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Master's Thesis

Heavy metal fractionation in thermochemical fluidised bed conversion to enable P-recovery from sewage sludge ashes

presented by
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Declaration of academic honesty

I certify that the master thesis at hand is to the best of my knowledge and belief the result of my own investigations and is composed by myself unless stated otherwise in the text. All content derived from the work of others has been specifically acknowledged. Furthermore, I confirm that I have not submitted this master thesis either nationally or internationally in any form.

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Abstract

Phosphorus recovery from sewage sludge is a central challenge for securing future food production, as fertiliser production is currently dependent on rock phosphate, a finite raw material declared a critical resource by the European Union in 2014. To face this challenge, the removal of heavy metals occurring in sewage sludge is essential, as is the bio-availability of the phosphate product to enable the application in agriculture. In this thesis, the recovery of phosphorus from sewage sludge is aimed in a single step process by thermochemical treatment. Experiments in a 10 kW bubbling fluidised bed reactor are conducted to identify the behaviour of different additives (NaCl, $CaCl_2$, $MgCl_2$, and Na_2SO_4) at 800 °C and 950 °C. A higher reduction of heavy metals (Pb, Cd, Zn, Cu, Ni, and Cr) is demonstrated with an increased additive amount of 2.2 wt% Cl compared to 0.7 wt% Cl. Thereby, $MgCl_2$ achieves the highest reduction for Cu and Zn to 67 % and 48 %, and $CaCl_2$ for Pb (54 %) and Cd (51 %), relative to samples without additives. Treatment with sub-stoichiometric oxygen supply shows a trend to higher reduction occurring for Cu, Zn, and Pb. The maximum phosphate solubility in neutral ammonium citrate of 42 % is achieved with $MgCl_2$ samples (0.7 wt% Cl, $\lambda < 1$). In the experiments, heavy metals accumulate in the filter ash fraction, while phosphates remain in the bottom ash fraction, that shows significant reduction of heavy metals. Bottom ash obtained in a single step thermochemical treatment process therefore provides the potential for further application in agriculture and for closing the gaps in phosphorus supply.

German Abstract

Um die Abhängigkeit von begrenztem Phosphatgestein zu verringern, bietet Klärschlamm das Potential zur Rückgewinnung von Phosphor. In der Aufbereitung des Klärschlamms spielt dabei die Abtrennung der vorkommenden Schwermetalle eine zentrale Rolle, sowie die Pflanzenverfügbarkeit der Phosphate, da beide Aspekte den Einsatz in der Landwirtschaft beschränken. In der vorliegenden Arbeit wird die Rückgewinnung von Phosphor aus Klärschlamm mittels thermochemischer Behandlung in einem einstufigen Prozess angestrebt. Unter der Zugaben von vier Additiven (NaCl, $CaCl_2$, $MgCl_2$, und Na_2SO_4) wurde Klärschlamm in einer 10 kW Wirbelschicht bei 800 °C und 950 °C behandelt. Bei einer erhöhten Additivkonzentration von 2,2 wt% Cl im Vergleich zu 0,7 wt% Cl zeigen die Ergebnisse eine allgemein verbesserte Reduktion der untersuchten Schwermetalle (Pb, Cd, Zn, Cu, Ni, und Cr). $MgCl_2$ erreicht dabei für Cu und Zn die höchsten Reduktionen auf jeweils 67 % und 48 % gegenüber den Versuchen ohne Additive, und $CaCl_2$ für Pb (54 %) und Cd (51 %). Bei der Variation der Prozessbedingungen zeigt die unterstöchiometrische Sauerstoffzufuhr einen Trend zur verbesserten Schwermetallabtrennung für Cu, Zn, und Pb. Seitens der Pflanzenverfügbarkeit weist $MgCl_2$ (0,7 wt% Cl, $\lambda < 1$) mit 42 % gegenüber den anderen Proben die höchste Phosphatlöslichkeit in einer neutralen Ammoniumcitrat-Pufferlösung auf. Aus den Ergebnissen geht eine Anreicherung der Schwermetalle in der Filterasche hervor, während die Phosphate in der Bodenasche verbleiben, die gleichzeitig den höchsten Schwermetallrückgang verzeichnet. Die Bodenasche bietet daher das Potenzial für den Einsatz in der Landwirtschaft und damit als nachhaltige Phosphorquelle.

Contents

1 Introduction

In order to obtain socially, economically, and environmentally balanced development throughout the planet, the United Nations declared the Agenda for Sustainable Development, and withal defined their core targets: the 17 Sustainable Development Goals (SDGs). These goals aim for improvement of human equality and compliance of human rights, as well as the sustainable management of bio-resources and worldwide climate justice (United Nations, 2015).

Sustainable management of phosphorus, including both the production and consumption, broaches the issue of multiple goals (Kanter and Brownlie, 2019). Jarvie et al. (2015) even emphasises on the unique role of phosphorus in the interacting relation of water, energy, and food security, and hence, is linking phosphorus to the majority of the Sustainable Development Goals.

Regarding the secure access to food on a global scale, phosphorus takes a pivotal role, as the demand for agricultural products will be increasing, due to global population growth and changes in dietary patterns (Malingreau et al., 2012; Kanter and Brownlie, 2019). Already now, food production strongly depends on the availability of inorganic fertiliser, and thereby its main components phosphorus, nitrogen, and potassium, but its dependence will be further increased by this predicted growth in demand (Kanter and Brownlie, 2019). The second Sustainable Development Goal, targeting the eradication of hunger, is hence directly related to the availability of phosphate rock or alternative phosphorus sources (Hermann et al., 2018). Similarly, the goal of water security is affected by phosphorus processing. Losses along the production chain lead to eutrophication of water and thus, induce a reduction of water security (Jarvie et al., 2015; Cordell et al., 2012).

However, phosphate rock, which covers the total phosphorus demand, is a finite resource and therefore characterised by scarcity (Cordell et al., 2009; Jasinski, 2020). According to Jasinski (2020) the worldwide reserves of phosphate rock account for 69 billion tons; the term reserves referring to identified resources, that are economically viable of mining with respect to their compliance with minimum criteria in chemical and physical conditions. A regional monopoly can certainly be discerned, as more than two thirds of the global reserves are situated in Morocco and the Western Sahara. Nevertheless, the biggest production mines are currently located in China. At the current ratio of production and reserves, the peak phosphorus will not be reached in short-term future, as predicted at the beginning of this century (Cordell et al., 2009). However, at the current consumption level of phosphate (47 million tons P_2O_5 in 2019), rock reserves will be scarce within the next 300 years (Cordell et al., 2012; Dawson and Hilton, 2011; Jasinski, 2020). Apart from scarcity, phosphate rock further bears an environmental impact due to mining processes and their energy intensity. Critical emissions include SO_2 and fine rock dust, that occur during the drying, calcining, grinding, and acidulation (Tonini et al., 2019).

In order to address the predicted phosphorus scarcity and eutrophication by mismanagement, the European Union declared phosphorus a critical resource in 2014. An imposed recycling quota on residues containing phosphorus, and the implementation of circular economy strategies are consequences (Ayet Puirgarnau, 2020). In Germany, the legislation is adapted since 2017, as a result of which waster water treatment plants are obliged to implement recovery measures until 2029 (BMJV, 2017). In addition, the ability to use recovered phosphorus will permit Europe to reduce its dependence on import from phosphate states (Ayet Puirgarnau, 2020). According to Daneshgar et al. (2018), up to 16 % of mined phosphorus can be covered solely by the recycling of human waste, which equals the actual consumption of phosphorus in human diet. Further losses are throughout the production chain and can be targeted by the circular economy strategies.

In general, waste water, sewage sludge, and sewage sludge ash are potential sources for phosphorus recovery from human waste. The increasing amount of sewage sludge and the resulting need for disposal and treatment techniques make sludge a particularly interesting source of phosphorus (Schnell and Quicker, 2020). Between 2003 and 2007 an annual amount of 11 million dry substance tons sewage sludge was produced in the European Union. Common disposal practises are varying in the EU member states, yet sewage sludge incineration is dominant in several countries like Germany and Belgium (Kelessidis and Stasinakis, 2012). Other pathways, including direct reuse for agricultural purposes and landfilling are controversial, due to different legislation standards regarding the content of organic pollutants and heavy metals and their ensuing entry to and accumulation in nature (Herzel et al., 2016; Kelessidis and Stasinakis, 2012). Similarly, the removal of heavy metal fractions is essential to enable the recovery of phosphorus and the further application of the phosphate product in agriculture. One possible removal technique is thermal treatment of sewage sludge blended with additives in a single-step process. In the same way as with mono-combustion, the organic matters are thermally destroyed, but simultaneously the heavy metals are fractionated, due to the additives. Through the use of sewage sludge, instead of the often used sewage sludge ash, a single-step process is created, that reduces the total energy consumption by heating the fuel only once. The additives, principally, fulfil two roles, firstly they promote the removal of heavy metals and secondly they affect the form of the phosphate product. The removal of heavy metals is enhanced by increasing their volatility. As a result phosphate bearing ash fractions are obtained, that are low in heavy metals, while heavy metals remain in the gaseous phase. As a second aspect, the form of the phosphate product indicates whether a direct application in the agricultural sector is possible. Only few phosphates are available for uptake in plants, hence, the direct formation of these phosphates is preferred to avoid further processing steps. The formation of phosphates is influenced by the applied additives, therefore the plant-availability of phosphorus is improved by a suitable selection of additives (Herzel et al., 2018).

This thesis aims to improve the understanding of the heavy metal removal potential by thermal treatment in a single-step process. For this purpose, experiments were conducted in a 10 kW bench scale bubbling fluidised bed reactor. Different alkaline chloride, alkaline earth chloride, and sodium sulphate based additives are tested for their suitability with respect to heavy metal fractionation, while also regarding the bio-availability of the product. Furthermore, the influence of process parameters, such as oxygen availability and temperature are discussed. In conclusion, recommendations for suitable additive and process parameter combinations are presented. Primarily, the results are discussed from the aspect of heavy metal removal. However, due to the relevance for further application, the bio-availability of phosphate products is also included in the discussion, to provide a holistic approach.

1.1 Phosphorus recovery

Phosphate rock is currently the only mined source of phosphorus for further processing (Jasinski, 2020). In general, the phosphate amount of the rock is expressed in P_2O_5 content, due to the processing of P_2O_5 in the fertiliser industry and improved comparability. The P_2O_5 content of phosphate rock ranges between 15 % to 30 %; high-grade ore contains more than 30 % P_2O_5 and can be used by the fertiliser industry without further treatment (Haldar, 2018). Nevertheless, by taking recovery processes into account, additional sources of phosphorus exist, which include waste water, sewage sludge, and sewage sludge ash. For these sources, the amount of phosphorus is expressed in elementary P content. The phosphorus content increases with preceding process steps and amounts to less than 0.001 % P in waste water, about 1 % P in sewage sludge, and 6 % P to 8 % P in sewage sludge ash, corresponding to about 18 % P_2O_5. Due to its high phosphorus concentrations and good availability as a product of widespread mono-combustion of sewage sludge, recent research focuses on recovery from sewage sludge ash (Adam, 2018). Regardless of the used medium (sewage sludge or sewage sludge ash), recovery processes are either performed by wet-chemical or thermochemical treatment (Schnell and Quicker, 2020). Further, pilot scale or even industrial scale processes for both recovery pathways exist. However, the focus of this thesis in on thermochemical treatment, due to its possible integration in existing mono-incineration processes. Thus, the method of wet-chemical processing is only introduced briefly.

1.1.1 Wet-chemical process

Wet-chemical processes are based on the extraction of fixed phosphorus by acidic or alkaline leaching solutions (Petzet et al., 2012). By adding acid and hence lowering the pH value, phosphorus is transferred into the liquid phase. Remaining solid particles are separated, and the acid solution is further neutralised for phosphorus recovery. When sewage sludge ash is used as source, the process becomes more complex, as heavy metals are dissolved as well in the leaching solution, due to the combustion of organic matter. Hence, the removal of heavy metal contents has to be performed additionally, although other leaching agents are favoured for this process (Schnell and Quicker, 2020). Inorganic acids like sulfuric acid (Shiba and Ntuli, 2017; Donatello et al., 2010) or nitric acid, show a better phosphorus recovery rate, precipitating phosphorus at pH 4, while organic acids (e.g. oxalic acid and citric acid (Fang et al., 2018)) show an increased removal of heavy metals (Fang et al., 2018). Hence, recent research discusses the combination of acidic and alkaline leachants (Petzet et al., 2012), and organic pretreatment and further precipitation of phosphorus by inorganic acids (Fang et al., 2018).

1.1.2 Thermochemical process

In thermochemical processes, the volatility of heavy metals compounds is used to separate the heavy metals from phosphorus fractions, while treated at temperatures between 750 °C and 1100 °C (Adam et al., 2007; Schnell and Quicker, 2020). Initially, the focus of research was on treatment in rotary kiln reactors, though in recent years several studies have been conducted in bubbling fluidised bed reactors. Due to a higher heat and mass transfer rate, the energy efficiency of the process can be improved by using fluidised bed reactors (Stemann et al., 2015).

In principal, thermochemical treatment can be conducted with sewage sludge or sewage sludge ash. Though sewage sludge ash is in the current focus research, sewage sludge bears increased potential by implementing thermochemical treatment in a single-step process. Due to the direct utilisation of sewage sludge, a heating and incineration step is eliminated, which contributes to an enhanced energy efficiency of the process (Schnell and Quicker, 2020). The process design of sewage sludge and sewage sludge ash treatment is yet similar. The feed material is blended with additives to improve the volatilisation behaviour of heavy metals. Investigated additives for thermochemical treatment are alkaline, and alkaline earth chlorides, as well as sodium carbonates and sulphates (Stemann et al., 2015; Schnell and Quicker, 2020). Heavy metal salts are built, which are vaporised at high temperature. Hence, heavy metals are partially transferred to the gaseous phase and separated from other ash fractions (Mattenberger et al., 2008). In addition, the selected additive influences the structure of phosphates in ash and thereby their availability for plants. Consequently, the additive is selected in respect of the heavy metal separation capacity and phosphate formation (Xia et al., 2020). Apart from the additive type, the yield of phosphorus and removal of heavy metals is affected by the amount of additive and several process parameters, like temperature and oxygen availability (Schnell and Quicker, 2020). However, the influence of additives and process parameters will be further discussed in chapter 1.2.3 ' Process parameters influencing heavy metal removal'.

1.1.3 Pilot and industrial scale processes

Regarding thermochemical processing, various pilot and industrial scale plants exist. However, the current focus of process designing is at rotating reactors. The EuPhoRec process and the AshDec process are further introduced, due to their temperature range and applied additives.

