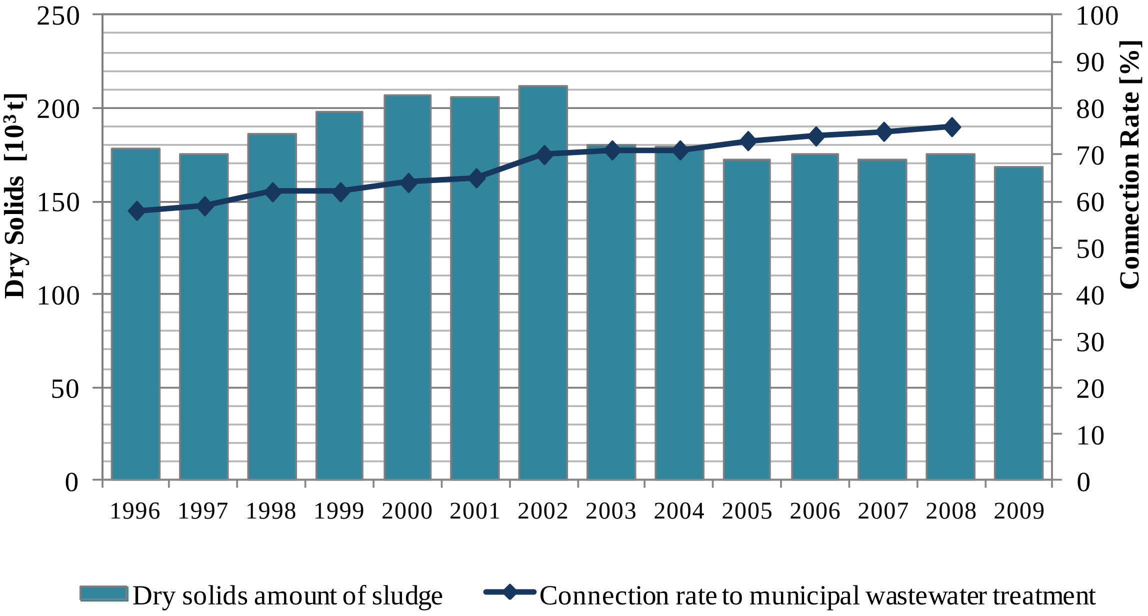


Figure 2 Annual sludge production of municipal WWTPs and connection rates in the Czech Republic [3], [4]

The amount of sludge shown in Figure 1 and Figure 2 represent the amount of total solids contained in sludge. However, the major portion of sludge is water and thus not included in statistics shown above. Prior to disposal, the water content of sludge is further reduced in dewatering units. The final total solid (TS) concentration is approximately 16.0-30.0 %. This means that 1 kg of dry solids represents a wet sludge amount, weighing 3.3-6.3 kg which has to be disposed of.

In 2008, according to [4], a total waste amount of 364.9×10^3 t was disposed of in the Czech Republic under waste code 19 08 05 - sludges from treatment of urban wastewater. Taking into account the amount of produced dry sludge in 2008, the solid concentration averaged 47 %. In 2009 the waste amount was 553.8×10^3 t. This represents an average solid concentration of 30 % in sludges that were disposed off. The determined average solid concentration for 2008 is very high and exceeds the technical feasibility of sludge dewatering. This suggests that in the 2008 statistics, the amount is partially given in dry solids.

The amount of sludge produced as an outcome of the indispensable wastewater treatment makes it necessary to establish a wise process of sludge utilization in the energy or fertilizer sectors.

2 PROBLEMS IN SLUDGE PROCESSING AND APPROACH TO SOLVING

The processing of sewage sludge represents a relatively broad range of interests, towards which attention is devoted not only from the operators of WWTPs, but also by various research institutions. From the operators' point of view, one can name the effort to reduce the sludge production to a minimum and with it the reduction of expenses for sludge disposal or to increase the production of biogas from the WWTP and, with it, to reach the self-sufficiency on energy.

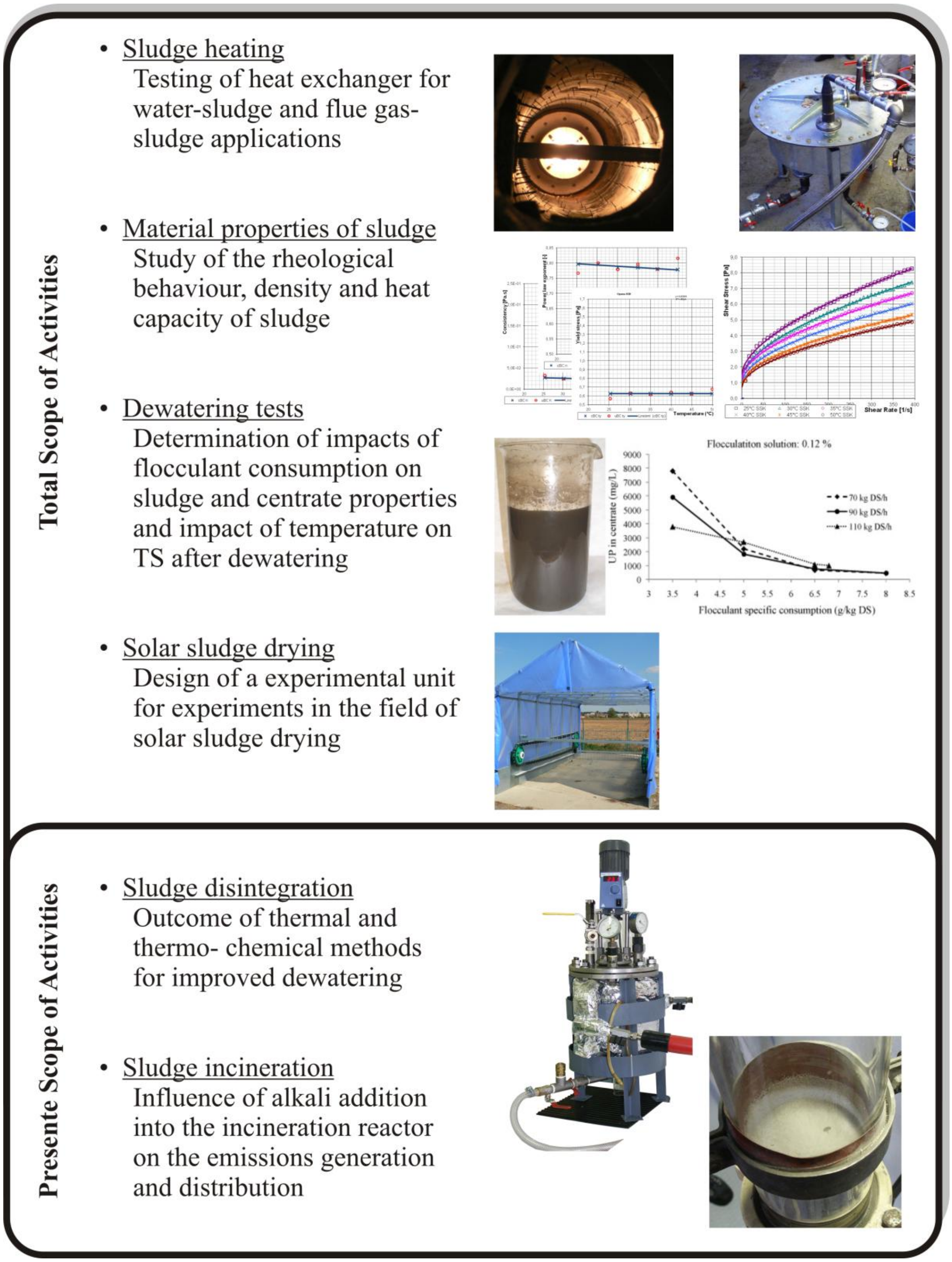
In research institutions, the material properties and the possibilities of its utilization are both investigated. One can find contributions on the rheological behavior of different types of sludges ([5], [6] and [7]), nutrient content utilized by crops ([8] and [9]), or contributions monitoring diverse pollutants contained in sludges ([10] and [11]). From the point of view of utilization, attention is paid to the possibilities of increased biogas production from anaerobic stabilization, the issue of sludge incineration and sludge drying respectively. One can find studies on the possibilities of phosphorous recovery from sludge, which can possibly be used for fertilizer production [12]. Moreover, attention is paid to improving the composting process and the production of so called fuel compost.

Although, during doctoral studies, attention was paid to several topics, which are related to the processing of sludge, this thesis summarizes only two relatively independent research fields. The first is the issue of sludge incineration, where the focus is given to the pollutants in the sludge. Due to the components contained in sludge, the incineration products arising from the incineration are different compared to the emissions from the incineration of fossil fuel and knowledge is required for the design and rating of sludge incineration plants. Conducted experimental sludge incineration tests under addition of limestone aimed at evaluating the influence of alkali on the distribution of pollutants in the combustion products. The experiment was carried out in a fluidized bed reactor and the arising flue gas and ashes were analyzed. Sulfur dioxide is the component, for which the most distinctive change was expected. The components nitrous oxides, hydrogen halides and persistent organic pollutants were tracked additionally. Furthermore, attention was drawn to heavy metals.

The second outstanding chapter in this work is the influence of sludge disintegration on its dewaterability. Currently, disintegration is primarily used to increase biogas production where the destruction of the microorganisms' cell walls makes the cell content available to fermentation bacteria. An obstacle for efficient sludge processing is the high water content ranging from 70 % to 84 % in dewatered sludge. The high water content affects the treatment costs and constrains the possibilities of waste to energy applications. For an efficient utilization, low water content is desired. From this reason, the possibility of using disintegration to increase the dewaterability of sludge was studied in laboratory scale and, based on the results, a operational scale unit was designed and its benefits in a possible application on a WWTP was assessed.

During the study period, next to those topics mentioned before, further studies and field experiments have been conducted (see Figure 3). The activities targeted at improving sludge processing for its subsequent utilization and comprised of:

- Design and testing of an experimental heat exchanger for flue gas-sludge applications. Determined results of heat transfer and flow behavior have been compared with values from CFD-Analysis using experimentally determined material properties [13].
- Development and performance tests on a helical water-sludge heat exchanger for sludge heating. Based on the results of measurement, the calculation relations for calculation of heat transfer coefficient and pressure drop have been corrected [14].
- Operational scale dewatering experiments of aerobic stabilized sewage sludge. The experiments aimed at studying the impacts of flocculant consumption and centrifuge load on the quality of dewatered sludge and centrate [15].
- Operational scale dewatering experiments of digested sewage sludge at different temperatures.
- Rheological study of the behavior of different types of sludges [16].



Total Scope of Activities

- Sludge heating
  Testing of heat exchanger for water-sludge and flue gas-sludge applications
- Material properties of sludge
  Study of the rheological behaviour, density and heat capacity of sludge
- Dewatering tests
  Determination of impacts of flocculant consumption on sludge and centrate properties and impact of temperature on TS after dewatering
- Solar sludge drying
  Design of a experimental unit for experiments in the field of solar sludge drying

Presente Scope of Activities

- Sludge disintegration
  Outcome of thermal and thermo- chemical methods for improved dewatering
- Sludge incineration
  Influence of alkali addition into the incineration reactor on the emissions generation and distribution

Figure 3 Scope of activities

3 SLUDGE GENERATION AND TREATMENT

Municipal wastewater consists of domestic wastewater discharged by households and industries. It also consists of surface water and water seeping into sanitary sewers. Industrial wastewater, which has a high level of pollution, is pre-treated at the plant and usually discharged into public sewer systems.

Thus, wastewater holds different pollutants such as:

- organic material,
- nitrogen,
- phosphorus,
- suspended solids,
- pathogenic organisms.

Water clarification from above mentioned pollutants is done in multiple stage treatment, starting with preliminary wastewater treatment and ends with the stabilization and utilization of the generated sludge. This comprehensive treatment is an energy consuming process and, as the wastewater treatment process holds possibilities for energy savings, it has come into focus of plant operators, communities and authorities during recent years. The biggest consumer is the biological treatment stage accounting for 50 % of the total energy consumption in case of anaerobic, and 70 % for aerobic sludge stabilization [17]. Energy and cost benchmarking of WWTPs is used to evaluate, compare and if applicable reduce the consumption of particular plants or processes. The distribution of energy consumption and operational costs gained in an Austrian benchmarking [18] are shown in Figure 4. The shown values represent the median values from 15 WWTPs with a treatment capacity ranging from 20 000-50 000 PE. One can read from this chart that the biological and mechanical stage holds a share of approximately 60 % of the total energy consumption and roughly 20 % of operational costs. Due to the high share in energy consumption, the biological treatment highly effects the total plant efficiency and thus, has to be in the focus considering intensifying or changing the wastewater treatment line or even sludge management.

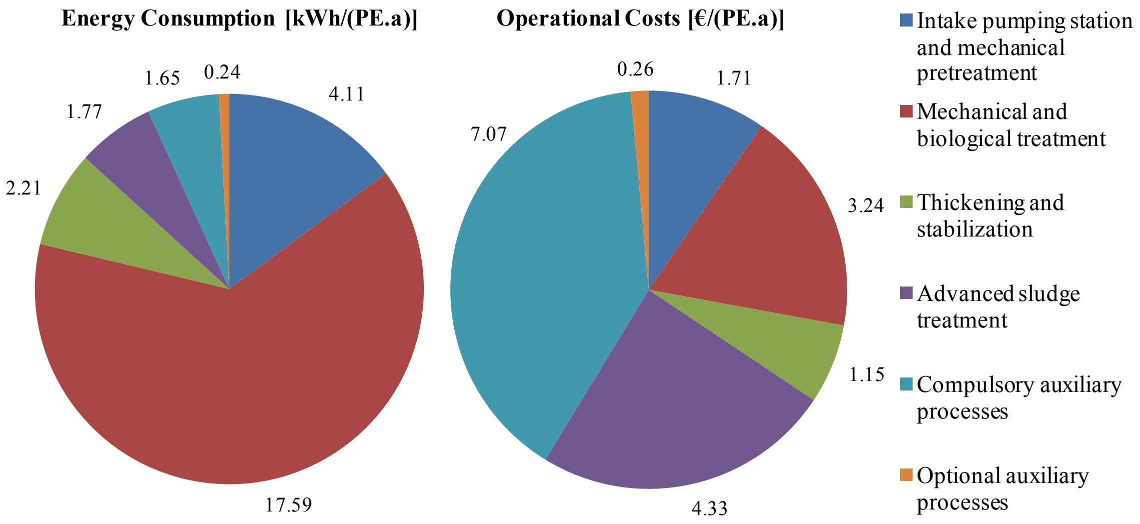


Figure 4 Energy consumption and operational costs of wastewater treatment for WWTPs of capacity (20 000-50 000) PE [18]

The production of sludge is a direct result of aerobic wastewater treatment. As good as the clarification from the view of clarified water may be, around 50 % of the biochemical oxygen demand (BOD_5) is converted by aerobic bacteria to additional biomass; only 50 % of the BOD_5 is mineralized to CO_2 and water. Thus, the amount of sludge increases within the wastewater treatment.

3.1 DESCRIPTION OF MUNICIPAL WASTEWATER TREATMENT

A typical wastewater clarification line for municipal wastewater comprises of mechanical and biological treatment, which is accomplished in different treatment stages as shown in Figure 5. The respective treatment stages are described in the following.

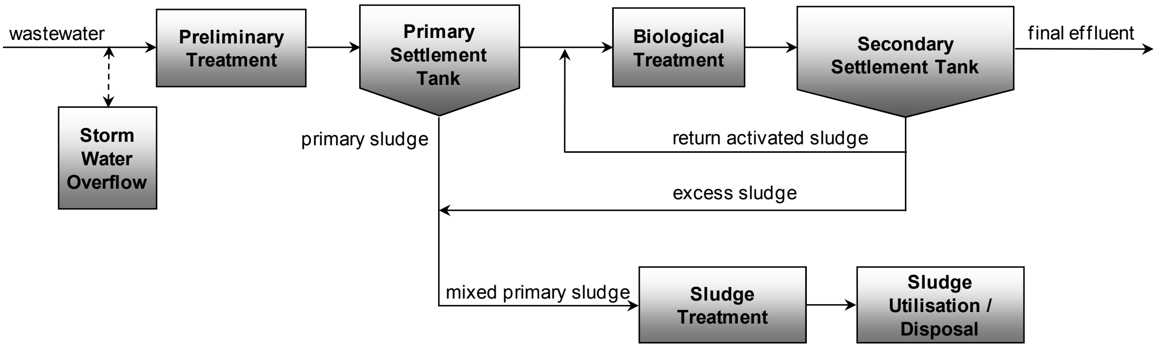


Figure 5 Flowsheet of a wastewater treatment line

3.1.1 Preliminary Wastewater Treatment

Preliminary treatment is mainly carried out in order to remove material that might damage equipment or hinder further treatment. In this treatment stage, sand, gravel and big floating pollutants are removed from the wastewater. After the preliminary treatment, wastewater is free of extraneous matter and thus prepared for further processing, which can be carried out without risk on the subsequent processing equipment.

3.1.2 Primary Clarification

Primary clarification takes place in the primary settlement tank. The primary clarification of raw wastewater is a classical float-sink separation. During this process, undissolved organic and inorganic material is removed from the wastewater. One scrapper is located at the surface of the wastewater in order to peel off floating debris from the water surface. The second scrapper is located at the bottom of the tank in order to strip settled debris from the settlement tank. Both types of debris are subsequently mixed and called primary sludge. Mechanically clarified water flows off through the overflow edge of the settlement tank.

3.1.3 Biological Treatment

Biological treatment takes place in the activation tank, where biodegradation of dissolved organic compounds takes place. The biodegradation is carried out within a cascade of anoxic and aerobic zones in the activation tank.

Considering the energy consumption of the biological treatment, outlines the aeration as the most demanding consumer (see Figure 6), where the aeration of the activation tanks accounts for 63 % of the total consumption of the biological treatment.

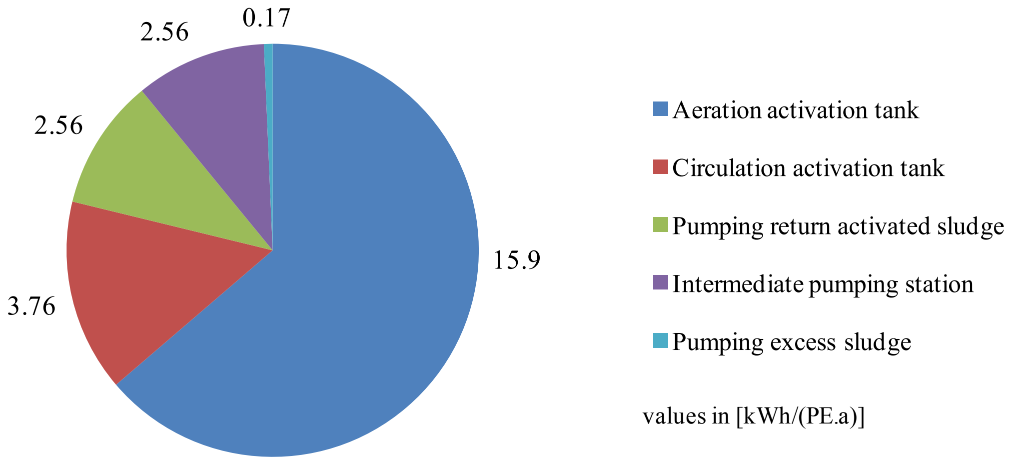


Figure 6 Allocation of electric power consumption for biological wastewater treatment; WWTPs of capacity >10 000 PE [17]

Denitrification Process

The first step within the biological stage is anoxic denitrification, where *Pseudomonas* degrade nitrate into nitrogen as described in equation (3-1).

$$2\ NO_3^- + 5\ H_2 \xrightarrow{\text{Pseudomonas}} 2OH^- + 4\ H_2O + N_2 \tag{3-1}$$

This reaction occurs in anoxic zones during the cascade [19]. As it - *Pseudomonas* takes oxygen from nitrate, one has to make sure that there is hardly any dissolved oxygen in the wastewater. Otherwise, the bacteria would consume dissolved oxygen instead of nitrate. Respiration of nitrate oxygen has a positive impact on the total oxygen consumption of the biological wastewater treatment. In denitrification, one kilogram of nitrate nitrogen represents 2.9 kg of oxygen [20]. As the oxygen, consumed in denitrification, comes from nitrate, denitrification reduces the total oxygen demand of the biological treatment stage.

Nitrification Process

Biodegradation of ammonium is done in two reaction steps. During nitrification, *Nitrosomonas* and *Nitrobacter* are necessary. The biodegradation of ammonium to nitrite is followed by the oxidation of nitrite to nitrate [19]. Both reactions, as shown in equations (3-2) and (3-3), take place in an aerobic milieu.

$$NH_4^+ + 1\tfrac{1}{2}\ O_2 \xrightarrow{\text{Nitrosomonas}} NO_2^- + 2\ H^+ + H_2O \tag{3-2}$$

$$NO_2^- + \tfrac{1}{2}\ O_2 \xrightarrow{\text{Nitrobacter}} NO_3^- \tag{3-3}$$

As the bacteria require atmospheric oxygen for their respiration, air or pure oxygen is injected at the tank bottom. The stoichiometric amount of required oxygen amounts to 4.57 kg for the removal of 1 kg of ammoniacal nitrogen [20]. In fact, the oxygen consumption is lower due to the utilization of oxygen bound to CO_2. A consumption of 4.3 g O_2/g N is widely accepted [21] and [22]. It is necessary to let the wastewater pass through aerobic and anoxic zones several times for better removal of nitrogen. The number of passes can be selected by choosing the ratio between excess sludge and return activated sludge.

3.1.4 Secondary Settlement Tank

Settling of bacteria produced in the biological treatment stage and, where applicable, chemical sludge from the precipitation of phosphates takes place in the final settlement tank. The diameters of the particles are much smaller than in raw wastewater. Thus, the sedimentation process takes longer compared to sedimentation in the primary clarification stage. Sludge withdrawn from the secondary settlement tank is partially returned into the activation tank. Excess sludge is mixed with primary sludge and referred to as mixed primary sludge. Water leaving the final settlement tank is clear and becomes discharged into receiving waters.

3.1.5 Sludge Treatment Section

The treatment of mixed primary sludge aims at its stabilization and eases subsequent handling. The extent of sludge treatment on WWTPs depends on the disposal route and can, amongst stabilization, involve dewatering, drying, sanitation and lime addition or a combination of these methods. Stabilization is not required if sludge stabilization is achieved by its final utilization or disposal.

3.2 SLUDGE TO ENERGY

The idea of Sludge to Energy is to take advantage of the energy content of organic compounds. The reduction of organic compounds goes along with stabilization, which is required prior to its final disposal. The following utilization methods represent proven methods of sludge stabilization.

3.2.1 Digestion of Sludge

Digestion is an approved method of sludge stabilization and the most frequently stabilization technology on WWTPs clarifying wastewater of 10 000 inhabitants or more. The outcome of anaerobic digestion is stabilized sludge and high calorific biogas. Biogas is utilized in gas engines to generate heat and electric power which is supplied into the public power network [23]. Typical sludge management with digestion is shown in Figure 7.

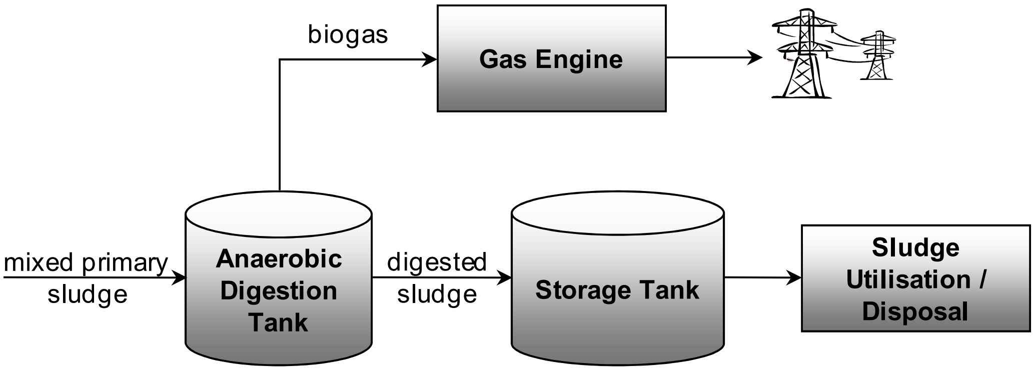


Figure 7 Digestion of mixed primary sludge

As supplying power into the public network is subject to subsidiaries according to Directive 2009/28/EC [24], anaerobic digestion holds a key role in the economical analysis of WWTPs.

3.2.2 Incineration of Sewage Sludge

Primarily, incineration aims at mass and volume reduction of sludge and reduction of organic matter in sludge; additionally, heat is produced. The products of incineration are flue gas and an inert material without biodegradable compounds. Heat recovered from incineration can be used for internal purposes, heating purposes or electricity production. Prior to its incineration, sludge needs to be dewatered and partially or entirely dried.

Sludge incineration plays a very limited role in the Czech Republic. Thus no operational data is available on a large scale. The following plant specific data and shares are based on operational data in Germany where the share of incineration in sludge disposal was 49 % in 2007 [25]. The incineration routes can be split up into mono-combustion (approx. 44 %), co-firing (approx. 44 %), cement plants (approx. 8-9 %) and municipal waste incineration plants (approx. 3-4 %).

Co-firing

In legal terms, co-firing (also referred to as co-combustion and co-incineration [26]) means any stationary or mobile plant whose main purpose is the generation of energy or production of material products and:

- which uses waste as a regular or additional fuel; or
- in which waste is thermally treated for the purpose of disposal.

These requirements apply to sludge utilization in cement production, where sludge and other alternative fuels are utilized both as fuel and as raw material. In 2007, 52 % of required fuel energy was supplied by alternative fuel, where the share of sludge in alternative fuels was 2.4 % of the calorific energy [27]. The advantage of using alternative fuels in cement production is that solid fuel is converted into clinker and the production of slag is avoided. Organic pollutants are avoided due to high temperatures in the clinker phase (1400-1450 °C) and gas phase (residence time 8 s above 1200 °C).

The second co-firing technology is the incineration of sludge in coal-fired power plants. In practice, the incineration capacity of brown coal power plants is limited to approximately 4 % and 1.5 % for black coal power plants (on a dry solid basis) [28]. However, the future of co-firing is uncertain in the upcoming generation of power plants. Due to the application of nickel-based materials, coal-fired power plants will face changes regarding incineration temperatures. This leads to difficulties predicting the impact of co-firing on the new materials. Consequently, operators of future power plants do not currently plan to introduce co-firing of sludge in newly built or planned equipment [25], [29] and will increase the importance of mono-combustion.

Mono-combustion

Mono-combustion, which refers to incineration plants using mainly sludge as fuel, are usually located on the premises of high capacity WWTPs. If so, incineration of unstabilized sludge is from a hygienic point of view possible. With regards to Germany, approximately 80 % of mono-combustion plants use fluidized bed technology [25]. As only sludge is incinerated in this process, the produced ash material has a specific composition which would subsequently allow - provided that suitable processing technology is available - to recover phosphorus from the ashes [30].

The main problem for energy efficient sludge incineration is the high water content ranging from 93 % to 98 % in thickened sludge and 70 % to 84 % after dewatering. The high water content of sludge restricts its incineration and counteracts the efficiency of the incineration process.

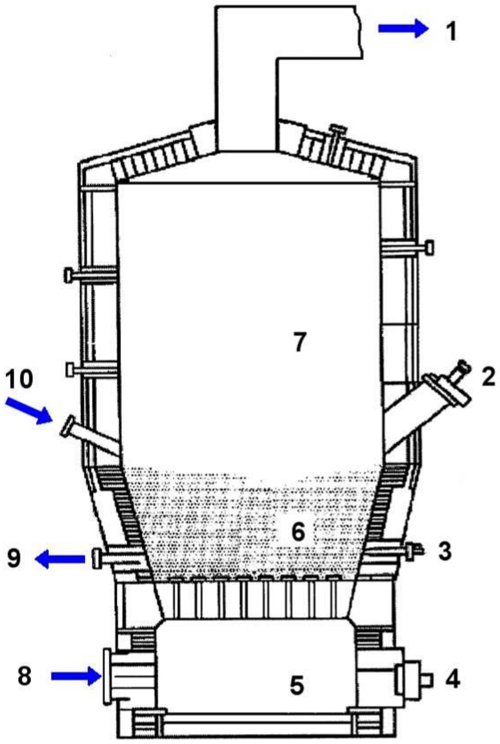
The best available technology (BAT) of sludge pre-treatment prior to its incineration is drying to such an extent that allows sludge incineration independent of support fuels. This is preferably achieved using heat recovered from the incineration [31]. Due to the higher efficiency of the fluidized bed technology, this technology may be designated as BAT in mono-combustion [31].

Fluidized Bed Combustors

In Europe, fluidized bed incineration was introduced in 1964 in Germany for the incineration of sludges from the refinery sector and the first plant for the incineration of municipal sludges followed in 1965 in Switzerland [32]. In the Czech Republic, the first fluidized bed combustor for the incineration of sludges is in operation since May 2009 in the city of Jihlava [33].

Fluidized bed combustors are particularly suitable for the incineration of wastes, homogenous in their particle size distribution. The distribution and mixture of sludge within the bed results in uniform burning and stable operation. The introduction of fluidization (or combustion) air under the bed causes turbulent flow in the freeboard and thus, good heat transfer and burnout in the gases. Depending on the movement of the fuel particles, the fluidized bed combustors can be classified in bubbling (stationary) fluidized bed (BFB) combustors (Figure 8) and circulating fluidized bed (CFB) combustors as shown in Figure 9.

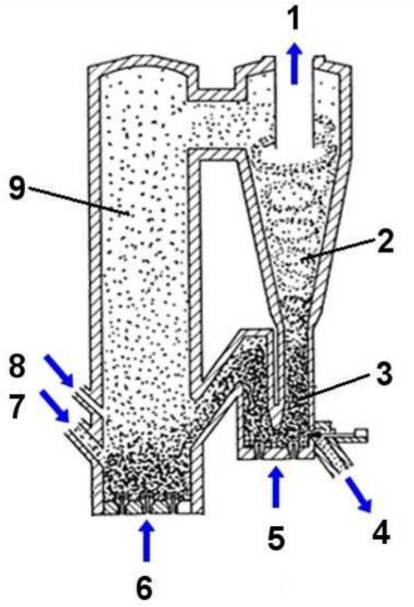
The BFB incineration represents the majority of sewage sludge mono-combustion plants and is suitable for the incineration of semi-dried or dried sludge. The term *bubbling fluidized bed* refers to a layer of sand or ash which, due to the introduction of pressurized air, behaves as a fluid. All instances of incineration (drying, volatilization and burnout) take place in the fluidized bed at temperatures in the range of 650 °C. The temperature above the fluidized bed (freeboard) is higher and usually in the range of 850-950 °C [31].



1: Flue gas exhaust
2: Burner
3: Fuel gun
4: Startup burner for hot windbox
5: Windbox
6: Fluidized bed
7: Freeboard
8: Fluidized air inlet
9: Ash and sand outlet
10: Sand inlet

Figure 8 Cross section of a typical bubbling fluidized bed incinerator [34]

In CFB incineration (Figure 9), the flow velocity in the freeboard is higher (4-6 m/s) compared to the BFB (0.7-1.1 m/s) and causes transport of the fuel particles. The CFB technology is mainly applied in coal fired power plants only, where dry sludge is co-combusted. The burnout of the fuel particles takes place while they are conveyed to the top of the incineration chamber, where the flue gas passes a cyclone. The particles, removed from the flue gas stream, are returned into the fluidized bed.



1: Flue gas exhaust
2: Cyclone
3: Loop seal
4: Ash outlet
5: Fluidization air
6: Fluidization (primary) air
7: Fuel inlet
8: Secondary air
9: Freeboard

Figure 9 Cross section of a typical circulating fluidized bed incinerator [19]

3.3 OTHER METHODS OF SLUDGE PROCESSING

Currently, sludge disposal in the Czech Republic is dominated by composting and agricultural utilization representing approximately 70 % over the last decade. Landfilling used to be important in sludge disposal but declined from 20 % in 2002 to 3.5 % in 2009. In the same period, agricultural utilization became more important and has reached 25 %. In 2009 an amount of 80 727 t of dry sludge was composted and 42 442 t was used in agriculture [4]. Although the amount of incinerated sludge increased from 290 t in 2002 to 712 t in 2008, and 2 179 t in 2009 (representing 1.3 % of the total sludge production) it still plays a limited role [4]. In comparison to data from Germany, the small share of sludge incineration becomes more evident. In 2009, according to [35] less than 15 % was composted and 52.5 % was incinerated. An overview of the disposal routs for the Czech Republic is given in Figure 10.