EuPhoRec process

The EuPhoRec process is a two step phosphorus recovery process, using sewage sludge as feed material (Figure 1.1). In a first step, blended sewage sludge enters the rotary kiln, which is operated in reducing atmosphere at temperatures between 650 °C and 750 °C. Typically, alkaline and alkaline earth chlorides are used as additives for improved heavy metal separation. Subsequently, the devolatilized sewage sludge enters the oxidation zone for further combustion at temperatures between 900 °C and 1000 °C (Schnell and Quicker, 2020). As a result, even heavy metals of low volatility are converted to the gas phase and fed into the flue gas cleaning system. Phosphorus remains in the ash and can be used directly as fertiliser. According to the manufacturer the phosphorus content of the product is affected by the sewage sludge composition and process parameters. However, a maximum phosphorus content of 8.7 % P or 20 %

P_2O_5 is achieved, with a solubility up to 60 % in neutral ammonium citrate. In total, the phosphorus recovery rate amounts to more than 98 % (Klose, 2018).

The process integration in a municipal solid waste incineration plant provides the possibility to operate the rotary kiln in countercurrent mode with an oxygen-enriched flue gas stream of the incineration plant. In addition, the flue gas cleaning system can be used for both treatments and the over all capital costs are decreased. Industrial scale plants are already operating (Klose, 2018).

AshDec process

The AshDec process is a market-available phosphorus recovery process, developed by Outotec (Figure 1.2). Sewage sludge ash is used as feed material and treated at 900 °C to 1000 °C in a rotating reactor. In the rotary kiln, the sewage sludge ash is blended with Na_2SO_4 and additional sewage sludge, used as reducing agent. In order to obtain the temperature range, natural gas is added (Schnell and Quicker, 2020). In case the ash treatment plant is adjacent to a sewage sludge mono-incineration plant, the gas cleaning system can be used for both treatments (Hermann and Schaaf, 2019). The phosphate product is rhenanite ($CaNaPO_4$), an established phosphate fertiliser. By adding Na_2SO_4 and additional K_2SO_4, a PK-fertiliser can be obtained, achieving a phosphorus content of 16.7 % P_2O_5. This is a slightly improved value, compared to the blending with Na only, where the phosphorus content amounts 15.8 % P_2O_5. The maximum P solubility in neutral ammonium citrate reaches 75 % in both cases (Hermann and Schaaf, 2019).

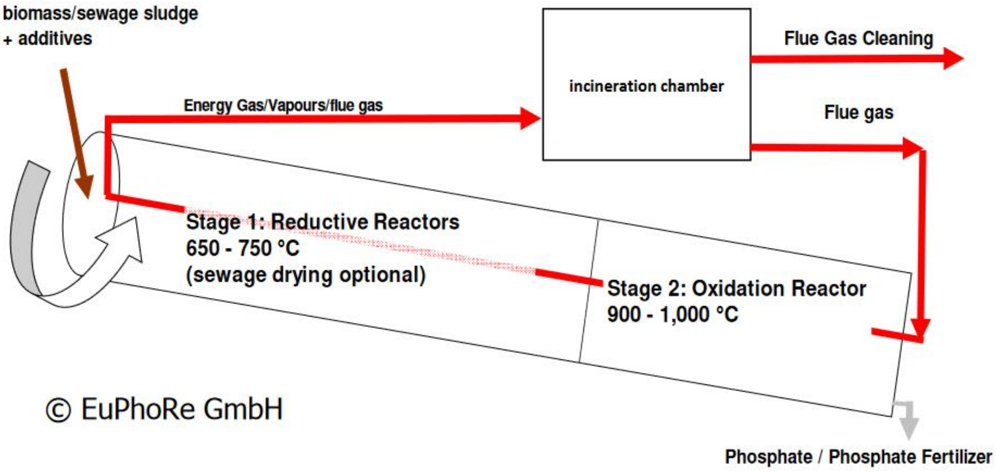

Figure 1.1: Flow chart of the EuPhoRe process (Hazard et al., 2018)

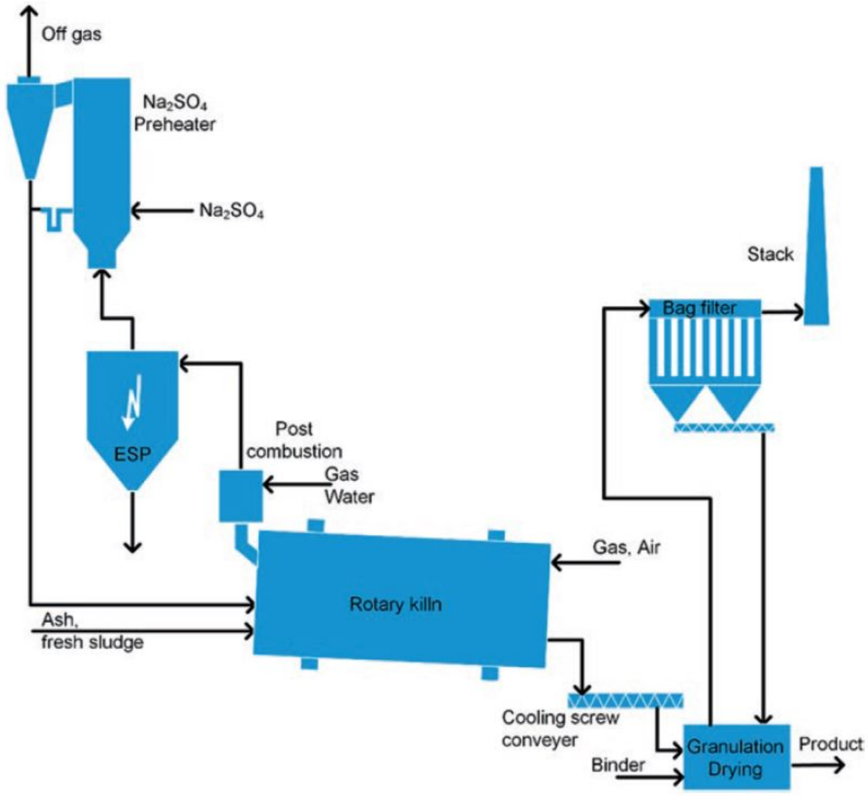

Figure 1.2: Flow chart of the AshDec process (Hermann and Schaaf, 2019)

1.1.4 Plant-availability of phosphorus

Although phosphorus is pivotal for the growth of plants, only few phosphate forms are absorbed in soil and further available for crops. They primarily occur as orthophosphates with Al, Fe, Mg, and Ca compounds, which additionally affect the ability of phosphorus absorption (Kratz et al., 2018, 2019).
Regarding the phosphorus release from the mineral, two main paths can be followed, the slow release or the fast release of phosphorus. Fast release phosphate products are characterised by their solubility in water, which allows an almost immediate availability for plants. However, water-soluble phosphates also leach easily and thus, do not provide a sustainable nutrients supply. The majority of commercial fertilisers, like monoammonium phosphate and triple super phosphate (Ca based phosphate) are water-soluble (Lustosa Filho et al., 2019; Everaert et al., 2017). Slow release phosphates are based on their solubility in citrate or neutral ammonium citrate. Though the phosphate is not immediately available for plants, they provide a long term fertilising effect in soil (Lustosa Filho et al., 2019).

Phosphate forms in sewage sludge and their abundance differ depending on the origin of the sewage sludge and the applied treatment methods. Among the most common compounds are Fe- and Al-phosphates. Their occurrence is due to waste water treatment processes, in which iron and aluminium salts are commonly used for chemical precipitation of phosphorus in waste water (Huang and Shenker, 2004). Initially, Fe- and Al-phosphates do not provide plant-available phosphorus, but thermochemical treatment proves a successful transformation to plant-available phosphate forms (Steckenmesser et al., 2017). The main phosphate form after thermal treatment without additives is $Ca_3(PO_4)_2$ (whitlockite), which remains non-available for plants. However, the formation from $Ca_3(PO_4)_2$ to $CaNaPO_4$ (buchwaldite) is successfully performed, based on the rhenania process. As mentioned before, rhenania fertiliser is a commercial phosphorus fertiliser, insoluble in water and primarily composed of $CaNaPO_4$. In the original rhenania process, rock phosphate is used and blended with Na_2CO_3 and SiO_2. After thermal treatment at 1100 °C to 1300 °C buchwaldite is formed, which is soluble in neutral ammonium citrate and alkaline. For sewage sludge ash treatment, the process parameters are slightly adjusted and Na_2CO_3 is substituted by Na_2SO_4, due to its superior ecological and economical performance (Stemann et al., 2015).

Apart from buchwaldite, $Mg_3(PO_4)_2$ (farringtonite) and $Ca_4Mg_5(PO_4)_6$ (stanfieldite) both showed promising bio-availability performance. They are formed in thermal treatment of sewage sludge ashes at 1000 °C and additional $MgCl_2$. At 750 °C first formation of $Mg_3(PO_4)_2$ is observed, whereas the formation of $Ca_4Mg_5(PO_4)_6$ starts at 850 °C. Thermally treated ash samples showed a phosphorus solubility up to 97 % in citric acid (Thomsen et al., 2017; Adam et al., 2009).

The measurement methods for plant-availability of phosphorus and their standardisation are a current topic of discussion. Though the European Union published a regulation and standardised sampling and analysis methods, the focus is merely on wet-chemical methods determining the solubility of phosphorus in various chemical extractants. They provide a reliable basis for comparison, whereas the predictive accuracy of the actual phosphorus uptake of the plants is limited (Kratz et al., 2019; Union, 2003). Hence, growth experiments offer the possibility of directly measuring the performance of phosphorus release and uptake with plants. The result is usually expressed in a relative agronomic efficiency, where the performance of the test fertiliser is set in relation to a benchmark fertiliser. A common benchmark fertiliser is triple super phosphate, but this benchmark is not standardised and can be selected individually. Besides the benchmark fertiliser, the duration of the experiment and the applied soil with its mineral composition affect the amount of plant-available phosphorus. As a result, the comparability of different sources is limited (Kratz et al., 2019).

1.2 Sewage sludge treatment in fluidised beds

Subsequent sewage sludge processing and disposal practises are still varying, dependent on the cultural and economic background. Nevertheless, certain consistent trends are identified, which provide information about technologies applied in the forthcoming years. In the beginning of this century, direct land application of sewage sludge dominated the end of the pipe sewage sludge disposal techniques in Europe. Recent development in more stringent legislations regarding the entry of pathogenes and heavy metals in the ecosystem, shifted the focus of disposal methods and lead to an still ongoing increase of sewage sludge incineration (Kelessidis and Stasinakis, 2012). In Europe, the Netherlands are the leading sewage sludge incineration nation with a share of 100 %, as their stringent legislation impedes the implementation of other disposal practices (Samolada and Zabaniotou, 2014). In Germany about 70 % of produced sewage sludge is incinerated, and on a global scale sewage sludge incineration is also the leading process in Japan, where more than 70 % of sewage sludge were thermally disposed in 2009 (Murakami et al., 2009).

The most significant advantages of sewage sludge incineration are the radical reduction of volume, leading to a decrease of further transportation and processing costs, and the simultaneous treatment of undesired components and sewage sludge stabilisation. Organic matters are thermally destroyed during the process and the compliance with potential limits of heavy metals for further applications is possible with additional methods, introduced in the following Chapter 1.3 (Schnell et al., 2020).

Within sewage sludge incineration, the mono-incineration in a fluidised bed is the dominant technology. Fluidised bed incinerators are characterised by high heat and mass transfer rates, induced by intensive mixing of the sewage sludge with the bed material and fluidisation agent. Silica sand is commonly used as bed material and air as fluidisation agent.

Additional fuel is added, if the calorific value of sewage sludge is below the requirements for autothermal combustion (Schnell et al., 2020). Based on air preheating being the only additional energy source, autothermal combustion is feasible with calorific values of 4.5 MJ per kg sewage sludge and above (Lehrmann, 2013).

The operation of the fluidised bed reactor is parted in two stages. In a first step, the sewage sludge is introduced in the fluidised bed and the primary air supply enters the reactor through a nozzle array at the bottom of the reactor. In this section, the oxygen supply is slightly sub-stoichiometric. The second air supply is added in the freeboard, leading to a post-combustion atmosphere, where the combustible gas is completely oxidised and good burnout is achieved. The air-fuel ratio in this section is about 1.2 (Schnell et al., 2020). The entire process is characterised by a low air supply, which leads to reduced heat losses through the flue gas and an overall compact flue gas cleaning system. Due to occurring agglomeration and sintering processes, the upper temperature limit is set at 950 °C. In Germany, an additional lower limit is set at 850 °C, according to the German Ordinance on the incineration and co-incineration of waste (BimSchV, 2013). The lower temperature limit aims to ensure a complete combustion, however, ash melting and nitrogen oxide formation are facilitated at these temperatures. Hence, operation at lower temperature is legally approved in most cases. Regarding the power of sewage sludge mono-incinerators, large scale mono-incineration plants in Germany achieve a heat output of up to 50 MW (Schnell et al., 2020).

Following the aforementioned combustion regime, the emissions are characterised by low values for nitrogen oxide and CO. In comparison to conventional municipal solid waster incineration, flue gas from sewage sludge incineration shows a lower HCl content, but an increased SO_2 content, though the flue gas composition is in general dependent on the sewage sludge composition (Schnell et al., 2020).

An identified challenge for the upcoming years is the reduction of N_2O, which is expected to be required in future legislation. Current high level of N_2O emissions are due to lower temperature operation, that enhances the reaction to N_2O. At increased incineration temperatures, N_2O emissions are significantly lower. By adding a afterburner chamber, the N_2O reduction can be achieved and thus, is technically feasible

(Kraus et al., 2018).

In contrast, sewage sludge co-incineration applications in Germany are coal-fired power plants, cement kilns, and waste incineration plants. The relevance of co-incineration is diminishing, as phosphorus recovery and recovery strategies are included in European legislation and already applied in German regulations. As a result, only sewage sludge with a content of less than 20 g phosphorus per kg dry mass is permitted to be co-incinerated. This is due to the lack of phosphorus recovery feasibility in waste incineration plants and cement kilns, that are characterised by increased impurities and low phosphorus content, due to the blending process. In coal power plants, the processing efforts are significantly increased as the additional coal ash leads to dilution of the phosphorus fraction and hence, impeded recovery potential. In addition, due to their fossil based energy conversion, their potential for future application is limited (Schnell et al., 2020).