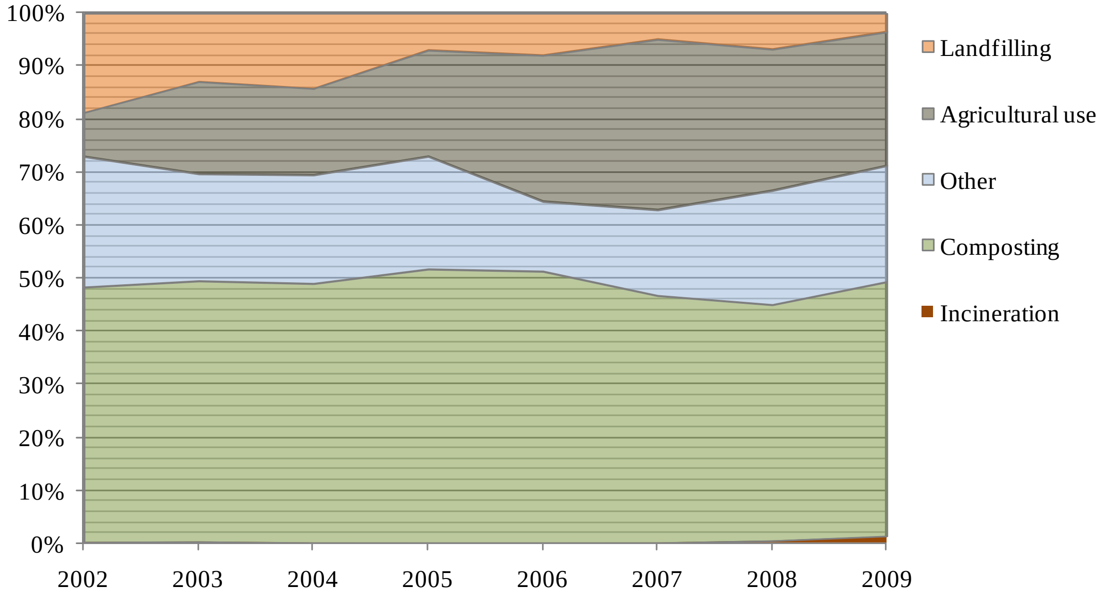


Figure 10 Disposal routes of municipal sludge in the Czech Republic [4]

3.3.1 Composting of Sludge

Stabilization of dewatered sludge under aerobic, thermophilic conditions is referred to as composting. During the exothermic process, the biodegradable material is converted into humus. Composting of biodegradable waste has a long tradition in the Czech Republic and peaked in 1987 with the production of 2.5×10^6 t of compost from biodegradeable waste [36]. In 2009 almost 50 % of the sludge produced was composted. Pre-treatment of sludge prior to composting is required to enhance sludge structure and enable aeration. For this reason dewatered sludge is mixed with structural material such as paper, wood chips and straw.

The first phase is aerated composting, which takes between 2 and 8 weeks. Exothermic reactions in the substrate cause an increase in temperature of 50 to 65 °C. Due to the heat treatment, the number of pathogens is reduced. The second phase is final composting in static piles which takes several weeks. Aerated composting of sludge can be carried out in aerated piles or pressure ventilated, closed boxes.

3.3.2 Landfilling of Sludge

Landfilling of biodegradable waste, which include sludge, leads to an uncontrolled production of carbon dioxide and methane. As a result, the methane emissions from biodegradable waste accounted for 3 % of total greenhouse gas emissions in the EU 15 member states in 1995 [37]. The release of carbon dioxide and methane into the air can be avoided collecting and flaring off landfill gases but the valuable organic matter contained in biodegradable waste is lost. Another disadvantage is that the biodegradation of the organic compounds in waste may lead to a subsidence in the landfill body as well as a long aftercare period. Consequently, the European Union issued regulations in its Landfill Directive 1999/31/EC [38] to gradually reduce the amount of biodegradable waste being landfilled.

Regarding the biodegradable waste, the Czech Republic implemented the Landfill Directive by setting limits restricting the amount of landfilled biodegradable waste. The amount of landfilled biodegradable waste will be reduced to 75 % by 2010, 50 % by 2013 and 35 % by 2020. The limits refer to the amount of landfilled biodegradable waste in 1995 amounting 1 530 000 t [39].

Some European countries have banned the landfilling of sludge. Landfilling is prohibited by law in Germany since June, 1st 2005. The landfill ban is regulated in the Abfall-ablagerungsverordnung (Directive on Landfilling of Waste) [40] which prohibits the landfilling of waste containing organic fraction higher than 5 % by weight, measured as loss on ignition (LOI). Thus, sludge needs to be incinerated or mechanically-biologically treated prior to its landfilling. Currently, the requirements can only be met by incineration.

3.3.3 Agricultural Utilization

Agricultural utilization is usually applied in rural areas, and from the technical point of view the most undemanding one. Although it provides a lot of advantages, land spreading is not widely accepted in public. Mainly because of odor nuisance, food safety scandals heated by the concentration of heavy metals which are accumulated in the soil, pathogen germs, persistent pollutants and organic halogen compounds. However, the organic matter and nutrients contained in sludge make the land spreading of waste arguable for agricultural use. According to legislation, the liquid or dewatered stabilized sludge may be used for fertilizer purposes if the pollutants' concentrations of heavy metals, organic pollutants and bacteria are below the limits set by the Czech Decree 382/2001 Sb. The limit values for heavy metals and organic pollutants are given in Table 1.

Table 1 Limit values for sludge utilization in agriculture [41]

	Concentration in Sludge Solids *[mg/kg]*
Arsenic	30
Cadmium	5
Chrome	200
Copper	500
Lead	200
Mercury	4
Nickel	100
Zinc	2500
Adsorbable organic halides	500
PCB ♣	Σ 0.6

♣ sum of the 6 congeners 28, 52, 101, 138, 153 and 180

3.4 PROBLEMS IN SLUDGE TREATMENT FOR ENERGY PRODUCTION

Sewage sludge is a versatile biofuel that is available in every urban area of the world. Due to its origin, the utilization in mono-combustion and co-firing, is subject to legal requirements regarding the incineration of waste, which sets more stringent requirements for the air emissions and treatment conditions. Furthermore, its constituent parts and fluctuating composition (ash content, chlorine, sulfur, heavy metals and water content) make sludge a complex biofuel that requires knowledge of its properties to identify bottlenecks and opportunities in its processing.

The effective utilization of sludge in Waste to Energy faces several constraints. The main restraints for the application of sludge in energy production can be summarized as follows:

Legal framework

- more stringent emission limits
- required incineration conditions

During operation, problems are caused by

- the low calorific value and
- the emissions produced

Their improvement requires detailed knowledge of

- material properties of sludge and
- the generation of emission in sludge incineration

4 SLUDGE PROPERTIES

Knowledge of sludge properties is required to design and evaluate treatment processes. In the following their classification, water distribution, chemical composition, viscosity, density and heat capacity is described.

4.1 CLASSIFICATION

In the process of wastewater treatment, the following types of sludge are distinguished:

Primary Sludge

Primary sludge is a mixture of solids separated from the wastewater during the primary clarification and contains approximately 4-5 % of solids. Primary sludge, in contrast to other types of sludges, has a fibrous and granular structure which in general eases water retention. However, the high organic content and biological degradability causes odor problems and complicates its sole processing.

Activated Sludge

Activated sludge is a mixture of microorganism generated in the biological treatment. It contains 0.5-1.5 % of solids and can be subdivided in waste activated sludge and recycle activated sludge. Waste activated sludge is thickened to a solids concentration of 2-6 % and subsequently mixed with primary sludge.

Mixed Primary Sludge

The mixture of waste activated and primary sludge represents mixed primary sludge (MPS), which accumulates in the wastewater treatment. Its high organic concentration (approx. 70 %) requires stabilization prior to disposal.

Stabilized Sludge

Stabilized sludge contains 2.5-4 % of solids. Stabilization of sludge is accomplished using either aerobic stabilization, where heat is produced due to the injection of oxygen, or digestion (also referred to as anaerobic stabilization), where biogas is produced. Sludge that has undergone digestion is referred to as digested sludge (DS). In contrast to mixed primary sludge, the organic share in sludge solids is lower and amounts to approximately 50 % in stabilized sludge. Used temperatures and retention time also secures hygienization of sludge.

Dewatered Sludge

In order to reduce its mass, stabilized sludge is dewatered from its original solid concentration to 16-30 %. The produced centrate is pumped into the biological treatment stage where it undergoes treatment. As the produced sludge cake is subject to disposal or utilization, its mass goes along with savings in disposal costs.

4.2 WATER DISTRIBUTION

The main challenge for energy efficient sludge incineration is the high water concentration in dewatered sludge. For an energy efficient utilization a low water content is desired, as the water contained in sludge leads to a low efficiency of the incineration. Thus, the increase of total solid concentration holds the key role to enhance the energy production of incineration.

Water can be divided in four groups according to a simple model shown in Figure 11:

- Free and interspace water
- Capillary water (bound)
- Adsorption water (bound)
- Inner water (bound)

The biggest share of water in sludge material is the water in sludge suspension which is not bound to particles (free and interspace water). Free and interspace water can be removed by means of gravitation or filtration. Thus, the total solid concentration by means of dewatering depends on the amount of free water. However, the attainable concentration of total solids, depends on the amount of bound water, which can only be removed by drying or improved pre-treatment.

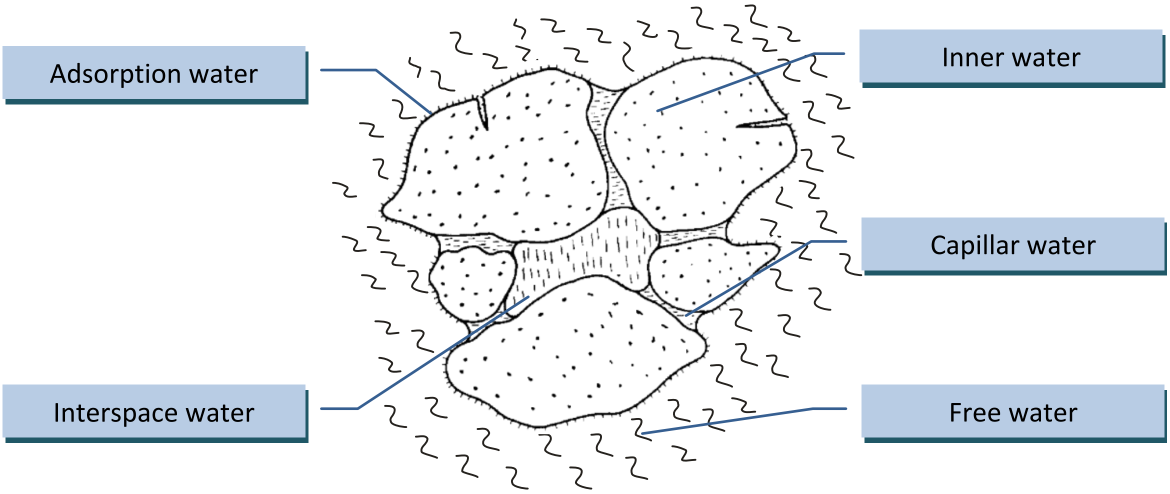


Figure 11 Water distribution in bulk material [42]

Drying processes are very energy consuming as the sludge needs to be heated up to the evaporation point and the water contained in sludge evaporated. The energy consumption in sludge drying processes is mainly caused by latent heat, necessary for water evaporation.

To enhance the total solid concentration after dewatering, several measures can be considered:

1. Increasing the temperature of dewatering

   The increase in temperatures reduces the viscosity of sludge and improves the settling velocity of sludge. The temperature should not exceed 70 °C as higher temperatures could decrease the effectiveness of available flocculants.

2. Disintegration of sludge

   The ratio between free and bound water is shifted towards free water, which can be removed by dewatering. The amount of biogas production can be expected to rise if disintegration is applied prior to anaerobic digestion.

3. Sludge drying

   Due to its high energy consumption, sludge drying is preferably performed using waste heat or dryer technologies requiring only small proportion of fossil energy.

4. Optimization regarding the dewatering flocculant

   Optimization regarding the type of flocculant and its dosage can lead to an increase in total solid concentration. The amount of flocculant however, has a bigger influence on the quality of centrate than the final solids content [15]. Thus, as the improvement is in most cases a result of earlier neglect and the potential of available flocculants is limited, this will not be subject of later considerations.

4.3 COMPOSITION

Sludge solids are composed of different organic and inorganic material, which makes it difficult to predict its properties.

The major element in the organic material is carbon, which accounts for approximately 53 to 67 %. Depending on the type of sludge, the elementary composition of volatile sludge solids differs as shown in Table 2. The organic fraction is build up on a large number of substances (proteins, fats and cellulose). The ash fraction contains a considerable amount of silicon. Further, the metals iron and aluminium, and the nutrients calcium, magnesium, phosphorus, potassium are contained. Table 3 shows the concentrations of ash forming elements in sludges from four WWTPs in the Czech Republic. The values represent mean concentrations determined in sludges from four WWTPs. Sludge contains different trace substances as it is the pollutant sink in wastewater treatment. Depending on the origin, different heavy metals and organic pollutants: dioxins and furans, polycyclic aromatic hydrocarbons, polychlorinated biphenyls are contained in the sludge solids.

Table 2 Typical composition of volatile sludge solids [34]

	Primary Sludge	Activated Sludge	Mixed Primary Sludge	Stabilized Sludge
Volatile substances in dry solids [%]	65	75	70	50
Carbon [%]	60.0	53.0	57.0	67.0
Hydrogen [%]	7.5	7.0	7.0	5.0
Oxygen [%]	28.0	30.5	30.0	25.0
Nitrogen [%]	3.0	9.0	5.0	2.2
Sulfur [%]	1.5	0.5	1.0	0.8

Table 3 Concentration of ash forming elements in ashes of digested sludge [43]

Si	Al	Fe	Ca	Mg	Ca	K	P
16.0 %	11.9 %	9.0 %	10.9 %	5.2 %	0.33 %	1.27 %	5.4 %

4.4 VISCOSITY

Since sewage sludge is a non-Newtonian liquid, the viscosity of sludge cannot be compared to water. Dynamic viscosity of sludge depends on the stress applied on the liquid while flowing. Sludge shows pseudoplastic behavior and has a yield stress. In order to cover these behaviors, an appropriate model needs to be selected in order to describe the dynamic viscosity. Among many others, a commonly used model to describe the flow behavior of sewage sludge is the Herschel Bulkley model, which is described by three model parameters. To fully describe the rheological model, the constants yield stress, consistency and power law coefficient are used as shown in equation (4-1).

$$\tau = \tau_y + k\dot{\gamma}^n \qquad Pa \qquad (4\text{-}1)$$

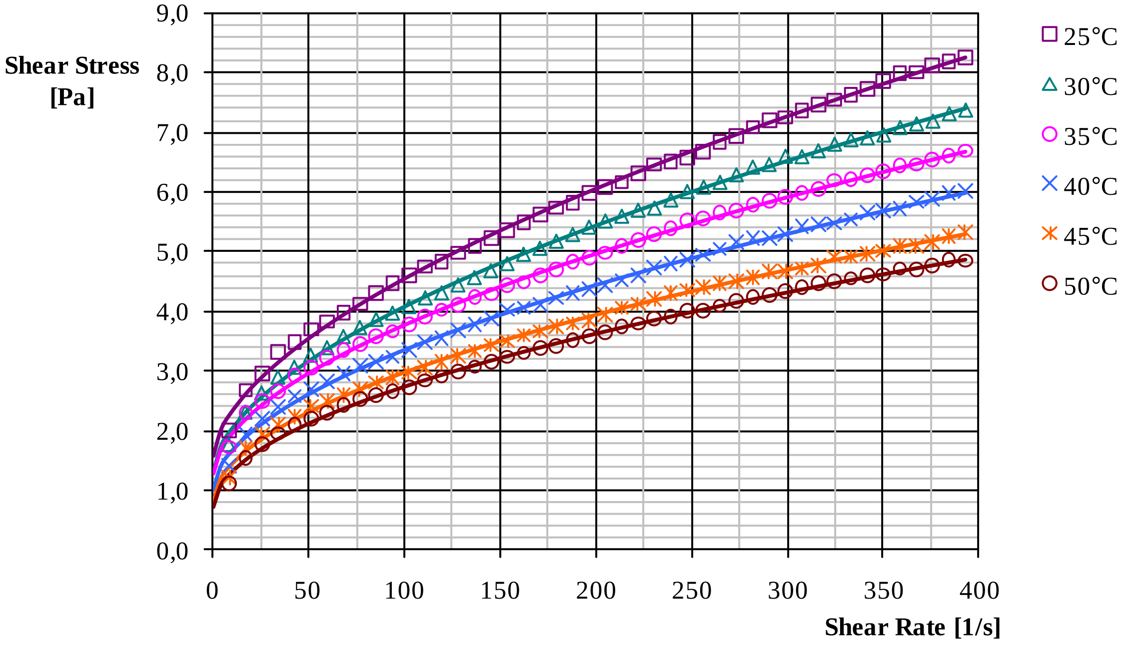
where τ = shear stress [Pa]
τ_y = yield stress [Pa]
k = consistency [Pa.s]
$\dot{\gamma}$ = shear rate [s^{-1}]
n = power law coefficient [-]

The viscosity is defined as the ratio of shear stress and shear rate as shown in equation (4-2).

$$\eta = \frac{\tau}{\dot{\gamma}} \qquad Pa.s \qquad (4\text{-}2)$$

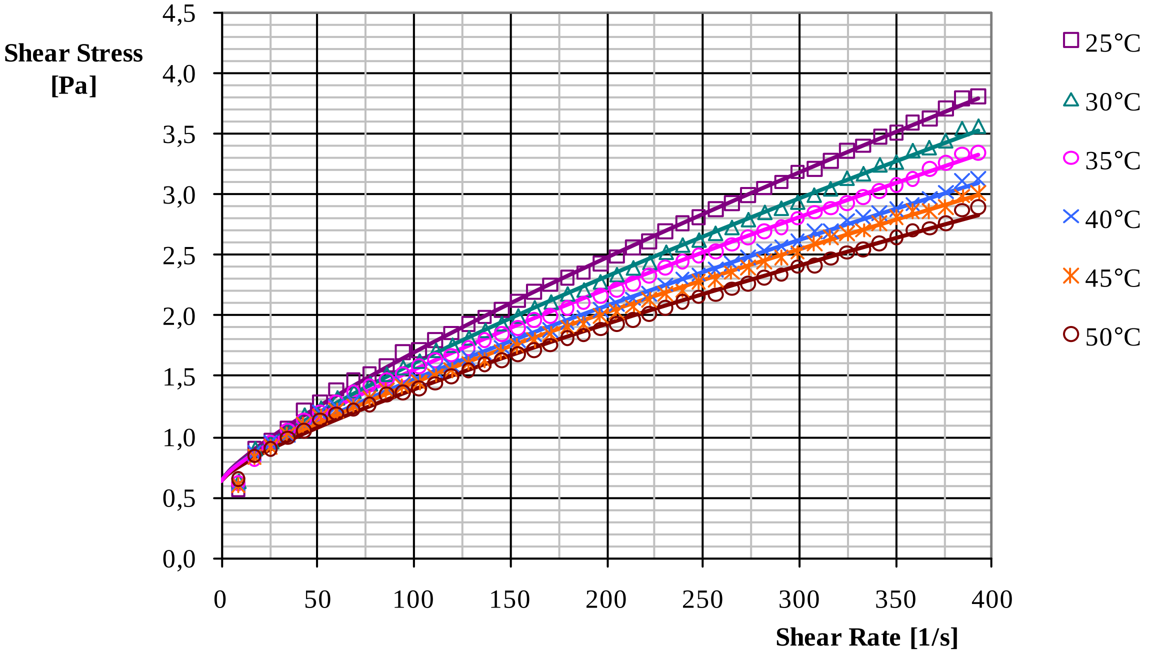
where η = dynamic viscosity [Pa.s]
τ = shear stress [Pa]
$\dot{\gamma}$ = shear rate [s^{-1}]

The flow behavior of sludge is commonly displayed in rheograms. Rheograms of mixed primary and digested sludge are shown in Figure 12 and Figure 13, respectively. From these figures it is easy to read, that shear stress and thus the viscosity of sewage sludge falls with increasing temperatures. The measured shear stress values of digested sludge are, in comparison with mixed primary sludge, lower and the underlying Herschel Bulkley model is unapparent from the plot. Compared to digested sludge, shear stress of mixed primary sludge varies in a wider range. It is approximately twice as wide as for digested sludge and the temperature dependence of mixed primary sludge is bigger compared to digested sludge.



Note: Sludge samples from the WWTP in the City of Opava; TS=2.1 %

Figure 12 Rheogram of mixed primary sludge for various temperatures



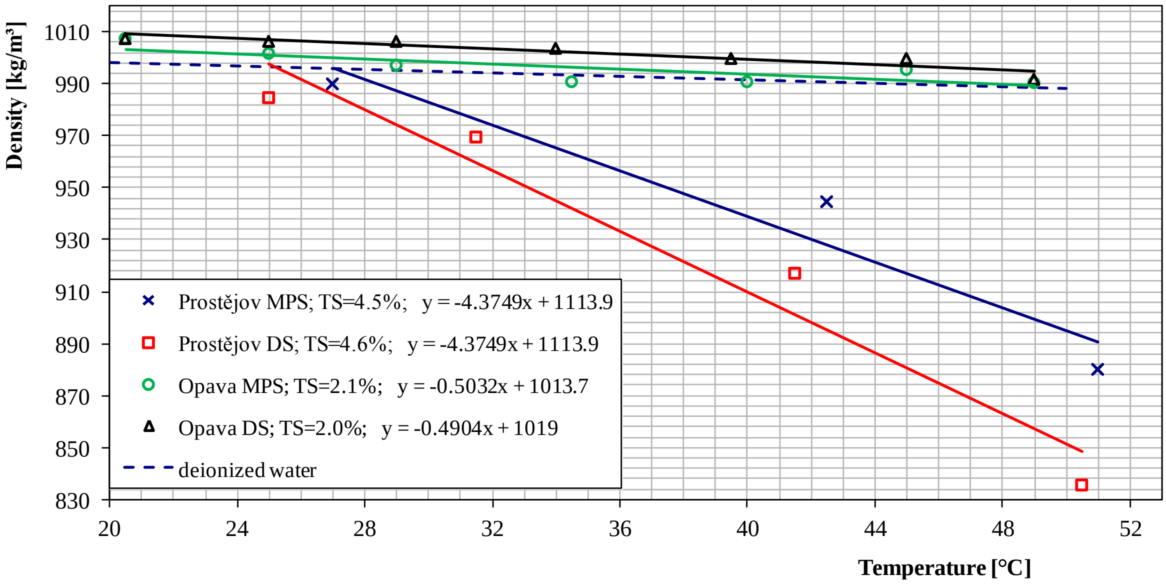
Note: Sludge samples from the WWTP in the City of Opava; TS=2.0 %

Figure 13 Rheogram of digested sludge for various temperatures

4.5 DENSITY

The density of sludge is preferably determined using a wide-neck pycnometer. This method holds an advantage over measurements using areometer or small-neck pycnometer. In density measurements the most serious mistake is caused by air bubbles that are generated at temperatures higher than 35 °C. By stirring the sample, trapped air bubbles are released from the sample and the density can be determined properly.

The density of sludge basically depends on the type of sludge. It was found, that mixed primary sludge has a lower density than digested sludge in general. However, depending on the origin of sludge this generalization can also be vice versa. In Figure 14, the temperature dependency of sludge density is shown for various sludges containing an average TS concentration of 4.6 % (sludge samples from the WWTP in Prostějov) and 2.1 % (sludge samples from the WWTP in Opava).



MPS: mixed primary sludge; DS: digested sludge

Figure 14 Density of various types of sludge

4.6 HEAT CAPACITY

Heat capacity is a thermodynamic quantity that describes the ability of a solid, liquid or gas to store energy. Storing energy under isobaric conditions, the temperature of the body changes. Especially the heat capacity at constant pressure is frequently used in heat balances, to calculate enthalpy and heat differences under isobaric conditions using expression (4-3), where C_p^* represents the real heat capacity [44].

$$\Delta H = \int_{T_1}^{T_2} C_p^* \ T \ dT \qquad J \qquad (4\text{-}3)$$

where
ΔH = enthalpy difference [J]
C_p^* = real heat capacity [J/K]
T = temperature [K]

Introducing the mean heat capacity at constant pressure (C_p), the expression (4-3) can be rewritten as

$$\int_{T_1}^{T_2} C_p^* \ T \ dT = C_p \ T_2 - T_1 \ , \qquad J \qquad (4\text{-}4)$$

where C_p is the mean heat capacity for a certain temperature interval specified by the temperatures T_1 and T_2. The specific heat capacity (c_p), which is the heat capacity per unit mass of a body, is used as a material property in heat balances to determine the heat, a body has stored. The term *heat capacity* used later refers to the *mean heat capacity*.

For setting up heat balances in the area of sludge utilization, awareness of the specific heat capacity (c_p) of sludge is required to calculate heat fluxes properly. Using the c_p of water instead of the c_p of sludge, provides a proper approximation for liquid sludges and is commonly used in literature such as [45], and is used to rate the heating of digestion tanks [21], [23] and [46]. However, this is not sufficient for dewatered and dried sludge, e.g. in heat balance as the share of solids is several times higher than in liquid sludge and amounts 16-30 % in dewatered sludge and 80-90 % in dried sludge. Balancing the heat for drying and incineration of dewatered sludge, [32] uses a c_p of 1.05 kJ/(kg K) for dry sludge solids. However, for a similar application, [47] uses a c_p of 2.0 kJ/(kg K) for sludge dry solids. As the values of c_p found in literature differ considerably, determination of sludge dry solid heat capacity is discussed in the following sections.

4.6.1 Heat Capacity Estimation of Solids

Determining the heat capacity of solids can be achieved using either the Dulong-Petit rule or the Neumann-Kopp rule. Both rules are described and discussed in the following two sections.

Dulong-Petit Rule

Considering sludge solids to be of crystal origin, the molar heat capacity of the particular crystals under isobaric conditions can be estimated using the Dulong-Petit rule which is shown in expression (4-5), where R [$J.mol^{-1}.K^{-1}$] is the universal gas constant [43].

$$c_{v,mol} = 3 \cdot R = 3 \cdot 8.314 \frac{J}{mol \cdot K} \approx 25 \frac{J}{mol \cdot K} \qquad (4\text{-}5)$$

The molar heat capacity at constant pressure can be estimated as follows [48]:

$$c_{p,mol} \approx 27 \frac{J}{mol \cdot K} \qquad (4\text{-}6)$$

The rule however provides only a first, rough estimation, as it turned out to be more a rule of thumb than a principle. Secondly, the rule is valid for high temperatures only. However, this circumstance can be considered to be fulfilled in the vicinity of room temperature.

The flaw in accuracy of the Dulong-Petit rule becomes evident comparing measured heat capacities ($c_{p,mol}$) of silver: 25.3 J/(mol K) and diamond: 6.7 J/(mol K) at 25°C. Due to its strong interatomic bonds, diamond has a lower heat capacity than silver and differs from the value determined by the Dulong-Petit rule.

The rule gives a first estimate of the molar heat, even if no further information on the solid is given. However it is impractical to apply on sludge solids, as the desired quantity is the mass based heat capacity, the molar weight of dry sludge would be required.

Due to its uncertainties and difficulties determining the mass based heat capacity, the Dulong-Petit rule was not pursued any further.

Neumann-Kopp Rule

The rule derives the heat capacity for a compound from the substances it is formed of, as it would be in a chemical reaction [49]: The general chemical reaction (4-7)

$$a\mathrm{A}(s)+b\mathrm{B}(s)\rightarrow \mathrm{A}_a\mathrm{B}_b(s)\,, \tag{4-7}$$

provides the molar heat capacity according to the Neumann-Kopp rule (NKR) as follows:

$$a\;\mathrm{c}_{\mathrm{p,mol}\;\mathrm{A}}+b\;\mathrm{c}_{\mathrm{p,mol}\;\mathrm{B}}=\mathrm{c}_{\mathrm{p,mol}\;\mathrm{A}_a\mathrm{B}_b}\,. \tag{4-8}$$

Thus, using $c_{p,mol}$ from [50], the heat capacity of the alloy $CuAl_2$ at 400 K can be calculated as follows:

$$2\mathrm{Al}+\mathrm{Cu}\rightarrow \mathrm{CuAl}_2 \quad \Rightarrow \quad 2\cdot 25.5+25.2=76.2\frac{J}{mol\cdot K} \tag{4-9}$$

Comparing the calculated $c_{p,mol}$ for $CuAl_2$ (76.2 J/(mol K)) with data from [50] (76.3 J/(mol K)) shows good fitness of the NKR for this example using inorganic components.

Yet, Kopp recommended to use lower values for several elements (B, C, P, S or Si), which were measured or derived from substance data with similar elementary composition [49].

Using the specific heat capacity instead of the molar heat capacity, the NKR and equation (4-8) can be rewritten, and the specific heat capacity of sludge is calculated from the mixtures' specific heat capacities $c_{p,i}$ multiplied by its mass fraction ω_i as shown in expression (4-10) [48] and [51].

$$\mathrm{c}_p=\sum_{i=1}^{N}\mathrm{c}_{p,i}\cdot\omega_i \qquad \left[\frac{J}{kg\cdot K}\right] \tag{4-10}$$

For liquid sludge, the NKR offers a simple method to determine the heat capacity of sludge based on the heat capacity of its compounds (water and dry sludge solids). Thus, the c_p of sludge, depending on the water content, can be calculated from the heat capacity of water and dry sludge determined in the following sections.

4.6.2 Evaluation Based on Experiments

Due to the lack of proper c_p values of sludge solids, the specific heat capacity was determined experimentally by calorimetry using the calorimeter shown in Figure 15. The general measurement procedure can be described as follows: A certain amount of water at a known temperature is in equilibrium with the calorimeter vessel. Both, water and calorimeter are in equilibrium with ambient temperature. A second substance at known, but different temperature is added to the calorimeter in order to induce a change in temperature on the mixture of both substances. As the substances have come to equilibrium, the temperature of the mixture is measured. Using two substances of known specific heat capacity or one substance of known specific heat capacity allows to either determine the calorimeter constant (C_{cal}) or the specific heat capacity of one substance.

Figure 15 Experimental setup for heat capacity measurement

Calorimeter Constant Determination

Expression (4-11) shows the energy balance describing the calorimeter method for mixtures. Based on which, both, the calorimeter constant and the specific heat capacity of sludge can be determined.

$$\Delta Q = \ m \cdot c_p + C_{cal} \ \cdot \Delta T \qquad J \qquad (4\text{-}11)$$

Inducing ΔQ from equation (4-11) using a second substance, the calorimeter’s heat constant (C_{cal}) is determined experimentally using the expression (4-12),

$$C_{cal} = m_2 \cdot c_{p,2} \cdot \frac{T_m - T_2}{T_1 - T_m} - \ m_1 \cdot c_{p,1} \qquad \left[\frac{J}{K}\right] \qquad (4\text{-}12)$$

where the indices are used as follows:

Index	*Substance and condition*
1	Water (in temperature equilibrium with the calorimeter)
2	Cooled water
m	Mixture of substance 1 and substance 2 (in temperature equilibrium)

The calorimeter constant had been determined using 600.0 g of water (substance 1) and 200.0 g of chilled water (substance 2). During the measurement series, the mean temperature of substance 1 was (22.79 ± 0.35) °C and (11.86 ± 0.38) °C for substance 2.

Thus determined values for C_{cal} average (0.1214 ± 0.0124) kJ/K. Determined values of the entire measurement series are shown in Figure 16. Descriptive statistics of the measurement series are included in Annex I.

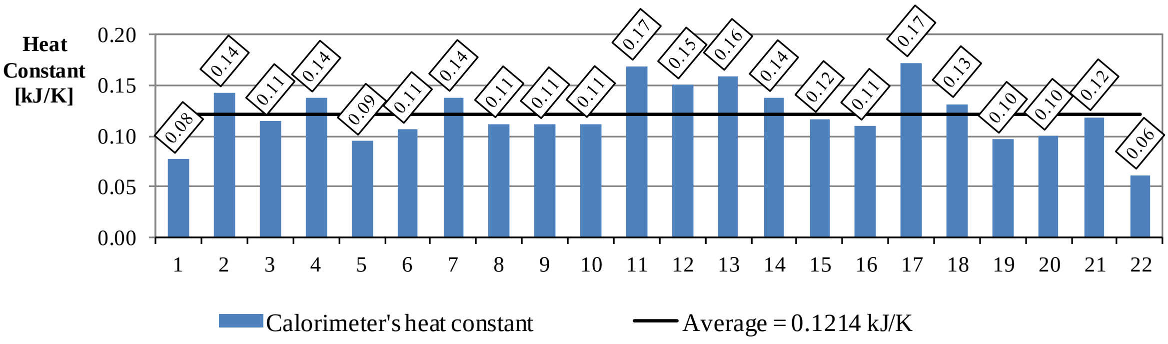


Figure 16 Determined values of calorimeter constant

Specific Heat Determination

Measuring the heat capacity of liquid sludge would be the most undemanding way to determine the specific heat capacity of sludge, as two liquids can be used. However, the accuracy of determined material property is low, as the influence of the unknown quantity (heat capacity of dry sludge solids) on the measured quantity is very small. This is due to the small amount of solids ranging from 0.5 to 6 % in liquid sludge. In order to gain higher repeatability of the measurements, dried sewage sludge was used as the amount of dry solid used within the particular measurements is higher. The dry solid concentration in sludge was 91.9 % within the conducted measurement series and an organic fraction of 0.556 was measured in dry solids.

From the law of energy conservation and expression (4-11) emerges that the heat absorbed by the water has to equal the heat dissipation of sludge. Thus, monitoring the temperature of water (T_1), the dried sewage sludge (T_2) and the mixture (T_m), the c_p of sludge can be calculated using expression (4-13).

$$c_{p,2} = \frac{\left(m_1 \cdot c_{p,1} + C_{cal}\right) \cdot \left(T_1 - T_m\right)}{\left(T_m - T_2\right) \cdot m_2} \qquad \left[\frac{J}{kg \cdot K}\right] \qquad (4\text{-}13)$$

The indices are used as follows:

Index	*Substance and condition*
1	Water (in temperature equilibrium with the calorimeter)
2	Cooled dried sludge
m	Mixture of substance 1 and substance 2 (in temperature equilibrium)

Figure 17 Measurement of specific heat capacity of sludge

Left: Sludge material used in heat capacity measurements. Right: Preparation of chilled sludge samples

The specific heat capacity of sludge was determined using 600.0 g of substance 1 (water in equilibrium with the vessel) and 200.0 g of dried sludge. During the measurement series, the mean temperature of substance 1 was (20.55 ± 0.89) °C and (5.95 ± 0.57) °C for substance 2.

The specific heat capacity of dried sludge determined in measurement series averages (1.17 ± 0.04) kJ/(kg K). Taking the water content of the used sludge sample into account, a specific heat capacity of 0.9 kJ/(kg K) in dry sludge solids is calculated using expression (4-10).

The measurement results of the conducted measurement series are shown in Figure 18. Descriptive statistics of the calculated values for specific heat capacity of dry sludge solids are included in Annex II.

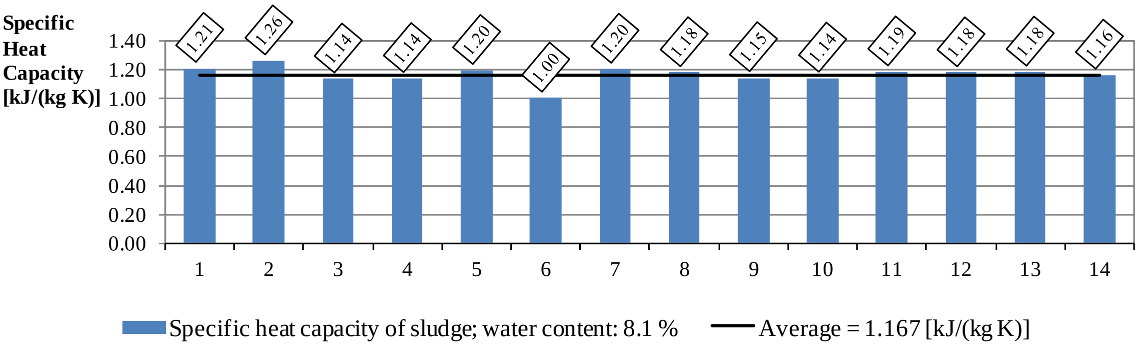


Figure 18 Measured values of specific heat capacity of dried sludge

4.6.3 Analytical Assessment

Analytical, the c_p value can be determined based on the ultimate analysis of dry sludge. However, it is necessary to distinguish between inert substances (ashes) and volatile substances as both types of substances possess a heat capacity in different vicinities. In the following, the specific heat capacities of two digested sludges (sludge A and sludge B) were analyzed. The ultimate analysis of both samples can be found in Annex III.

Estimation for Volatile Substances

The elementary composition of volatile substances contained in sludges can be determined in ultimate analysis. However, its distribution and molecular structure and thus the molar heat of the volatile substances cannot be determined. From this reason, a simplification is made and the composition of sludge is justified using three organic compounds which are likely contained in sludge solids. This permits using the specific heat capacity data of the used compounds that hypothetically form the volatile solids contained in dry sludge. Thus, the flaw, caused using c_p values of elements which are not in solid state or depend on their molecular structure (C, H, O and N), can be avoided [49]. Using the above described modification, an estimate value of the dry solid heat capacity can be calculated.

Table 4 shows the elementary, organic composition of the two analyzed sludge samples. Although the composition of both samples differs significantly, both samples represent digested sludge. The content of sulfur and chlorine contained in the samples amounted to 1.05 % or less and thus, was neglected.

Table 4 Composition of volatile substances used for c_p-determination

	SLUDGE A *[%]*	SLUDGE B *[%]*
Volatile substances	52.36	31.39
Carbon	64.41	49.50
Hydrogen	8.07	7.10
Oxygen	20.25	43.33
Nitrogen	7.28	0.06

Based on the composition shown in Table 4, different substances were tested to find the chemical composition that represents the elementary composition of both sludge samples. Independently, a combination of the following three substances was found most suitable:

- Dextrin $C_6H_{10}O_5$ a degradation product of starch,
- Palmitic acid $C_{16}H_{32}O_2$ a typical fatty acid and
- Melamine $C_3H_6N_6$ a nitrogen carrier resp. organic base.

In order to represent the elementary composition of the real samples at the best, the optimum share of each of the three components for the hypothetical mixture was determined. The determined concentration of dextrin, palmitic acid and melamine in the hypothetical samples is given in Table 5.

Table 5 Composition of hypothetical samples used for c_p-determination

	SLUDGE A *[%]*	SLUDGE B *[%]*
Palmitic acid	67	16
Dextrin	23	84
Melamine	10	0

Figure 19 shows the chemical composition of the real and hypothetical samples. The composition is normalized to 100 %.

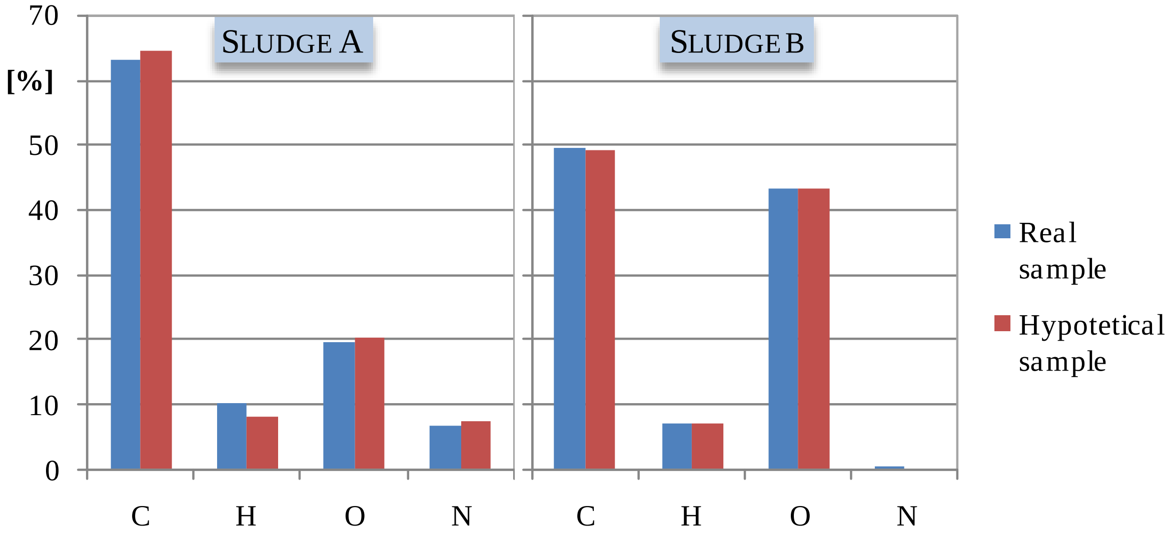


Figure 19 Components contained in sludge solids and model compounds

By using expression (4-10), and c_p of each component, the specific heat capacity of the hypothetical samples can be calculated. For the calculation, values given in the Annex IV were used for dextrin, palmitic acid and melamine. Determined specific heat capacities of volatile dry solid at 20 °C amount to 1.65 kJ/(kg K) in sludge A and 1.38 kJ/(kg K) in sludge B.

Determination for Inorganic Substances

The specific heat capacity of inorganic substances (ashes) contained in sludge can be calculated using the NKR and the ash composition determined in ultimate analysis.

Due to the availability of c_p data, the original ash composition of the original sludge samples - as it is given in Annex III - had to be changed for the c_p determination and is shown in Table 6.

The following amendments were made:

- SO_3 and K_2O form K_2SO_4. The stoichiometric surplus of either one of the compounds is neglected and
- two mole of P_2O_5 form one mole of P_4O_{10}.

Table 6 Composition of inorganic substances used for c_p-determination

	SLUDGE A *[%]*	SLUDGE B *[%]*
Ashes	47.64	68.61
SiO_2	38.12	41.92
Fe_2O_3	23.14	13.39
MnO	0.10	-
Mn_3O_4	-	0.18
Al_2O_3	11.29	13.86
TiO_2	0.88	0.96
CaO	15.32	16.74
MgO	2.26	2.70
Na_2O	0.73	0.70
K_2SO_4	1.07	3.95
P_4O_{10}	7.10	5.60

Using expression (4-10), and c_p values of the ash components, the specific heat capacity of the hypothetical samples can be calculated. For its determination, data given in Annex IV was used. Thus, the specific heat capacity of inorganic solids calculated at 20 °C amounts to 0.72 kJ/(kg K) in sludge A and 0.74 kJ/(kg K) in sludge B.

Recapitulation

Using the above mentioned analytical method gives an estimate value for the c_p of volatile substances. Due to the unclear presence of compounds in volatile substances, the composition has to be estimated and thus, the analysis results in an estimate value. The c_p of inorganic substances contained in sludge can be calculated based on the Neumann-Kopp rule using available data for the respective compounds.

Values determined for the c_p of ashes are in very good agreement for both sludge samples. The values of volatile substances are in same vicinity but vary from each other due to the different content of nitrogen and oxygen.

Table 7 Analytically determined specific heat capacity

	SLUDGE A *[kJ/(kg K)]*	SLUDGE B *[kJ/(kg K)]*
Volatile substances	1.65	1.38
Ashes	0.72	0.74
Total solids	1.21	0.94

Assuming that the elementary composition of volatile substances and ashes is comparable within its group, allows to conclude an expression in order to calculate the specific heat capacity of dry sludge material from the share of volatile material. The advantage of this method is that the determination of the volatile share (determined as LOI) is less demanding than measurement of the elementary composition.

Based on the c_p analysis of sludge A and B, an average value of c_p can be calculated for the volatile and inorganic substances:

- 0.73 kJ/K per kg of ashes
- 1.52 kJ/K per kg of volatile substances

These values allow estimating the specific heat capacity of dry sludge solids as a function of the LOI according to expression (4-14),

$$c_{p,TS} = 0.79 \cdot \omega_{vs} + 0.73 \qquad \left[\frac{kJ}{kg \cdot K}\right] \qquad (4\text{-}14)$$

where $c_{p,TS}$ = specific heat capacity of total sludge solids (dry)
ω_{vs} = mass fraction of volatile solids in dry sludge

4.6.4 Discussion

Although the c_p of dry sludge solids can be found in literature, the data is not sophisticated as it is not very precise. The value stated in [32] is given by *»approximately 1.05 kJ/(kg K) for ashes and dry sludge solids«*. In contrast to this, the value used in [47] amounts to 2.0 kJ/(kg K), whereas [23] gives the same number (2.0-2.4 kJ/(kg K)) for centrifuge dewatered sludge. Values for c_p as a function of the water content and organic matter in sludge can be derived from [52] where the c_p of sludge, that consists of 80 % of solids, amounts 2.2 kJ/(kg K) for a LOI of 90 % and 1.5 kJ/(kg K) for a LOI of 10 %.

Table 8 contains an overview of values found in literature as mentioned above, as well as experimentally and analytically values determined in the sections above.

Table 8 Specific heat capacity of dry sludge solids

	DATA ORIGIN	CONDITIONS	VALUE *[kJ/(kg K)]*
Dry sludge solids and ashes	[32]	(20-900) °C	approx. 1.05
Dry sludge solids	[47]	(25-850) °C (organic fraction: 72 %)	2.0
Dry sludge solids	[52]	20 °C (organic fraction: 50 %)	1.3
Dry sludge solids	experimentally determined from dried sludge	20 °C (organic fraction: 55.6 %)	0.90 ± 0.04
Dry sludge solids Sludge A	analytically determined	20 °C (organic fraction: 52.4 %)	1.21
Dry sludge solids Sludge B	analytically determined	20 °C (organic fraction: 31.4 %)	0.95

The experimental determination of c_p of dry sludge solids using dried sludge gives repeatable results and thus, holds an advantage over the determination using liquid sludge. Recalculating the c_p of dry sludge solids from experiments conducted by the author [16] using liquid sludge result in values that were approximately a threefold of the values determined by using dried sludge. Comparing these values with values found in literature shows a higher reliability for the values determined using dried sludge samples.

Values of the specific heat capacity of sludge solids are rarely in literature, but easy to determine from an ultimate analysis of sewage sludges. However, the LOI is a regularly determined sludge characteristic and thus more available. The correlation found to calculate the specific heat capacity of dry sludge solids represents a one-parametric, linear equation, which is a function of LOI. The dependencies found with expression (4-14) are in agreement with data published in [52] and the values are in the same vicinity as values shown in Table 8. The temperature dependency of the heat capacity is hardly predictable, as the huge variety of volatile substances, possibly contained in sludge solids, makes it difficult to determine the heat capacity as a function of temperature. Even in a narrow temperature range (20-60 °C), phase transition of carbon compounds has an unpredictable impact on the value.

The composition of sludge not only complicates predicting the parameters density, viscosity and heat capacity but also its pollutants production in incineration, which is a topic of the following chapter.

5 EMISSIONS GENERATED BY SLUDGE INCINERATION

This section is devoted to experimental tests in the field of emissions generation in sewage sludge incineration. Primarily, the experiment aimed at evaluating the influence of limestone addition in sludge incineration on the generation of acidic components (hydrogen halides, sulfur dioxide). Additionally, further gaseous emissions as well as heavy metals were tracked.

In legislative terms, sludge falls into the category of waste. The incineration and the air emissions generated in sewage sludge incineration are subject to legal regulations regarding the incineration of waste [53]. The main difference between sludge incineration and conventional power generation lies in the incineration conditions and more stringent standards for air emissions, which are summarized in Table 9.

Table 9 Air emission limit values in waste incineration [53]

	354/2002 Sb. *Daily Average Limits*
Carbon monoxide	50 mg/m^3
Polychlorinated dibenzodioxins and dibenzofurans (PCDD/F) ♦	Σ 0.1 ng TEQ/m^3
Gaseous and vaporous organic substances (total organic carbon)	10 mg/m^3
Heavy metals As, Co, Cr, Cu, Mn, Ni, Pb, Sb, V and their compounds ♣	Σ 0.5 mg/m^3
Heavy metals Cd, Tl and their compounds ♣	Σ 0.05 mg/m^3
Heavy metal Hg and its compounds ♣	0.05 mg/m^3
Inorganic chlorine and its compounds expressed as HCl	10 mg/m^3
Inorganic fluoride and its compounds expressed as HF	1 mg/m^3
NO_x expressed as NO_2 for existing incineration plants exceeding a capacity of 6 tonnes per hour or new incineration plants	200 mg NO_2/m^3
NO_x expressed as NO_2 for existing incineration plants with a capacity of 6 tonnes per hour or less	400 mg NO_2/m^3
Sulfur dioxide (SO_2)	50 mg/m^3
Total dust	10 mg/m^3

Note: Concentrations are given at normal conditions (101.325 kPa and 0 °C) and 11 vol.% oxygen in dry exhaust gas

♦ Sample period: 6-8 hours

♣ Sample period: 0.5-8 hours

5.1 GENERATION OF AIR EMISSIONS

In waste incineration, the acidic components (hydrogen halides and sulfur dioxide) contained in flue gas are often removed in wet scrubbers, where the neutralization agent is either calcium or sodium hydroxide. The expressions (5-1) to (5-4) show the neutralization reactions of sulfur dioxide and hydrogen chloride in a single stage wet scrubber using sodium hydroxide:

$$2NaOH\,(aq) + SO_2 \rightarrow Na_2SO_3 + H_2O \tag{5-1}$$

$$2NaOH\,(aq) + SO_2 + \tfrac{1}{2}O_2 \rightarrow Na_2SO_4 + H_2O \tag{5-2}$$

$$NaOH\,(aq) + HCl \rightarrow NaCl + H_2O \tag{5-3}$$

Dry flue gas cleaning refers to the use of dry chemicals which are usually lime or bicarbonate. These methods are particularly suitable for fluidized bed incineration. The use of sodium bicarbonate in flue gas treatment is also referred to as BICAR-process, which is applied in flue gas treatment of the industrial sludge incineration plant Slovnaft in Bratislava, Slovak Republic. Sodium bicarbonate reacts under the influence of heat to sodium carbonate:

$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2 \tag{5-4}$$

The resulting sodium carbonate binds sulfur dioxide and gives sodium sulfite and sodium sulfate:

$$Na_2CO_3 + SO_2 \rightarrow Na_2SO_3 + CO_2 \tag{5-5}$$

$$Na_2SO_3 + \tfrac{1}{2}O_2 \rightarrow Na_2SO_4 \tag{5-6}$$

Further, hydrogen fluoride and chloride give sodium chloride and sodium fluoride:

$$Na_2CO_3 + 2HCl \rightarrow 2NaCl + CO_2 + H_2O \tag{5-7}$$

$$Na_2CO_3 + 2HF \rightarrow 2NaF + CO_2 + H_2O \tag{5-8}$$

The treatment costs of flue gas produced in waste incineration is very demanding due to different and fluctuating pollutants concentration in waste fuel. Within the frame of this thesis, emissions emerging from the incineration of sludge are investigated.

5.1.1 Oxygen (O_2)

The oxygen concentration in flue gas has its origin in the excess air supplied to the reactor. It serves as process parameter and thus, is measured continuously. The European Directive on Waste Incineration [26] demands pollutants' concentration at a certain flue gas condition. For the incineration of solid waste, the Directive requires concentrations to be given at temperature 273.15 K, pressure 101.3 kPa and 11 vol.% oxygen in dry gas.

As the given oxygen concentration regards the pollutants' reference condition but not the required oxygen excess for the incineration, the concentrations at the standard percentage oxygen concentration are calculated using equation (5-9).

$$E_S = \frac{21 - O_S}{21 - O_M} \cdot E_M \tag{5-9}$$

where E_S = emission concentration at the standard percentage oxygen concentration [mg/m_N^3]
E_M = measured emission concentration [mg/m_N^3]
O_S = standard oxygen concentration [vol.% in dry gas]
O_M = measured oxygen concentration [vol.% in dry gas]

5.1.2 Carbon Monoxide (CO)

High concentration of carbon monoxide (CO) in flue gas is the result of insufficient burnout and can be avoided either intensifying the mixture of flue gas or increasing the temperature in the riser or the air excess.

The CO concentration highly depends on the dimensions of the incinerator and location of the flue gas probe. Sänger [54] showed for a 9 m BFB reactor, that a mixing element in the riser reduces the CO concentration from 270 mg/m^3_N to less than 50 mg/m^3_N at 6 vol.% oxygen in dry gas, where the flue gas was probed from the center of the reactor. For a 15 m high CFB reactor, Leckner [55] measured a concentration of less than 5 mg/m^3_N at 6 vol.% oxygen in dry gas. Here, the flue gas was probed downstream the cyclone and had undergone intense mixing.

5.1.3 Nitrogen Compounds

In incineration technology, nitrogen emissions comprise of nitrogen containing oxides, mainly nitric oxide (NO), nitrogen dioxide (NO_2) and nitrous oxide (N_2O) and are formed during incineration from nitrogen and oxygen. Although all species contribute to NO_x concentrations, the species should be distinguished in NO_x and N_2O and evaluated separately as their formation mechanisms and effects on the atmosphere are different. The distinction is also made in legislation on flue gas limits for the incineration of waste. The European Directive on the Incineration Waste [26] as well as the national Czech regulation 354/2002 [53] require NO_x emission to be given for NO and NO_2.

Nitrogen Oxides (NO_x)

Of all NO_x compounds, nitrogen monoxide (NO) and nitrogen dioxide (NO_2), from which NO outweighs massively, are the most important in combustion technology. The sources of NO can be described by the mechanisms formation out of fuel nitrogen, thermal formation and prompt formation.

The formation of NO is related to the nitrogen content in fuel. Fuels, rich in nitrogen tend to produce higher NO concentrations. In comparison to coal, which contains approximately 1-2 % of nitrogen in the volatiles, sludge contains 2-5 % and thus counts among the fuels containing high amount of nitrogen. The high content of fuel nitrogen concludes in high NO_x emissions. The conversion rate of fuel nitrogen into NO nitrogen depends on the combustion conditions such as air excess ratio, temperature and the nitrogen concentration in the gas phase. The conversion of nitrogen to NO can be reduced by primary measures such as air staging [54], [55] and [56].

In thermal formation, molecular nitrogen from the air reacts with oxygen radicals, which are formed at temperatures above 1300 °C. The reaction forms NO and atomic nitrogen. As the reaction highly depends on the combustion temperature as obvious from Figure 20, the influence of thermal NO formation remains considerably low by selecting a suitable incineration temperature. For sludge incineration, the fluidized bed technology allows temperatures as low as 850 °C (limited by legal requirements [26]).

Prompt NO is formed at the flame-gas interface, where atmospheric nitrogen reacts with hydrocarbon to fixed nitrogen compounds, which become further oxygenated to form NO. The influence of prompt NO_x on the total NO_x emissions is very small and is estimated to amount less than 10 ppm in pulverized coal combustion [57].

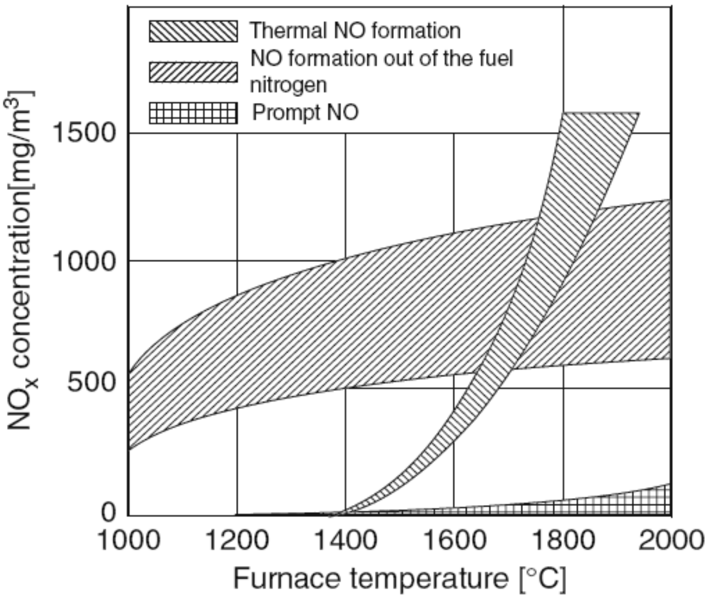


Figure 20 NO emissions in coal combustion (Zelkowski 2004) from [57]

Nitrous Oxide (N_2O)

Nitrous Oxide (N_2O) is a colorless gas, which is expected to nowadays overweigh the ozone depletion of singular chlorofluorocarbons [58]. Nevertheless it is not yet regulated by international agreements, protocols or treaties.

The amount of Nitrous Oxide (N_2O) emerging from sludge incineration is considerably low compared to NO. Shimizu [56] found the volumetric concentration of NO_x ($NO+NO_2$) to be a fivefold of the N_2O concentration. However, low incineration temperatures, suitable for NO_x reduction, have the reverse effect on N_2O reduction. Thus, the concentration of N_2O in the flue gas, decreases with increasing temperature as verified by [54] and [59].

5.1.4 Sulfuric Compounds

Sulfur dioxide (SO_2) is formed during incineration from oxygen and sulfur contained in sludge volatiles. The volatile sulfur is converted to SO_2 and in oxidizing conditions transferred partially to SO_3. This means that in contrast to nitrogen compounds, the concentration of SO_2 in flue gas can be estimated from the proximate and ultimate analysis of sludge.

In fluidized bed combustion, SO_2 can be easily reduced using dry desulfurization by the addition of limestone into the reactor. The ongoing decarbonization process is described by reaction (5-10).

$$CaCO_3 \rightarrow CaO + CO_2 \tag{5-10}$$

And triggers the reaction of quicklime and sulfur oxides (5-11) and (5-12)

$$2CaO + 2SO_2 + O_2 \rightarrow 2CaSO_4 \tag{5-11}$$

$$CaO + SO_3 \rightarrow CaSO_4 \tag{5-12}$$

where sulfur oxides are bound to calcium as $CaSO_4$, in solid phase.

5.1.5 Hydrogen Halides (HCl and HF)

Halogens, contained in sewage sludge, are mainly represented by chlorine and fluorine as shown in Table 12. Under incineration conditions, halogens contained in sludge are bound to hydrogen as hydrogen chloride (HCl) and hydrogen fluoride (HF). Thus, most of chlorine and fluorine can be found in the flue gas.

Calcium oxide, formed in reaction (5-10), reduces HCl and HF emissions. CaO reacts with hydrogen halides contained in flue gas as shown by reaction (5-13) and (5-14). The equilibrium concentration of HCl in equation (5-14) highly depends on the temperature [60], and rises with increasing temperature.

$$CaO + 2HF \rightarrow CaF_2 + H_2O \tag{5-13}$$

$$CaO + 2HCl \rightarrow CaCl_2 + H_2O \tag{5-14}$$

5.1.6 Persistent Organic Pollutants – POPs

Within the field of incineration technology, persistent organic pollutants (POPs), refer to the following three substances: polychlorinated dibenzodioxins and polychlorinated dibenzofurans (short form 'dioxins and furans', or PCDD/F), polycyclic aromatic hydrocarbons and polychlorinated biphenyls.

Dioxins and Furans

The term 'dioxins and furans' (PCDD/F) describes certain types of chlorinated carbon rings, which can be found in air, soil, sediments and food. The main contribution to the environment comes from the following sources: [61]

- Incineration of waste (municipal and medical),
- Forest fires and residential wood burning,
- Land application of sewage sludge and
- Coal fired power plants.

PCDD/F are formed from chlorine and organic carbon, whereas the formation can be catalyzed by metal-ions. The formation of dioxins is suppressed by SO_2 contained in hot flue gases as it reduces chlorine in the presence of water vapor as shown in expression (5-15).

$$SO_2 + H_2O + Cl_2 \rightarrow SO_3 + 2HCl \tag{5-15}$$

As a byproduct in incineration processes, the formation occurs at temperatures between 300 °C and 600 °C. Temperatures of 900 °C and above result in the temporary destruction of dioxins. During the cooling of flue gases to the formation temperature, dioxins are partly regenerated [62].

Due to their toxic, persistent and bioaccumulative properties, PCDD/F are subject to regulations and their release is restricted by threshold limits. The emission limits of dioxins and furans are given as mass rated toxicity equivalent (TEQ), which is determined as product of the individual PCDD/F concentration and its toxic equivalence factor (TEF). The factors of regulated PCDD/Fs are given in Annex I of the European Directive on Waste Incineration [26]. The total emission limit for PCDD/F amounts to 0.1 ng TEQ/m_N^3 representing the sum of individual TEQs.

Polycyclic Aromatic Hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) are formed as a byproduct of fuel combustion and are the result of partial combustion, which makes them omnipresent in the environment. As they are known to be carcinogenic, mutagenic and teratogenic, their prevention is of concern for environmental protection. From the hundreds of existing PAHs, the U.S. Environmental Protection Agency (USEPA) listed 16 of them as 'priority pollutants', which are nowadays analyzed in lieu of the substance group.

Polychlorinated Biphenyls

Polychlorinated biphenyls (PCBs) were produced from the late 1920s until the late 1970s [63] and found technical application in electrical systems (transformer oil and capacitors) and in plastics as flame retardants. Nowadays, PCBs are produced as byproducts in the burning of wastes from the industrial and municipal sector.

PCBs count among the family of chlorinated hydrocarbons and, in contrast to PAHs and PCDD/Fs, PCBs have a general chemical formula. The 10 isomers of PCB correspond to the general chemical formula $C_{12}H_{10-n}Cl_n$, where n ranges from 1-10. There are, depending on the arrangement of chlorine atoms, 209 PCB substances which are assigned a congener number (1-209). Due to their chemical structure, several congeners show dioxin-like properties. These congeners are classified as dioxin-like PCB (dl-PCB) and comprise the congeners 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169 and 189. In recent years, the effects of PCBs on health and environment are well investigated and PCBs (especially dl-PCBs) are accepted to be carcinogenic in animals and probable in humans.

5.1.7 Heavy Metals

The term heavy metals is often used for metals which exceed a certain density and are linked to toxicity or contamination. The borderline however, was never defined by an authorized body. Thus, several borderline densities, ranging from 3.5 to 7 g/cm^3 were used over the last decades. In legal terms of air pollution control of the European Community [26], heavy metals include: As, Cd, Co, Cu, Cr, Hg, Mn, Ni, Pb, Sb, Sn, Tl, V and Zn.

5.1.8 Reduction of Air Emissions

In order to fulfill the emission limits set by legislation, a tailored multiple-stage flue gas treatment is required, where the individual pollutants are removed from the flue gas stream. Table 10 shows the basic treatment methods used in pollution control.

Table 10 Overview of flue gas treatment for pollution control; based on [64]

POLLUTANT	TREATMENT
Dioxins and Furans (PCDD/F)	Primary measures Adsorption Catalytic and oxidative destruction
Fly ash	Filtration, electrostatic precipitation
Gaseous heavy metals (such as Hg)	Absorption, adsorption
Hydrogen halides (HF, HCl)	Chemical absorption
Nitric oxide (NO_x)	Primary measures Non-catalytic reduction (SNCR) Catalytic reduction (SCR)
Particle bound and partly gaseous heavy metals (such as Cd)	Filtration, absorption, adsorption
Particle bound heavy metals (such as Zn, Pb)	Filtration
Sulfur dioxide (SO_2)	Chemical absorption

5.2 METHODS AND MATERIALS FOR EMISSIONS EVALUATION

Within the frame of this thesis, the generation of emissions from the incineration of dried municipal sludge has been evaluated, and the influence of calcium oxide on the generated emission was investigated. The experiments have been conducted at the Czech Academy of Science in cooperation with the Institute of Process and Chemical Fundamentals.

5.2.1 Experimental Fluidized Bed Apparatus

The fluidized bed reactor consists of a cylindrical riser (1), which is 93.6 mm in diameter and 980 mm in height. It is separated by the gas distributor (2) from the windbox (3). The reactor tube, which accommodates the riser and windbox, is coated with electrical heating panels (4) to provide adequate incineration temperatures also for low calorific fuel. Dried sludge from the fuel hopper (5) is dosed by the slide feeder (6) into the pneumatic transport tube (7). Carrier gas transports the sludge particles into the fluidized bed (8). Preheated combustion air (inlet air) is supplied under the gas distributor (2) and ensures fluidization of the bed material and air excess for the combustion. Feeding of fuel results in growth of the fluidized bed (8). As the bed height reaches the overflow hopper (9), particles contained in the upper layer of the bed leave the reactor and are collected in the ash collector (not depicted). The amount of fuel can be adjusted by diameter variation of the feeding pockets or by changing the time interval of the slide feeder. Thermocouples, which are placed in protection tubes, are used to measure the temperatures of the incineration process. Temperatures in the fluidized bed (10a), the freeboard (10b), in the head of the reactor (10c) and under the gas distributor (11) are measured. The composition of the flue gases in the reactor can be measured using a height adjustable tube (12). Coarse ash is separated from the flue gas stream by cyclone (13) and collected in the ash hopper (14). The flue gas leaves the system through the hot exhaust at (14) and enters the flue gas test section (not depicted; described in section 5.2.5). The reactor is constructed of high alloy CrNi steel, which is heat resistant up to 1100 °C.