1.3 Heavy metal fractionation from sewage sludge

The removal of heavy metals from sewage sludge is the key objective for the feasibility of phosphorus recovery, since any further application of sewage sludge is limited by the presence of heavy metals and their legal threshold (Pradel and Aissani, 2019). In general, copper (Cu), zinc (Zn), lead (Pb), chromium (Cr), nickel (Ni), and cadmium (Cd) are most abundant heavy metals in sewage sludge and therefore, their removal is the topic of current research (Yang et al., 2020; Adam et al., 2007; Nowak et al., 2011). Their presence is due to enrichment of heavy metals by activated sludge in the sewage treatment plant and further integration into cells. There, they are most likely to occur in Fe-Mn oxide bounds, carbonate bounds, organic matter bounds, or exchangeable fractions (Yang et al., 2020).

As already discussed above, thermal treatment is one pathway for heavy metal removal and as a result for the recovery of phosphorus. Due to the fact that mono-incineration is an established treatment for sewage sludge in Europe, the main infrastructure for thermal treatment is already present (Adam et al., 2007; Schnell and Quicker, 2020). Furthermore, organic contaminants are destroyed during thermal treatment, thus, hygienisation of sewage sludge is already integrated in the process (Schnell and Quicker, 2020). Taking these considerations into account, further discussed fractionation techniques focus on thermal treatment.

1.3.1 Characterisation of removable heavy metals

In order to fractionate heavy metals from further sewage sludge components, the volatility is the most significant property. Taking a look at the volatilisation behaviour of trace elements in the coal combustion process, Clarke and Sloss (1992) characterised three categories. The first category includes elements, that are hardly volatile, and thus remain in the bottom ash and coarse residues. Elements, which are concentrated in fine-grained particles, since they volatilise and further condense within the system, are part of the second category. In the case of sewage sludge, this category is represented by Cd, Cu, Pb, and Zn. The third category includes volatile elements, that do not condense within the system and therefore may not be collected, but have to be recovered from the off-gas. Intermediate behaviours occurs with Cr and Ni, that can be classified between category one and two.
Sørum et al. (2003) studied the volatility of heavy metals in municipal solid waste combustion and identified similar behaviour. As Cr hardly volatilises, up to 96 wt% remain in the bottom ash. For Ni the share in bottom ash increases up to 98 wt% (Rigo and Chandler, 1994), whereas Cu is varying between 89 and 96 wt%. The fraction for Zn, Cd, and Pb are showing a high variation, by ranging from 37 to 86 wt% (Zn), 17 to 83 wt% (Cd), and 58 to 94 wt% (Pb) in the bottom ash (Sørum et al., 2003). However, these numbers solely serve to evaluate the feasibility of heavy metals fractionation based on their volatility. Process parameters influencing removal be-

haviour will be discussed later on in this chapter.

In general, the initial groups applied for coal combustion (Clarke and Sloss, 1992) correlate with characterisations used in current research. Fraissler et al. (2009) identified three main groups for heavy metal volatility during thermal treatment of sewage sludge (Table 1.1).

Table 1.1: Volatility of heavy metals in thermal treatment of sewage sludge based on Fraissler et al. (2009)

low-volatile	semi-volatile	high-volatile
Cr, Ni	Cu, Zn	Cd, Pb

1.3.2 Additives for heavy metal removal

Due to their availability, selectivity, and established application in metallurgy (Jena and Brocchi, 1997), the majority of publications focuses on chlorine based additives for heavy metal removal from sewage sludge. In general, chlorination is suitable, because metal chlorides have lower boiling points than their corresponding metal oxides. Hence, the volatility of heavy metals is increased by chlorination (Abanades, 2001). Suitable removal performance is achieved with alkaline and earth alkaline chlorides, such as NaCl, $MgCl_2$, and $CaCl_2$ (Mattenberger et al., 2008; Adam et al., 2007). However, chloride based additives are characterised by strong corrosiveness. Unless anti-corrosion equipment is installed, their application is thus limited (Xing et al., 2020; Fraissler et al., 2009).

A different approach is a focus on the bio-availability of the phosphate product. In order to obtain enhanced bio-availability, sodium sulphate or carbonate based additives, like Na_2SO_4 or Na_2CO_3 are added during sewage sludge treatment. In this case, heavy metals are removed in their elementary form by the reduction of present heavy metal oxides (Herzel et al., 2018).

Alkaline and alkaline earth chlorides

Depending on the metal group, two different reaction pathways for chlorides are identified, the direct chlorination and the indirect chlorination. In direct chlorination, the chlorides react with heavy metal oxides, which are presumably formed during incineration or partial incineration. Typically, chlorination with NaCl occurs directly, as no reaction with H_2O and O_2 takes place (Chan et al., 1996).

$$2NaCl + ZnO \longrightarrow Na_2O + ZnCl_2 \tag{1.1}$$

However, in indirect chlorination HCl or Cl_2 is formed in a first step (Equations 1.2 and 1.3), which react with H_2O or O_2, dependent on the moisture of the atmosphere. In general, indirect chlorination occurs with alkaline earth chlorides, as $MgCl_2$ and $CaCl_2$ (Chan et al., 1996; Fraissler et al., 2009).

$$CaCl_2 + H_2O \longrightarrow CaO + 2\,HCl \tag{1.2}$$

$$CaCl_2 + \frac{1}{2}\,O_2 \longrightarrow CaO + Cl_2 \tag{1.3}$$

Further, heavy metal oxides react with the intermediate chlorides, HCl and Cl_2, and form mainly volatile heavy metal chlorides (Nowak et al., 2011). According to Fraissler et al. (2009), possible compounds in thermodynamic equilibrium are, inter alia, $ZnCl_2$, CdO, CuCl, and $NiCl_2$.

$$2\,HCl + ZnO \longrightarrow ZnCl_2 + H_2O \tag{1.4}$$

$$Cl_2 + ZnO \longrightarrow ZnCl_2 + \frac{1}{2}\,O_2 \tag{1.5}$$

The volatile heavy metal chlorides may be integrated in the matrix (Abanades, 2001). Similarly, at high temperatures (1150 °C) heavy metal oxide ZnO may react directly with matrix material (Equations 1.7 and 1.8). As a result, the amount of removable heavy metals is decreased (Jakob et al., 1995).

$$Al_2O_3 + CdCl_2O + H_2O \longrightarrow CdO \cdot Al_2O_3 + 2HCl \tag{1.6}$$

$$SiO_2 + ZnO \longrightarrow ZnSiO_3 \tag{1.7}$$

$$Al_2O_3 + ZnO \longrightarrow ZnAl_2O_4 \tag{1.8}$$

Sodium carbonate and sulphate

The application of sodium carbonate is based on the rhenania process for phosphorus fertiliser production. By adding Na_2CO_3 and silica sand, the phosphates, apatite $Ca_5(PO_4)_3(OH,F,Cl)$ and whitlockit $Ca_3(PO_4)_2$, are forming bio-available $CaNaPO_4$ at 1100 °C to 1300 °C in a rotary kiln (Herzel et al., 2018).

$$Ca_3(PO_4)_2 + Na_2CO_3 + SiO_2 \longleftrightarrow 2CaNaPO_4 + CaSiO_3 + CO_2 \tag{1.9}$$

Heavy metals primarily occur as oxides and are reduced to their elementary form. Due to the increased vapour pressure, they are further volatilised (Vogel et al., 2016). Compared to Na_2SO_4 the costs for Na_2CO_3 are rather high, as well as the environmental footprint, thus, in recent studies Na_2CO_3 is substituted by Na_2SO_4 (Herzel et al., 2016). The application of Na_2SO_4 requires a reducing atmosphere in order for the sulphate to be reduced and the reaction of alkaline and phosphate to take place (Herzel et al., 2018).

1.3.3 Process parameters influencing heavy metal removal

Apart from differing reaction pathways due to additive type and amount, process parameters such as temperature and oxygen availability also influence the removal behaviour of heavy metals (Schnell and Quicker, 2020). The influence of granulate type is not further discussed in this thesis, since Mattenberger et al. (2010) stated its negligible impact. Various examples of the following literature discuss heavy metal removal from municipal solid waste (MSW) fly ash. However, according to Nowak et al. (2013) the removal processes from MSW fly ash and sewage sludge or sewage sludge ash follow the same patterns and are thus comparable. Moreover, the performance of sewage sludge ash may exceed removal amounts accomplished with MSW fly ash. Hence, publications discussing heavy metal removal from MSW fly ash will be included in the following chapter for enhanced process comprehension. An overview of influencing process parameters and additives is presented on Table 1.2.

Additive amount and type

The selection of additive not only influences the obtained phosphate structure, but also the separability of heavy metals. In addition, the volatilisation behaviour is also affected by amount of additive and, in case of chlorine based additives, is limited by corrosion effects (Nowak et al., 2012).

Taking a look at the low-volatile heavy metals, Cr separability is affected negatively by chlorides, when treated in a rotary reactor at temperature below 1000 °C (MSW). In principle, Cr volatilises in form of hydroxides above 600 °C, but by adding chlorides the formation of CrO_4^{-2} is favoured and hence, the removable amount of Cr decreased. Only with high chloride concentrations (20 wt% Cl), a positive removal effect is observed, since Cr volatilises as CrO_2Cl_2. Due to its deviant reaction pathway, NaCl stands out as an exception and increases the separability (Nowak et al., 2012; Fraissler et al., 2009). No Cr is removed by thermochemical treatment with Na_2SO_4 in a rotary kiln (Herzel et al., 2016).

In contrast, Ni removal without any chlorides is only possible at temperatures above 1100 °C and its removal behaviour is strongly dependent on the additive type (Nowak et al., 2012). By adding $MgCl_2$ a negative effect occurs, as $MgCl_2$ may increase the spinel amount ($MgAl_2O_4$). $MgAl_2O_4$ tends to bound with Ni, and thus, reduces the volatile amount of Ni (Nowak et al., 2012; Le Forestier and Libourel, 2008). The highest amount of removed Ni is observed with $CaCl_2$ flakes in a rotary kiln at 1000 °C (MSW). Nowak et al. (2012) stated, that the rate limiting step for Ni chlorination is given by the reaction of Ni with HCl or Cl_2 and $CaCl_2$ provides sufficient Cl. In contrast, NaCl removes no Ni at all, according to thermodynamic equilibrium calculations. Similarly to Cr, experiments conducted with Na_2SO_2 showed no Ni removal as well.

Zn removal is linked to the presence of $MgCl_2$ and $CaCl_2$, which increase the removable amount significantly. Experiments in a muffle oven showed, that up to 85 % Zn is removable by using $MgCl_2$ additives (MSW). The removable Zn fraction is also dependent on the additive amount and increases with an increase of added Cl. NaCl has no effect at all or even a negative effect on Zn removal (Nowak et al., 2012). By adding Na_2SO_4, up to 9 % Zn is removed when treated in reducing atmosphere (Herzel et al., 2016).

According to Nowak et al. (2012), Cu volatilisation decreases with increasing chloride amount. This decrease may occur, since the diffusion of the chloride and the phase change are limiting steps and during chloride forming a liquid barrier accrues, that impedes diffusion (Nowak et al., 2011). Further, the formation of negative azeotrops with CuCl is shown (Nowak et al., 2012). However, thermochemical equilibrium calculations showed, the volatility of all Cu in form of $(CuCl)_3$ by adding minimum chloride amount of 5 wt% (Fraissler et al., 2009). The performance of $CaCl_2$, $MgCl_2$, and NaCl are very similar, and do not show any significant deviation in removal behaviour (Nowak et al., 2012). By adding Na_2SO_4, no Cu is removed (Herzel et al., 2016).

Due to the already high volatility of Pb and Cd, the dependence of chloride amount and type chloride is neglected in most studies and therefore not discussed in this chapter. According to Fraissler et al. (2009), they may as well volatilise without chlorination as hydroxides or oxides. When adding Na_2SO_4, Pb and Cd are removed successfully up to 80 % and 39 % (Herzel et al., 2016).

Overall, the chloride concentration significantly affects heavy metal removal, since increasing chloride amount also increases the removal of heavy metals. However, Adam et al. (2007) showed, that the highest rate increase occurs between 5 wt% and 10 wt% chloride. Different additive types generally influence the amount removed, though no unitary behaviour pattern for one additive with every heavy metal is observed. For Na_2SO_4 more data is required to discuss its removal efficiency. Nevertheless, Herzel et al. (2016) observed the removal of only three out of six relevant heavy metals.

Temperature
According to various studies, temperature influences heavy metal removal from sewage sludge ashes significantly (Adam et al., 2007; Mattenberger et al., 2010, 2008; Vogel et al., 2016). In general, an increase in temperature is directly linked to an increase in volatility of heavy metals compounds, and therefore positively affects the feasibility of heavy metal removal. However, experimental research focused on sewage sludge ashes in rotary kiln reactors and muffel furnaces. Schnell and Quicker (2020) investigated the behaviour of sewage sludge in a muffle furnace with increasing temperature and demonstrated a reduction of Ni and Zn removal, when adjusting the temperature from 850 °C to 950 °C. According to thermodynamic equilibrium calculations for sewage sludge ash (Fraissler et al., 2009), especially Pb shows a strong dependence on temperature, followed by Cr and Ni. A lower temperature limit is given at 500 °C, where Cl release starts, whereas the upper temperature limit is given due to occur-

ring melting processes (Fraissler et al., 2009). Further increase in temperature may also lead to the formation of solid oxides and hence, a decline in heavy metal removal (Jakob et al., 1995). Overall, the optimal temperature depends on raw ash or material composition (Adam et al., 2007).

Influence of reducing conditions

The term 'reducing conditions' here refers to the operation of the systems with nitrogen and a smaller proportion of air as fluidisation agent, leading to a sub-stoichiometric oxygen supply. The term air gasification is frequently found in literature and describes the same setting of process parameters. In this thesis, the terms reducing atmosphere and reducing conditions are used synonymously to sub-stoichiometric oxygen supply.

The influence of sub-stoichiometric oxygen supply is studied in few publications only. Equilibrium calculations of Sørum et al. (2003) showed, that the behaviour of Zn and Cu changes, when altering the conditions from oxidising to reducing atmosphere. Cu becomes less volatile in reducing conditions, while the volatility of Zn increases in reducing condition. Nevertheless, both are fully volatilised with $\lambda = 0$ at 1077 °C (Cu) and 727 °C (Zn). With Ni removal, no change of behaviour is observed when varying the conditions. Similar results can be found at Schnell and Quicker (2020), who conducted experiments with sewage sludge in a muffle furnace with nitrogen atmosphere and post combustion. Thereby, Ni and Cr are not affected by altered oxygen conditions. However, Cu, Zn, and Pb show an increased dependence from the added chlorine amount, when shifting to reducing conditions. In total, Pb removal increases, as reactivity of high-volatile heavy metals enhances in reducing conditions (Herzel et al., 2016).

Thermochemical treatment of sewage sludge ash in a muffle furnace showed significant removal of Cd, Zn, and Pb. These experiments are conducted at 950 °C in reducing conditions, the additives selected in this study are Na- and K- based sulphates and carbonates. However, Cu, Cr, and Ni remained in solid phase (Herzel et al., 2016).

Table 1.2: Qualitative influence of process parameters and additives on heavy metal removal. Due to already high separability of Pb and Cd, they are not represented. As temperature influence is always positive, it is not represented. Symbols represent: (+) positive influence, (+o) moderately positive influence, (o) neutral influence, (o-) moderately negative influence, (-) negative influence

Heavy metal	Additive amount	$\lambda < 1$	NaCl	$MgCl_2$	$CaCl_2$	Na_2SO_4
Zn	+	+	o-	+	+	+
Cu	o-	-	o	o	o	o
Ni	+	o	o	-	+	o
Cr	+o	o	+	-	-	o

1.4 Legislation in Austria

In Austria, legal regulations of heavy metal input into the soil via products of sewage sludge processing are addressed in the fertiliser ordinance (BGBl. No. 100/2004) and the compost ordinance (BGBl. No. 292/2001). In order to allow the application as compost, raw sewage sludge needs to comply with legal thresholds before any possible treatment. After processing, heavy metal contents of quality class A+ have to be achieved to enable the application in agriculture (Bundeskanzleramt, 2001). Both limits for raw sewage sludge and compost of quality class A+ are presented in Table 1.3.

Another option is the direct declaration as fertiliser, in which case the limit values are based on the fertiliser ordinance. The composition of fertiliser and its required nutrients contents are dependent on fabricated fertiliser typ. However, the limit values for heavy metals contents only differ between fertiliser and mineral fertiliser whose P_2O_5 content exceeds 5 % (Table 1.3) (Bundeskanzleramt, 2004).

Table 1.3: Heavy metal limits for pretreatment sewage sludge, compost, and fertilisers in Austria (Bundeskanzleramt, 2004, 2001)

Heavy metal	Sewage Sludge in mg/kg DM	Compost in mg/kg DM	Fertiliser in mg/kg DM	Mineral fertiliser in mg/kg DM	Mineral fertiliser in mg/kg P_2O_5
Cd	3	0.7	3	-	75
Pb	200	45	100	100	-
Cr	300	70	2	2	-
Ni	100	25	100	100	-
Cu	500	70	-	-	-
Zn	2000	200	-	-	-
Hg	5	0.4	1	1	-
V	-	-	-	1500	-
As	-	-	40	40	-

1.5 Key objectives

The aim of this thesis and experimental series is to increase the knowledge about heavy metal fractionation from sewage sludge blended with additives and treated thermochemically in a bench scale fluidised bed reactor. Particularly, the deviant behaviour in reducing and oxidising atmosphere is of great interest, as well as further information about the influence of differing additives. For enhanced understanding, three process related and one product related research questions are phrased and will be discussed and answered in the following chapters.

- Is the amount of removed heavy metals dependent on the amount of additive?
- Which additive is most suitable for heavy metal removal during thermal treatment of sewage sludge in terms of maximum removable amount?
- Is it possible to enhance the removal of heavy metals by conducting the thermal treatment with sub-stoichiometric oxygen supply?
- Is the product of thermal treatment suitable for fertiliser application?

2 Experimental

In order to study the influence of additives and process parameters on the separability of heavy metals and on the bio-availability of the phosphorus product, three experimental series in a 10 kW bubbling fluidised bed reactor are performed. For this purpose, pelletized sewage sludge is blended with chloride additives, like NaCl, $MgCl_2$, $CaCl_2$, and Na_2SO_4. In the first series, experiments are conducted in oxidising atmosphere at 950 °C; the concentration of the additive amount 2.2 wt% Cl. The second series focused on chloride based additives with 0.7 wt% Cl in oxidising atmosphere at 950 °C. The experiments of the third series are conducted with sub-stoichiometric oxygen supply, further referenced as reducing atmosphere. $MgCl_2$ at 0.7 wt% Cl and Na_2SO_4 at 2 wt% Na are studied at 800 °C. In addition, one experiment without any additives is conducted in each series as a reference value.
The bio-availability of phosphorus is determined by solubility experiments, standardized by the European Union (Union, 2003)

2.1 Sample preparation

Sewage sludge samples are pelletized by an external company. To blend the samples with the additives, the additives are first solved in water and afterwards mixed with the pelletized sewage sludge. In order to obtain a share of 0.7 wt% chloride, 11.54 g NaCl are added per kg sewage sludge. In the case of $MgCl_2$, 9.40 g are added per kg sewage sludge, and 10.95 g $CaCl_2$. Na_2SO_4 stands out as an exception, as its share amounts 2 wt% Na and thus, 61.78 g per kg sewage sludge. This is due to its noncorrosive effect, in contrast to chloride base additives. The measured additives are mixed with 300 ml water and stirred until they are entirely dissolved. Afterwards, the solution is mixed with sewage sludge pellets.

During the first experimental series, the additives are added directly into the reactor through a valve. Hence, no pellet preparation is required.

2.2 Fluidised bed experiments

All experiments were performed in a 10 kW bench-scale bubbling fluidised bed reactor.

2.2.1 Bubbling fluidised bed reactor

The fluidised bed reactor is constructed from stainless steel. The inner diameter of the fluidised bed section is 13.6 cm and 30 cm of the freeboard section. The fluidised bed section is also provided by a electrical heating system, although an additional preheating is installed, before the reactor entry. Three temperature sensors are installed at the lower part of the reactor (Figure 2.1: T1-3). For this, thermocouples of type K are used. In addition, one thermocouple is installed in the splash zone (Figure 2.1: T4) and one in the freeboard zone (Figure 2.1: T5). The entire reactor, as well as cyclone and filter are covered with an isolating layer to minimise heat losses (Figure 2.1 left). However, the isolation of the filter is afterwards removed, in order to improve the temperature difference from cyclone to filter and hence, the condensation of heavy metals.

Two bunkers of 15 l and 25 l supply the feedstock. In this experimental series, bunker 2 (25 l) provides wooden pellets and the smaller one supplies pelletized sewage sludge. Both fuels are continuously transported by screw conveyors from each bunker to the reactor. In order to assure a largely inert atmosphere, the bunkers are flushed with N_2.

The fluidisation medium is supplied through air nozzles at the bottom of the reactor.

The bottom part is fixed as flange and can be taken off to remove the accumulated bottom ash. After passing the reactor, the produced gas steam is led from the top of the reactor through a cyclone in order to separate coarse particles. For temperature measurement, a K-type thermocouple is installed (Figure 2.1: T6). The bottom of the cyclone is equipped with a container and valve for separate collection of wood ash and sewage sludge ash. Hence, the valve is closed after the heating with wooden pellets, and the sewage sludge ash is merely accumulated in the cyclone. Further, the gas is led through a filter in order to remove fine ash particles. The filter is filled with quartz wool and another K-type thermocouple is installed there (Figure 2.1: T7). Before being fed to a torch and burned with CH_4, part of the gas bypasses a gas analyser (Figure 2.1: A1). Here, the content of O_2, CO_2, CO, H_2 and CH_4 is continuously measured.

2.2.2 Oxidising atmosphere

The first and second experimental series are conducted in oxidising atmosphere. Although the experimental implementation varies slightly, the procedure is the same at the beginning.

At first, an air flow of 6000 Nl/h is set in order to fluidise the bed material in the reactor. For these series, silica sand ranging between 300 µm to 1000 µm is used as bed material. The reactor is heated up by the electrical heating system in steps of 30 °C per 10 minutes until 500 °C in the fluidised bed (Figure 2.1: T1-3) are reached. As the experiments in oxidising atmosphere are conducted at 950 °C, further heating with wooden pellets is necessary in order to obtain the temperature. Hence, the nitrogen supply for bunker flushing is opened, then the valve for the wooden pellets supply is opened, and the conveyor screw set at 17.5 Hz (1.14 kg per hour). In order to obtain heavy metal fractionation, the cyclone is preheated to a temperature of 400 °C (Figure 2.1: T6), while the temperature in the following filter reaches up to 300 °C (T7) and the reactor temperature is not exceeding 950 °C. Due to the temperature difference in the cyclone and filter, the heavy metal components are gaseous in the cyclone and may condense in the filter.

As soon as all temperatures are reached, the wooden pellets supply is stopped and the container for wooden ash at the bottom of the cyclone is closed. The bunker filled with sewage sludge pellets is flushed with nitrogen, and the valve for the sewage sludge supply is opened, while the conveyor screw is set at 50 Hz, which corresponds to about 1 kg per hour. In total, the amount of sewage sludge used ranges between 1.5 kg and 2.8 kg. In case the temperature declines, the wooden pellet supply is switched on at a set point below 10 Hz, to stabilize the temperature in the reactor at 950 °C. The additional wooden pellets are measured to identify and separate the wooden ash from sewage sludge ash. The electrical heating system is adjusted and set at temperatures from 400 °C to 550 °C in the reactor and preheating area.

However, in the first series the additives are not blended with sewage sludge and thus added separately. After about one hour of sewage sludge combustion, all chloride enters through a valve (Figure 2.1: V1) into the reactor.

As soon as the temperatures are decreasing, the sewage sludge sample is entirely consumed and the cooling down of the reactor starts.

2.2.3 Reducing atmosphere

The preparation and preheating of experiments with sub-stoichiometric oxygen supply proceed identically to the oxidising atmosphere experiments. However, no temperature difference between cyclone and filter is targeted in this experimental series, and the reactor set point temperature is at 800 °C. This is done, because the reactions with sub-stoichiometric oxygen supply are endothermic and higher temperatures demand a disproportionate amount of additional fuel. Additionally, all experiments are conducted with bed material at particle size between 100 µm and 200 µm, in order to achieve bubbling bed condition. Silica sand is used as bed material.

Once the temperature is reached, the wooden pellets supply is stopped and the container for wooden ash at the bottom of the cyclone is closed. The fluidisation gas is switched to one part of air to four to five parts of nitrogen, at about 600 Nl/h and 2800 Nl/h. In total, an air-fuel ratio of $\lambda < 0.1$ is achieved. Then, the bunker filled with sewage sludge pellets is flushed with nitrogen and the valve for the sewage sludge supply is opened, while the conveyor screw is set at 50 Hz. As a decline in temperature occurs, the wooden pellet supply is added at a rate of below 10 Hz for process stabilization. The additional wooden pellets are measured to identify and separate the wooden ash from sewage sludge ash.

As soon as the temperatures are decreasing, and no CO and O_2 is measured, the sewage sludge sample is entirely consumed and the cooling down of the reactor starts.

2.3 Ash analysis

Three different ash fractions are identified, the bottom ash in the reactor, the cyclone ash, and the filter ash. In order to separate the bottom ash from the bed material, the whole fraction is sieved through a 300 µm sieve. Cyclone ash and filter ash are applied without any further processing in the analysis. The heavy metal content and occurring types are identified in each ash sample with ICP OES, inductively coupled plasma-optical emission spectrometry. Afterwards, the samples are treated with neutral ammonium citrate to determine the solubility of phosphate fractions.

2.3.1 Heavy metal content

Each ash fraction is homogenised in order to improve the representativeness of the samples and 5 g are yielded. The heavy metal content of each ash fraction is identified by ICP OES (Inductively coupled plasma-optical emission spectrometry). It was performed according to relevant standards based on ISO 16967 and ISO 16994.

2.3.2 Phosphorus solubility

The phosphorus amount in the bottom ash fraction is identified by ICP OES. The solubility of phosphorus in neutral ammonium citrate was conducted following the standardized method of the Union (2003).

100 ml of a ammonium citrate solution at pH 7,0 are heated to 65 °C and 1 g of the bottom ash sample is added. In order to suspend the sample, the flask is shaken and placed in a water bath to maintain the temperature of 65 °C. The sample is stirred for one hour and afterwards cooled to ambient temperature under running water, and transfer into a 500 ml flask, that is filled with water. After mixing, the content is filtered.

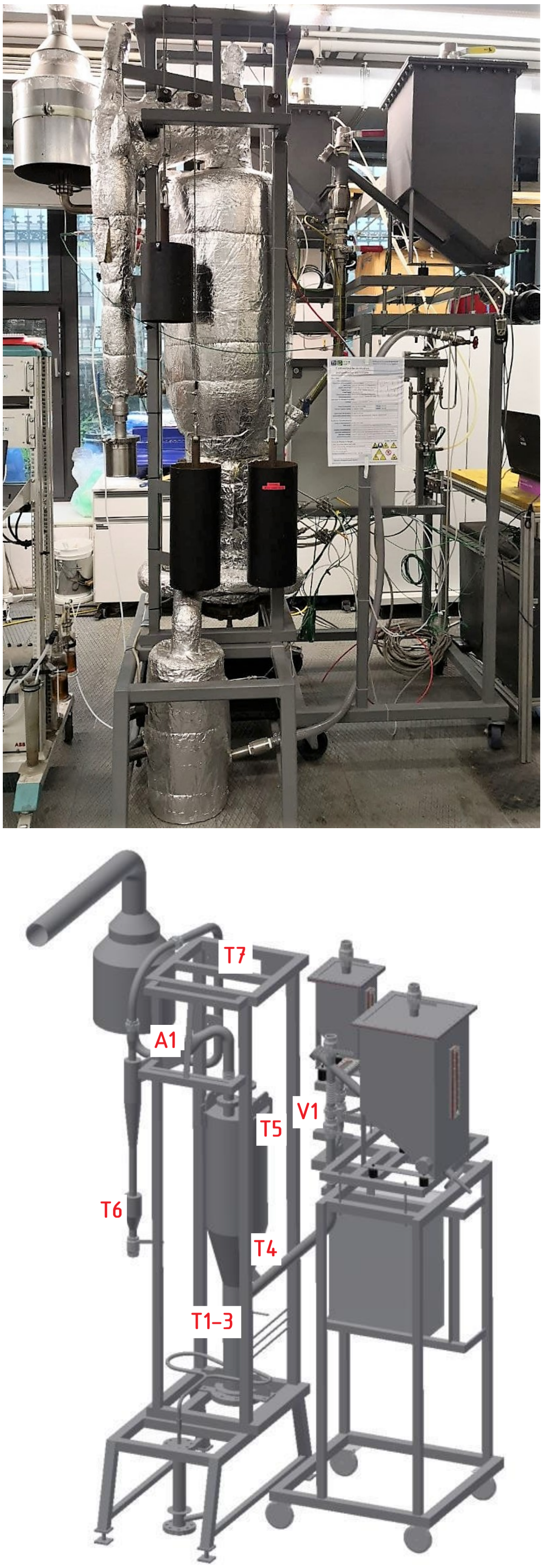

Figure 2.1: Photo of bubbling fluidised bed reactor and CAD drawing, modified after Langer (2020)

3 Results

The results of this thesis focus on six heavy metals (Cr, Ni, Cu, Zn, Cd, and Pb), due to their legal threshold for fertiliser application. In addition, Hg, V, and As are included in legal regulations, however they are not considered in this thesis for different reasons. The amount of V occurring in sewage sludge is significantly below the threshold for the application as mineral fertiliser, which is the only legal regulation including V. For Hg and As, the concentration in sewage sludge and ash samples is not quantitatively measurable and hence, not studied in this thesis.