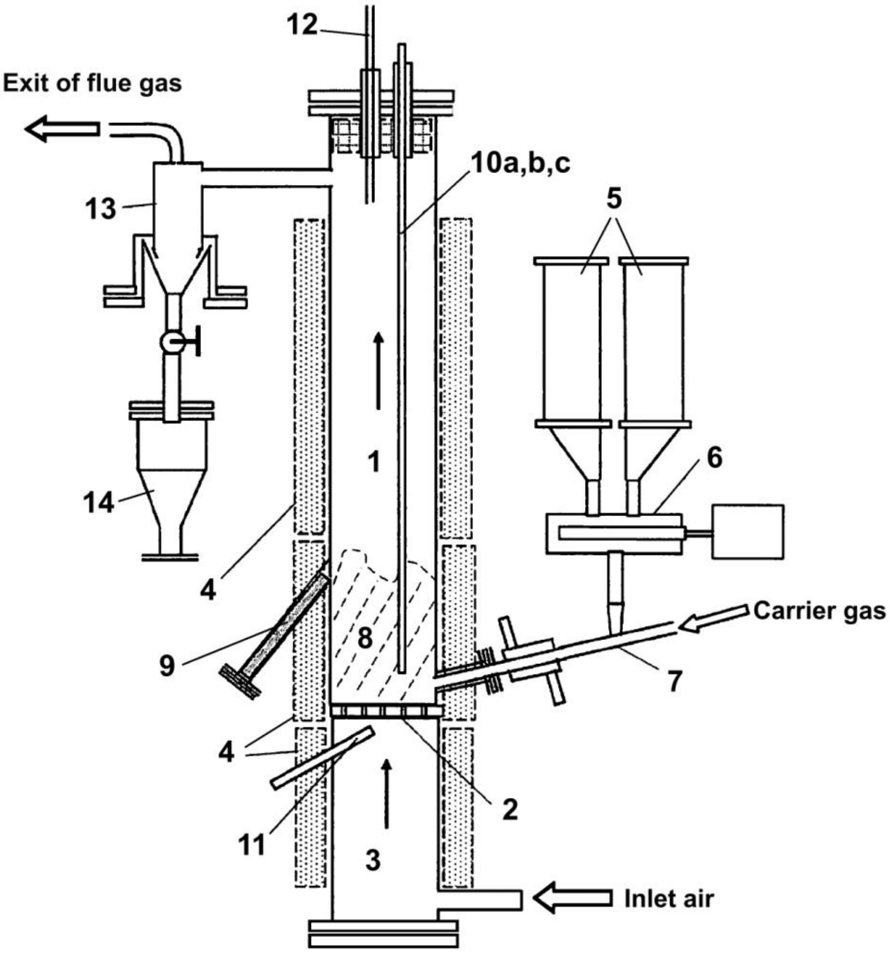
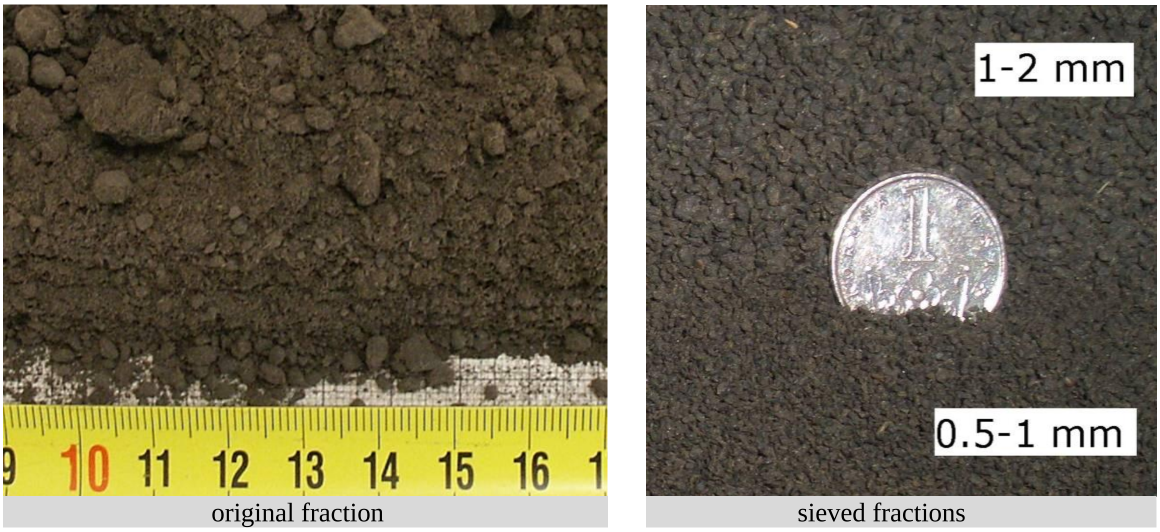


Figure 21 Cross section of the experimental fluidized bed reactor [59]

5.2.2 Fuel Preparation

Dried digested sludge from the WWTP in Brno-Modřice was used for the combustion experiments. The original sludge sample showed a great variety in particle size with particles up to 16 mm in diameter (Figure 22, left).



original fraction

sieved fractions

Figure 22 Particle size fractions of sludge

Sieving was obligatory in order to unify the particle size distribution and thus guarantee unproblematic pneumatic transportation into the reactor and constant dosage by the slide feeder. Furthermore, unification in particle size is necessary as the fluidization velocity of particles depends on the particle diameter and shape. The fuel used in experiments had a particle diameter of 0.5-2 mm expressed as mesh width (Figure 22, right). The fractions used as fuel represents approximately 30 % of the original sludge fraction (see Table 11) and was prepared using a *Retsch AS 200* sieving machine.

Table 11 Particle size distribution of sludge

MESH WIDTH *[mm]*	MASS DISTRIBUTION *[%]*
0.0-0.5	19.78
0.5-1.0	11.03
1.0-2.0	21.41
2.0-4.0	24.37
4.0-6.3	12.14
> 6.3	11.26

5.2.3 Chemical Composition of Employed Materials

The generation and reduction of emissions depends on the chemical composition of employed materials. The materials sludge, limestone and the bed material (comprising of sand and fuel ash) were used in experiments.

Sludge

The composition of sludge used in experiments gives an overview of the expected flue gas composition. Within the experiments, three batches of sludge were used (fuel A, B and C). The main difference in used fuels A and B is the lower share of volatile substances in fuel A. The fuel contains approximately 8.5 % of water and 52 % of volatile matter. The composition of volatiles varied slightly and is shown in Table 12. The nitrogen concentration in volatile matter is higher in comparison to typical values given in [34] and amounts to 6.8 % on average. The heating value of fuel A was measured 10.4 MJ/kg and, due to the lower volatile matter, slightly lower than for fuel B which was 10.8 MJ/kg. Fuel C is a mixture of fuel A (50 %) and fuel B (50 %). The mixture was assumed to be ideal and concentrations for fuel C are calculated from A and B. As the water concentration of fuel A and B had changed, the values of fuel C proximate analysis‘ were determined individually. The composition of fuel was determined in the size fraction 0.5-2 mm, which was used in experiments.

The theoretical flue gas composition is determined for the fuel feeding rate of the particular experiment and the fluidization air flow. For more information than presented in Table 13, see Annex V.

Table 12 Composition of fuel used in experiments

	FUEL A	FUEL B	FUEL C
Proximate analysis, [%] in raw sample			
Water	8.59	8.62	8.17
Ash	41.03	38.51	40.06
Volatile substances	50.38	52.87	51.77
Ultimate analysis, [waf.%]			
Carbon	52.08	51.64	51.86
Hydrogen	7.26	7.66	7.47
Oxygen	32.37	32.31	32.47
Nitrogen	6.67	6.98	6.83
Sulfur	1.49	1.29	1.39
Chlorine	0.093	0.098	0.096
Fluorine	0.036	0.033	0.035
Bromide	0.003	0.003	0.003

Table 13 Calculated flue gas composition

	FUEL A	FUEL B	FUEL C
Air components [vol.%]			
O_2	9.04	7.70	9.69
N_2	79.69	80.06	79.69
CO_2	10.20	11.18	9.57
Ar	0.94	0.95	0.94
Pollutants concentration [mg/m$_N^3$] given at 11 vol.% O_2			
SO_2	2854	2441	2656
HCl	88.8	98.1	88.6
HF	30.2	30.1	30.2

Note: Concentrations are adjusted for transport nitrogen
Pollutants concentrations are given in dry gases for 100 % conversion

The heavy metal concentration in fuel A and B was determined for As, Cd, Co, Cu, Cr, Hg, Mn, Ni, Pb, Sb, Sn, Tl, V and Zn. The analysis shows that heavy metals in sludge mainly comprise of zinc, copper, manganese and lead, which exceed 96 % of the total heavy metals contained in sludge. Table 14 gives the heavy metal concentrations of the fuels and lists the heavy metals tracked in input and output streams (used in distribution analysis) and heavy metals analyzed in input streams solely (not used in distribution analysis).

Table 14 Heavy metals characteristics of fuel

	FUEL A	FUEL B
Tracked in input and output streams [mg/kg] dry		
As	6.72	6.53
Cd	0.44	< 0.4
Co	5.98	5.58
Cu	266	273
Mn	256	253
Pb	33.3	29.1
Sb	4.76	4.84
Sn	15.5	15.9
V	25.0	23.9
Zn	982	986
Tracked in input streams [mg/kg] dry		
Cr	81.7	55.1
Hg	1.46	2.07
Ni	30.7	25.8
Tl	< 5	< 0.5

Limestone

Limestone from the cement plant Čížkovice was employed in experiments. The calcium concentration of the employed fraction was 29.5 % in the raw sample. Feed limestone contains little amount of SO_3, which amounted to 0.05 waf.%. As the initial concentration is very low compared to used limestone containing approximately 8.9 % SO_3, the initial concentration is neglected in distribution analysis. The detailed composition of limestone is shown in Table 15.

Table 15 Composition of additive used in experiments

	LIMESTONE
Proximate analysis [%] in raw sample	
Water	0.75
Ash	64.75
Volatile substances	34.50
Ultimate analysis [waf.%]	
CaO	66.71
SiO_2	19.95
Al_2O_3	7.73
Fe_2O_3	2.55
K_2O	1.37
MgO	0.88
TiO_2	0.40
SrO	0.15
P_2O_5	0.14
MnO	0.05
SO_3	0.05
Σ NiO, V_2O_5, ZrO_2, ZnO, Cr_2O_3	0.03

Bed Material

The initial bed material was 600 g of sand, which was replaced by fuel ash with the ongoing dosage of fuel. In fluidized bed incineration, only small ash particles are removed from the reactor. The bigger particles remain in the reactor and act as bed material. Knowledge of the bed material composition can be very revealing in terms of emission prevention. Shimizu [56] and Ho [65] reported that pollutant control is related to the chemical bed composition. The composition of fuel ash was determined only once as the ash composition of fuel A and B can be expected to be quite similar as suggested by Table 14. The composition of used bed materials is shown in Table 16.

Table 16 Composition of bed material

	Fuel A *Ash*	Sand
Expressed as oxides [%] in dry sample		
SiO_2	30.74	98.48
Fe_2O_3	18.12	0.03
CaO	15.09	-
P_2O_5	13.37	-
Al_2O_3	10.56	1.38
MgO	1.65	-
K_2O	1.37	-
TiO_2	0.75	-
Na_2O	0.66	-
MnO	0.08	-
NiO	0.01	-

5.2.4 Physical Properties of Employed Materials

The physical properties of sludge, limestone and bed material used in experiments are summarized in Table 17 and in the following, explained in more detail.

Table 17 Physical properties of employed materials

	Sludge	Bed Material		Limestone	
		Sand	*Ash*	*Raw*	*Calcinated*
Particle size♦ [mm]	0.5 - 2.0	0.5 - 0.71	0.63 - 2.0	0.71 - 1.0	0.71 - 1.0
Poured bulk density [kg/m^3]	694	1421	743	-	700
Particle density♣ [kg/m^3]	1542	2530	940	-	1084
True solid density♠ [kg/m^3]	1740	2530		-	2853
U_{mf} at 25 °C [m/s]	0.29	0.22	0.22	0.38	0.28

♦ As mesh width
♣ Determined by mercury pycnometry
♠ Determined by helium intrusion analysis

Bulk Density

Bulk density marks the density of a granular solid in a continuous fluid, whereas the fluid is almost exclusively air. It is determined including the fluid in between the granular material and is e.g. used to calculate the static bed height for a given amount of bed material.

Particle Density

Particle density marks the density of solids, whereas the related volume includes the particles' pore volume. Thus, for continuous solids, the particle density corresponds to the true solid density. Particle density is used to calculate fluidization properties of bulk material.

True Solid Density

True solid density refers to the density of the homogenous material. Compared to particle and bulk density, the true solid density is related to the volume of the solid material only. The pore volume and interspaces remain unconsidered.

Particle Fluidization and Discharge

Minimum fluidization velocities (U_{mf}) of used materials were determined measuring the pressure drop induced by the bed material versus flow rate of fluidization air. The air flow velocity was then calculated for the empty flow pipe and is shown in Figure 23. Values for U_{mf} are read from the x-axis at the inflection point of the graph.

Comparing the U_{mf}-values for the materials, a determination can be drawn on their discharge order. Low U_{mf}-values result in quick discharge, whereas particles having the highest U_{mf}-values tend to remain in the fluidized bed reactor. Thus, fuel sludge and raw limestone won't be discharged from the bed until their U_{mf}-values drop due to burnout and calcination. For sand and ash, the same velocities were determined.

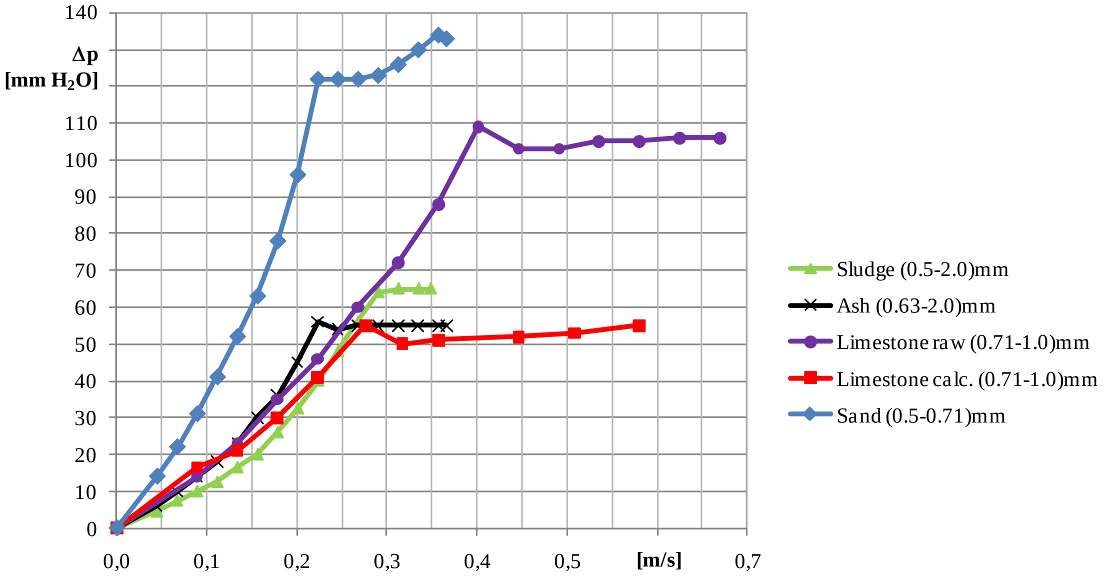


Figure 23 Pressure drop of bulk materials

Evidence of the correct discharge order gives the material distribution in the ash collector, which is shown in Figure 24. It shows the material from the bottom of the collector on the right hand side and the top of the collector on the left hand side. Sand outweighs fuel ash on the right hand side representing the beginning of the experiment. The sand concentration decreases with increasing fuel ash concentration from right to left and advancing experiment duration. Fuel ash represents the main proportion of bed material on the left hand side, representing the end of the experiment. In this fraction, the white limestone particles can be clearly distinguished from the red fuel ash and few sand particles.

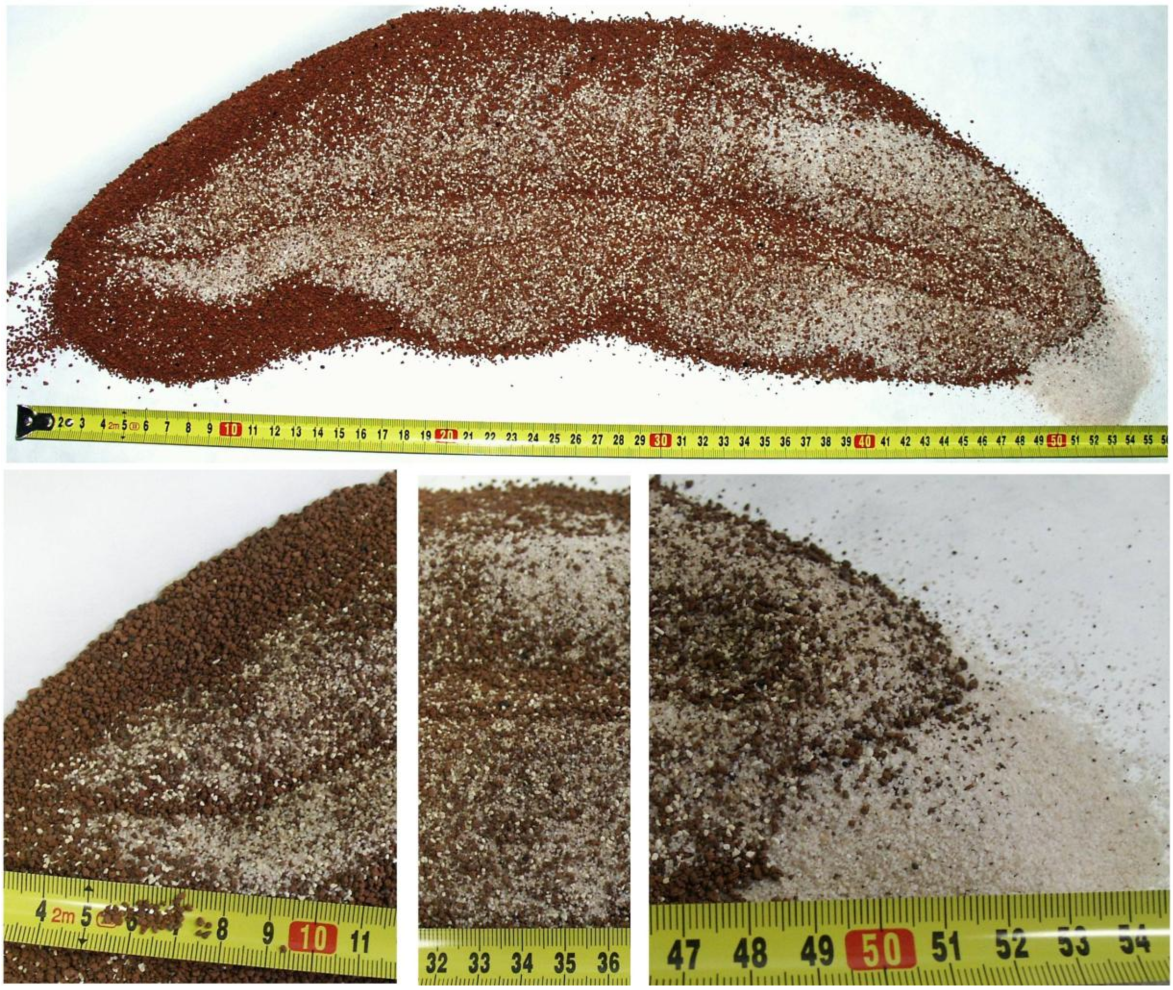


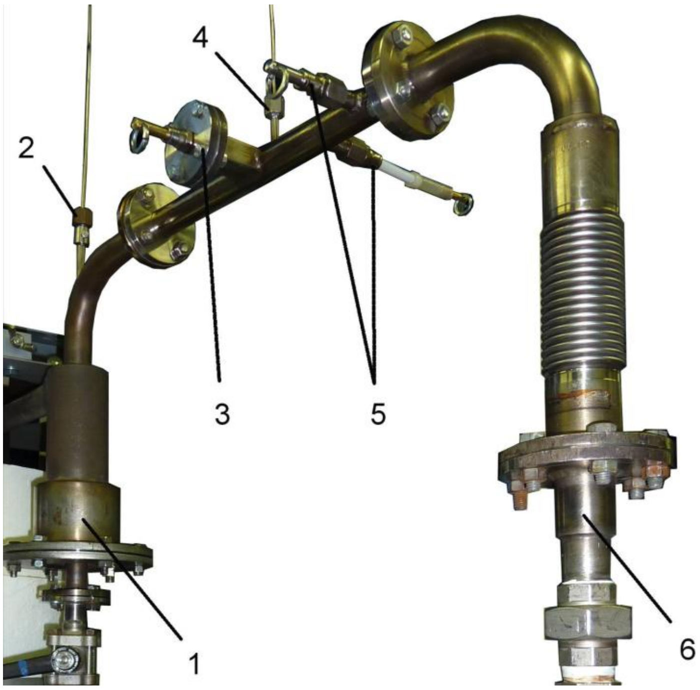
Figure 24 Material distribution in the ash collector

5.2.5 Pollutants Measurements

Produced pollutants (gaseous and particle bound) were mapped in the flue gas and the ashes were analyzed for heavy metals. The analysis of heavy metals in the ashes was aimed at determining the distribution in the output streams (fluidized bed, bed ash, cyclone ash and flue gas). The reactor used for experiments (described in chapter 5.2.1) was constructed from temperature resistant alloy, which is high in chromium and nickel. The elements Cr and Ni have not been analyzed as abrasive wear caused by the fluidized bed would falsify the balance. Within preliminary experiments, the distribution of mercury turned out to be difficult to verify. This observation was due to the constructive arrangement and the high volatility of Hg, which is above 100 °C present as Hg(g) or $HgCl_2$(g) [66]. From this reason, Hg distribution was not analyzed. The distribution of heavy metals was analyzed for the elements: As, Cd, Co, Cu, Mn, Pb, Sb, Sn, V and Zn.

The flue gas composition was measured downstream of the cyclone for coarse ash separation. The pollutants CO, N_2O, NO and SO_2 were continuously mapped using the gas analyzer ABB-EL3020. Heavy metals, SO_2, HCl and HF were measured manually by means of absorption and condensation methods. The measurement of PCDD/F, PAH and PCB was carried out by the authorized testing laboratory TESO-Brno, cited as [67].

The arrangement of sampling ports and temperature measuring point is shown in Figure 25, where flue gas leaves the reactor through the cyclone (1) and passes the temperature measuring point (2). Particle bound pollutants contained in flue gas are measured at sampling point (3), and the temperature is measured by thermocouple in (4). Measurement of gaseous pollutants takes place at sampling ports (5), before the flue gas enters the off gas stack (6). During the performed incineration measurements, a mean temperature between 225.7 and 231.4 °C was measured at the sampling port of particle bound pollutants. The sampling port for gaseous pollutants is located little downstream, where the temperature can be expected to be in the same range.



1: Cyclone
2: Temperature measurement in cyclone
3: Sampling point for particle bound pollutants
4: Temperature measurement at particle bound sampling point
5: Sampling ports for gaseous pollutants
6: Off gas stack

Figure 25 Flue gas measuring section

5.2.6 Experimental Procedure

Firstly, evaluation tests were carried out to verify fluidization and ash discharge. Secondly, four experiments were conducted to monitor emissions of sludge incineration and the influence of limestone on the emissions generated by sludge incineration (see Table 18). In all experiments, the fluidization of the bed material was assured supplying 2.48 m_N^3/h of air to the reactor. The transportation of fuel and additive into the reactor was assured by 0.93 m_N^3/h of nitrogen. Prior to the experiments, the reactor was heated to 720 °C in the fluidized bed and 780 °C in the freeboard. Then, the slide feeder was started and fuel and additive was feed to the reactor.

The experiments can be classified in long-term experiments (experiment 1 and 2), where fuel A and B was used, and short-term experiments (experiments 3 and 4), where fuel C was used. The influence of limestone was investigated in experiment 2 and 4.

The long-term experiments 1 and 2 were conducted in order to provide sufficient sampling time for PCDD/F and POP measurements, where the sampling time was 6 h. During measurements 1 and 2, hydrogen halides were also measured, where samplings took place three times over a period of 120 minutes each. The short-term experiments 3 and 4 served for tracking the emissions of hydrogen halides and SO_2 by means of absorption (only one sampling) and continuous tracking of CO, CO_2, NO, NO_2, and SO_2. The concentration of O_2 was continuously tracked during each of the experiments.

It is apparent from Table 18 that the amount of limestone in experiment 2 differs from experiment 4 although the feeding pocket diameter is constant. The plate used in experiment 2 had been used previously in evaluation and dosage tests and thus, due to the extended use, the pocket's edge was worn out after experiment 2. This caused a higher feeding rate during experiment 2. The feeding plate used in experiment 4 was newly produced and thus, the feeding rate was lower.

Table 18 Scope of conducted experiments

	Exp. 1	Exp. 2	Exp. 3	Exp. 4
Date	2011/02/08	2011/02/10	2011/04/08	2011/02/08
Duration	7h 28min	7h 52min	2h 30min	3h 50min
Fuel supplied	Fuel A	Fuel B	Fuel C	Fuel C
Material supplied	Fuel/Fuel	Fuel/Limestone	Fuel/-	Fuel/Limestone
Feeding pocket diameter [mm]	12.0/12.0	13.8/4.0	13.8/-	13.8/4.0
Sludge feeding rate [g/h]	547	575	501♦	501♦
Limestone feeding rate [g/h]	-	116	-	67
Ca/S - ratio [mol/mol]	-	7.3	-	4.4
Pollutants evaluated in flue gas	HM, PCBs, PAHs, HF, HCl, PCDD/F, Fly Ash	HM, PCBs, PAHs, HF, HCl, PCDD/F, Fly Ash	HF, HCl, NO, N_2O, CO, CO_2, SO_2	HF, HCl, NO, N_2O, CO, CO_2, SO_2
Pollutants evaluated in cyclone ash	HM	HM	-	-
Pollutants evaluated in bottom ash	HM	HM	-	-
Pollutants evaluated in ash collector	HM	HM	-	-

HM: Heavy metals
♦ Average in experiment 3 and 4

5.3 RESULTS OF MEASUREMENTS

In the following, unless otherwise specified, the concentrations of the pollutants and oxygen in the dry flue gas are adjusted for the amount of nitrogen used for the fuel transport.

5.3.1 Conditions of Incineration

Incineration conditions were selected to assure complete fuel burnout. This was achieved for an oxygen concentration of approximately 6 vol.% in dry gases. In experiment 2, the measured oxygen concentration was lower compared to measurement 1. This difference is reasonable and caused by the following three circumstances: Firstly, fuel with a higher amount of volatiles was employed, resulting in a higher oxygen consumption. Secondly, the release of CO_2 caused by the decomposition of limestone increases the total amount of flue gas, reducing the O_2 concentration (see expression (5-10)). Thirdly, desulfurization consumes oxygen as evident from equation (5-11). The measured oxygen concentrations are in agreement with the calculated oxygen concentration.

Table 19 Incineration conditions in experiments

	Exp. 1 *Fuel A*	Exp. 2 *Fuel B+Limest.*	Exp. 3 *Fuel C*	Exp. 4 *Fuel C+Limest.*
λ [-]	1.6	1.4	1.7♦	
O_2 measured [vol.%]	6.21	5.21	6.95	6.44
O_2 calculated [vol.%]	6.55	5.57	7.02	7.02
T in fluidized bed [°C]	866.8	868.1	865.6	865.1
T in freeboard [°C]	836.7	836.7	837.1	835.5
T in flue gas sampling port [°C]	228.1	225.7	231.4	229.2
Unburned matter in cyclone ash [%]	1.111 ± 0.075	3.632 ± 0.072	1.865 ± 0.242♦	
Unburned matter in bed material [%]	≤ 0.01	≤ 0.01	≤ 0.01♦	

♦ Average in experiment 3 and 4

5.3.2 Ash Distribution

The validity of performed emission measurement as well as the mass balance of pollutants depends on the goodness of the total mass balance of the experiments. Balancing the total amount of ash in input and output streams allows assessing the goodness of performed experiments. The resulting ash distribution (shown in Table 20) is corrected by the unburned matter of the particular ash stream. The values demonstrate a reliable incineration process: The main ash fraction is contained in the bed ash, minor loss of bed material through the distributor plate and total ash yield ranging from 99.2 to 100.1 % of the input stream.

Table 20 Ash distribution of conducted experiments

	Exp. 1 *Fuel A*	Exp. 2 *Fuel B+Limest.*	Exp. 3 *Fuel C*	Exp. 4 *Fuel C+Limest.*
Under distributor plate [%]	0.02	0.01	0.01	
Fluidized bed and ash collector [%]	97.65	98.56	97.52	
Cyclone [%]	2.17	1.47	1.68	
Airborne particle in flue gas [%]	0.11	0.09	not determined	
Percentage of input [%]	99.95	100.11	99.20	

5.3.3 Oxygen (O_2)

Oxygen concentrations between 7.21 and 9.59 vol.% were measured in experiments 1-4. The values presented in Table 21 are used to adjust the measured pollutants concentration to the standard oxygen concentration.

Table 21 Oxygen concentration in flue gas

	Exp. 1 *Fuel A*	Exp. 2 *Fuel B+Limest.*	Exp. 3 *Fuel C*	Exp. 4 *Fuel C+Limest.*
O_2 [vol.%]	8.60	7.21	9.59	8.90

Note: Concentrations are average values over the entire measurement and adjusted for transport nitrogen

Oxygen concentrations of experiment 3 and 4, where in both experiments fuel C was used, are shown in Figure 26. The addition of Limestone decreased the O_2 concentration from 9.59 vol.% in experiment 3 to 8.90 vol.% in experiment 4. The concentration measured in experiment 4 during the time interval 15:34-15:50 is relative high and indicates irregularities in the feeding rate.

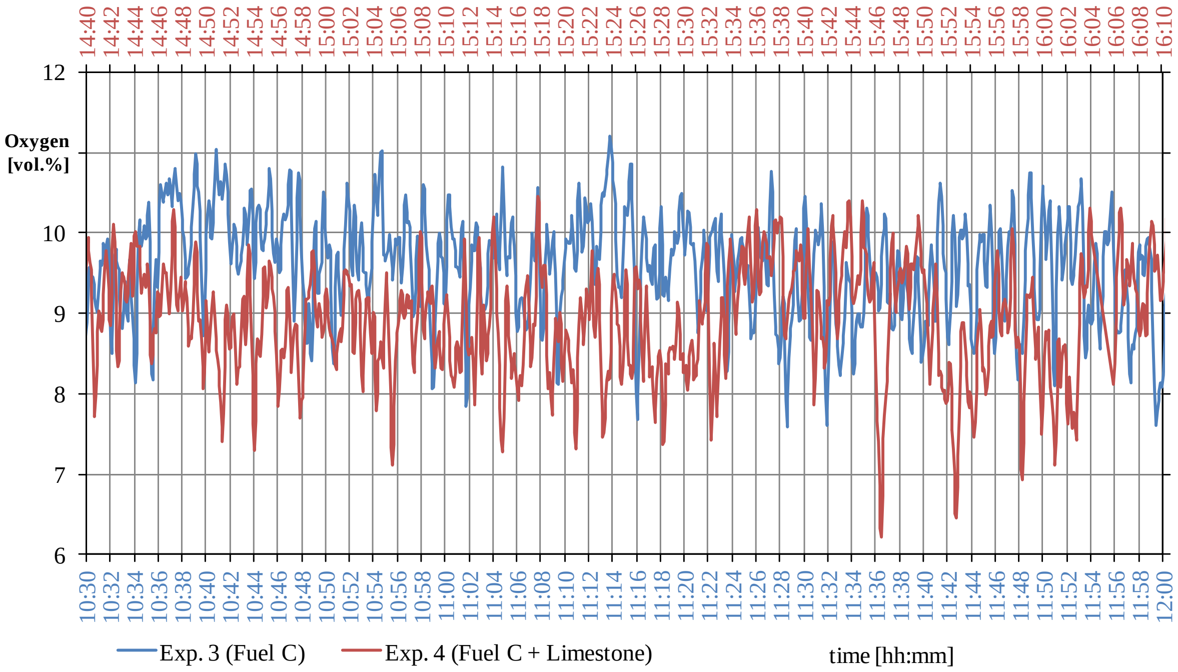


Figure 26 Oxygen concentration of experiment 3 and 4

5.3.4 Carbon Dioxide (CO_2)

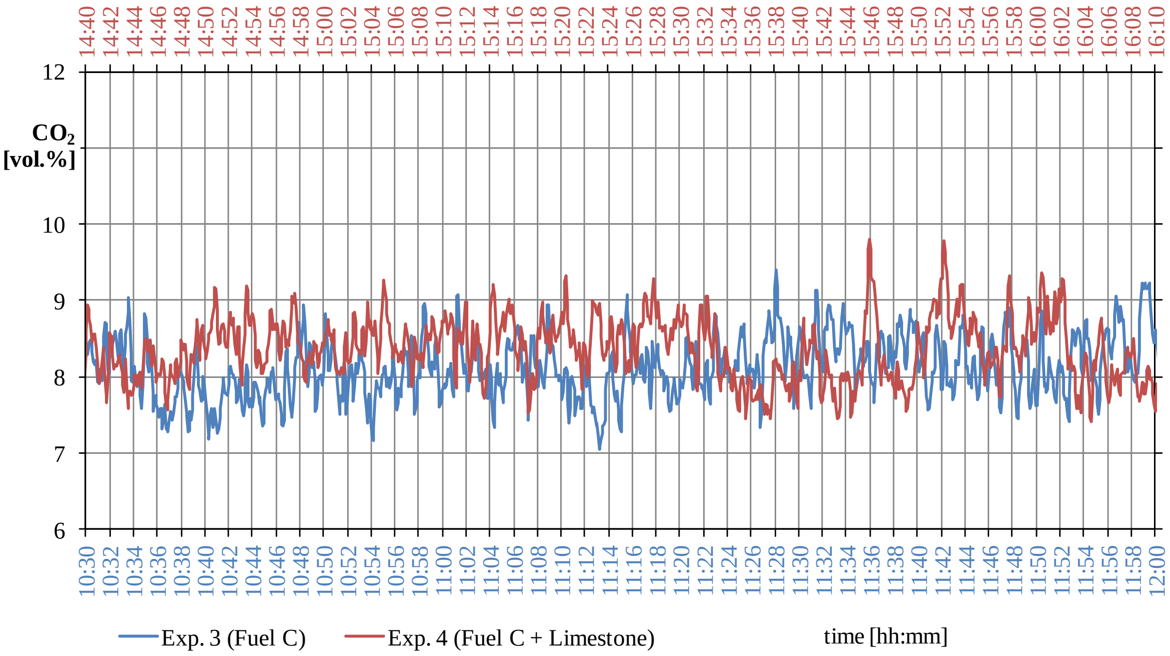
CO_2 concentration measured for particular oxygen concentrations diverge in experiment 3 and 4. Resulting from the addition of limestone in experiment 4, the CO_2 concentration is higher in comparison with experiment 4. The values given at 11 vol.% O_2 are in good agree as the same fuel is used (see Table 22). The slightly higher CO_2 concentration is caused by the addition of limestone.