An overview of the conducted experiments and their process parameters is shown in Table 3.1.

Table 3.1: Overview of conducted experiments

No.	Additive	Additive concentration	λ	Temperature
1.1	no additive	-	>1	950 °C
1.2	Na_2SO_4	2 wt% Na	>1	950 °C
1.3	$MgCl_2$	2.2 wt% Cl	>1	950 °C
1.4	$CaCl_2$	2.2 wt% Cl	>1	950 °C
1.5	NaCl	2.2 wt% Cl	>1	950 °C
2.1	no additive	-	>1	950 °C
2.2	NaCl	0.7 wt% Cl	>1	950 °C
2.3	$MgCl_2$	0.7 wt% Cl	>1	950 °C
2.4	$CaCl_2$	0.7 wt% Cl	>1	950 °C
3.1	no additive	-	>1	800 °C
3.2	no additive	-	<1	800 °C
3.3	$MgCl_2$	0.7 wt% Cl	<1	800 °C
3.4	Na_2SO_4	2 wt% Na	<1	800 °C

3.1 Sewage sludge composition

The composition of the sewage sludge is shown in Figure 3.1, whereas sewage sludge 1 (Figure 3.1: left) is used in the first experimental series and sewage sludge 2 (Figure 3.1: right) in the second and third series. In both samples the most abundant compounds are Fe, Ca, P, and Si with concentration above 10 g per kg dry mass sewage sludge. However, sewage sludge 2 contains more than 30 g Al per kg dry mass, which is about 10 times higher than the Al content in sewage sludge 1.

The concentrations of the heavy metals evaluated in this thesis (Cd, Cr, Cu, Ni, Pb, and Zn) are in both sewage sludge samples in the same order of magnitude. The most abundant heavy metal is Zn with 500 mg per kg dry mass in sewage sludge 1 and about 800 mg per kg dry mass in sewage sludge 2. Zn is followed by Cu (both 200 mg per kg dry mass), Pb, Ni, and Cr. The concentration of Pb, Ni, and Cr are in both samples varying between 10 mg per kg dry mass (Ni, sample 1) and 80 mg per kg dry mass (Cr, sample 2), and Cd only occurs in small concentration of 0.4 mg per kg dry mass and 0.2 mg per kg dry mass.

The elements As, Sb, Tl, and Hg are not presented in Figure 3.1, as their content is not exactly quantifiable. Their concentration does not exceed 15 mg per kg dry mass (Sb and Tl) and 5 mg per kg dry mass (Hg and As).

The ash content of the sewage sludge samples accounts for 17.9 % in sample 1 and 42.4 % in sample 2. Moreover, the lower heating value is 17.8 MJ per kg dry substance in sample 1 and 13,1 MJ per kg dry substance in sample 2.

3.2 Abundance of phosphorus in ash fractions

The abundance of phosphorus in the ash fractions in varying, affected by the amount and type of additive and the applied sewage sludge (Figure 3.2). In the first experimental series with 2.2 wt% Cl added, the phosphorus content over all ash fractions is increasing in comparison with the no additive sample (about 225 g per kg dry substance). Not containing any chloride, the Na_2SO_4 sample displays the same level of

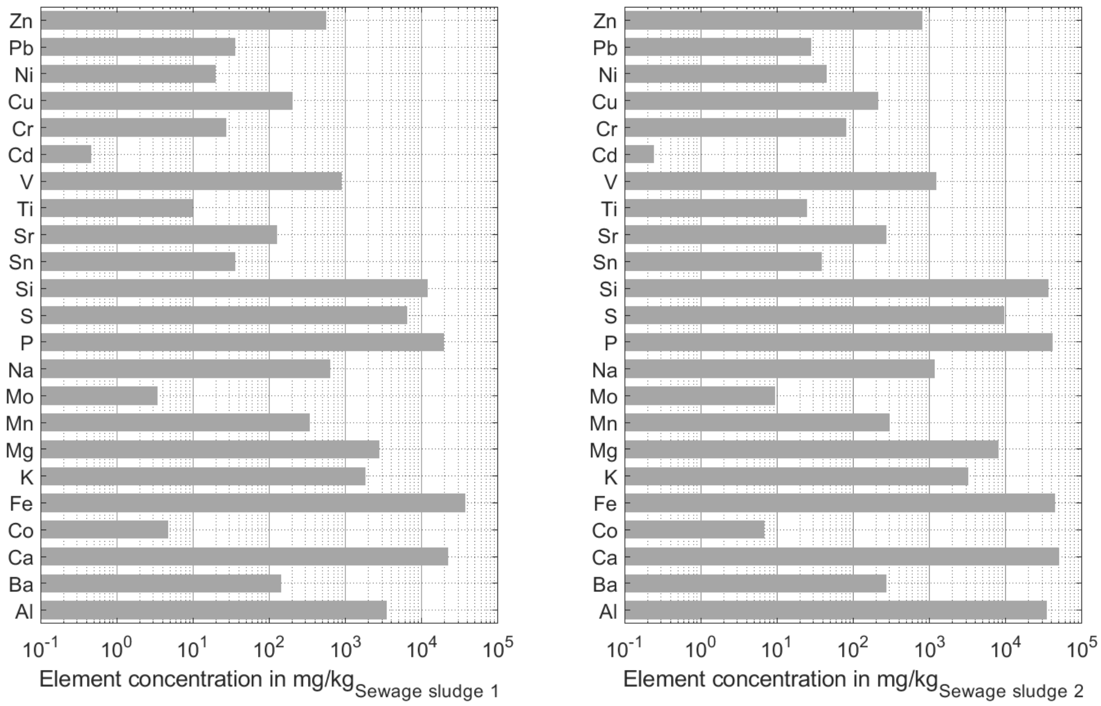

Figure 3.1: Composition of raw sewage sludge samples. Left figure: Sewage sludge 1. Right figure: Sewage sludge 2.

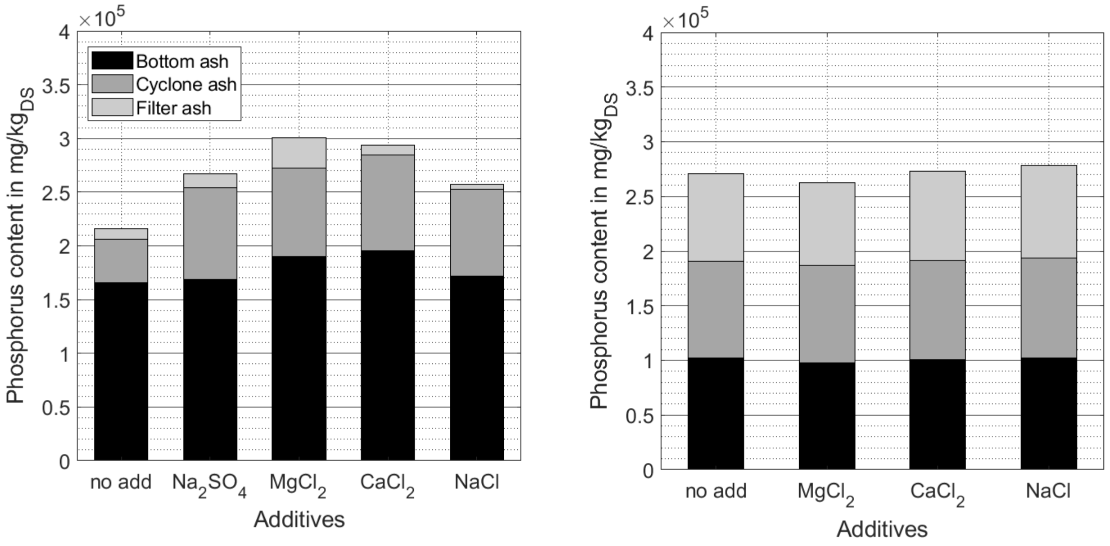

Figure 3.2: Phosphorus content in all ash fractions of sewage sludge 1 (left) and sewage sludge 2 (right) experiments.

increase as the NaCl sample. Samples involving $MgCl_2$ and $CaCl_2$ are both higher (up to 300 g per kg dry substance). In each sample, the bottom ash fraction bears the majority of phosphorus.

In the second and third experimental series, sewage sludge with significantly increased Al content is applied. The abundance of phosphorus in each ash fraction deviates from former experiments, as it is about the same in each fraction. Though the bottom ash fractions still represents the largest proportion (100 g per kg dry substance), the difference to the other fractions is marginal. The overall phosphorus content in sewage sludge 2 is higher than in sewage sludge 1, whereas the phosphorus content in the ash fraction of the benchmark experiment is equally higher in sewage sludge 2 ash samples. However, no trend in deviation is identified by the addition of 0.7 wt% Cl.

3.3 Occurrence of heavy metals

In order to investigate the occurrence and possible removal of heavy metals during thermal treatment, the results are subdivided by the influence of additives and the influence of reducing conditions. The influence of additives is evaluated in consideration of differing additive amount and additive type, while the effects of reducing atmosphere are compared to the result in oxidising atmosphere.

In the follow chapter the results are expressed as the relative concentration of an element. Hence, each element concentration is set in relation to the its concentration in the benchmark experiments, which are conducted without additives (Table 3.1: No. 1.1, No. 2.1, No. 3.2).

The distribution of heavy metals over the ash fractions allows the localisation of heavy metal removal. Figure 3.3, left shows the relative amount of heavy metals in filter ash in relation to the heavy metal amount in the total ash. Originally, filter ash amounts 20 % to 50 % of the total ash, which is represented by the 'no add' bar of each heavy metal. However, blending with additives causes a shift for most heavy metals and thus, heavy metal accumulation occurs in the filter ash fraction. With some samples the increase of heavy metals in the filter ash fraction even exceeds the amount of heavy metals over all ash fractions in the benchmark sample. In contrast, the concentrations of heavy metals is generally decreasing in bottom ash, as shown in Figure 3.3, right, where heavy metals in bottom ash are set in relation to the heavy metals in bottom ash of the benchmark experiment. The few exceptions occurring are described in detail in the following chapter.

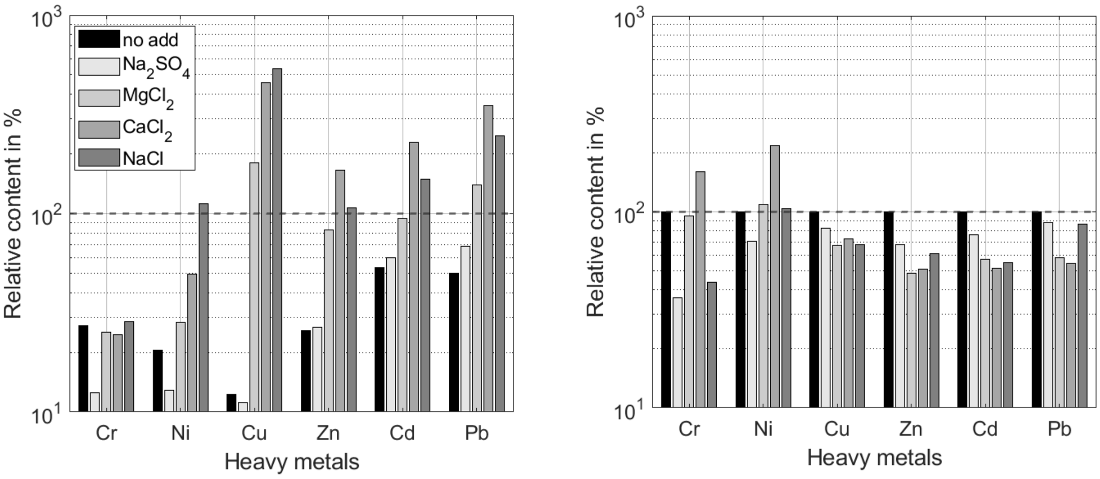

Figure 3.3: Left figure: Heavy metal content in filter ash fraction relative to total ash fractions of the no add experiment; Right figure: Heavy metal content in bottom ash fraction relative to the bottom ash fraction of the no add experiment

3.3.1 Influence of additives

Each heavy metal is presented with differing additive type and, for Cl-based additives, with differing additive amount. The comparison of additive amount considers 0.7 wt% Cl per kg sewage sludge and 2.2 wt% Cl per kg sewage sludge. Experiments with Na_2SO_4 are always conducted with a concentration of 2 wt% Na per kg sewage sludge and are, hence, not considered in the comparison of additive amount. The comparison of additive types includes all applied additives, NaCl, $MgCl_2$, $CaCl_2$, and Na_2SO_4.

Chromium

When comparing the influence of the additive amount over all ash fractions, 0.7 wt% Cl and 2.2 wt% Cl both show reduction in Cr content for $MgCl_2$ and NaCl (Figure 3.4: left). Though, with 0.7 wt% Cl the reduction is higher, including the highest decrease of Cr amount to only 50 % of the benchmark sample ($CaCl_2$, 0.7 wt% Cl). In contrast, the only sample with increased Cr content is $CaCl_2$ with 2.2 wt% Cl, distinguished by the atypically big proportion of bottom ash. Overall, the Cr content of bottom ash is significantly higher in 2.2 wt% Cl samples than in 0.7 wt% Cl samples.

The relative Cr content in the bottom ash fraction is varying strongly with no significant relation between additive amount and type (Figure 3.4: right). Hence, no additive shows a consistent reduction of Cr content with high and low Cl concentration, and no trend of Cr reduction is detected with increasing Cl amount. With 0.7 wt% Cl, $MgCl_2$ and NaCl both achieve increased contents of 110 %, though $CaCl_2$ accomplishes a reduction to 50 %. The most reduction occurs with NaCl, 2.2 wt% Cl (to 45 %). By contrast, high reduction values with $MgCl_2$ (up to 55 %) are found in literature, when studying the thermal treatment behaviour of sewage sludge and $MgCl_2$ in a muffle oven. In addition, no dependence from the added Cl amount is shown (Schnell and Quicker, 2020).

Na_2SO_4 achieves the smallest amount of Cr in all ash fractions (Figure 3.3: right). As corrosion occurred during the experiments of series 1 (2.2 wt% Cl), part of the Cr amount in Cl-based experiments presumably does not originate from the sewage sludge, but from the reactor body. Thus, Na_2SO_4 is the only additive with reliable values without corrosion.