Table 22 CO_2 concentration in flue gas

	Exp. 3 *Fuel C*	Exp. 4 *Fuel C+Limest.*
CO_2 for particular O_2 [vol.%]	9.26	10.13
CO_2 for 11 vol.% O_2 [vol.%]	8.12	8.37

Note: Concentrations are average values over the entire measurement

Same as for the oxygen concentration, a disturbance can be seen in experiment 4. For the time interval 15:34-15:50, the concentration is even lower than the concentration measured during experiment 3.



Note: Concentrations given at 11 vol.% O_2

Figure 27 CO_2 concentration of experiment 3 and 4

5.3.5 Carbon Monoxide (CO)

Carbon monoxide concentrations of 9.18 mg/m_N^3 in experiment 3 and 8.15 mg/m_N^3 in experiment 4 were measured. The freeboard temperatures in both experiments were nearly the same - 837.1 °C in experiment 3 and 835.5 °C in experiment 4. The CO concentrations measured during experiments are below the detection limit given by the European norm on the determination of the mass concentration of carbon monoxide [68]. The low concentrations give evidence for a complete burnout of employed fuels.

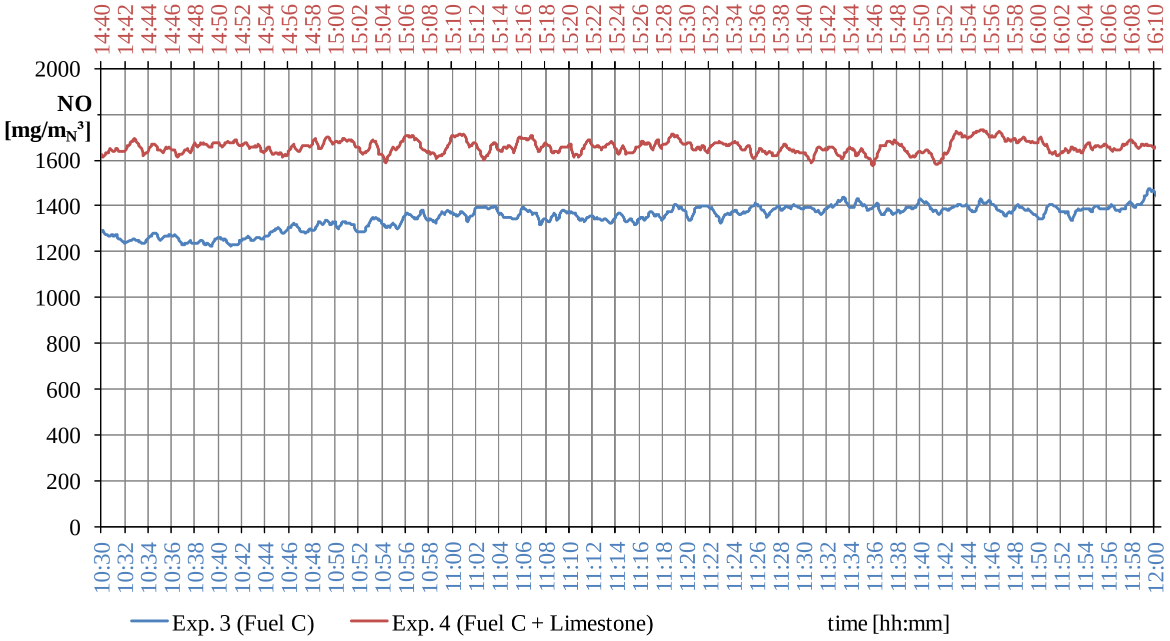
The measured concentrations are in accordance with literature and in the magnitude of the values determined in a CFB reactor [55], where the concentrations amounted to 3.3 mg/m_N^3 - measured at a freeboard temperature of 850 °C.

5.3.6 Nitrogen Oxides (NO_x)

In comparison to coal combustion, high NO concentrations were measured due to the high nitrogen content in fuel. The NO concentration of experiment 3, which is shown in Figure 28, is partially in transition due to changes in the fluidized bed material. The transition is caused by the bed material catalyzing the formation of NO [56]. Steady state is reached after time 11:04 as the bed material reached constant composition. At steady state, a concentration of 1450 mg/m_N^3 at 11 vol.% O_2 is obtained for the incineration of sludge without limestone (exp. 3). The NO concentration measured under the addition of limestone (exp. 4) amounts to 1658 mg/m_N^3 at 11 vol.% O_2.

The fuel-N to NO conversion ranges, according to [34], between 2 and 7 wt.% for the incineration of sludges. In accomplished measurements, the conversion is relatively high and amounts to 10.3 % for experiments without limestone and 13.5 % where limestone was used in experiments. The addition of limestone increases NO concentration. This is in accordance with literature where coal combustion, under the addition of limestone, resulted in higher NO concentration [56].

In terms of pollution control, the concentration of NO_x is of higher importance than the concentration of NO. Considering the NO_x emissions to be made up on 5 % of NO_2 and 95 % of NO, the concentration of NO_x in flue gas, results in 2340 mg NO_2/m_N^3 in experiment 3 and 2676 mg NO_2/m_N^3 in experiment 4. In order to fulfill legal requirements, NO_x reduction (e.g. air staging and SNCR) is of high concern in order to fulfill environmental regulations.



<u>Note:</u> Concentrations given at 11 vol.% O_2

Figure 28 NO concentration of experiment 3 and 4

5.3.7 Nitrous Oxide (N_2O)

Measured concentrations of N_2O varied from 250 to 400 mg/m_N^3 for 11 vol.% O_2 and are in the range given by [54], which amounts to 300-400 mg/m_N^3. The transient period for the N_2O emissions is shorter in comparison to NO [56]. Thus, concentrations shown in Figure 29 give the N_2O concentration for experiments 3 and 4 at steady state conditions.

Incineration of sludge (exp. 3) showed a mean N_2O concentration of 323 mg/m_N^3 for 11 vol.% O_2. The addition of limestone had a positive effect and decreased the N_2O concentration to 271 mg/m_N^3. Shen reported in [69] a decrease in N_2O concentrations for the addition of limestone in coal combustion, where limestone catalyzes the decomposition reactions of N_2O. The N_2O concentration is influenced by several substances contained in sludge ash. The compounds Fe_2O_3 and Al_2O_3 contained in sludge ash have a higher N_2O decomposition potential than SiO_2 [69] which was the initial bed material in conducted experiments.

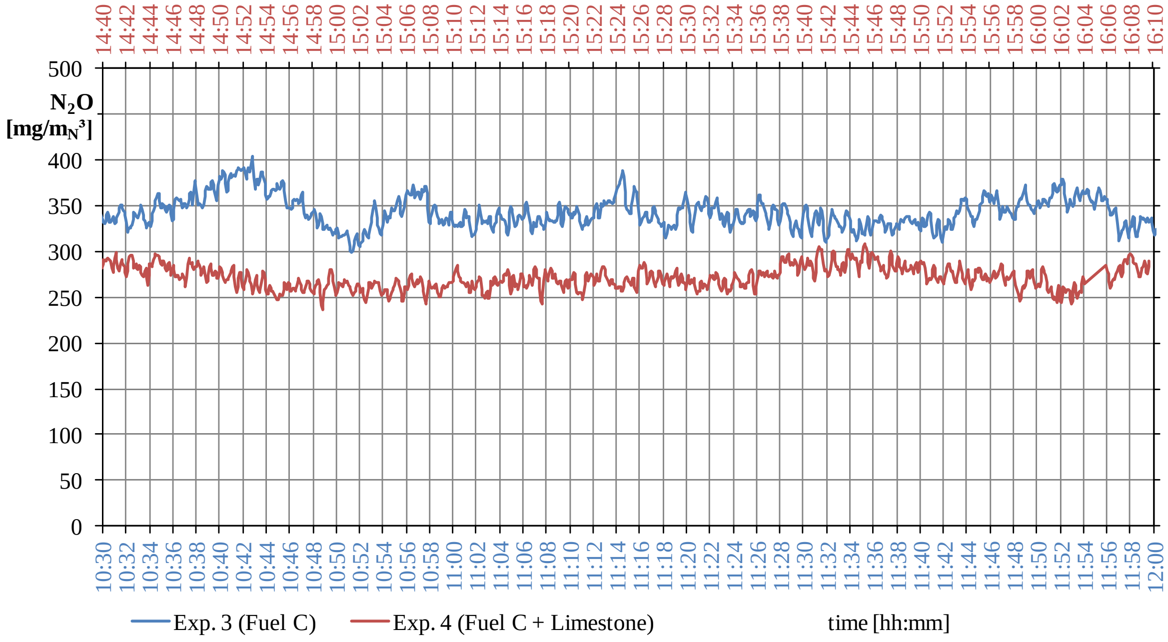
For the incineration of sludge (exp. 3), 3.4 % of the fuel-N was converted to N_2O-N. Under addition of limestone (exp. 4), the conversion was lower and amounted to 3.0 %.

In legal terms, nitrous oxide does not contribute to the NO_x emissions regulated by legislation [53]. Under atmospheric conditions, N_2O contributes to the formation of NO_2 which is regulated by pollution legislation. Thus, from the technical point of view, N_2O emissions has to be included in the calculation of NO_x emissions as it contributes significantly to NO_x emissions. Comparing the contribution of NO and N_2O in the formation of NO_x, the contribution of N_2O amounts to 23 % in experiment 3 and 18 % in experiment 4 as evident from Table 23.

Table 23 NO_2 formation from NO and N_2O

	EXP. 3 *Fuel C*	EXP. 4 *Fuel C+Limest.*
NO [mg NO_2/m_N^3]	2219	2537
N_2O [mg NO_2/m_N^3]	675	566

Note: Concentrations are average values over the entire measurement and given at 11 vol.% O_2



Note: Concentrations given at 11 vol.% O_2

Figure 29 N_2O concentration of experiment 3 and 4

5.3.8 Sulfur Dioxide (SO_2)

The SO_2 emissions were measured simultaneously by absorption method and gas analyzer in experiment 3 and 4. The results of both methods differ, whereas no drift could be determined. In experiment 3, the higher concentration was measured by analyzer and in experiment 4, the higher SO_2 concentration was determined by absorption method.

On average, a SO_2 concentration of 1290 mg/m_N^3 for 11 vol.% O_2 was measured in experiment 3. This is lower than the calculated SO_2 concentration in flue gas (2656 mg/m_N^3 for 11 vol.% O_2) and gives a sulfur conversion of 49 %. In experiment 4, where limestone was used, the SO_2 concentration was lower and averaged to 460 mg/m_N^3 for 11 vol.% O_2. From this follows a SO_2 capture of 60.8 % for the addition of limestone at a Ca/S ratio of 4.4.

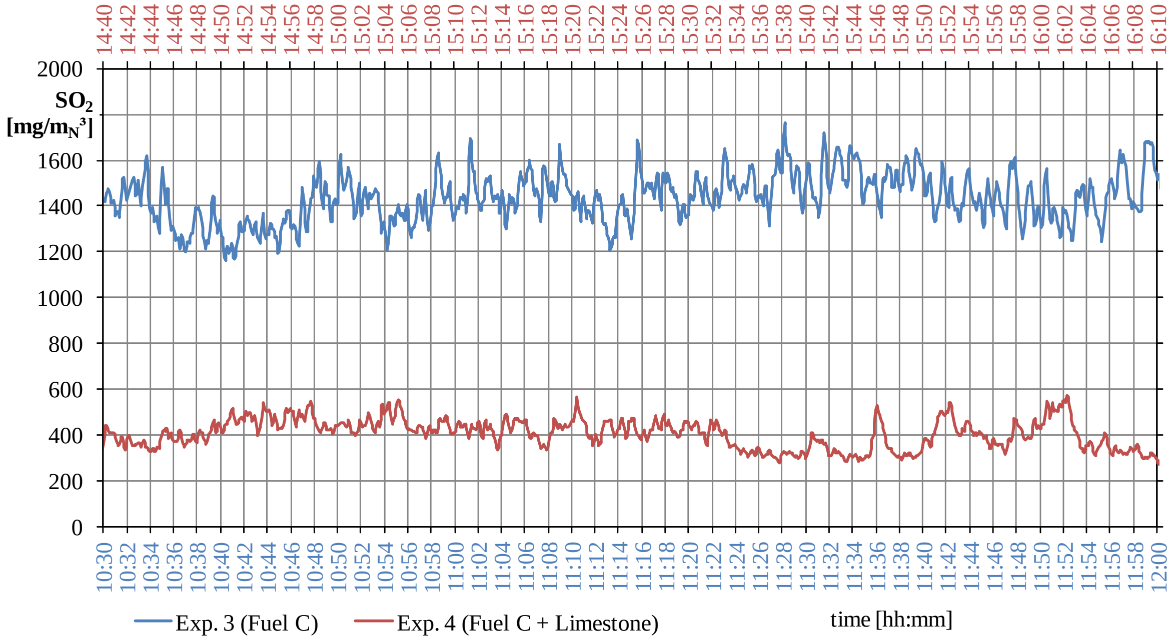
The SO_2 concentrations measured in experiment 3 and 4 are presented in Table 24 and Figure 30.

Table 24 SO_2 emissions measured by gas analyzer and absorption method

	EXP. 3 *Fuel C*	EXP. 4 *Fuel C+Limest.*
Absorption method [mg/m_N^3]	1141	514
Gas analyzer [mg/m_N^3]	1434	404

Note: Concentrations are average values over the entire measurement and given at 11 vol.% O_2

Regarding the irregularities in feeding rate (discussed in section 5.3.3), one can see, that in the same time interval (15:34-15:50) the SO_2 concentration dropped. This indicates a drop in the sulfur feeding and subsequently irregularities in the volatiles contained in fuel and not in the feeding rate of limestone.



<u>Note:</u> Concentrations given at 11 vol.% O_2

Figure 30 SO_2 concentration of experiment 3 and 4

5.3.9 Hydrogen Halides (HCl and HF)

The concentrations of hydrogen halides were measured in experiment 1, 2, 3 and 4. The main part of chlorine is transferred into the flue gas. In sludge incineration (exp. 1 and 3), approximately 90 % of chlorine was verified in the flue gas, where the HCl concentration averaged 81.1 mg/m_N^3. A slight decreased in HCl emissions was observed for the addition of limestone in experiment 2 and 4. The amount of limestone had no influence on the capture rate of chlorine. The equilibrium concentration of HCl for its capture (as in reaction (5-14)) highly depends on the temperature. For HCl concentrations determined in flue gas, the capture can take place downstream the head of the reactor only, where the temperature is below 510 °C. The HCl removal is very low as CaO is mainly present in the fluidized bed, where the temperature is too high for the given HCl concentration. Probably, the HCl reduction occurred downstream the head of the reactor.

The transfer rate of fluorine into the flue gas was 48.3 % in experiment 1. The addition of limestone in experiment 2 captured 45.8 % of HF from the flue gas (Ca/S = 7.3). The capture of HF depends on the amount of limestone. For a Ca/S ratio of 4.4 (exp. 3 vs. 4), the capture was 27 %. For experiment 3 and 4, the amount of fluorine in the flue gas was higher than the fluorine input. The values shown in Table 25 are adjusted for 100 % fluorine input. The measured concentrations are summarized in Table 26.

Table 25 Transfer of chlorine and fluorine into flue gas

	EXP. 1♦ *Fuel A*	EXP. 2♦ *Fuel B+Limest.*	EXP. 3 *Fuel C*	EXP. 4 *Fuel C+Limest.*
Chlorine [%]	86.0	78.4	91.8	80.9
Fluorine [%]	48.3	26.2	100.0♣	73.3♣

♦ Average of three samplings
♣ Adjusted for fluorine input

Table 26 Concentration of hydrogen halides in flue gas

	EXP. 1♦ *Fuel A*	EXP. 2♦ *Fuel B+Limest.*	EXP. 3 *Fuel C*	EXP. 4 *Fuel C+Limest.*
Chlorine [%]	76.2	72.5	85.9	71.5
Fluorine [%]	17.1	8.4	47.1	32.7

Note: Concentrations given at 11 vol.% O_2
♦ Average of three samplings

5.3.10 Dioxins and Furans (PCDD/F)

The flue gas from experiment 1 and 2, was analyzed for 7 PCDDs and 10 PCDFs. The analysis showed that the concentration of each PCDD/Fs was under the limit of determination. Table 27 summarizes the upperbound concentrations, which are determined from the limit of determination and thus, represent the highest concentration of PCDD/Fs which is possibly contained in the flue gas. The sum of upperbound concentration is in the magnitude of 300 pg/m_N^3. The upperbound TEQ concentration is lower and in the range of 30 pg TEQ/m_N^3. The overview of the analyzed PCDD/Fs upperbound concentration is given in Annex VI and Annex VII.

Table 27 Concentration of dioxins and furans in experiment 1 and 2

	EXP. 1 *Fuel A*	EXP. 2 *Fuel B+Limest.*
Total concentration [pg/m_N^3]	< 387	< 299
TEQ concentration [pg TEQ/m_N^3]	< 36	< 28

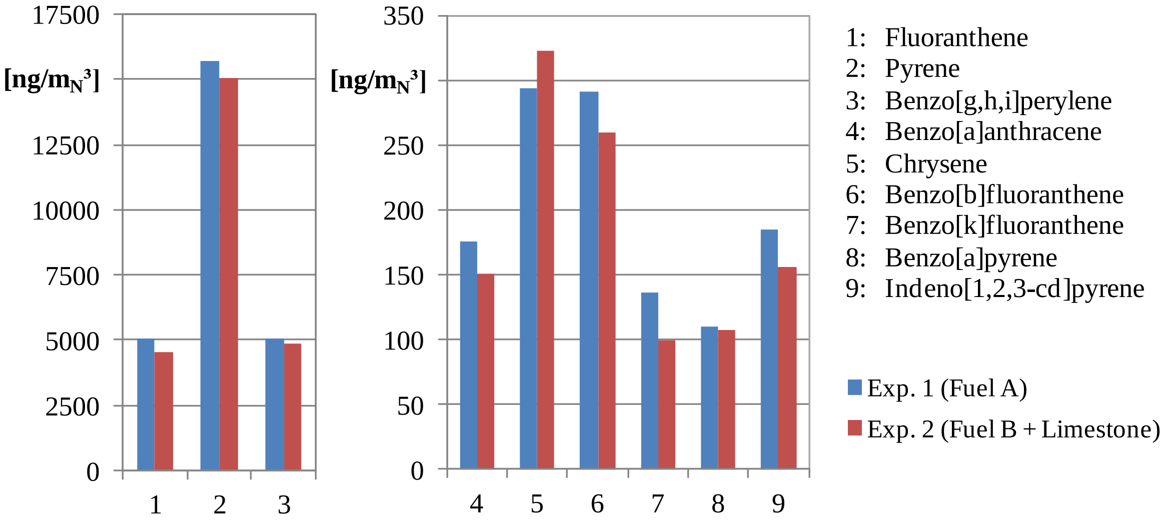
Note: Values represent the upperbound concentrations given at 11 vol.% O_2

5.3.11 Polycyclic Aromatic Hydrocarbons (PAH)

Flue gas from experiment 1 and 2, was analyzed for 10 polycyclic aromatic hydrocarbons which are subject to the USEPA list of priority pollutants. Except for one

(Dibenzo[a,h]anthracene), the concentrations of the analyzed PAHs were above the limit of quantification. The concentration of the three dominant PAHs in flue gas (fluoranthene, pyrene and benzo[g,h,i]perylene) was in the range of 5000-15000 ng/m_N^3 and about two orders of magnitude higher than of the other PAHs. The other PAHs are namely benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene and indeno[1,2,3-cd]pyrene. Figure 31 shows the concentration of the three dominant PAHs and the other PAHs. The concentrations of all 10 PAH, analyzed in experiment 1 and 2, are given in Annex VIII.

In this work, an amount of 180 µg PAH/kg of dry fuel was produced in experiment 1 and 2. The sum of PAH concentrations determined in measurement 1 amounts to 27 µg/m_N^3. In measurement 2, the total PAH concentration was slightly lower and amounted to 25.5 µg/m_N^3. The difference is, although very low, significant as there is a clear shift in the concentration values. The concentrations determined during measurement 1 are for 8 of 9 PAHs higher than in experiment 2. Solely the concentration of chrysene is higher for experiment 2.



Note: Concentrations given at 11 vol.% O_2

Figure 31 PAH emissions in experiment 1 and 2

5.3.12 Polychlorinated Biphenyls (PCB)

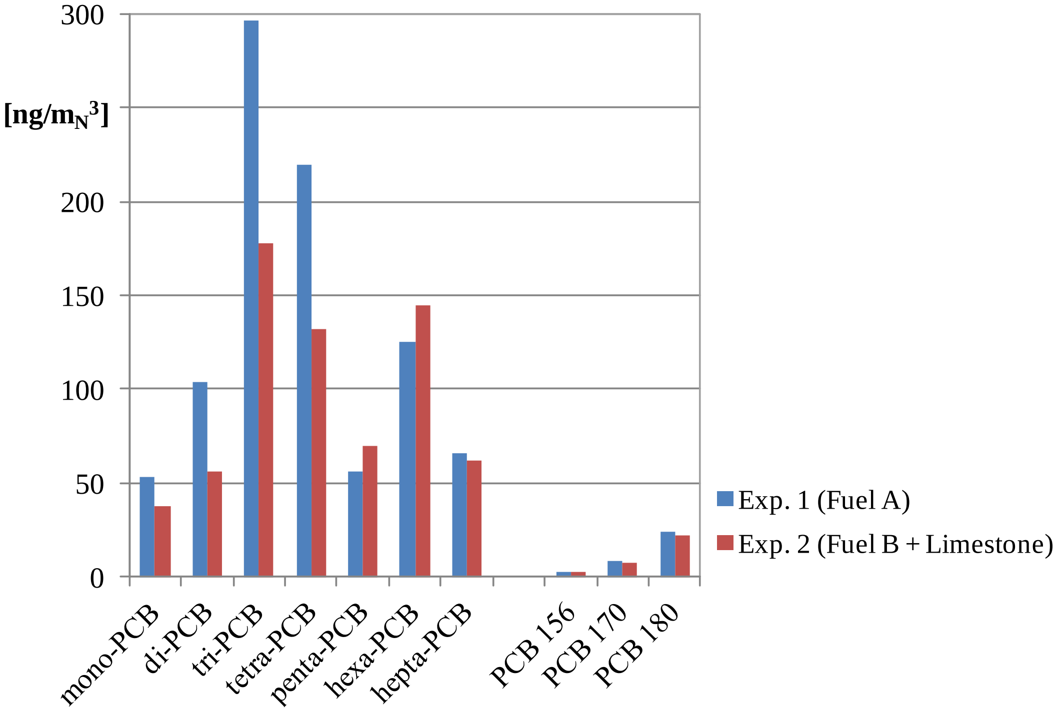
The concentrations of PCBs were measured for experiment 1 and 2. The concentration was determined for PCB 170, PCB 180, the 10 isomeric PCBs and 12 dioxin-like congeners. Except for octa, nona and deca-PCB, each isomer was determined in the flue gas. The highest concentration was determined for tri and tetra-PCB as evident from Figure 32.

Except for PCB 156, no dl-PCBs were determined at concentrations above the limit of quantification. The dl-PCB 156 was present at low concentrations amounting to 1.98 ng/m_N^3 in experiment 1 and 2.12 ng/m_N^3 in experiment 2.

The concentration of PCB 180 in flue gas amounted to 21.09 ng/m_N^3 in experiment 1 and 21.48 ng/m_N^3 in experiment 2. The concentration of PCB 170 amounted to 7.21 ng/m_N^3 in experiment 1 and 7.25 ng/m_N^3 in experiment 2.

The addition of limestone marginally decreased the PCB concentration in flue gas. The concentration determined as the sum of the 10 isomeric PCBs was reduced from 921 ng/m_N^3 in experiment 1 to 680 ng/m_N^3 in experiment 2. The specific production per kg dry fuel amounts to 6.3 µg for the incineration of sludge (exp. 1) and 5.0 µg for sludge incineration under addition of limestone (exp. 2).

Figure 32 shows the concentration of PCBs contained at concentrations higher than the limit of quantification. The concentrations of all PCB isomers and congeners, analyzed in experiment 1 and 2, are given in Annex IX.



Note: Concentrations given at 11 vol.% O_2

Figure 32 PCB emissions in experiment 1 and 2

5.3.13 Fly Ash

The concentration of fly ash increased within the course of experiments (see Table 28). This is caused by the change of bed material. At the beginning of the experiments, the fluidized bed consists of sand, which is gradually replaced by fuel ash causing higher concentrations of fly ash in the flue gas. With increasing time, the movement of bed ash causes attrition of the ash, resulting in higher fly ash concentrations.

Table 28 Concentration of fly ash in experiment 1 and 2

	EXP. 3 Fuel C	EXP. 4 Fuel C + limest.
Sampling 1 [mg/m_N^3]	86.3	79
Sampling 2 [mg/m_N^3]	131	111
Sampling 3 [mg/m_N^3]	170	134
Average [mg/m_N^3]	129	108

Note: Concentrations given at 11 vol.% O_2

5.3.14 Heavy Metals (As, Cd, Co, Cu, Mn, Pb, Sb, Sn, V and Zn)

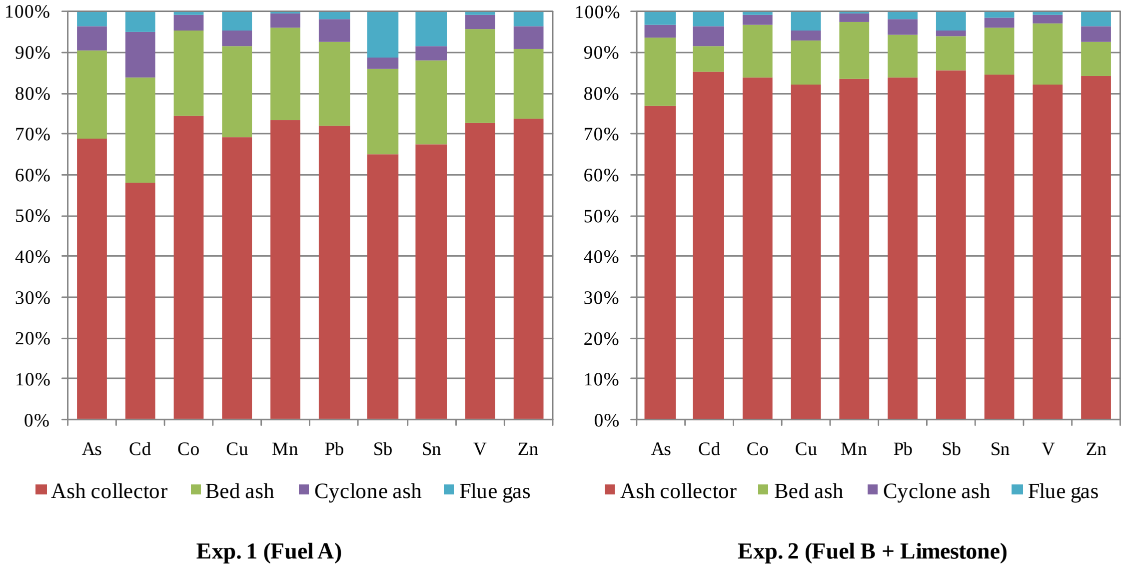
For experiment 1 and 2, the amount of heavy metals was determined in the output streams: ash collector, bed ash, cyclone ash and flue gas. The yield of the heavy metals is shown in Table 29. It indicates the goodness of balance and interrelates the amount of heavy metals in the output to the amount of heavy metals in the input. The determined yield for Cd is very high due to a very low concentration in the fuel.

Table 29 Yield of heavy metals in output streams for experiment 1 and 2

	AS	CD	CO	CU	MN	PB	SB	SN	V	ZN
Exp. 1 (Fuel A) [%]	89.4	146.6	105.3	77.2	88.7	74.6	69.9	93.1	102.4	63.0
Exp. 2 (Fuel B + Limest.) [%]	94.8	226	106.5	77.7	97.7	82.5	88.6	84.0	125.6	64.7

Distribution of Heavy Metals

The major part of heavy metals remains in the ash fraction and is present in the ash collector and bed ash. Only approximately 5 % of the total heavy metals emissions is contained in the flue gas. This is evident from the heavy metals’ distribution in output streams presented in Figure 33.



Note: Values are calculated from the emission and not adjusted for metal feed

Figure 33 Distribution of heavy metals determined in experiment 1 and 2

Heavy Metals in Flue Gas

The heavy metal concentration in flue determined in experiment 1 and 2 increased within the course of the particular experiments. The increase goes along with the increase in fly ash concentration.

The sampling port is located downstream the cyclone. However the air emission limits for heavy metals (50 µg/m$_N^3$ for Cd+Tl and 500 µg/m$_N^3$ for the sum of As, Co, Cr, Cu, Mn, Ni, Pb, Sb and V) are not fulfilled as the cyclone aimed at separation of unburned matter than the separation of heavy metals. In operational scale the requirements on heavy metal concentration can be fulfilled by means of further mechanical or chemical cleaning.

The average values of experiment 1 and 2, as shown in Table 30, are determined from three samplings. In the measurement of Sb and Sn, a measurement error (blunder) occurred in experiment 1. The concentrations of Sb and Sn given in Table 30 are the mean of the two samplings. The highest three HM concentrations in flue gas are the elements Zn, Cu, and Mn, which represent the highest three concentrations in fuel. The lowest concentration in flue gas is Cd, which represents the lowest share of HM in used fuels.

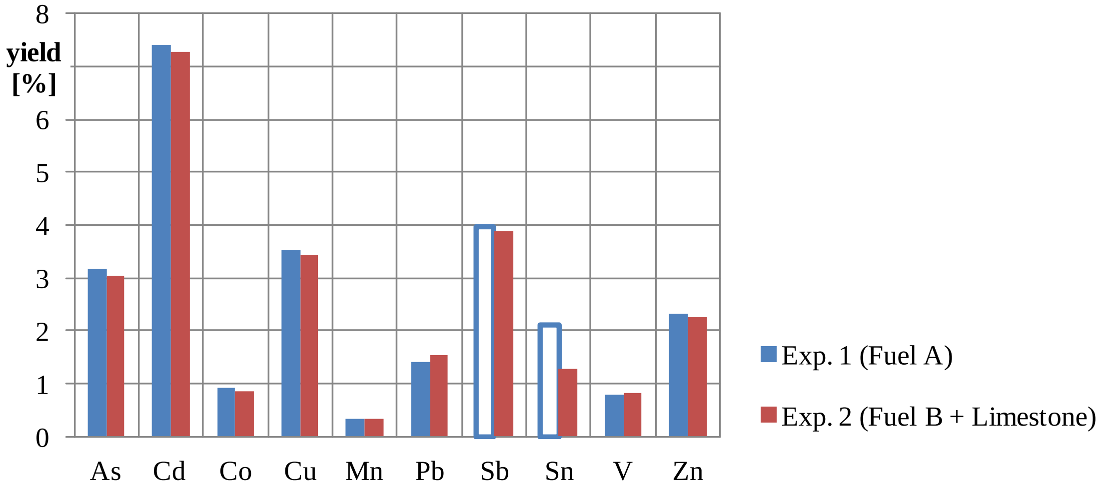
Table 30 Heavy metal concentration in flue gas

	As	Cd	Co	Cu	Mn	Pb	Sb	Sn	V	Zn
Exp. 1 (fuel A) [µg/m_N^3]	35.7	5.47	9.10	1569	142	78.6	(36.0)♦	(62.2)♦	33.6	3842
Exp. 2 (fuel B + limest.) [µg/m_N^3]	31.6	4.65	7.41	1498	130	71.4	29.9	32.4	30.5	3527

Note: Concentrations represent the mean of three samplings and are given at 11 vol.% O_2
♦ Average of two samplings

Due to a different composition and amount of used fuels, the emission reduction cannot be judged based on the flue gas concentrations but based on the yield of heavy metals in flue gas. The yield, as given in Figure 34, is determined as the ratio of heavy metals contained in flue gas to the amount of heavy metals contained in fuel. The highest yield gives Cd, of which 7.3 % is transferred from the fuel into the gas phase. For the metals As, Cu, and Zn, 3.5-2.3 % of the input is present in the flue gas. A minor yield between 1.4 and 0.3 % was determined for Co, Mn, Pb and V. As an error occurred for Sb and Sn in experiment 1, their yield in flue gas is not significant.

The average yield of heavy metals (As, Cd, Co, Cu, Mn, Pb, V and Zn) in flue gas amounts to 2.5 % for the incineration of sludge (exp.1) and 2.4 % for the addition of limestone (exp.2). The addition of limestone had no significant influence on heavy metal emissions and marginally decreased the yield of As, Cd, Co, Cu and Zn.



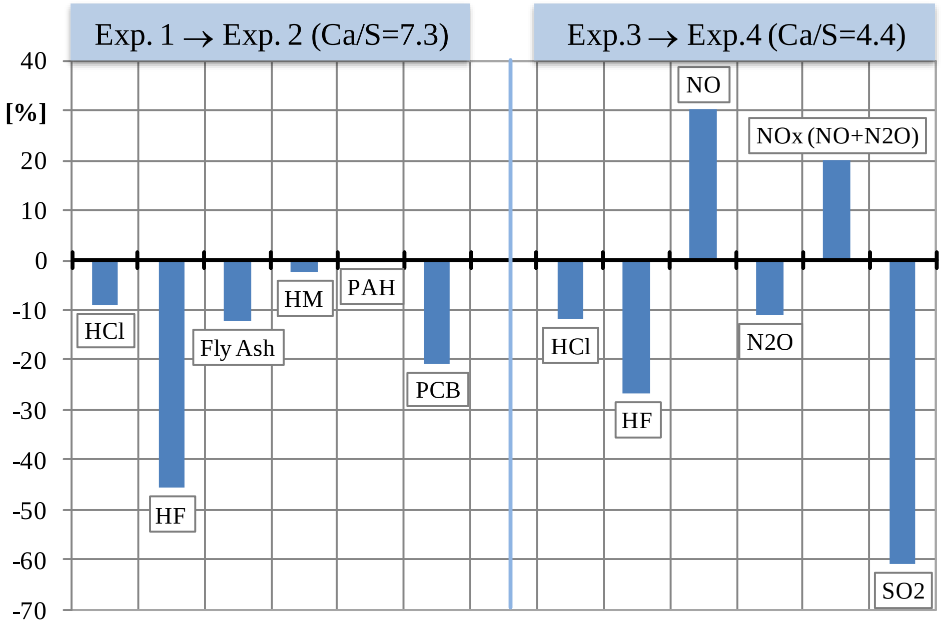
Note: Values are adjusted for metal feed
Values of Sb and Sn in exp. 1 are determined from two samplings

Figure 34 Yield of heavy metals in flue gas in experiment 1 and 2

5.4 DISCUSSION

Emission production from the incineration of sludge was described and the influence of alkali on the emissions was investigated in experiments. The change in pollutants' emissions for each pollutant class is summarized in Figure 35. However, the change in pollutants' emissions requires careful consideration - the reduction of PCB is determined from concentrations which are close to the limit of determination. Thus, the reduction cannot be taken for granted and is discussed in the following. The PCDD/F emissions are not listed as the concentration was below the limit of determination.

The addition of limestone achieved the highest pollutants' reduction for sulfuric compounds. SO_2 emissions could be reduced by 61 %. The downside of limestone addition is a higher production of nitrogen oxides, resulting in an increase of NO_x emissions.



Note: HM Σ (As, Cd, Co, Cu, Mn, Pb, V, Zn)

Figure 35 Change of emissions in conducted experiments

Nitrogen Compounds

Sludge counts among biofuels containing high amount of nitrogen and produces emissions high in nitrogen oxide. The concentrations of NO and N_2O in flue gas were measured within this work. The conversion of fuel-N to NO-N and N_2O-N results from the organic nitrogen content in fuel and depends on the composition of sludge ash serving as bed material.

For NO, metal oxides contained in sludge ashes (e.g. Fe_2O_3, MgO and Al_2O_3) are reported to catalyze its formation [56]. Calcium oxide (CaO, $CaCO_3$), which is constituent of both, sludge ash and alkaline additive used in experiment, increases the conversion of fuel-N to NO-N [69]. In conducted experiments (exp. 3+4), an increase was determined for the addition of limestone. The addition of limestone at an Ca/N ratio of 2.5 (Ca/S = 4.4) increased the NO concentration in dry flue gas from 1450 to 1658 mg/m_N^3 at 11 vol.% O_2.

Oxides and sulfates present in sludge ashes (e.g. Fe_2O_3, Al_2O_3 and $CaSO_4$) have a higher N_2O decomposition potential than SiO_2 [69], which is usually used as bed materials. In conducted experiments (exp. 3+4), the conversion of fuel-N to N_2O-N decreased by 0.3 percentage points. As a result of limestone addition, the concentration of N_2O in dry flue gas dropped from 323 to 271 mg/m_N^3 at 11 vol.% O_2.

The NO_x emissions increase from 2894 to 3103 mg NO_2/m_N^3 at 11 vol.% O_2 due to the addition of limestone. This is a disadvantage as it increases the efforts of pollutants control in sludge incineration.

Sulfur Dioxide

The amount of sulfur contained in fuel (1.39 waf.%) yields a calculated SO_2 concentration of 2656 mg/m_N^3 at 11 vol.% O_2 (for 100 % conversion).

The measured concentration during sludge incineration (exp. 3) was considerably lower amounting to 1290 mg/m_N^3 at 11 vol.% O_2. This represents 49 % of sulfur contained in fuel. The low SO_2 yield in the flue gas is the result of CaO contained in sludge ash, which captures approximately 50 % of the sulfur contained in fuel. The Ca/S ratio, naturally given was 4.8.

The addition of limestone in experiment 4 (Ca/S = 4.4 %) reduced the SO_2 concentration in flue gas to 460 mg/m_N^3 at 11 vol.% O_2, representing 19 % of sulfur contained in fuel. From the sulfur balance of experiment 3 and 4 follows, as a result of limestone addition, a SO_2 capture of 61 %.

Hydrogen Halides

The reaction of CaO with HCl is constrained by the temperature dependency of the equilibrium concentration [60]. For the capture of chlorine using limestone, the equilibrium concentration is higher than 1000 mg/m^3 at conditions in the fluidized bed (T = 860 °C). In experiments, a minor reduction of chlorine in the flue gas was observed. The capture of chlorine was independent from the limestone dosage and amounted to approximately 10 % during experiments. The capture is likely to take place downstream the head of the reactor, where the flue gas was at temperature between 510 and 230 °C.

The reduction of fluorine emissions goes along with the amount of limestone used in the particular experiment. Comparing experiment 1 and 2, (Ca/S: 7.3), the chlorine emissions were reduced by 45.8 %. For experiment 3 and 4 (Ca/S: 4.4), the reduction in fluorine amounted to 27 %.

Dioxins and Furans

The formation of dioxins and furans from the incineration of sludge was investigated by Deng [70], who reported a sum concentration of 8955 pg/m_N^3 (TEQ = 69.14 pg/m^3) for the combustion of sludge containing a chlorine concentration of 6.3×10^{-2} waf.%. The chlorine concentration in sludge used in this study amounts to 9.5×10^{-2} waf.%. Dioxins and furans were not detected in conducted experiments. Thus, from the conducted experiments, the influence of limestone on the production of dioxins and furans cannot be judged. The upperbound concentrations suggest a PCDD/F concentration below 390 pg/m_N^3 representing a TEQ of 36 pg/m_N^3 (values at 11 vol.% O_2).

Polycyclic Aromatic Hydrocarbons

The sum of measured PAH concentrations in flue gas amounts to 25.5 µg/m_N^3 at 11 vol.% O_2. The addition of limestone gave a concentration of 27 µg/m_N^3 at 11 vol.% O_2. The measured PAH concentrations are lower compared to Deng [70], who reported 107 µg/m_N^3. The total production in both experiments is 180 µg PAH/kg of dry fuel. The addition of limestone did not influence the PAH emissions. This finding is supported by [70], where no influence could be determined in co-firing of sludge.

Polychlorinated Biphenyls

The PCB emissions from sludge incineration do not depend on the addition of limestone. The dominant PCBs in the flue gas stream are tri-PCB, tetra-PCB and hexa-PCB. The concentrations of PCB 156, which represents the only detected dioxin-like PCB, were considerable low amounting to approximately 2 ng/m_N^3 at 11 vol.% O_2. The sum of isomeric PCBs produced in the combustion experiments amounts to approximately 5.5 µg/kg dry fuel.

Fly Ash

Fly ash emission increased within the experiments due to attrition in the ash bed. The measured concentrations at 11 vol.% O_2 average 129 mg/m_N^3 in experiment 1 (no additive) and 108 mg/m_N^3 in experiment 2 (addition of limestone). The change in concentration is probably the result of the different fuel composition (ash and volatile fraction).

Heavy Metals

The major part of heavy metals was detected in the ash fraction. The minor part of HM contained in fuel is transferred into the flue gas. For the heavy metals As, Cd, Co, Cu, Mn, Pb, V and Zn, a consistent balancing was possible for the mass streams of the incineration process. The transfer of these HMs from the fuel into the flue gas averaged 2.5 %. The addition of limestone decreased the average yield of HM marginally to 2.4 %.

According to Ho [65], limestone is, in contrast to sand, a more effective sorbent for the capture of Pb and Cd. The higher Pb capture in the use of limestone could not be verified in this work. In conducted experiments 1 and 2, the addition of limestone increased the Pb yield from 1.4 to 1.5 % in flue gas. The Cd yield for the addition of limestone decreased marginally from 7.4 to 7.3 %. The difference to the results published by Ho is based in the different bed material. Ho compared the bed materials sand and limestone. The conducted experiments suggest that the addition of limestone into the ash bed does not influence the HM yield in flue gas.

Legal Aspects

The incineration of sludge falls into the category of waste incineration, which is subject to stringent air emissions requirements, where the standard is set by legal regulations regarding the incineration of waste [53]. Experiments conducted on emissions generation aimed to identify bottlenecks and possibilities of emissions‘ reduction in sludge incineration. For this purpose, limestone was used as additive in fluidized bed combustion. The addition of limestone influences the concentrations of SO_2 and HF positively (✓), for NO_x negatively (✗) and the other emissions remain unchanged (-). For the evaluation of legal aspects, the air emissions concentrations determined in experiments are compared with legal requirements (see Table 31). It is obvious, that compliance with limit values cannot be reached and additional flue gas treatment is required to primarily reduce the concentration of SO_2, HCl, HF, heavy metals and dust.

Table 31 Determined pollutants’ concentrations and limit values

	LIMIT VALUE	SLUDGE INCINERATION *Fuel A/C*	ALKALI ADDITION *Fuel B/C + Limest.*	EFFECTIVENESS OF LIMESTONE
Carbon monoxide $[mg/m_N^3]$	50	9.2	8.2	-
Dioxins and Furans $[ng/m_N^3]$	0.1	$< 36\times10^{-6}$	$< 28\times10^{-6}$	-
Heavy metals Σ (As, Co, Cr, Cu, Mn, Ni, Pb, Sb, V) $[\mu g/m_N^3]$	500	1867 ♦	1769 ♦	-
Heavy metals Σ (Cd, Tl) $[\mu g/m_N^3]$	50	5.5 ♣	4.7 ♣	-
HCl $[mg/m_N^3]$	10	80	72	-
HF $[mg/m_N^3]$	1	17.1	8.4	✓
NO_x expressed as NO_2 $[mg/m_N^3]$	200	2894 ♠	3103 ♠	✗
SO_2 $[mg/m_N^3]$	50	1290	460	✓
Total dust $[mg/m_N^3]$	10	129	108	-

Note: Concentrations are given at normal conditions and 11 vol.% oxygen in dry exhaust gas
♦ Comprising of As, Co, Cu, Mn, Pb, V, Zn
♣ Comprising of Cd
♠ Including N_2O

6 SLUDGE DISINTEGRATION

Disintegration of sewage sludge refers to hydrolysis of sludge solids. The three most important methods of sludge disintegration are mechanical, chemical and thermal disintegration. This work is, in theory and experimental work, devoted to the thermal disintegration, which in terms of energy efficiency holds advantages over mechanical and chemical disintegration due to measures of heat recovery and thus, has high potential for future applications.

Disintegration is applied on selected WWTPs for example in Denmark, the Czech Republic, Great Britain, Germany and Ireland. The first thermal disintegration process, which was patented in 1935 by PORTEOUS, required sludge temperatures of 180 to 200 °C at operational pressure up to 2.8 MPa. The process aimed at improving sludge thickening in picket fence thickener [71]. The process after PORTEOUS causes odor nuisance which made the process unpopular [32].

Besides stand-alone thermal disintegration, a combination of thermal and chemical methods can be used. Chemical hydrolysis can be attained using appropriate chemical agents (acid, lye) [72] and [73]. By chemical hydrolysis, the cell walls of microorganisms are damaged and the sludge structure breaks up. The combination of thermal and chemical disintegration allows reducing the operational temperature of the thermal disintegration process. Thereby, the energy demand can be reduced.

6.1 PURPOSE OF SLUDGE DISINTEGRATION

Currently, disintegration methods are applied to increase the biogas production in digestion or in case of operational problems (floating and bulking sludge) caused by filamentous bacteria. In order to increase biogas production, waste activated sludge is disintegrated. Here, mainly mechanical disintegration methods e.g. ball mill, ultrasound, lysate-thickening centrifuge are applied.

Disintegration of stabilized sludge before dewatering influences the dewaterability of sludge ([23], [32], [74] and [75]). Here, during disintegration the sludge flakes are disrupted and bound water becomes available for gravitational means of dewatering. The increase in total solids concentration in dewatered sludge goes along with the reduction of water contained in dewatered sludge. This reduces the total amount of sludge for disposal and increases the possibilities of sludge utilization in waste to energy as less water needs to be evaporated by drying or during incineration.

Gaining process parameters for the design of a suitable disintegration process which aims at improved dewatering, experiments using thermal and thermo-chemical methods were conducted, which aimed at:

- finding a suitable laboratory scale dewatering method for disintegrated sludge,
- determining the suitable temperature level for disintegration,
- data collection for process design and
- the evaluation of impacts on the centrate after centrifugation.

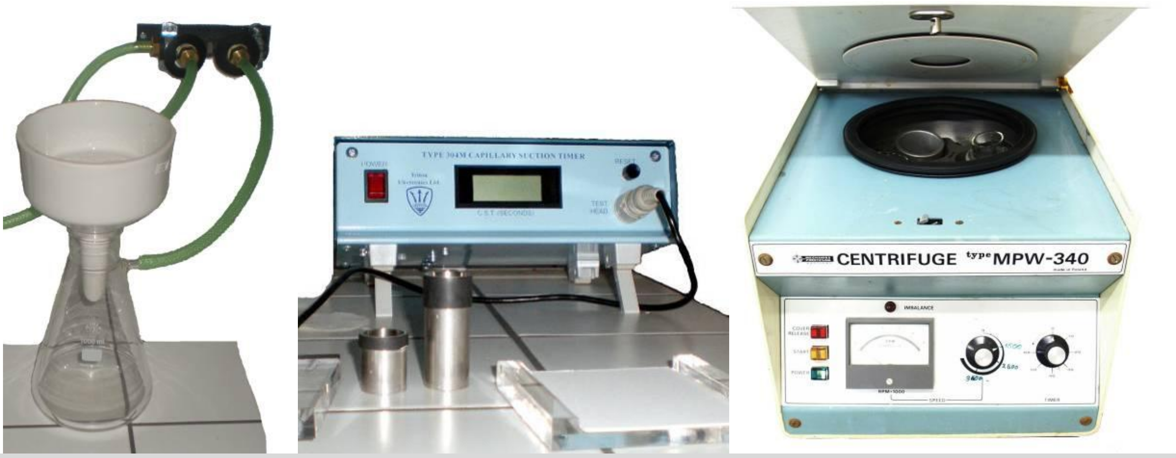
6.2 METHODS AND MATERIALS USED FOR DISINTEGRATION EXPERIMENTS

The impact of thermal and thermo-chemical treatment of sludge on its dewaterability was assessed in laboratory measurements. For this purpose, a laboratory-scale disintegration unit was designed within the frame of FSI-Junior grant BD 138 3011 and used in experimental work (see Figure 36). The disintegration unit is built as a double jacket vessel designed to operate under pressure or atmospheric conditions and can hold up to 2.7 l of sludge. The admissible pressure is 1 MPa at an operating temperature of 180 °C. The unit is heated by means of an external heat source and liquid heat transfer medium. Thermometer, pressure sensor and mixing device are attached to the vessel's flange. For sealing the agitator shaft to the flange, a mechanical cartridge seal is used. Mixing of the reactor was realized using an overhead stirrer, which was inserted into a holder that was attached to the flange. Additional information can be found in [76].

Figure 36 Disintegration unit used in experiments

Treatment was accomplished for liquid digested sludge from the WWTP in Brno-Modřice in all measurement runs. The TS concentration in sludges ranged from 3 to 4 % containing an volatile concentration around 53 %.

For evaluation of the attainable dry matter in sludge cake, it is important to select a method of dewatering that provides reliable results in laboratory-scale measurements. Therefore, measurements were carried out comparing three different methods. Namely, suction filtration, capillary suction time (CST) and centrifugation tests were performed (Figure 37).



suction filtration CST-meter laboratory centrifuge MPW-340

Figure 37 Measurement devices for dewatering test

It was found that disintegration of sewage sludge influences the validity of sludge dewatering tests. Not all types of dewatering test, allow a conclusion to be drawn with respect to dewaterability of disintegrated sewage sludge. Both, CST-meter and suction filtration use filter material, which apparently tends to clog during dewatering test of disintegrated sludge. This finding is supported by [77]. Thus, these two types of dewatering tests turned out to be inappropriate. Comparing the dewatering tests' significance, centrifugation can be considered to be the most significant of the three methods applied. For additional information regarding conducted experiments and conclusions see [78].

Thermal sludge treatment was performed at temperatures ranging from 50 to 170 °C. Besides stand-alone thermal disintegration, a combination of thermal and chemical methods was used. In contrast to thermal treatment, thermo-chemical treatment was accomplished under addition of chemical agents (acid, lye) and at lower temperatures (110 °C).

Subsequently, samples were dewatered in a beaker centrifuge. The resulting sludge cake and centrate were then analyzed. After centrifugation, the centrate was poured off and used to determine the total amount of solids at 105 °C and pH. The determination of total solids in sludge cake was done by a reference-based approach. The method of direct comparison was chosen due to different conditions during particular centrifugation. Samples of disintegrated and original (non-disintegrated) sludge were processes simultaneously. By this approach, a higher comparability among the measurements was achieved.

For the analysis, the following devices were used:

- centrifuge MPW-340 with a maximum acceleration of 2600×g,
- pH-meter WTW-3210,
- rheometer RheolabQC,
- optical microscope with digital image capture.

6.3 DETERMINATION OF REQUIRED TEMPERATURE LEVEL

For determining the required temperature level for thermal disintegration, digested sludge was heated to a temperature of 70, 100, 130 and 160 °C. Then, temperature and pressure (> 0.8 MPa) were maintained for 30 minutes. The total solid concentration in sludge cake was determined in treated and untreated samples. Dewatering conditions used were 1000×g for 10 minutes.

The results of total solid measurements after centrifuge are shown in Table 32. Comparing the total solid concentration of treated samples with untreated samples shows an improvement in dewatering for samples treated at 100 °C and above.

Table 32 Total solid concentrations for thermally treated sludge; 10 min at 1000×g

SLUDGE TEMPERATURE	70 °C	100 °C	130 °C	160 °C
TS of untreated cake [%]	8.5	7.8	8.4	8.2
TS of treated cake [%]	8.8	8.5	12.4	15.5
Change [%]	+ 3	+ 9	+ 47	+ 88

Thermal disintegration of sewage sludge has a positive effect on sludge dewatering by means of centrifuge. The outcome is a higher amount of suspended solids in the centrate and a higher total solid concentration in the cake. Figure 38 illustrates the difference between untreated sludge sample (left) and treated sludge samples at 160 °C (right) after dewatering. The treated sample has a smaller cake volume and a higher amount of centrate. The treated centrate is darker due to the higher concentration of solids.

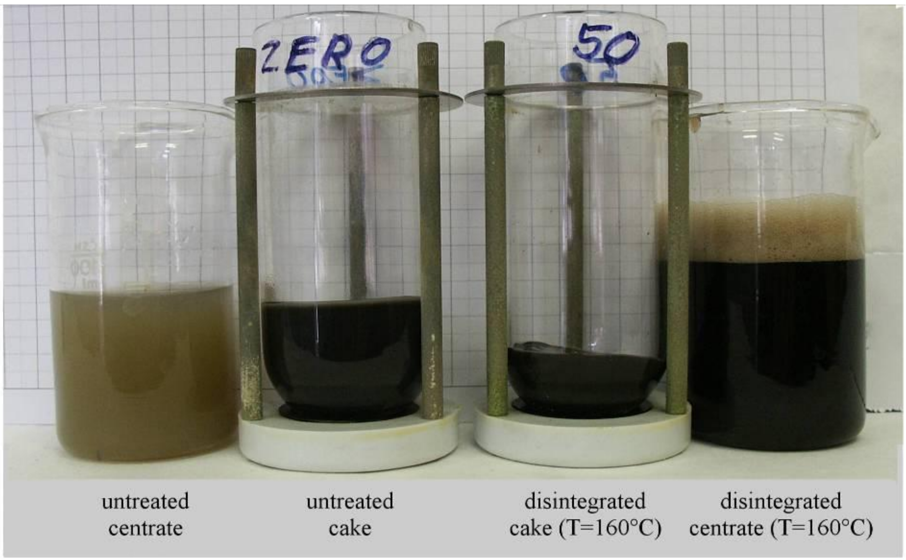


Figure 38 Sludge samples after dewatering

As disintegration changes the structure of sludge, it influences also the flow behavior of liquid sludge (see Figure 39). Samples heated to 70 and 100 °C show similar flow behavior as untreated samples. Dynamic viscosity had been noticeably changed and was far lower after treatment at 160 °C.

In viscosity measurements, in contrast to dewatering tests, treatment at 100 °C did not result in a change of sludge properties and suggested a disintegration temperature in the magnitude of 130 °C for thermal disintegration. Beneath this treatment temperature the sludge properties are not permanently changed.

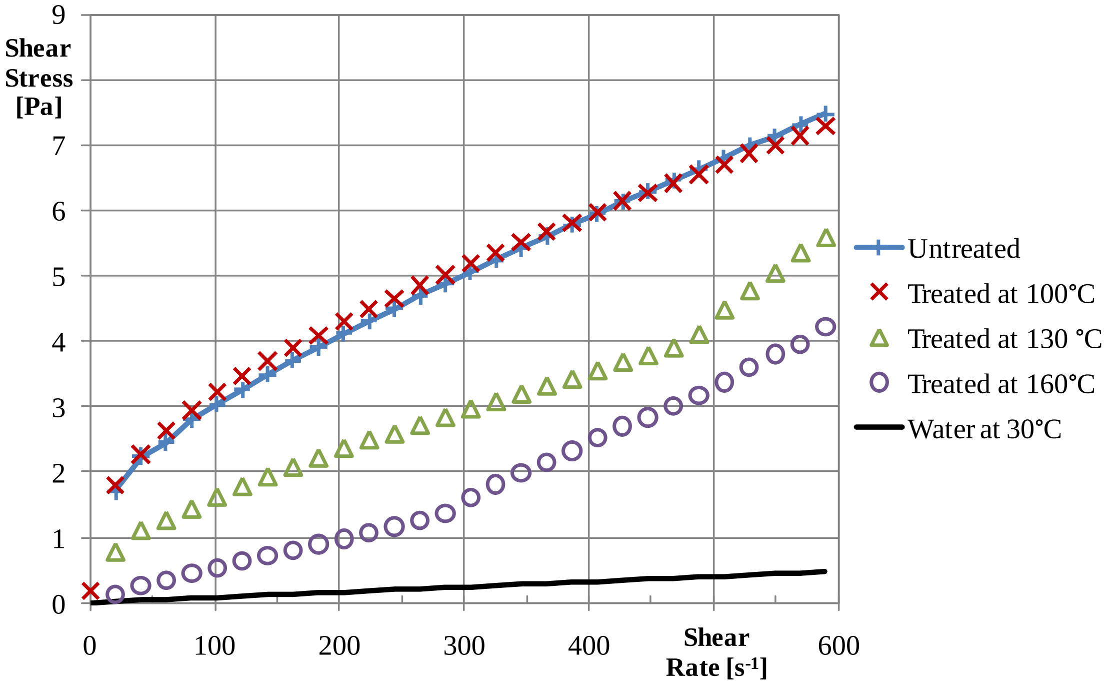


Figure 39 Rheograms of heat treated sludge samples; measured at 30 °C

6.4 INFLUENCE OF THERMO-CHEMICAL DISINTEGRATION

The temperature required for thermal disintegration can be decreased using a combination of thermal and chemical disintegration which is described in the following.

Thermo-chemical experiments were conducted adding sodium hydroxide (NaOH) and citric acid ($C_6H_8O_7$) respectively. The temperature for thermo-chemical disintegration was selected below the required temperature for thermal disintegration (130 °C as determined in section 6.3) and was adjusted to 110 °C. Equal conditions (temperature, pressure and time) were selected for the reference sample (XT-01) and the samples where the amount of agent was increased from zero to 200 g/kg of sludge solids. Table 33 summarizes the conditions and agent dosage used in experiments. The disintegration unit was filled with digested sludge (approx. 2 kg) and agent, then pressurized to 0.5 MPa. Accordingly to experiments for thermal disintegration, the holding time was selected 30 minutes. Centrifugation of sludge was done at an acceleration of 2500×g over 10 minutes. After centrifugation, the centrate was poured off and used to determine the total amount of solids at 105 °C and pH. A detailed overview of conducted measurements and used ratio of agents is shown in Table 33.

Table 33 Overview of measurements and agents used in thermo-chemical disintegration

SAMPLE CODE	AGENT AND TREATMENT METHOD	AGENT DOSAGE *[g/kg TS]*
XT-01	30 min at 110 °C	0
LT-01	NaOH + 30 min at 110 °C	35
LT-02	NaOH + 30 min at 110 °C	120
LT-03	NaOH + 30 min at 110 °C	200
KT-01	citric acid + 30 min at 110 °C	43
KT-02	citric acid + 30 min at 110 °C	112
KT-03	citric acid + 30 min at 110 °C	200

Influence on Dewatering Behavior

The dewatering tests after thermo-chemical disintegration were done using a higher acceleration (2500×g in contrast to 1000×g, as used in section 6.3). This resulted in a higher TS concentration in sludge cakes of untreated and disintegrated sludge. The total solid concentration in untreated liquid sludge amounted to 3.7 % and after dewatering 11.6 %. From the measurements of total solid concentration follows, that thermo-chemical disintegration improves the attainable solid concentration in sludge cake compared to stand-alone thermal disintegration (see Table 34). The lowest values of TS (15.0 and 15.5 %) in thermo-chemically treated samples were obtained for the lowest agent dosage. The highest value of TS (19.1 %) was obtained using 200 g NaOH per kg of sludge solids.

Table 34 Total solid concentrations of thermo-chemically treated sludge; 10 min at 2500×g

SAMPLE CODE	TREATED SAMPLE *[%]*	UNTREATED SAMPLE *[%]*
XT-01	14.4	11.6
LT-01	15.0	12.1
LT-02	15.7	11.7
LT-03	19.1	11.5
KT-01	15.5	11.5
KT-02	16.7	11.8
KT-03	15.7	12.1

Influence on Centrate

As a result of thermo-chemical treatment, the total amount of solids in centrate increased (see Table 35). The values ranged from 7 800 to 22 500 mg/kg of centrate in treated samples, whilst the total amount of solids in original samples accounted for approximately 3 000 mg/kg. Using stand-alone thermal disintegration (XT-01), approximately 16 % of the total solids in sludge sample remained in centrate. Using sodium hydroxide in sludge treatment, the content increased up to 41 % and ranged between 23 and 31 % for citric acid. After centrifugation of original sludge samples only 6 % of the total amount of solids contained in sludge samples remained in centrate. This phenomenon can be traced back to the decrease in sludge particle size. Measured values of pH in reference samples showed only a small deviation from the average value 7.4. The measured values of pH in treated centrate are shown in Table 35.

Table 35 Measured amount of total solids in centrate at 2500×g and pH value

SAMPLE CODE	TREATED SAMPLE *[mg/kg]*	ORIGINAL SAMPLE *[mg/kg]*	PH IN CENTRATE OF TREATED SAMPLES *[-]*
XT-01	7 800	2 800	-
LT-01	10 100	2 800	-
LT-02	17 900	2 800	9.4 at 22.7 °C
LT-03	22 500	2 900	10.1 at 23.7 °C
KT-01	11 500	2 900	7.8 at 23.1 °C
KT-02	14 400	3 200	7.4 at 23.1 °C
KT-03	17 500	3 100	6.6 at 21.4 °C

Influence on Sludge Structure

From the rheograms, shown in Figure 40, it is noticeable that thermal disintegration decreases the dynamic viscosity of sludge. Thermo-chemical disintegration, leads to the most considerable decrease of viscosity, which is not only influenced by the dosage but also by the type of agent. From Figure 40 emerges, that using the lowest dosage of NaOH (LT-01) results approximately in the same dynamic viscosity as stand-alone thermal disintegration (XT-01). Here, only a small change in structure was observed. The highest decrease in viscosity was observed at a dosage of 200 g/kg NaOH (LT-03).

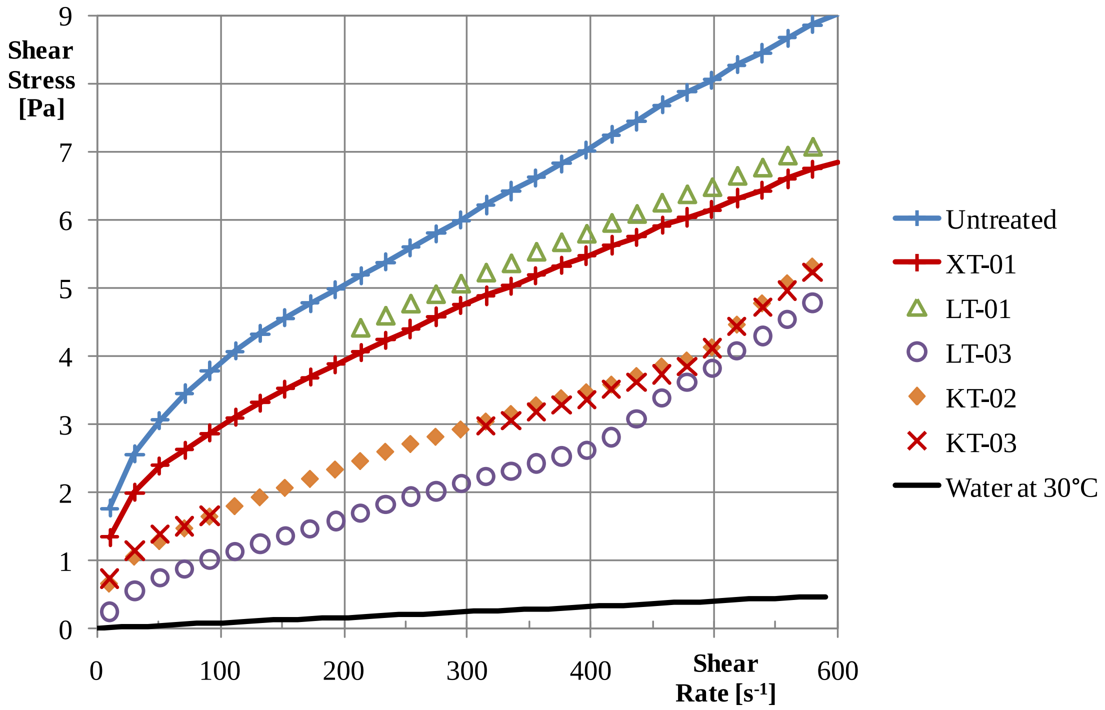


Figure 40 Rheograms of thermo-chemically treated sludge samples; measured at 30 °C

From the microscopic images of sludge (Figure 41 KT-02) a rather considerable change clearly emerges in the sludge structure after its thermo-chemical treatment using higher dosage of agents (irrelevant if lye or acid). The structural change of samples treated by thermal disintegration (Figure 41 XT-01) and for low agent dosage (LT-01, KT-01) is hardly noticeable.