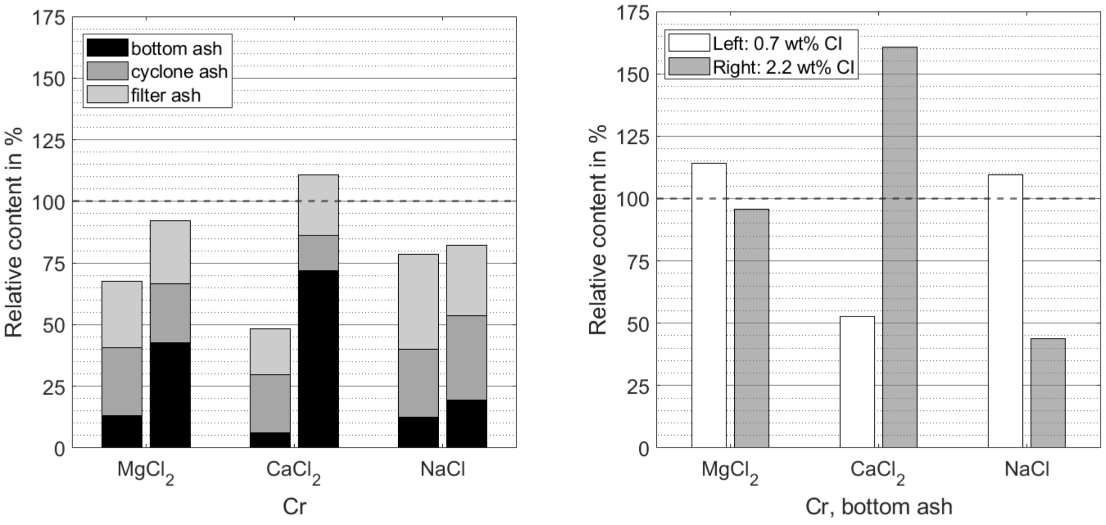

Figure 3.4: Cr content relative to benchmark experiment. Left figure: Cr content over all ash fractions. Right figure: Cr content in bottom ash

Nickel

Regarding the Ni content over all ash fractions, all 0.7 wt% Cl samples are below 100 %, $CaCl_2$ showing the smallest content at about 60 % (Figure 3.5: left). However, all 2.2 wt% Cl samples exceed 100 %, with NaCl at a significantly high value of 350 %. Another characteristic value is the bottom ash content of the $CaCl_2$, 2.2 wt% Cl sample, which alone exceeds 100 %, and thus, is higher than the total Ni content of the benchmark sample. Similarly to Cr, the proportion of bottom ash is higher at 2.2 wt% Cl samples,and further increase in Ni content occurs, when regarding the bottom ash fraction only. Although only the $CaCl_2$, 0.7 wt% Cl sample shows reduction of Ni content, a reduction to 35 % is achieved (Figure 3.5: right). Na_2SO_4 gives the biggest reduction over all ash fractions by achieving a relative Ni content of 70 % (Figure 3.3: left). Overall, these results resemble the results of Cr. They indicate corrosion of the Ni-Cr steel reactor and thus, are not representative. The effects of corrosion are detectable in the inner reactor wall. Literature data shows an additive amount independent reduction of Ni at a low level under similar conditions with $MgCl_2$ (Schnell and Quicker, 2020).

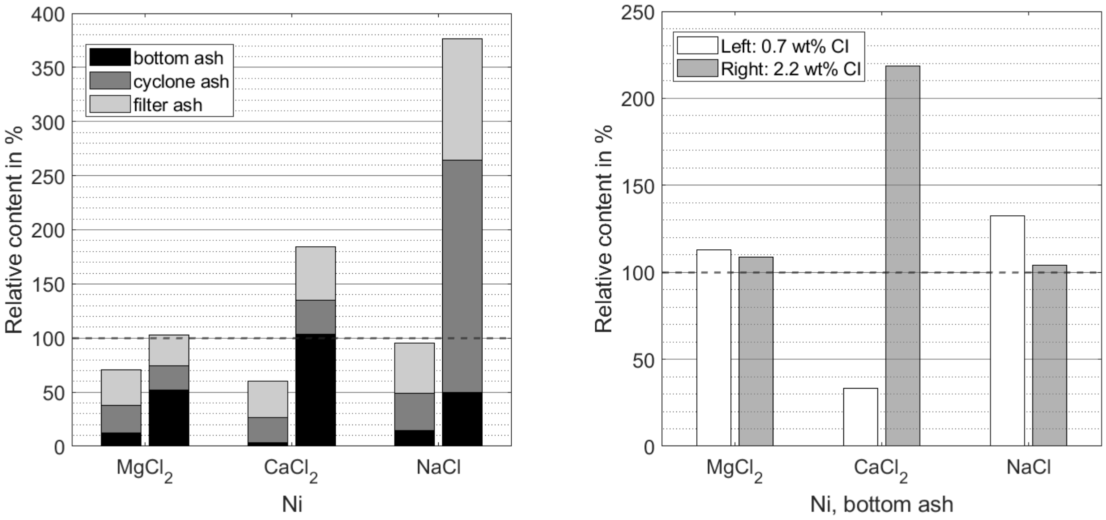

Figure 3.5: Ni content relative to benchmark experiment. Left figure: Ni content over all ash fractions. Right figure: Ni content in bottom ash

Copper

The blending with 2.2 wt% Cl based additives leads in every experiment to an increase of Cu amount over all ash fraction, reaching from 260 % ($MgCl_2$) up to 630 % (NaCl) (Figure 3.6: left). However, the increase is primarily in the filter ash fraction, which also is the predominant fraction in these samples. Samples with 0.7 wt% Cl are all based around 100 % and thereby equal the content of the benchmark experiment. $CaCl_2$ is marginally below 100 % and $MgCl_2$ above 100 %.

In the bottom ash fraction the Cu content records a decrease in every sample, compared to the benchmark bottom ash sample (Figure 3.6: right). Samples with 2.2 wt% Cl achieve higher reduction with all three additives, NaCl and $MgCl_2$ having the lowest content with both at 67 %. Schnell and Quicker (2020) obtain corresponding Cu removal dependence, when adding an increased amount of $MgCl_2$ (1 % $MgCl_2$, 2 % $MgCl_2$, and 5 % $MgCl_2$). There, the maximum reduction to 85 %, is achieved with 5 % $MgCl_2$ (corresponding to 3.7 wt% Cl) at 950 °C in a muffle oven.

Na_2SO_4 leads to a relative Cu content of 80 % over all ash fractions, which exceeds the Cu content achieved by Cl-based additives (Figure 3.3: left).

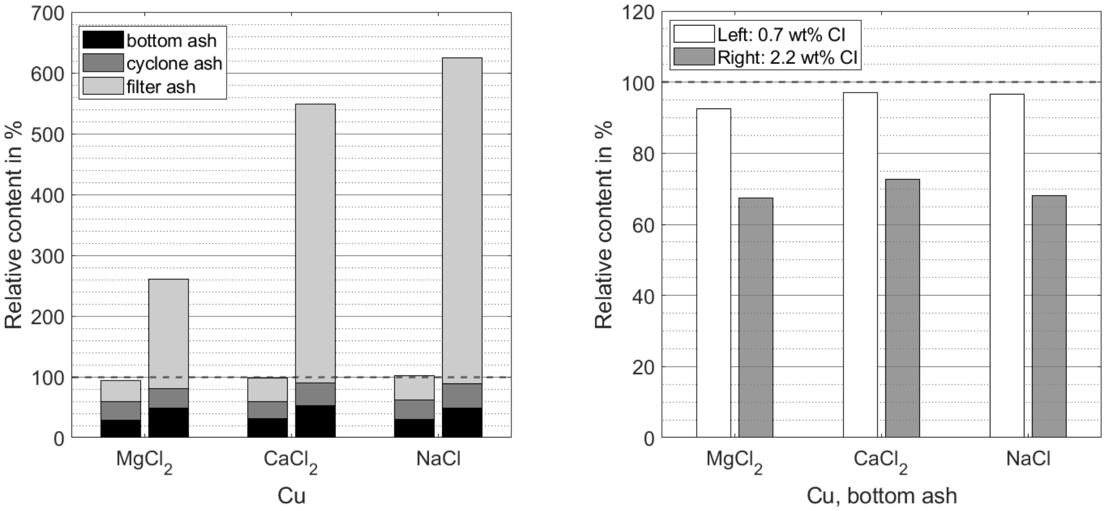

Figure 3.6: Cu content relative to benchmark experiment. Left figure: Cu content over all ash fractions. Right figure: Cu content in bottom ash

Zinc

All 0.7 wt% Cl samples are below 100 %, and thereby are showing a reduction of Zn content over all ash fractions (Figure 3.7: left). $CaCl_2$ and NaCl achieve the smallest Zn content, both showing reduction to 87 %. In contrast, all 2.2 wt% Cl samples are exceeding 100 %, with filter ash representing the biggest fraction is in every sample. Bottom ash makes up between 10 % and 20 % of the total ash in these samples.

Despite the overall reduction, almost no reduction is detected in the bottom ash samples with 0.7 wt% Cl (Figure 3.7: right). Thus, the reduction only concerns cyclone and filter ash. In contrast, the 2.2 wt% Cl bottom ash samples show reductions to 48 % ($MgCl_2$) and 60 % (NaCl), indicating a shift from bottom to filter ash and further accumulation. Literature data shows a similar dependence on the added chloride amount, though the removal occurs at a lower level (Schnell and Quicker, 2020).

The relative Cu content induced by Na_2SO_4 is slightly higher, than the results with Cl-based additives (Figure 3.3: left).

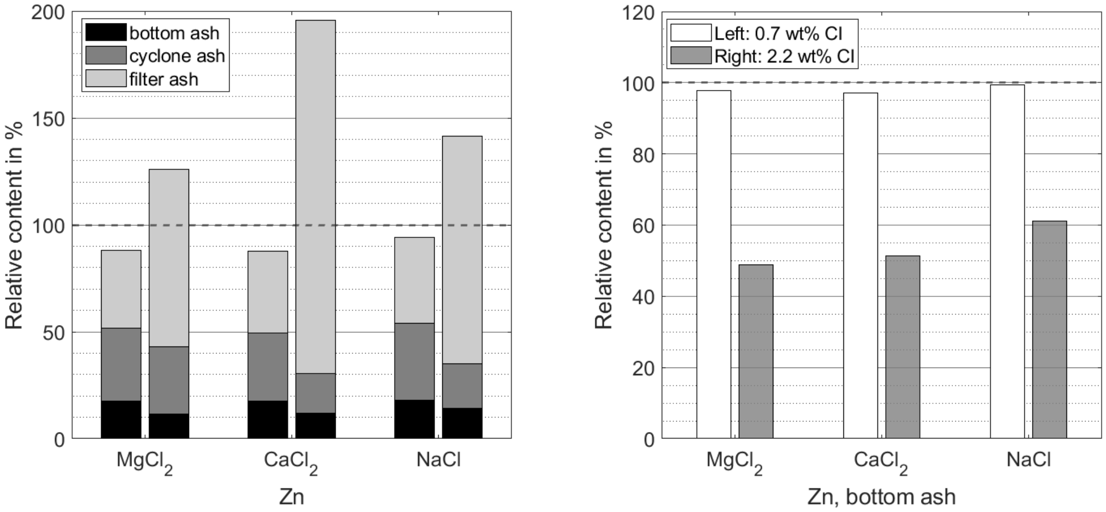

Figure 3.7: Zn content relative to benchmark experiment. Left figure: Zn content over all ash fractions. Right figure: Zn content in bottom ash

Cadmium

0.7 wt% Cl samples show no significant variation in Cd content over all ash fractions, NaCl alone exceeding 100 % (Figure 3.8: left). 2.2 wt% Cl, however, leads to an increase of Cd content in every additive sample, with $CaCl_2$ reaching up to 250 %. In both cases, the majority of Cd is found in the filter ash fraction.

The bottom ash fractions displays a reduction of NaCl (75 %) and $MgCl_2$ (below 100 %) with 0.7 wt% Cl. In contrast, blending with $CaCl_2$ leads to an increased Cd amount of 160 %. All samples of 2.2 wt% Cl show a reduced Cd content varying between 50 % ($CaCl_2$) and 57 % ($MgCl_2$ %).

Adding Na_2SO_4 leads to a relative Cd content of 75 %, which exceeds the reduced Cd amount of Cl-based additives.

Lead

Over all ash fraction, the $MgCl_2$, 0.7 wt% Cl sample is the only sample, that shows reduction for Pb. However, the 0.7 wt% Cl samples record only small increase in relative Pb content, whereas all 2.2 wt% Cl samples exceed 100 %, reaching from 180 %

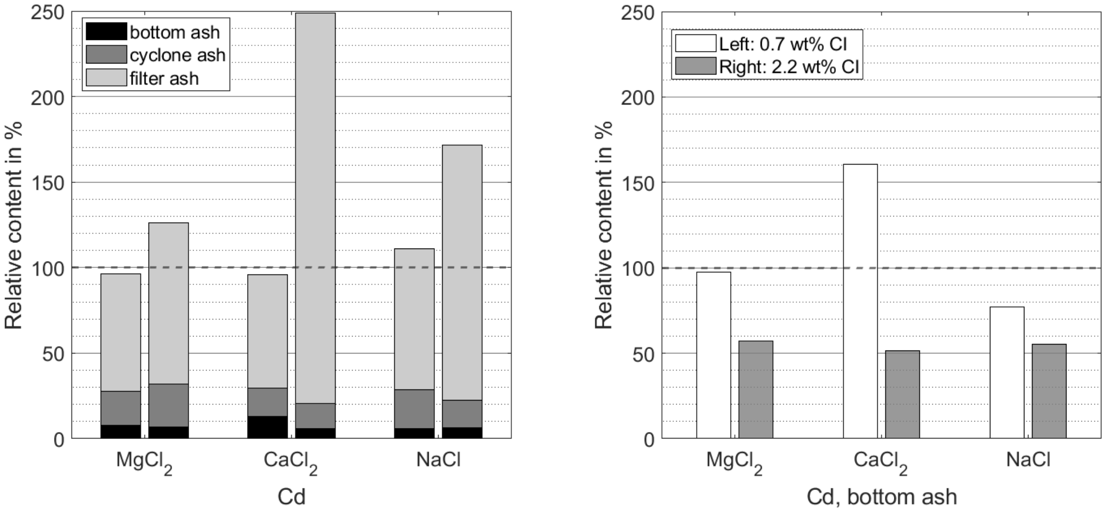

Figure 3.8: Cd content relative to benchmark experiment. Left figure: Cd content over all ash fractions. Right figure: Cd content in bottom ash

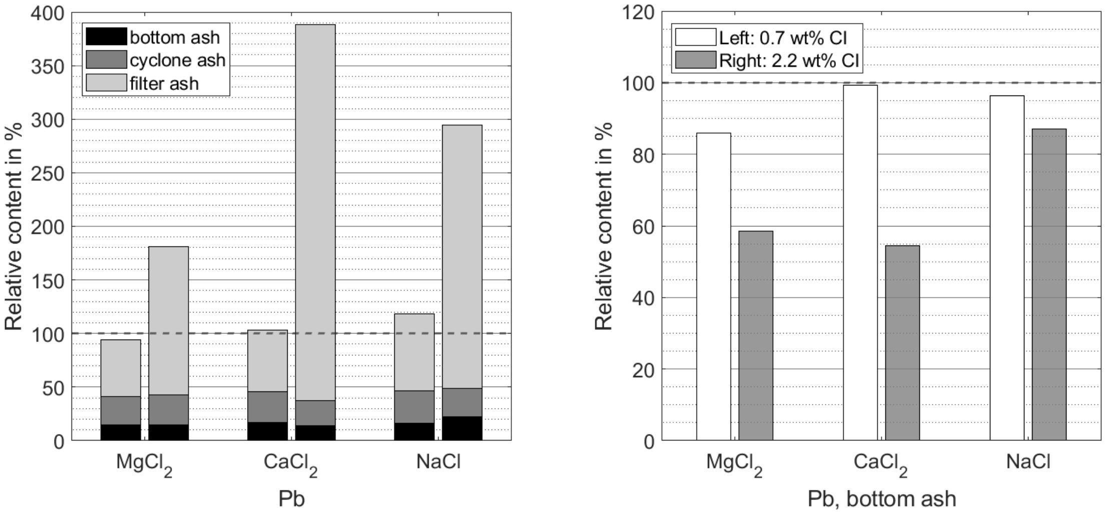

Figure 3.9: Pb content relative to benchmark experiment. Left figure: Pb content over all ash fractions. Right figure: Pb content in bottom ash

($MgCl_2$) to 380 % ($CaCl_2$) (Figure 3.9: left). Similarly to Cu, Zn, and Cd, filter ash makes up the biggest part of all ash fractions.