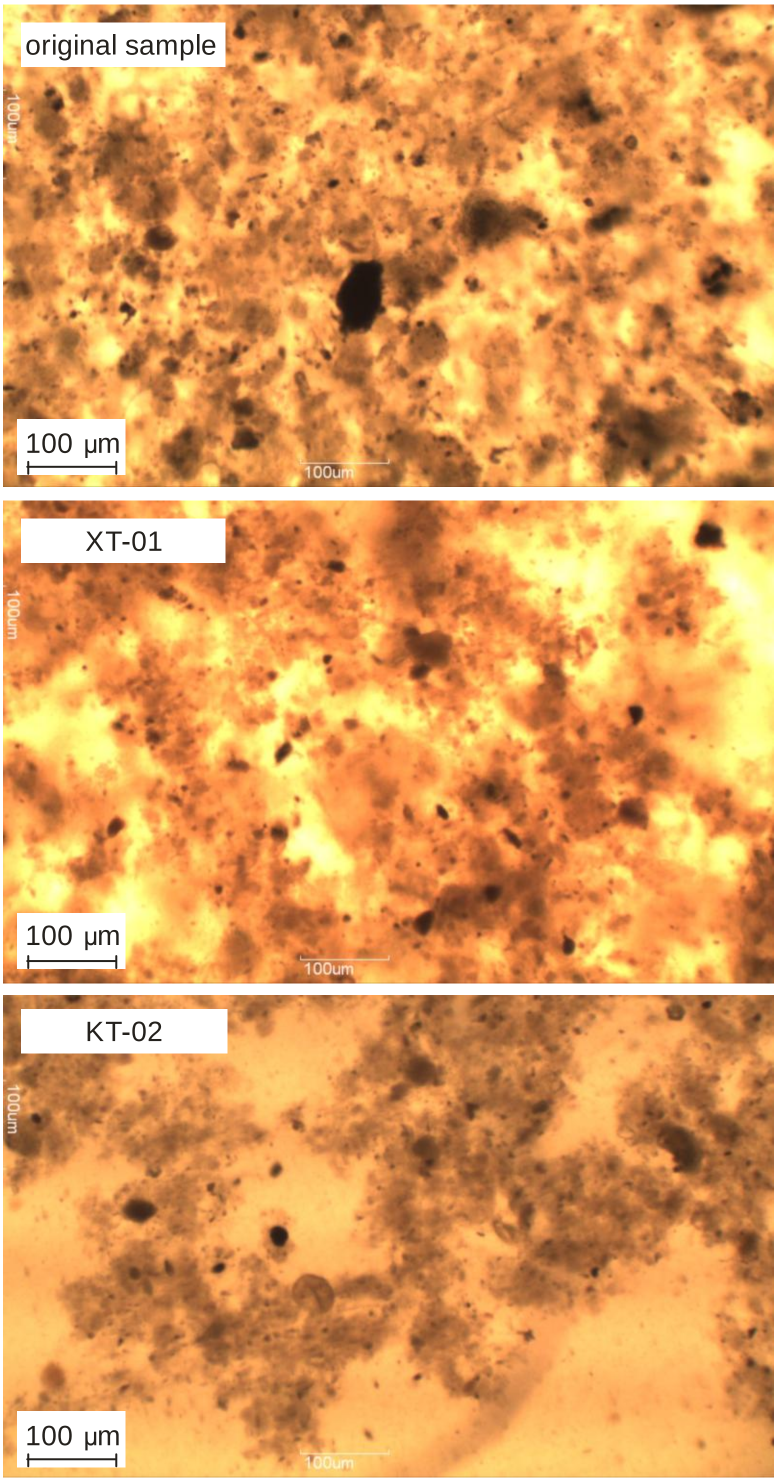


Figure 41 Image of untreated, thermally and thermo-chemically treated sludge (top down)

The influence of thermo-chemical disintegration on sewage sludge dewatering, centrate and sludge structure was investigated and described in this section. The conducted experiments showed that the dewaterability increases for a treatment temperature of 110 °C under addition of NaOH and citric acid, respectively. Using thermo-chemical disintegration in contrast to solely thermal disintegration, the treatment temperature can be decreased by 30-40 °C. Thus, from the energy point of view, thermo-chemical disintegration can be operated using less heating energy than thermal disintegration. A disadvantage is the higher pollution in centrate, which increases the return load of the biological wastewater treatment stage. The influence of thermo-chemical disintegration on the operation of a WWTP is discussed in the following section.

6.5 INFLUENCE OF THERMO-CHEMICAL DISINTEGRATION ON WWTP OPERATION

For determining the influence of thermo-chemical treatment on the WWTP operation, it was necessary to evaluate the dewatering experiments using flocculant agent. In experiments, NaOH was used as an agent in thermo-chemical treatment. The treatment conditions were selected accordingly to previous thermo-chemical treatment experiments (110 °C for 30 minutes at 0.5 MPa). In experiments, the NaOH amount was adjusted to 100 g/kg of sludge solids. Based on indicative measurements, the polymer flocculant Ciba ZETAG 8185 was chosen out of three flocculant agents and used in dewatering experiments. The flocculant dosage for untreated samples amounted to 6 g/kg sludge solids. Based on experience gained from experiments investigating the influence of flocculant on centrate, which were described in [15], a higher flocculent dosage was selected and amounted to 8 g/kg sludge solids. Thus, the concentration of undissolved solids in centrate of treated samples was reduced.

6.5.1 Attainable Total Solid Concentration under Operational Conditions

The experimentally determined total solid concentration using a beaker centrifuge is considerably lower in comparison with TS concentration attained in operational-scale using a dewatering centrifuge or filter press. Transferring experimentally determined results to operational-scale was subject to research summarized in [79] and [80]. The dependencies were determined for different centrifuge accelerations (in lab-scale) and different operational-scale dewatering machinery (see Figure 42).

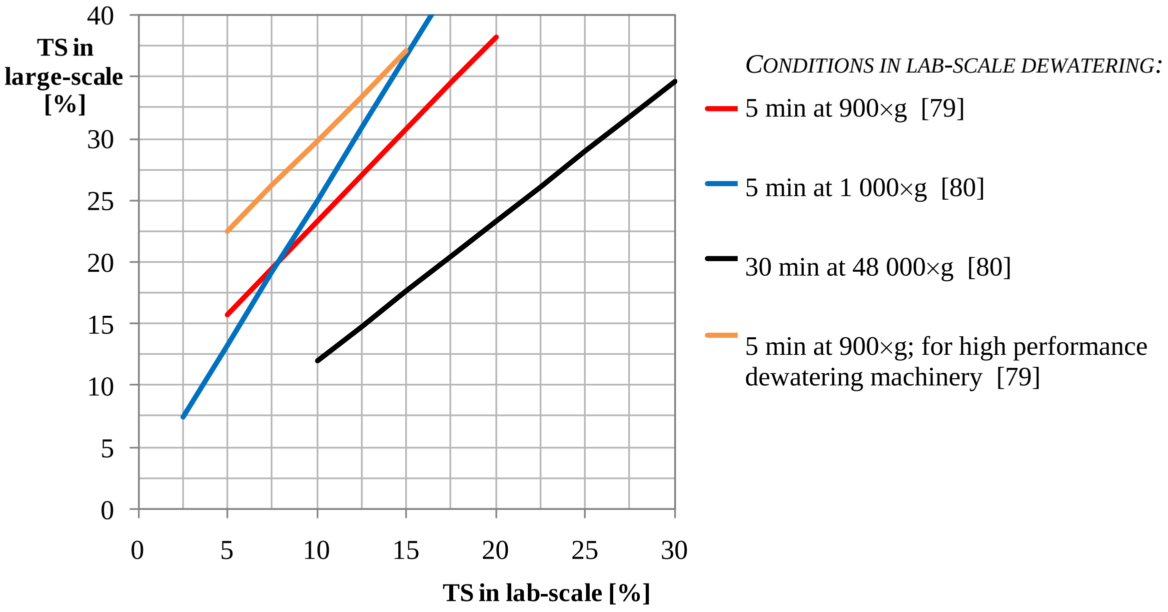


Figure 42 Dependence of attainable TS concentrations in operational-scale and lab-scale

The lab-scale dewatering conditions for this work were chosen 1000×g for 5 minutes. The dependency of TS concentration in operational-scale was selected accordingly to [80] and is given by equation (6-1).

$$TS_{op-scale} = 2.35 \cdot TS_{lab-scale} + 1.49 \tag{6-1}$$

where $TS_{op-scale}$ = total solid concentration attained under operational conditions [%]
$TS_{lab-scale}$ = total solid concentration attained under laboratory conditions [%]

6.5.2 Sludge Dewaterability and Centrate Composition

The total solid concentration of digested liquid sludge amounted to 3.1 %. The results of total solids after dewatering in lab-scale, and in operational-scale are given in Table 36. The dewatering tests, conducted in lab-scale, of untreated sludge and thermo-chemically treated sludge suggest an increase by seven percentage points in operational-scale. This corresponds to a reduction of 25 % for the disposal of dewatered sludge.

Table 36 Total solid concentration of thermo-chemically treated sludge; 5 min at 1000×g using polymeric flocculant

	TS IN LAB-SCALE ♦ *[%]*	TS IN OPERATIONAL-SCALE ♣ *[%]*
Untreated sludge – cake	8.3	21.0
Treated sludge - cake	11.3	28.1

♦ Average of three samplings
♣ Proposed by equation (6-1)

The centrate properties were determined in an accredited laboratory. The protocol of measurement is listed in [81]. The amount of total solids in centrate was reduced by the addition of flocculant and ranged between 1540 mg/kg in untreated, and 9850 mg/kg in treated sample. For thermo-chemically treated samples, the COD was in the range of 9000 mg/l. The COD in the untreated sludge amounted to 1500 mg/l, which corresponds to operational data given in [82], where the COD in centrate amounts to 1795 mg/l. Sludge disintegration has minor influence on the ammonium concentrations in centrate. The concentrations determined in experiments amount to 1062 mg/l in treated sludge.

Table 37 Centrate properties of thermo-chemically treated sludge; 5 min at 1000×g using polymeric flocculant

	UNTREATED SLUDGE	TREATED SLUDGE
COD_{Cr} [mg/l]	1500	8700
Undissolved solids [mg/l]	330	3720
Total solids [mg/kg]	1540	9850
pH [-]	8.0	9.2
NH_4 [mg/l]	1031	1062
NO_3 [mg/l]	< 0.20	1.58
NO_2 [mg/l]	0.13	1.09
Total nitrogen [mg/l]	844	1319

6.5.3 Additional Load on the WWTP

Dewatering of disintegrated sludge causes a higher pollution in centrate. Treatment of this water is accomplished in the biological treatment stage of the wastewater treatment plant. The additional oxygen consumption is calculated from the carbonaceous organic pollutants and the nitrogenous compounds (NH_4^+ and NO_3^-) contained in the centrate. Here, the oxygen consumption for the removal of organic (carbonaceous) pollutants is calculated using equation (6-2) [83]:

$$OC_C = \frac{S_0 - S}{1000} \cdot \left(\frac{1}{f} - 1.42 Y_{obs} \right) \qquad \left[\frac{g}{l} \right] \qquad (6\text{-}2)$$

where
OC_C = specific O_2 consumption for the removal of organic matter [g/l]
S_0 = influent BOD_5 concentration [mg/l]
S = effluent BOD_5 concentration [mg/l]
f = conversion factor for converting BOD_5 to BOD_u; usually amounts to 0.67
Y_{obs} = observed yield of produced biomass; usually amounts to 0.5 g/g

The oxygen consumption for degradation of ammonium during nitrification is calculated from the concentration of ammoniacal nitrogen using equation (6-3) [22].

$$OC_N = \frac{4.3\ S_0 - S}{1000} \qquad \left[\frac{g}{l}\right] \qquad (6\text{-}3)$$

where OC_N = specific O_2 consumption of nitrification [g/l]
S_0 = influent $N\text{-}NH_4^+$ concentration [mg/l]
S = effluent $N\text{-}NH_4^+$ concentration [mg/l]

In denitrification (anoxic conditions), the oxygen contained in nitrate is consumed. The consumption reduces the amount of required oxygen as evident from equation (6-5) [22].

$$OC_D = \frac{2.9\ S_0 - S}{1000} \qquad \left[\frac{g}{l}\right] \qquad (6\text{-}4)$$

where OC_D = specific O_2 consumption of denitrification [g/l]
S_0 = influent concentration $\Sigma(N\text{-}NO_3^-$, $N\text{-}NH_4^+$ and $N\text{-}NO^{2-})$ [mg/l]
S = effluent concentration $\Sigma(N\text{-}NO_3^-$, $N\text{-}NH_4^+$ and $N\text{-}NO^{2-})$ [mg/l]

The individual oxygen consumption in the biological treatment stage is calculated from the pollutants' reductions (S_0-S) given in Table 38. The outflow concentrations of the biological treatment stage were selected according to operational data [82]. The BOD_5 is determined from the measured COD, where the BOD_5/COD ratio was 0.5.

Table 38 Pollution reduction (S_0-S) used in the calculation of oxygen requirement

	Untreated Centrate	Treated Centrate
BOD_5 [mg/l]	745	4345
$N\text{-}NH_4^+$ [mg/l]	796	821
$N\text{-}NO_3^-$ [mg/l]	-11.2	-10.8
$N\text{-}NO_2^-$ [mg/l]	-0.5	-0.2

The total oxygen consumption (OC_{total}) consists of the individual oxygen consumptions as given in equation (6-5).

$$OC_{total} = OC_C + OC_N - OC_D \qquad \left[\frac{g}{l}\right] \qquad (6\text{-}5)$$

The total oxygen consumption amounts to 1.72 g/l for untreated, and 4.57 g/l for treated centrate (see Table 39).

The consumption of electricity for the supply of air into the aeration tanks is influenced by the aeration efficiency (AE), which is defined as the ratio of the oxygen amount (OC) and the input power of the aerator and includes losses by transmission and frequency converter. The AE used in this work amounts 1.23 kg O_2/kWh and was evaluated for an existing WWTP with a capacity higher than 1 000 000 PE.

The calculated values are given in Table 39. The additional energy consumption for the treatment of centrate in the biological treatment stage is given by the difference of the specific energy consumptions of treated and untreated centrate and amounts to 2309 Wh/m³.

Applying the calculation on municipal wastewater described in [82], the specific energy consumption of the aeration amounts to 8.3 kWh/a per population equivalent (expressed as PE-COD110). Considering that the determined value represents solely the aeration, it is in agreement with benchmarks described in [17] and [18] and represents 35 % of the total electricity consumption of the WWTP.

Table 39 Oxygen consumption of centrate in the aeration process

	UNTREATED CENTRATE	TREATED CENTRATE
OC_{total} [g/l]	1.72	4.57
Electricity consumption [Wh/m^3]	1406	3715

6.6 DISINTEGRATION PROCESS FOR ENHANCED DEWATERING

Sludge dewatering can be improved by the disruption of sludge flakes. In order to benefit from this, disintegration is integrated between digestion and dewatering unit as shown in Figure 43. For this application a reduction of approximately 30 % in the dewatered sludge mass has been observed in experiments.

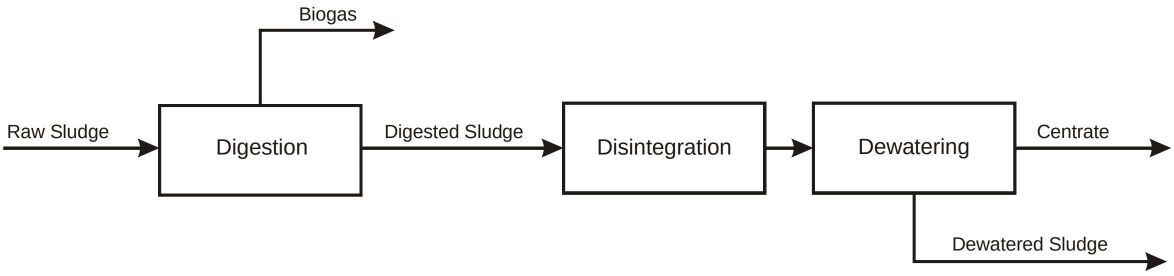


Figure 43 Flow diagram of sludge management for enhanced dewatering

The considered process of thermo-chemical disintegration aims at enhanced dewatering of sewage sludge and is rated for a liquid sludge amount of 10.8 t/d containing 4 % of solids. The resulting amount of total solids (432 kg/d) refers to a WWTP capacity of 10 000 PE.

The disintegration process, as shown in Figure 44, is operated continuously and consists of the disintegration unit and a heat exchanger which recovers heat from the hot sludge, and thus raises the temperature of cold sludge from 10 to 50 °C. Further increase in temperature is accomplished in the disintegration unit, where the required disintegration temperature is reached by thermo-oil. Prior to leaving the system, disintegrated sludge is recooled in the heat recovery.

The internal heat recovery is constrained by the availability of heat exchangers suitable for the considered process. For balancing the process, the amount of recovered heat refers to a double pipe heat exchanger.

For operational use of thermo-chemical disintegration, liquid agent is used to ease its handling. The considered specific dosage of NaOH 50% into the sludge corresponds to the concentrations used in conducted experiments (described in section 6.5.3) and amounts to 0.2 kg/kg TS. The temperature level for disintegration is selected according to conducted experiments of thermo-chemical disintegration (described in section 6.5).

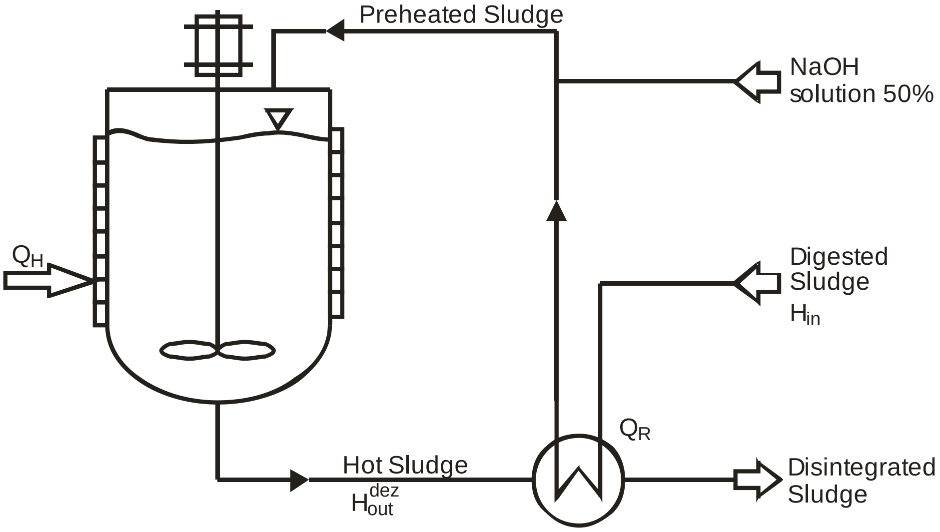


Figure 44 Flow diagram of disintegration process

6.6.1 Design of Disintegration Unit

The disintegration unit shown in Figure 45 is designed as a stirred pressure vessel suitable for thermal or thermo-chemical disintegration of sludge. The required additional heat (Q_H) is transferred by heat transfer medium. This flows through heating ducts, welded on the cylindrical shell of the unit. Sludge enters the unit continuously at the top of the vessel, remains for a mean retention time of 4 h and leaves the tank at the bottom of the tank. The heat transfer inside the vessel is intensified by means of a stirrer.

In experiments a treatment temperature around 170 °C had been found unfavorable as it changes the properties of sludge. From this reason, the maximum temperature of heat transfer medium should be selected lower. For the designed disintegration unit, the maximum temperature of the heat transfer medium is selected 160 °C, which results in a minimum heating period of 80 minutes.

Table 40 Design parameters of disintegration unit

Diameter [m]	1.2
Volume [m³]	2.0
Admissible pressure [MPa]	1.0
Admissible temperature [°C]	160

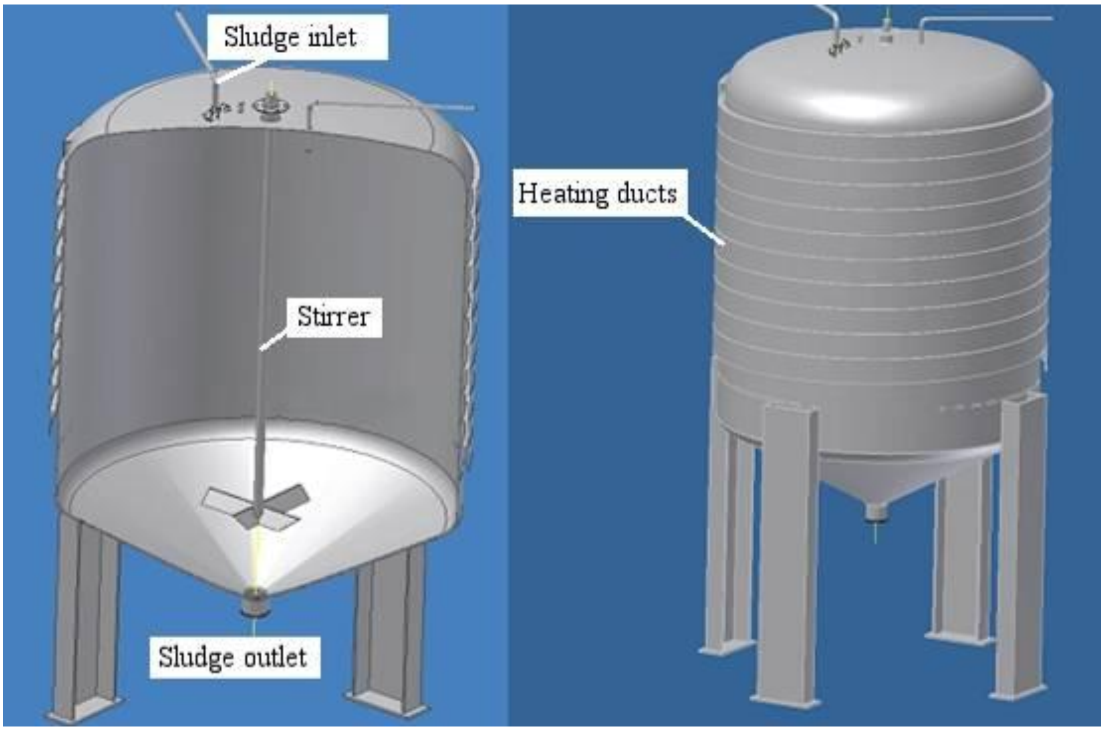


Figure 45 Disintegration unit for thermal and thermo-chemical disintegration [84]

6.6.2 Heat and Mass Balance

The flow rates after disintegration and conventional treatment is shown in Table 41 where the considered amount of liquid sludge amounts to 10.8 m³/d at a total solids concentration of 4 %. According to disintegration measurements (described in section 6.5.1), an increase in solid concentration in the dewatered sludge from 21.0 % to 28.0 % can be expected. The amount of dewatered sludge decreases by 25 % and the amount of centrate increases by 6 %.

Table 41 Mass streams in sludge handling process

	CONVENTIONAL	DISINTEGRATION
inlet		
Digested sludge [kg/d]	10 800	
Total sludge solids [kg/d]	432	
NaOH solution 50 % [kg/d]	-	86.4
outlet		
TS in dewatered sludge [%]	21.0	28.0
Dewatered sludge [kg/d]	2057	1543
Centrate [kg/d]	8743	9257
COD load in centrate [kg/d]	13.1	80.5

In terms of heat balance, the disintegration process (Figure 44) can be described as shown in equation (6-6).

$$H_{out}^{dez} = Q_H + H_{in} + Q_R \qquad J \qquad (6\text{-}6)$$

where H_{in} = enthalpy of digested sludge [J]
Q_R = recovered heat in heat exchanger [J]
Q_H = required additional heat supplied by heat transfer medium [J]
H_{out}^{dez} = enthalpy of hot sludge [J]

The thermal power of the heat exchanger allows recovering a daily heat amount of 1.74 GJ from the hot sludge leaving the disintegration unit and reduces the amount of required heat to 2.66 GJ per day. Table 42 summarizes the heat streams and temperatures.

Table 42 Heat fluxes and temperatures in disintegration process

	HEAT FLUX *[MJ/d]*	STREAM TEMPERATURE *[°C]*
Digested sludge H_{in}	440	10
Required additional heat Q_H	2658	-
Recovered heat in heat exchanger Q_R	1737	-
Hot sludge $H_{out, dez}$	4835	110
Preheated sludge	-	49.5
Disintegrated sludge	-	70.5

For sludge digestion, waste heat from the incineration of biogas can be supplied to the disintegration process. With respect to the amount of available waste heat from biogas utilization, the heat demand of the disintegration process (Q_H) is covered by internal sources or has to be acquired in the form of natural gas.

6.6.3 Economical Evaluation

Sludge disposal costs vary depending on the disposal route. The major part of sludge, produced in the Czech Republic is disposed of in agriculture and composting. As a result, the costs for disposal are relatively low and range from approximately 450 to 600 Kč/tonne. For the following economical evaluation, the costs are assumed 500 Kč/tonne.

Capital costs for the disintegration unit account for approximately 1 085 thousand Kč and include the stirred vessel, heat exchanger, burner for the heat transfer medium, dosage system for the chemical agent, project engineering and expenses for construction. The costs for the disintegration vessel and heat exchanger are determined based on the material costs of used steel. The material costs for the used agents remain unconsidered in this evaluation as the application allows to use a suitable chemical agent of low purity at low cost.

The produced centrate has an adverse influence on the cost-effectiveness of the process as it requires more oxygen for its cleaning in the aeration process (discussed in section 6.5.3). The resulting increase in electricity consumption depends on the amount of produced centrate and amounts to 21.85 kWh/d for a TS increase from 21 to 28 % after dewatering. Additional electricity consumption is caused by the stirring of the disintegration unit and summarized in Table 43.

Table 43 Additional electricity consumption caused by disintegration

Vessel mixer [kWh/d]	3.1
Additional blower consumption [kW/m³ of centrate]	2.3
Electricity costs [Kč/kWh]	2.5

For TS concentrations determined in experiments, the payback period amounts to at least 15 years (in case the heat demand of the disintegration process is completely covered by waste heat) and probably exceeds the lifetime of the equipment. The payback period depends highly on the amount of acquired heat. For covering 5 % of the required heat by natural gas, the payback period is prolonged to 20 years. As shown in Figure 46, where the plumb line marks the TS concentration obtained from experiments for a increase in TS concentration from 21 to 28 %.

Analyzing the types of costs and savings (capital costs, electricity costs and savings from sludge disposal) shows that the capital costs highly influence the economy of the process. For a final TS concentrations of 28 % and covering the heat demand by waste heat, the daily capital costs are a fourfold of the costs for electricity and thus strongly influence the payback period (see Figure 47).

Due to the long payback period of 15 years, the influence of increasing sludge disposal costs should be taken into account. During recent years, the fee for landfilling of sludge has risen by 5 % p.a. Thus, the price adjustment for sludge disposal by the private sector can be expected to be in the same magnitude. For a 5 % p.a. increase in disposal costs, and TS increase from 21 to 28 %, the payback period will be reduced by 4 years and amounts to 11 years - see Figure 48, where the plumb lines mark the operation period after which the savings cover the total expenses (break-even point).

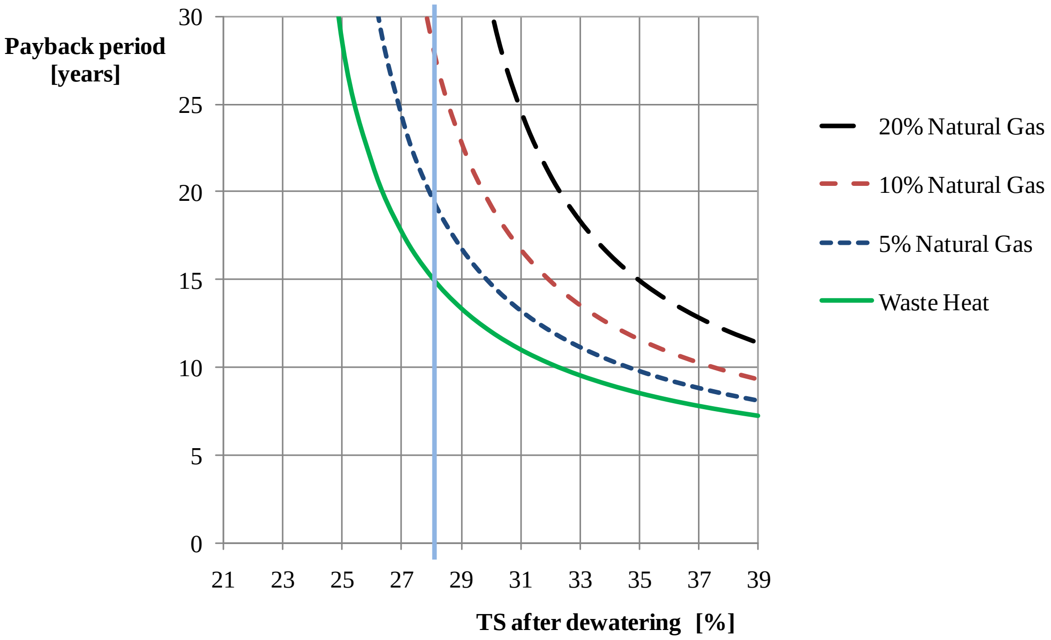


Figure 46 Payback period depending on attained TS and amount of acquired heat

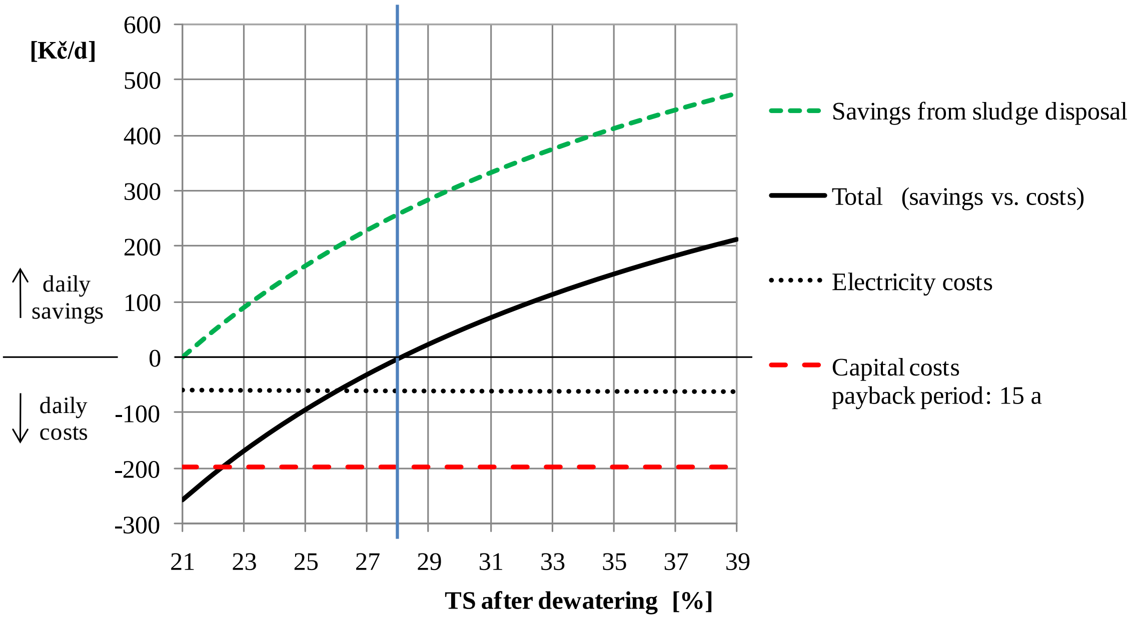


Figure 47 Daily costs and savings of disintegration for a 15 year payback period

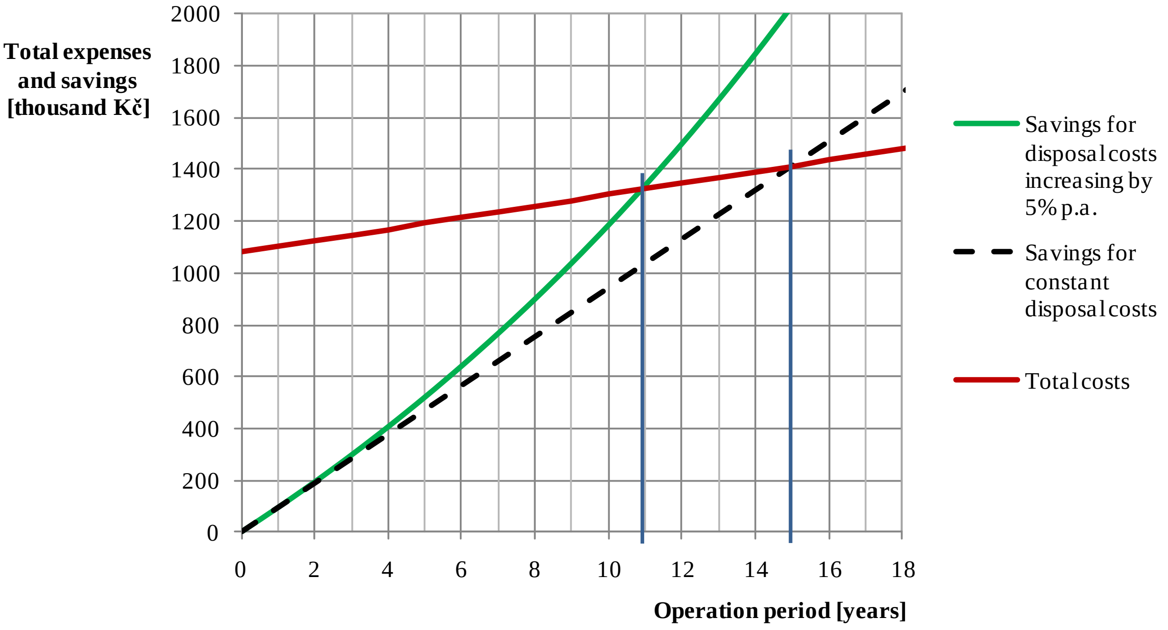


Figure 48 Total expenses and savings for constant and increasing disposal costs

6.6.4 Discussion

Disintegration of digested sludge offers a convenient way of improving sludge dewaterability, and thus reducing its disposal costs. However, the costs (especially the capital costs) strongly impair its economy and the payback over the lifetime cannot be taken for granted.