In contrast, a reduction of Pb content occurs in every samples of the bottom ash fraction (Figure 3.9: right). 0.7 wt% Cl samples indicate only small reduction with $CaCl_2$ and NaCl, both marginally below 100 %, and $MgCl_2$ to 85 %. The results of

2.2 wt% Cl samples show higher reduction, ranging between 54 % ($CaCl_2$) and 85 % (NaCl). Schnell and Quicker (2020) observed similar chloride dependent behaviour with $MgCl_2$. Hereby, the maximum reduction is reached at 80 % with 5 % $MgCl_2$. Na_2SO_4 reaches with reduction to 90 % the same amount as NaCl, but still exceeds the Pb content induced by $MgCl_2$ and $CaCl_2$.

3.3.2 Influence of reducing conditions

In order to estimate the influence of the oxygen supply, two experiments without additives are conducted at 800 °C; experiment 3.1 in oxidative atmosphere and experiment 3.2 in nitrogen-based atmosphere. Figure 3.10 demonstrates the absolute heavy metal content in the bottom ash fraction. As the amount is not exactly measurable for Cd and Pb with under stoichiometric oxygen supply, these bars are not shown. Nevertheless, a value of less than 7 mg per kg dry substance is detected for Pb, and hence below the amount in oxidising atmosphere. In reducing atmosphere higher reduction occurs with Cu and Zn, whereas Ni and Cr show higher reduction in oxidising atmosphere.

The benchmark experiment for reducing atmosphere samples is experiment 3.2, conducted with sub-stoichiometric oxygen supply at 800 °C. Reducing atmosphere experiments are further conducted with an additive amount of 0.7 wt% Cl for $MgCl_2$ and 2 wt% Na for Na_2SO_4. In order to facilitate comparability, the following results are compared to samples with the same additive amount, hence $MgCl_2$, 0.7 wt% Cl and Na_2SO_4, 2 wt% Na represent samples in oxidising atmosphere. However, the temperature of oxidising atmosphere experiments exceeds the temperature of experiments in reducing atmosphere, as it is set at 950 °C. Thus, the temperature difference has to be respected, when evaluating the results.

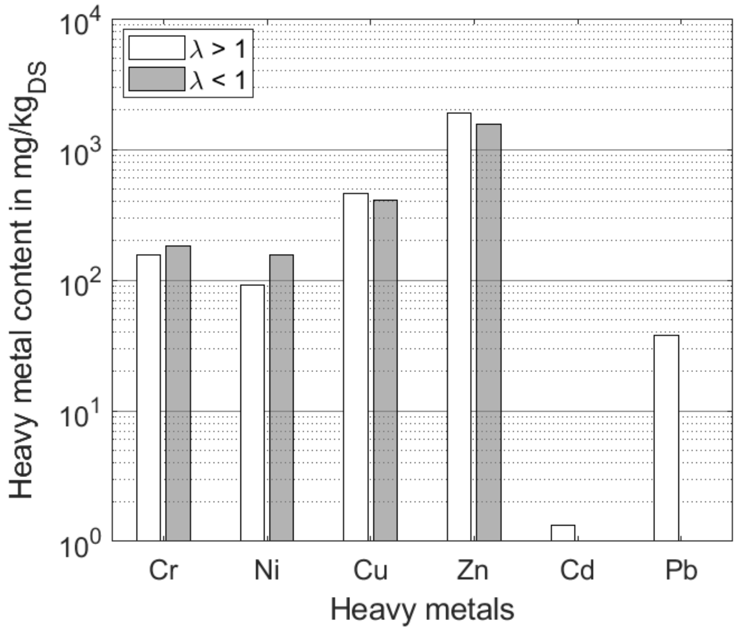

Figure 3.10: Comparison of heavy metal content in the bottom ash with $\lambda > 1$ (left) and $\lambda < 1$ (right) at 800 °C; bars not shown correspond to non-measurable values.

Chromium

The oxidising atmosphere induces a higher reduction of relative Cr content over all ash fractions. An increase of Cr in reducing conditions occurs with $MgCl_2$.

Similar results occur in the bottom ash fraction, though the only increase is recorded with $MgCl_2$ in oxidising atmosphere. In reducing atmosphere, $MgCl_2$ records a relative content of 90 %, which is marginally above the 82 % in literature data (Schnell and Quicker, 2020).

Nickel

An increase occurs in reducing atmosphere with both additives. However, the increase predominantly concerns the filter ash, which leads to a relative Ni content of 160 % (Na_2SO_4) and 170 % ($MgCl_2$) over all ash fractions.

The bottom ash fraction records a lower relative Ni content in reducing atmosphere, than in oxidising atmosphere. The occurring reduction to 90 % by $MgCl_2$ matches the 95 % achieved in a muffle oven with similar temperature and additive amount (Schnell and Quicker, 2020).

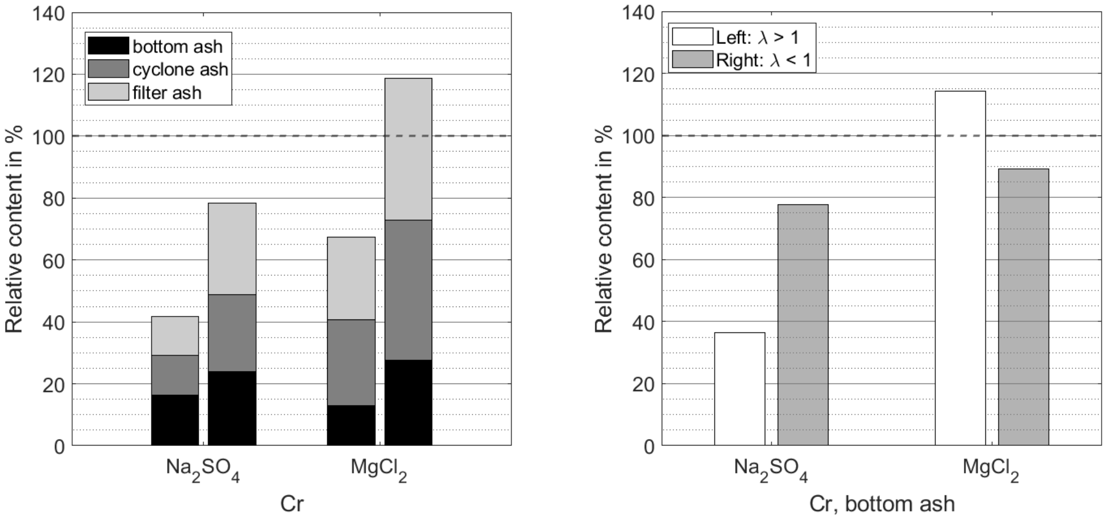

Figure 3.11: Cr content relative to benchmark experiment. Left figure: Cr content over all ash fractions. Right figure: Cr content in bottom ash

Copper

In reducing atmosphere, $MgCl_2$ shows a better performance in Cu reduction, than in oxidising atmosphere and with Na_2SO_4 over all ash fractions. Compared to literature data, where a reduction to 95 % is achieved, the sample records a marginally higher reduction to 82 % (Schnell and Quicker, 2020). In the bottom ash fraction, $MgCl_2$ records the same performance. In contrast, relative Cu content increases with Na_2SO_4 over all ash fractions and in the bottom ash fraction.

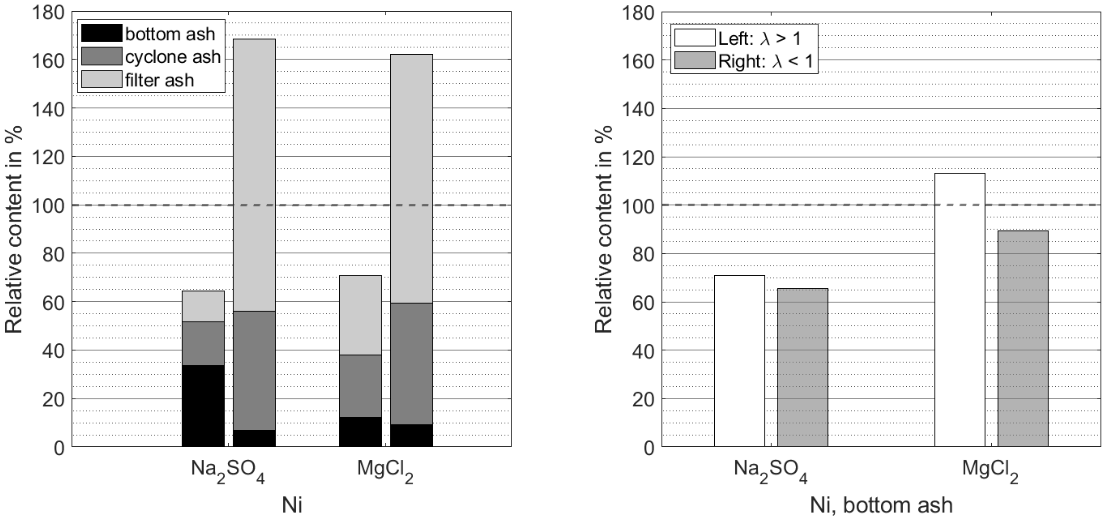

Figure 3.12: Ni content relative to benchmark experiment. Left figure: Ni content over all ash fractions. Right figure: Ni content in bottom ash

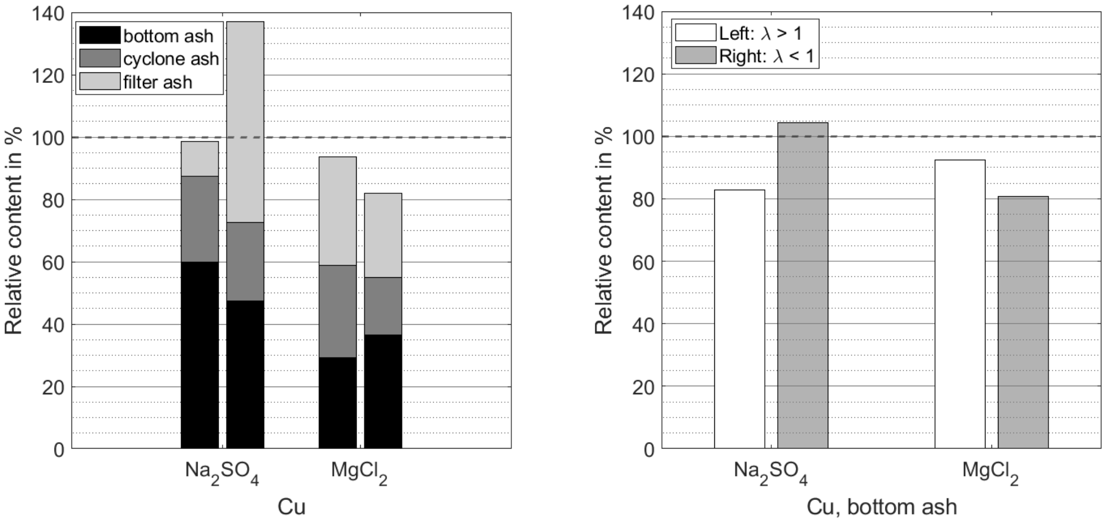

Figure 3.13: Cu content relative to benchmark experiment. Left figure: Cu content over all ash fractions. Right figure: Cu content in bottom ash

Zinc

Oxidising conditions achieves higher reduction of the relative Zn content for both additives. With $MgCl_2$ in reducing atmosphere even an increase above the benchmark experiment is recorded. This increase is also found in the bottom ash fraction with $MgCl_2$ and Na_2SO_4. In contrast, a reduction to less than 90 % is shown in experiments

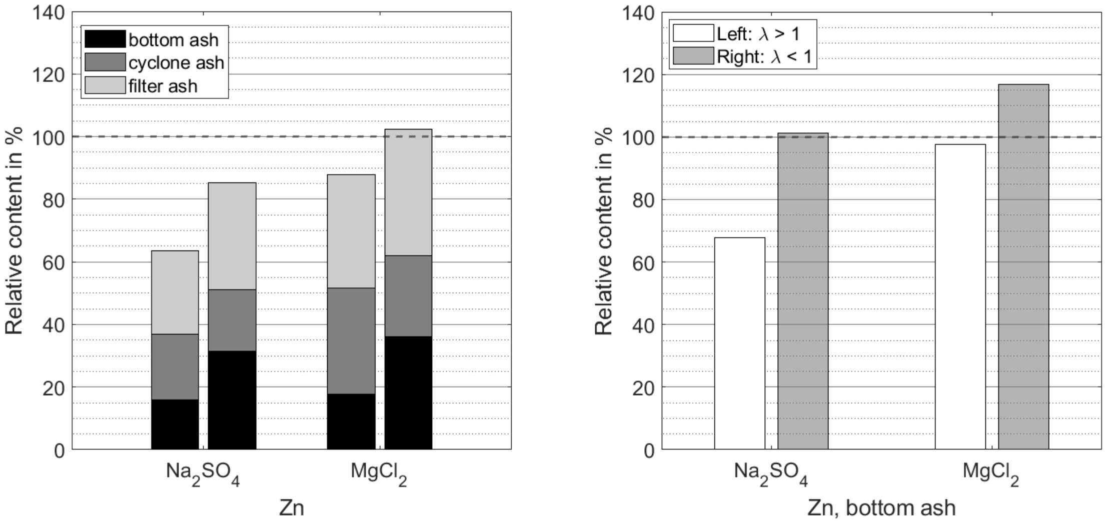

Figure 3.14: Zn content relative to benchmark experiment. Left figure: Zn content over all ash fractions. Right figure: Zn content in bottom ash

by Schnell and Quicker (2020).