The efforts undertaken for sludge disintegration should not only be seen as the reduction of waste for disposal, but also as an improvement of sludge quality. Thermal and thermo-chemical disintegration use similar process parameters as required for the sanitation of sewage sludges generated in the processing of animal by-products not intended for human consumption (e.g. from slaughterhouses). Here, the suggested disintegration process could provide a capable method to produce a harmless material fulfilling corresponding legal requirements. Moreover, the reduction of the water contained in dewatered sludge improves the possibilities of sludge utilization in incineration.

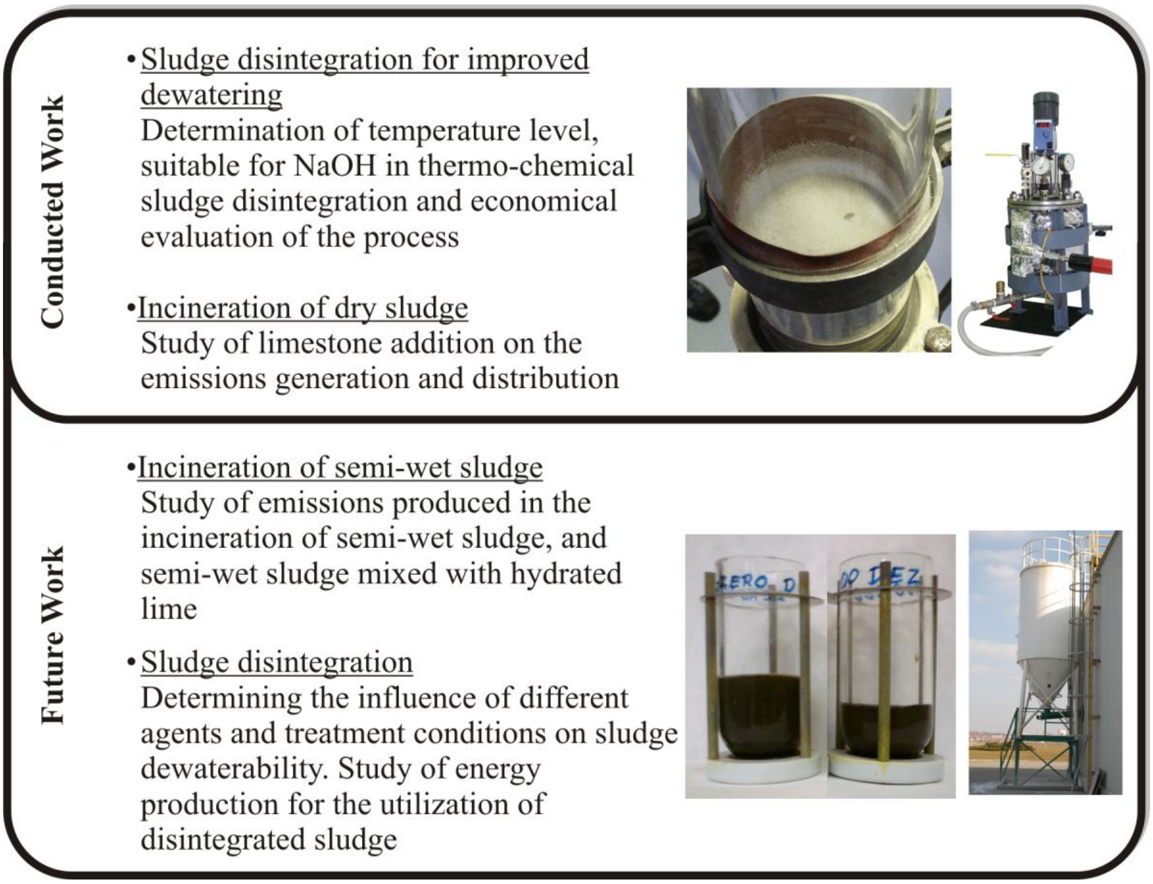
7 CONCLUSION

In current sludge management, the conversion of waste to energy is achieved by incinerating sludge solids or biogas, produced during the anaerobic stabilization of sludge. The incineration of sludge in waste to energy applications falls into the stringent legal frame of waste incineration and their operation is constrained by the low calorific value of sludge and contaminants contained in sludge solids. For the improvement of sludge incineration processes, knowledge of sludge properties, emissions generation and the possibilities of water reduction in the sludge is required. This thesis on the processing of sewage sludge in waste to energy applications contains a description of sludge material properties (density, specific heat capacity and dynamic viscosity), and is, in its main chapters, devoted to sludge disintegration for improved dewatering and the experimental study of emissions in fluidized bed incineration, where the influence of alkali addition is examined.

The material property specific heat capacity was determined for dried sludge using the calorimeter method, and compared with values, estimated from the sludge composition. The estimation, based on the Neuman-Kopp rule (NKR), gave a value of 1.2 kJ/(kg K) and the experimental determination 0.9 kJ/(kg K). Both values are in accordance with values used in literature [32], [47] and [52]. The flow behavior of liquid sludge shows non-Newtonian (yield-pseudoplastic) behavior and the viscosity of disintegrated sludge is lower. The density of liquid sludge is comparable to the density of water. However, air bubbles contained in sludge can lower the density of the liquid.

The energy production from the incineration of sludge solids is constrained by the material properties of sludge – mainly the high water content, which usually ranges between 70 and 84 % after dewatering. As a means of reducing the water content, thermo-chemical disintegration of stabilized sewage sludge before dewatering is considered within this thesis. For this process, the outcome is a reduction of the water content in sludge and a higher pollution concentration in the centrate. Experiments conducted on a laboratory scale suggest a reduction in the water content from 79 % to 72 % after dewatering. The comparison of costs (costs for additional centrate treatment and capital costs for the disintegration unit) with the savings from the reduction of sludge disposal costs result in a long payback period, which probably exceeds the lifetime of the equipment. However, sludge which underlies legal requirements of sludge sanitation can be treated appropriately using the disintegration process considered in this thesis. Furthermore, the water content is reduced and the possibility of its utilization in incineration is improved. Testing the dewaterability of sludge for further agents, as for example salts, in thermo-chemical disintegration, can widen the possible range of suitable agents. Investigating the influence of further agents, which are favorably waste or by-products from production or other processes, can reveal the influence of the agent’s oxidation state, treatment temperature, retention time and pressure on the dewaterability of sludge.

In incineration, the contaminants of dried sludge result in air emissions exceeding the allowed limit values, making comprehensive flue gas treatment mandatory. Experiments were conducted in sludge incineration with the aim of determining the behavior of the gaseous pollutants generated and heavy metals contained in sludge, and the influence of limestone on the distribution of pollutants was also investigated. Using dried sludge (TS = 8.5 %), the experiments confirmed that the addition of limestone into the incineration reactor cannot replace the flue gas treatment. The addition of limestone reduced the emissions of SO_2 and HF and increased the NO_x emissions. The utilization of semi-wet sludge (TS = 31 %) in incineration is in favor of reducing NO_x emissions as reported by [54]. However, with respect to the experimental incineration apparatus, this could not be verified in own measurements as the apparatus is appropriate for dry fuel only. Using a mixture of semi-wet sludge and hydrated lime (as it is used in the treatment of dewatered sludge) can possibly limit the NO_x emissions and reduce the emissions of acidic substances.



Conducted Work

- Sludge disintegration for improved dewatering
  Determination of temperature level, suitable for NaOH in thermo-chemical sludge disintegration and economical evaluation of the process
- Incineration of dry sludge
  Study of limestone addition on the emissions generation and distribution

Future Work

- Incineration of semi-wet sludge
  Study of emissions produced in the incineration of semi-wet sludge, and semi-wet sludge mixed with hydrated lime
- Sludge disintegration
  Determining the influence of different agents and treatment conditions on sludge dewaterability. Study of energy production for the utilization of disintegrated sludge

Figure 49 Future activities

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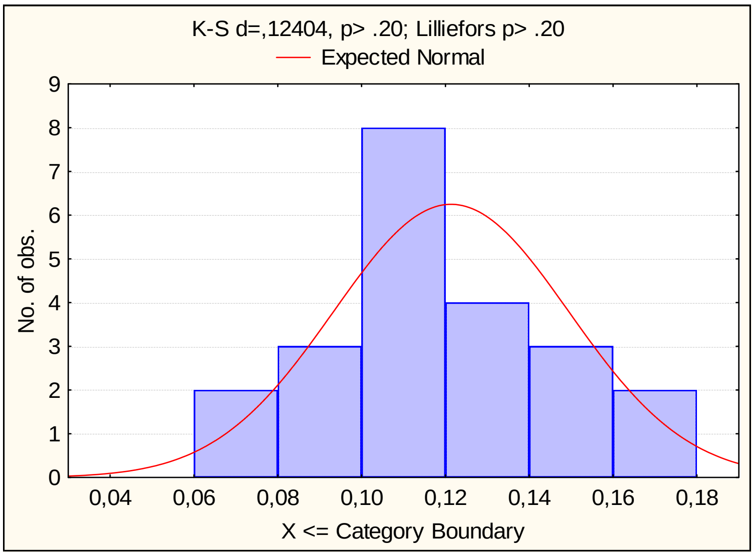
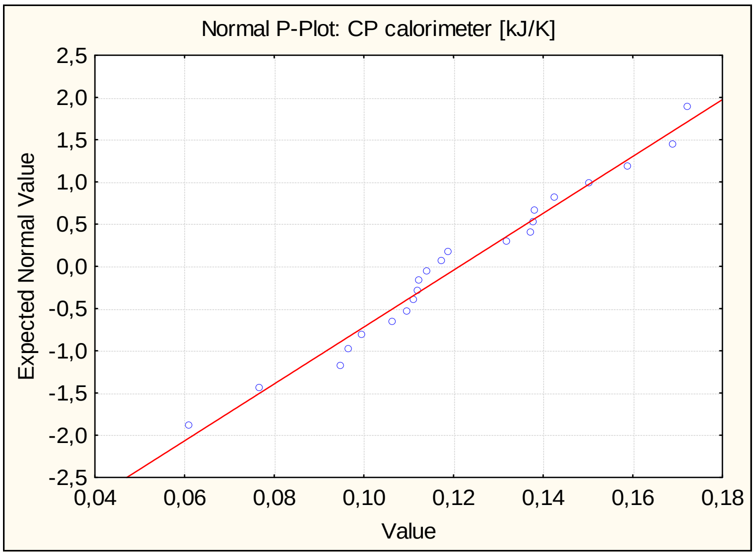
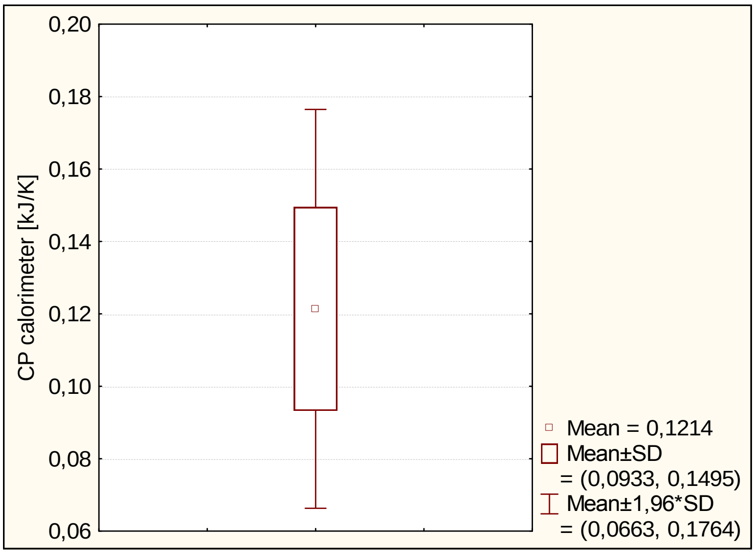
ANNEX

Annex I Statistical analysis of measured calorimeter constant: Ccal



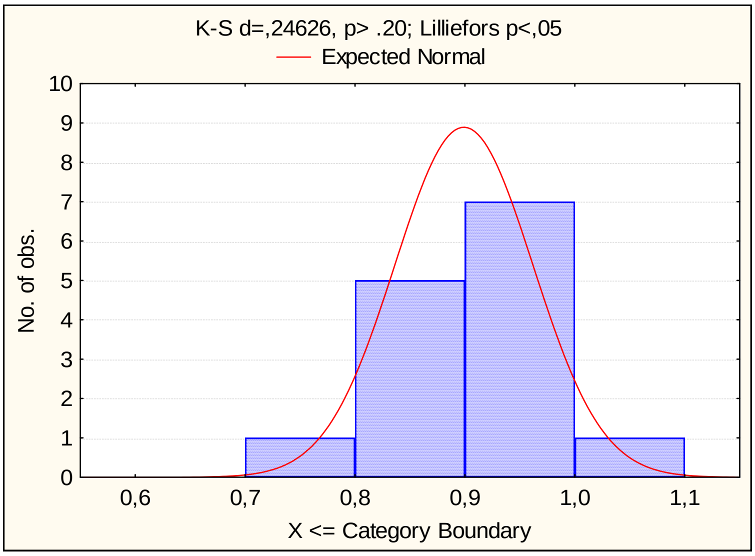


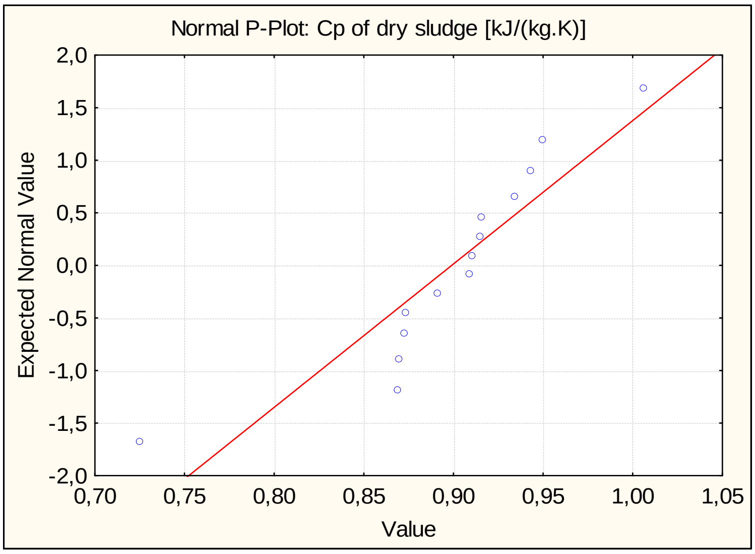


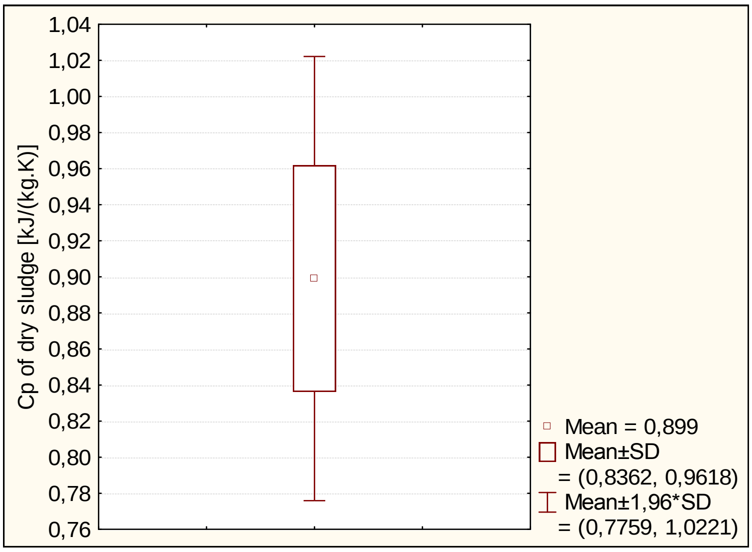
Values of C_{cal} (kJ/K)
0.06119
0.07681
0.09480
0.09669
0.09968
0.10648
0.10960
0.11116
0.11209
0.11229
0.11426
0.11732
0.11903
0.13200
0.13743
0.13794
0.13810
0.14259
0.15043
0.15893
0.16890
0.17229

Total Number:	22
Mean:	0.1214
Confidence Interval(P=.95):	± 0,0124
Variance:	0.000789
Std.Dev.:	0.028097

Annex II Statistical analysis of measured specific heat capacity of dry sludge solids: c_p







Values of c_p (kJ/kg.K)
0.72558
0.86924
0.86953
0.87274
0.87324
0.89159
0.90930
0.91045
0.91472
0.91611
0.93427
0.94359
0.95004
1.00597

Total Number:	14
Mean:	0.8990
Confidence Interval(P=.95):	± 0,0360
Variance:	0.003946
Std.Dev.:	0.062813

Annex III Ultimate analysis of water free dried sludge samples

	SLUDGE A *[%]*	SLUDGE B *[%]*
Ashes	47.64	68.61
Volatile substances	52.36	31.39
Composition of volatile substances		
Hydrogen	8.07	7.03
Carbon	64.41	48.98
Nitrogen	7.28	0.06
Oxygen	20.25	42.88
Sulfur	1.05	0.89
Chlorine	-	0.16
Composition of ashes		
SiO_2	35.18	39.08
Fe_2O_3	21.36	12.48
MnO,	0.09	-
Mn_3O_4	-	0.16
Al_2O_3	10.42	12.92
TiO_2	0.82	0.90
CaO	14.14	15.61
MgO	2.08	2.52
Na_2O	0.67	0.65
K_2O	1.69	1.99
SO_3	0.44	3.24
P_2O_5	13.10	10.45

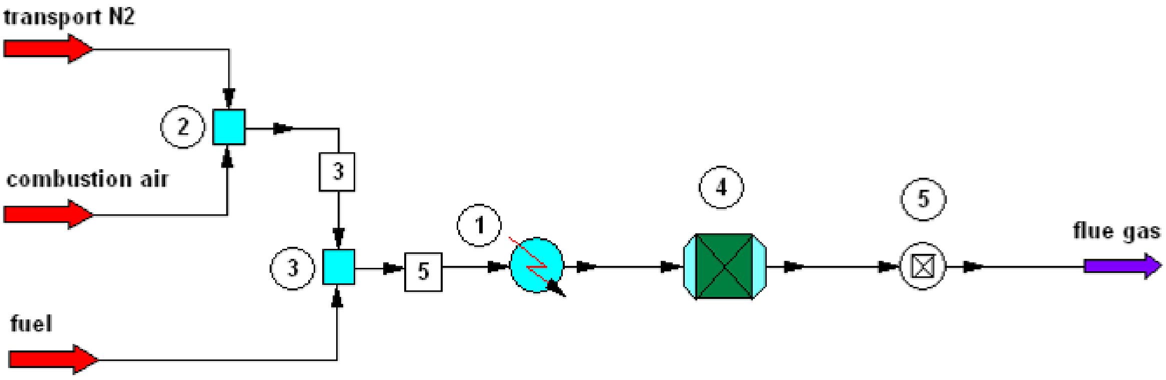
Note: Composition of sludge B according to [59]

Annex IV Specific heat capacity of various components at 20 °C

ORGANIC COMPOUNDS [50]	*[kJ/(kg K)]*
Palmitic acid	1.80
Dextrin	1.30
Melamine	1.47
INORGANIC COMPOUNDS [51]	
SiO_2	0.73
Fe_2O_3	0.64
MnO [50]	0.60
Mn_3O_4	0.49
Al_2O_3	0.76
TiO_2	0.68
CaO	0.76
MgO	0.92
Na_2O	1.18
K_2SO_4 [50]	0.79
P_4O_{10} [50]	0.70

Annex V Results of theoretical flue gas determination using CHEMCAD

Flow diagram



Inlet streams and composition in experiments 1-4

	Transport N_2	*Combustion air*
Total std.V [m^3/h]	1	2.66
Oxygen [vol.%]	0	20.94
Nitrogen [vol.%]	100	78.13
CO_2 [vol.%]	0	0
Ar [vol.%]	0	0.93

Concentration in dry flue gas

Experiment 1	Calculated	Measured	*Fuel A (dry): 500 g/h*
Oxygen [vol.%]	6.55	6.21	
Nitrogen [vol.%]	85.29	-	
CO_2 [vol.%]	7.39	-	
Ar [vol.%]	0.68	-	
SO2 [mg/m^3]	2263	-	
HF [mg/m^3]	24.0	13.4	
HCl [mg/m^3]	70.3	60.9	

Experiment 2	Calculated	Measured	*Fuel B (dry): 525 g/h*
Oxygen [vol.%]	5.57	5.21	
Nitrogen [vol.%]	85.57	-	
CO_2 [vol.%]	8.09	-	
Ar [vol.%]	0.68	-	
SO_2 [mg/m^3]	2150	-	
HF [mg/m^3]	26.5	7.32	
HCl [mg/m^3]	86.4	64.5	

Experiment 3 & 4	Calculated	Measured		
		Exp. 3	Exp. 4	*Fuel C (dry): 460 g/h*
Oxygen [vol.%]	7.02	6.95	6.45	
Nitrogen [vol.%]	85.29	-	-	
CO_2 [vol.%]	6.93	6.73	7.35	
Ar [vol.%]	0.68	-	-	
SO_2 [mg/m^3]	1993	975	382	
HF [mg/m^3]	22.7	33.9	24.9	
HCl [mg/m^3]	66.4	63.4	55.9	

Annex VI PCDD/F concentrations in flue gas for experiment 1

Excerpt from the measurement protocol [67]:

Measurement results PCDD/F concentrations in flue gas

Place	**ICPF AS CR, Praha**
Date	**08.2.2011**
Characteristics	**Incineration of sludge without addition of limestone**
Sampling Point	Sampling port for gasous emissions
Sample Number	2037/1
Journal	Journal 2037/01, TESO Brno spol. s r.o., Brno

Measurement of toxic PCDD/F pollutants				
Toxic congeners		relative toxicity	concentration	
Toxic congeners PCDD			ng/m_N^3	$ng\ TEQ/m_N^3$
2,3,7,8-TCDD	2,3,7,8-Tetrachlorodibenzodioxin	1,00	< 0,007	< 0,0070
1,2,3,7,8-PeCDD	1,2,3,7,8-Pentachlorodibenzodioxin	0,50	< 0,009	< 0,0045
1,2,3,4,7,8-HxCDD	1,2,3,4,7,8-Hexachlorodibenzodioxin	0,10	< 0,010	< 0,0010
1,2,3,6,7,8-HxCDD	1,2,3,6,7,8-Hexachlorodibenzodioxin	0,10	< 0,010	< 0,0010
1,2,3,7,8,9-HxCDD	1,2,3,7,8,9-Hexachlorodibenzodioxin	0,10	< 0,010	< 0,0010
1,2,3,4,6,7,8-HpCDD	1,2,3,4,6,7,8-Heptachlorodibenzodioxin	0,01	< 0,024	< 0,00024
OCDD	Octachlorodibenzodioxin	0,001	< 0,059	< 0,00006
Toxic PCDD total		-	**n.d.**	**n.d.**
Toxic congeners PCDF				
2,3,7,8-TCDF	2,3,7,8-Tetrachlorodibenzofuran	0,10	< 0,018	< 0,0018
1,2,3,7,8-PeCDF	1,2,3,7,8-Pentachlorodibenzofuran	0,05	< 0,013	< 0,0007
2,3,4,7,8-PeCDF	2,3,4,7,8-Pentachlorodibenzofuran	0,50	< 0,013	< 0,0065
1,2,3,4,7,8-HxCDF	1,2,3,4,7,8-Hexachlorodibenzofuran	0,10	< 0,019	< 0,0019
1,2,3,6,7,8-HxCDF	1,2,3,6,7,8-Hexachlorodibenzofuran	0,10	< 0,019	< 0,0019
1,2,3,7,8,9-HxCDF	1,2,3,7,8,9-Hexachlorodibenzofuran	0,10	< 0,019	< 0,0019
2,3,4,6,7,8-HxCDF	2,3,4,6,7,8-Hexachlorodibenzofuran	0,10	< 0,019	< 0,0019
1,2,3,4,6,7,8-HpCDF	1,2,3,4,6,7,8-Heptachlorodibenzofuran	0,01	< 0,023	< 0,0002
1,2,3,4,7,8,9-HpCDF	1,2,3,4,7,8,9-Heptachlorodibenzofuran	0,01	< 0,023	< 0,00023
OCDF	Octachlorodibenzofuran	0,001	< 0,053	< 0,00005
toxic PCDF total		-	**n.d.**	**n.d.**
toxic PCDD+PCDF total		-	**n.d.**	**n.d.**
Upperbound - concentration			**0,348**	**0,032**

Note: values are given at experimental conditions (6,21 % O_2 in dry gases)

Annex VII PCDD/F concentrations in flue gas for experiment 2

Excerpt from the measurement protocol [67]:

Measurement results PCDD/F concentrations in flue gas

Place	**ICPF AS CR, Praha**			
Date	**10.2.2011**			
Characteristics	**Incineration of sludge under addition of limestone**			
Sampling Point	Sampling port for gasous emissions			
Sample Number	2037/2			
Journal	Journal 2037/01, TESO Brno spol. s r.o., Brno			
Measurement of toxic PCDD/F pollutants				
Toxic congeners		relative toxicity	concentration	
Toxic congeners PCDD			ng/m_N^3	ng TEQ/m_N^3
2,3,7,8-TCDD	2,3,7,8-Tetrachlorodibenzodioxin	1,00	< 0,008	< 0,0080
1,2,3,7,8-PeCDD	1,2,3,7,8-Pentachlorodibenzodioxin	0,50	< 0,009	< 0,0045
1,2,3,4,7,8-HxCDD	1,2,3,4,7,8-Hexachlorodibenzodioxin	0,10	< 0,011	< 0,0011
1,2,3,6,7,8-HxCDD	1,2,3,6,7,8-Hexachlorodibenzodioxin	0,10	< 0,011	< 0,0011
1,2,3,7,8,9-HxCDD	1,2,3,7,8,9-Hexachlorodibenzodioxin	0,10	< 0,011	< 0,0011
1,2,3,4,6,7,8-HpCDD	1,2,3,4,6,7,8-Heptachlorodibenzodioxin	0,01	< 0,023	< 0,00023
OCDD	Octachlorodibenzodioxin	0,001	< 0,048	< 0,00005
Toxic PCDD total		-	**n.d.**	**n.d.**
Toxic congeners PCDF				
2,3,7,8-TCDF	2,3,7,8-Tetrachlorodibenzofuran	0,10	< 0,010	< 0,0010
1,2,3,7,8-PeCDF	1,2,3,7,8-Pentachlorodibenzofuran	0,05	< 0,011	< 0,0006
2,3,4,7,8-PeCDF	2,3,4,7,8-Pentachlorodibenzofuran	0,50	< 0,011	< 0,0055
1,2,3,4,7,8-HxCDF	1,2,3,4,7,8-Hexachlorodibenzofuran	0,10	< 0,012	< 0,0012
1,2,3,6,7,8-HxCDF	1,2,3,6,7,8-Hexachlorodibenzofuran	0,10	< 0,012	< 0,0012
1,2,3,7,8,9-HxCDF	1,2,3,7,8,9-Hexachlorodibenzofuran	0,10	< 0,012	< 0,0012
2,3,4,6,7,8-HxCDF	2,3,4,6,7,8-Hexachlorodibenzofuran	0,10	< 0,012	< 0,0012
1,2,3,4,6,7,8-HpCDF	1,2,3,4,6,7,8-Heptachlorodibenzofuran	0,01	< 0,022	< 0,0002
1,2,3,4,7,8,9-HpCDF	1,2,3,4,7,8,9-Heptachlorodibenzofuran	0,01	< 0,022	< 0,00022
OCDF	Octachlorodibenzofuran	0,001	< 0,054	< 0,00005
toxic PCDF total		-	**n.d.**	**n.d.**
toxic PCDD+PCDF total		-	**n.d.**	**n.d.**
Upperbound - concentration			**0,299**	**0,028**

Note: values are given at experimental conditions (5,21 % O_2 in dry gases)

Annex VIII PAH concentrations in flue gas for experiment 1 and 2

Excerpt from the measurement protocol [67]:

Measurement results of PAH concentrations in flue gas

Place	ICPF AS CR, Praha	
Journal	Journal 2037/01, TESO Brno spol. s r.o., Brno	
Sampling Point	Sampling port for gasous emissions	
Sample Number	2037/1	2037/2
Date	08.2.2011	10.2.2011
Characteristics	sludge A	sludge B + Limestone
Amount of sampled gas	374,55 dm^3	372,39 dm^3
pollutant	concentration (ng/m_N^3)	concentration (ng/m_N^3)
Fluoranthene	5051	4568
Pyrene	15748	15049
Benzo[g,h,i]perylene	5051	4838
Benzo[a]anthracene	176	150
Chrysene	294	322
Benzo[b]fluoranthene	292	260
Benzo[k]fluoranthene	137	99
Benzo[a]pyrene	110	107
Indeno[1,2,3-cd]pyrene	185	156
Dibenz[a,h]anthracene	< 59	< 54
total PAH	**27044**	**25550**

Note: values are adjusted for carrier nitrogen and given at 11 %O_2 in dry gases

Annex IX PCB concentrations in flue gas for experiment 1 and 2

Excerpt from the measurement protocol [67]:

Measurement results of PCB concentrations in flue gas

Place	ICPF AS CR, Praha	
Journal	Journal 2037/01, TESO Brno spol. s r.o., Brno	
Sampling Point	Sampling port for gasous emissions	
Sample Number	2037/1	2037/2
Date	08.2.2011	10.2.2011
Characteristics	sludge A	sludge B + Limestone
Amount of sampled gas	374,55 dm^3	372,39 dm^3
pollutant	concentration ($\mathrm{ng/m_N^3}$)	concentration ($\mathrm{ng/m_N^3}$)
mono-PCB	53,49	37,63
di-PCB	104,00	56,43
tri-PCB	297,13	177,37
tetra-PCB	219,88	131,68
PCB#77	< 1,04	< 0,86
PCB#81	< 0,10	< 0,09
penta-PCB	56,46	69,87
PCB#105	< 1,16	< 2,39
PCB#114	< 0,11	< 0,13
PCB#118	< 7,13	< 6,44
PCB#123	< 0,10	< 0,13
PCB#126	< 0,11	< 0,12
hexa-PCB	124,80	145,12
PCB#156	2,20	2,12
PCB#157	< 0,41	< 0,54
PCB#167	< 0,71	1,02
PCB#169	< 0,41	< 0,32
hepta-PCB	65,37	61,80
PCB#170	8,02	7,26
PCB#180	23,47	21,50
PCB#189	< 0,92	< 0,81
octa-PCB	< 13,08	9,14
nona-PCB	< 5,05	< 2,95
deca-PCB	< 0,17	< 0,20

Note: values are adjusted for carrier nitrogen and given at 11 %O_2 in dry gases