Cadmium

For Cd, the quantitative expression of the relative content is not applicable, as Cd is detectable in bottom ash but not quantitatively measurable. However, even with out the bottom ash fractions, reducing atmosphere samples are exceeding the benchmark sample for both additives. Due to the small amounts of Cd in sewage sludge, no literature data is available.

Lead

Similarly to Cd, the exact amount of Pb in bottom ash is not measurable for the benchmark and Na_2SO_4 sample in reducing atmosphere. Both values are below 7 mg per kg sewage sludge and thus, significantly low. When also including the other ash fractions, an increase to more than 200 % is recorded with Na_2SO_4 in reducing atmosphere, due to the significant growth of the filter ash fraction. Samples with $MgCl_2$ in reducing atmosphere are marginally exceeding the benchmark, while literature data shows a reduction of Pb amount under reducing conditions (Schnell and Quicker, 2020).

3.4 Phosphorus solubility

The extraction of phosphorus soluble in neutral ammonium citrate is conducted for selected bottom ash samples, to obtain knowledge about possible bio-availability of the phosphorus in the ash fractions. Due to their performance in the removal of heavy metals, the bottom ash samples of experimental series 1 with 2.2 wt% Cl are analysed and the bottom ash samples of experimental series 3, which was conducted with sub-stoichiometric oxygen supply.

In oxidising atmosphere, $MgCl_2$ and NaCl achieve the highest extraction with 22 %. Similarly, $MgCl_2$ shows the highest phosphorus extraction in literature, though the extracted amount and the applied $MgCl_2$ amount of literature data surpasses values of this thesis. With a concentration of 150 mg $MgCl_2$ per kg sewage sludge a phosphorus extraction of 40 % is achieved (Schick, 2009).

Experiments with sub-stoichiometric oxygen supply show an over all increased amount of extracted phosphorus. With $MgCl_2$ an extraction up to 42 % occurs, which is the highest amount achieved in this thesis. However, biochar samples with $MgCl_2$ reach up to 60 % at 800 °C (Xia et al., 2020). With Na_2SO_4, an extraction of 28 % is observed, the Na/P ratio of the initial sewage sludge and additive blending being 0.73. At the same Na/P ratio, Herzel et al. (2016) achieves similar results with sewage sludge ash.

4 Discussion

In order to discuss the removal of heavy metals and possible fertiliser application of the phosphate product, two aspects concerning the fractionation have to be considered. Primarily, the fraction of high phosphorus occurrence is identified and further, the fraction of low heavy metal occurrence.

The sewage sludge samples in this thesis are characterised by divergent compositions, however, in both cases phosphorus is most abundant in the bottom ash fraction. With sewage sludge 1 even an increase of phosphorus in bottom ash induced by thermal treatment with additives is observed.

Regarding the abundance of heavy metals, an opposite trend occurs. The amount of heavy metals in bottom ash is decreasing when blended with additives, exceptions are due to corrosion effects. In contrast, an accumulation of heavy metals occurs in the filter ash. Thereby, the heavy metal concentration after thermochemical treatment exceeds the total heavy metal amount in the benchmark experiments. When analysing the occurrence of an individual heavy metal, the correlation with their volatility is reasonable. The majority of the low volatile heavy metals, Cr and Ni, are expected to remain in the bottom ash fraction, albeit with a decreasing concentration, when treated thermochemically. This trend is observed in selected samples, however, the results are not representative due to corrosion. Cu and Zn as semi-volatile heavy metals increase significantly in filter ash, when blended with additives. The concentration of the high volatile heavy metals, Cd and Pb, is already set at a high level in the benchmark filter ash fractions. An even further increase occurs while thermochemical treatment. In total, the bottom ash fraction is the most suitable for phosphorus recovery, due to the reduced heavy metal content and high phosphorus concentration.

Apart from the localisation of heavy metals in the ash fractions, the potential of the individual heavy metals for the indication of removal is evaluated. These six heavy metals are primarily chosen as indicators, since their relevance in further applications is given. During and after the conduction of experiments, certain difficulties concerning unintentional interaction with reactor components or impeded measurability emerged, creating the need for a discussion of suitability.
As mentioned before, in this thesis Cr and Ni do not comply with the criterion of representativeness, due to occurring corrosion. As stringent restrictions for Cr exist regarding the further phosphorus applications in agriculture, Cr bears the potential to be established as strong indicator. However, current Cr content in sewage sludge ash exceeds the legal thresholds by several orders of magnitude, hence, subsequent removal techniques have to be considered. On Cu and Zn, as most abundant heavy metals in sewage sludge, the correlation of Cl amount dependence is well observed. As no stringent regulations exist, they serve as general indicator of whether the conditions applied are effective and suitable.
With Cd, the analytical method encounters its limitations and in many cases only the detection of Cd is possible, due to the small content in ash samples. As a critical element in soil with stringent legal thresholds, Cd serves as an essential indicator for further application. As a result, the applied measurement methods must ensure that the limit is not surpassed. In this thesis, concentrations below 1 mg per kg dry mass are no longer measured, but only detected. With legal limits at 3 mg per kg dry mass, the detection limit is sufficient. Similar limitations in measurement occur with Pb, while its legal restriction are identical to Ni, the total abundance in sewage sludge is decreased, rendering it a less critical element.

In total, phosphorus recovery is feasible with thermochemical treatment in a single-step process. The amount of phosphorus in bottom ash is suitable for further applications and complies with selected standards for phosphorus solubility. However, the following considerations have to be taken into account for a holistic evaluation. In this thesis, only one method is applied to identify the bio-availability, and this method is based on comparison with literature data. The results correspond to observations in literature, where two main paths of additive adding are identified. The selection of additive can be based on promoting the formation of bio-available phosphates or focusing on improved heavy metal removal. In sum, both criteria need to be fulfilled for phosphorus recovery, although certain knowledge gaps exist regarding the bio-availability. For improved understanding of bio-availability behaviour, further bio-available phosphate formations have to be qualitatively identified on the analytical aspect. Further, these observations need to be empirically approved with growth experiments.

In order to comply with legal heavy metal restrictions with the current process design, further treatment is necessary. Primarily, this implies a targeted Cr separation, implemented for example by a subsequent extraction in leaching processes.

Further discussion focuses on answering the research questions.

Is the amount of removed heavy metals dependent on the amount of additive?

The dependence on additive amount differs with the individual heavy metal. No significant trend occurs with Cr and Ni, however, the results are not representative. With Cu, Zn, Cd, and Pb, the dependence on the chloride amount in the additive exits in the bottom ash fraction. An increased amount of chloride induces a significant increase of heavy metal removal. In general, the reduction with 0.7 wt% Cl ranges within 90 %, and is thus marginal. As a result, increased Cl amount is recommended for significant removal of heavy metals, but an upper limit is given imposed by corrosive effects. Due to the accumulation and transport of heavy metals discussed above, the results differ for the filter ash fraction, where the content of Cu, Zn, Cd and Pb is increased.

Which additive is most suitable for heavy metal removal during thermal treatment of sewage sludge in terms of maximum removable amount?

In comparison to chloride based additives, the overall lowest reduction occurs with Na_2SO_4. Nevertheless, Na_2SO_4 is primarily introduced to enhance the bio-availability of the phosphate product and is characterised by a more complex reaction mechanism. Hence, the focus of Na_2SO_4 is not on heavy metal removal, but it is applicable for this purpose as well.

In contrast, $CaCl_2$ and $MgCl_2$ remove the over all highest amount of heavy metals, though their results are differing. $MgCl_2$ achieves the most reduction for Cu and Zn, and $CaCl_2$ for Pb and Cd. Hence, $CaCl_2$ induces the most reduction for heavy metals, that are already known for their high volatility. In addition, the amount of Cd is in general very low and for some samples only detectable.

The performance of NaCl is located between Na_2SO_4 and $MgCl_2$ and $CaCl_2$. For Cd and Cu, the reduction behaviour is similar to the other chloride additives, this coincides with literature, where all chloride additives perform similarly for Cu (Nowak et al., 2012). For Zn and Pb, NaCl shows more correlation with results from Na_2SO_4, and for Zn, no effect is shown with NaCl.

Due to the performance with semi-volatile heavy metals, $MgCl_2$ appears as most suitable additive for heavy metal removal.

Is it possible to enhance the removal of heavy metals by conducting the thermal treatment with sub-stoichiometric oxygen supply?

Experiments conducted with sub-stoichiometric oxygen supply show an improved reduction of Cu, Zn, Cd, and Pb at 800 °C. However, additives are not considered in these results and the behaviour with additives is varying strongly in bottom ash. The $MgCl_2$ samples show a reduction of Ni, Cr, and Cu in bottom ash with sub-stoichiometric oxygen supply, but Na_2SO_4 samples are characterised by a dominant variation and no trend of improved reduction with sub-stoichiometric oxygen supply. It also must be considered that, the experiments in oxidising atmosphere are conducted at 950 °C, while reducing atmosphere experiments are conducted at 800 °C. The influence of temperature is not studied in this thesis, as a broad consensus of its influence already exits in literature. Hence, the comparison of reducing and oxidising atmosphere is affected by the difference in temperature, which proves to play a pivotal role.

Overall, sub-stoichiometric oxygen supply leads to a lower content of four heavy metals, when compared to experiments conducted in oxidising atmosphere at the same temperature. At different temperature levels, an improved removal occurs with sub-stoichiometric oxygen supply, despite being at the lower temperature level. Thus, a positive removal effect is observed, and the reduction of heavy metals can be enhanced with sub-stoichiometric oxygen supply. For further specification including the effects of additives, more experiments conducted at the same temperature level are necessary.

Is the product of thermal treatment suitable for fertiliser application?

The suitability for fertiliser application depends primarily on the heavy metal concentration limited by the legal threshold of the Austrian and European fertiliser ordinance. Currently, none of the samples after thermochemical treatment complies with the legislation, due to the limit for Cr, which is set at 2 mg per kg dry mass. All samples exceed this limit by multiple orders of magnitude. The restrictions for Pb are achieved in every bottom ash sample treated with additives. However, restrictions for Ni are only met in experimental series 1 with Na_2SO_4 and $MgCl_2$, where sewage sludge 1 with a significant smaller Ni content is applied.

Hence, for fertiliser application the concentration of Cr has to be reduced significantly. The compliance of the other heavy metals depends on the applied additive, and the initial composition of the sewage sludge.

Another factor taken into account for the fertiliser application is the bio-availability of phosphorus. The bio-availability is qualitatively determined by the phosphorus solubility in neutral ammonium citrate. Thereby, the highest extraction occurs with

$MgCl_2$ and sub-stoichiometric oxygen supply. Due to the relatively low Na/P ratio, Na_2SO_4 samples show lower phosphorus extraction; with an increased Na/P ratio to greater than 1.75, extraction similar to triple super phosphate are expected. However, it has to be taken into account that the method is chosen for facilitated comparability. The predictive accuracy of the actual phosphorus uptake of plants is limited, as not all phosphates soluble in neutral ammonium citrate are available for plants, Al-phosphates being an example (Steckenmesser et al., 2017). Further, no information about the standard deviation is available, due to the sample size. Thus, the dependence on homogeneous mixing of each sample is given. In total, growth experiments are recommended for improved reliability on plant availability.

5 Conclusions and outlook

The origin of heavy metal removal by thermochemical treatment lies in the treatment of municipal solid waste, and research for application in sewage sludge is still in the beginning. Although the knowledge of application with municipal solid waste can be adopted, adaptations are necessary to meet the demands of sewage sludge processing. The general objective of this thesis is the implementation of phosphorus recovery from sewage sludge. Within this objective, the removal of heavy metals from sewage sludge to enhance phosphorus recovery is considered to be the primary aspect. However, the bio-availability of obtained phosphates is additionally relevant for further applications. Hence, chloride based additives and Na_2SO_4 are applied, to investigate the potential for heavy metal removal and enhanced plant availability. In total, very homogeneous results occur in bottom ash, where an increased heavy metal reduction is induced by an increase of additive amount. The best results for heavy metal removal are achieved with $MgCl_2$, though reduction occurs with every additive. Bio-availability is expressed in extraction of phosphorus soluble in neutral ammonium citrate, and shows improved results when treated with sub-stoichiometric oxygen supply. Similarly to heavy metal removal, $MgCl_2$ outperforms the other additives in terms of bio-availability of phosphate.

For future experimental design a consistent temperature level is recommended, when comparing oxidising and reducing condition, in order to study the differing behaviour more detailed and without the significant influence of temperature.
Due to occurring corrosion, the behaviour of Cr and Ni is not studied in depth. Exper-

iments in a brick-lined reactor provide representative values to close these knowledge gaps. As the Cr concentration is currently exceeding the legal threshold for fertiliser application, a focus on Cr behaviour during thermochemical treatment and customised removal strategies bear potential for further research. Since the limit value is considerably exceeded, the implementation of the entire Cr removal during the single-step process is not assumed. Thus, the consideration of a subsequent Cr extraction with wet-chemical methods is recommended.

Regarding the bio-availability of phosphate bearing ash, the extraction in neutral ammonium citrate is a standardised method, which provides a considerable basis for comparability with literature data. However, the actual phosphorus uptake of plants differs and is not in total represented by values, obtained with wet-chemical methods. When focusing on the bio-availability of phosphates, growth experiments provide reliable results for fertiliser performance. Apart from an empirical approach to validate bio-availability of phosphates, general knowledge gaps of bio-available phosphate formations are identified. Thus, the combination of a qualitative phosphate analysis and growth experiments is recommended to improve understanding of plant available phosphorus. In a further step, additives enhancing the formation of bio-available phosphorus can be applied during thermochemical treatment for a targeted phosphate formation.

The fate of chlorides in the flue gas is not addressed in this thesis and bears potential for further research. Chlorides may occur as HCl emissions, that promote corrosion within the system, or heavy metal chlorides not condensed in the filter. The occurring concentrations and abundance of chloride formations is yet unknown, however, improved understanding is necessary in order to adapt the flue gas system.

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