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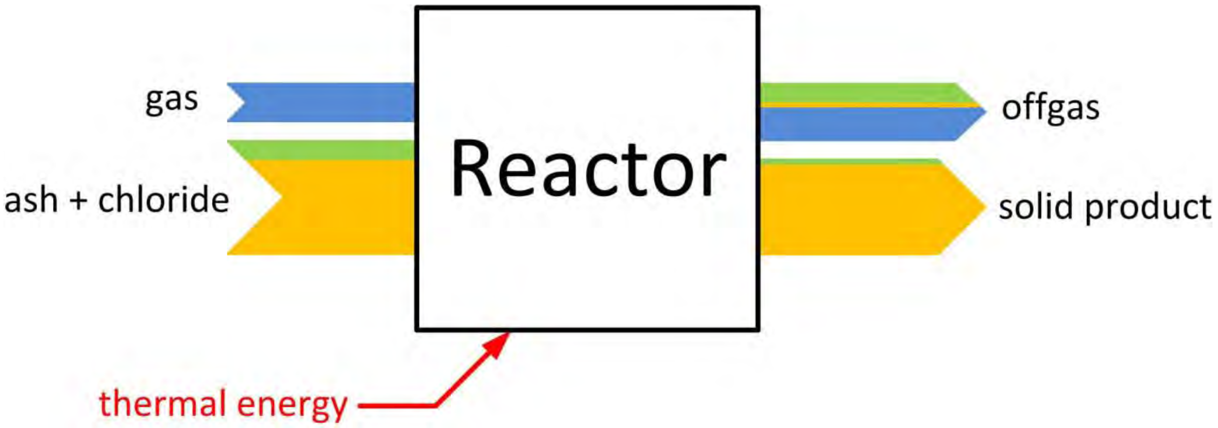
Heavy metal separation from incineration ashes by chlorination and thermal treatment

Dissertation

Institute of Chemical Engineering
Vienna University of Technology

Benedikt Nowak



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Heavy metal separation from incineration ashes by chlorination and thermal treatment

Dissertation

prepared for the purpose of obtaining the academic degree Doctor of Engineering Sciences (Doktor der technischen Wissenschaften)

under the supervision of
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Institute of Chemical Engineering

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Abstract

Incineration is considered as an environmentally friendly disposal option for waste such as municipal solid waste (MSW) or sewage sludge. One of the residues from incineration is fly ash. MSW fly ash requires special handling and disposal because of its leaching behavior. Sewage sludge ash is an important secondary resource for phosphorus. However, heavy metals have to be considered carefully for direct utilization as fertilizers because their concentrations are usually too high according to current regulations.

Heavy metal removal from fly ash can be performed by mixing the ash with environmentally compatible chlorides (e. g. $CaCl_2$, $MgCl_2$) and treating the mixture at temperatures between 900 and 1100°C. In order to avoid the entrainment of significant amounts of dust in the treatment process, the mixture can be pelletized (after addition of water). The thermal treatment can be conducted in rotary or fluidized bed reactors.

In this work, experiments concerning the influence of the ash type (sewage sludge ash and MSW fly ash), chloride type ($CaCl_2$, $MgCl_2$, NaCl), chloride amount (0 to 230 g Cl added per kilogram ash), pelletization, reactor type (rotary reactor, fluidized bed reactor), treatment temperature (800 to 1200°C), and residence time (1 min to 20 h) on the separation efficiency for different heavy metals (Cd, Cr, Cu, Ni, Pb, Zn) were carried out. In addition, specific tests were performed in a muffle oven and by thermogravimetric analysis.

During the treatment process, volatile heavy metal compounds (mainly chlorides) are formed. Depending on the type of chloride added, heavy metals are either directly (e. g. $ZnO + 2\,NaCl \longrightarrow ZnCl_2 + Na_2O$) or indirectly chlorinated. When chlorinated indirectly, chlorides react first with water vapor or oxygen to form HCl or Cl_2 (e. g. $CaCl_2 + H_2O \longrightarrow CaO + 2\,HCl$); these gases subsequently chlorinate. NaCl follows the route of direct chlorination but evaporates in significant amounts without reacting as well. $CaCl_2$ and $MgCl_2$ are more effective for heavy metal removal; they indirectly chlorinate.

Treating a pelletized mixture of sewage sludge ash and $CaCl_2$ (150 g Cl added per kilogram of ash) in a laboratory-scale rotary reactor, at 1050°C, more than 99% of Cd, approximately 97% of Cu, 95% of Pb, and 95% of Zn can be removed after 25 min. More than 50% of these heavy metals are already volatilized during the heat-up period (i. e. after 2 min when heating from ambient temperature).

For MSW fly ash, the same procedure leads to significantly lower amounts of heavy metals removed; even when using 230 g Cl per kilogram of ash, at 1050°C after 45 min approximately 95% of Cd, 60% Cu, 97% Pb, and 80% Zn can be released. These differences in heavy metal removal are caused by different heavy metal concentrations, different grain sizes, and different matrix compositions of both ashes.

Without pelletization, but also depending on other conditions, higher amounts of Cu and Zn can be removed from MSW fly ash. Using $CaCl_2$ (150 g Cl added per kilogram of ash) and a treatment temperature of 1000°C, up to 80% of Cu and Zn are volatilized after 60 min. If pelletized before treating thermally, 25% of Cu and 60% of Zn can be removed after 45 min.

Further enhancement of heavy metal removal from MSW fly ash is possible by adding organic material to the ash-chloride mixture, although thermodynamic equilibrium calculations reveal that reducing conditions decrease the amount of Cu removed. Prior reduction and subsequent oxidization under chlorination condition increases the amount of Cu removed as well.

For heavy metal removal from sewage sludge ash, both a rotary reactor and a fluidized bed reactor are suitable. By comparing the separation efficiency of Cu, Pb, and Zn in both reactors, the limitations of heavy metal removal concerning the external mass transfer were identified: Cu removal is limited by the evaporation and/or diffusion of its chloride; Pb and Zn removal are limited by the availability of HCl and Cl_2.

Kurzfassung

Die Verbrennung von Abfällen wie Hausmüll oder Klärschlamm wird als umweltfreundliche Entsorgung angesehen. Einer der Verbrennungsrückstände ist Flugasche. Lagerung und Transport von Flugasche aus Hausmüllverbrennungsanlagen (Hausmüllasche) gestaltet sich auf Grund des Auslaugungsverhaltens kompliziert. Klärschlammasche ist eine wichtige Sekundärrohstoffquelle für Phosphor. Die Schwermetallgehalte sind jedoch üblicherweise zu hoch für die direkte Nutzung als Düngemittel gemäß aktueller Düngemittelverordnungen.

Schwermetalle können aus Asche durch Mischen mit umweltverträglichen Chloriden (z. B. $CaCl_2$, $MgCl_2$) und anschließender thermischer Behandlung zwischen 900 und 1100°C abgetrennt werden. Um den Austrag großer Staubmengen im thermischen Prozess zu vermeiden, kann die Mischung (nach Zugabe von Wasser) pelletiert werden. Die thermische Behandlung kann in Drehrohr- oder Wirbelschichtreaktoren erfolgen.

In der vorliegenden Arbeit wird der Einfluss der Asche (Klärschlammasche und Hausmüllasche), des Chlorids ($CaCl_2$, $MgCl_2$, NaCl), der Menge an zugegebenem Chlorid (0 bis 230 g Cl pro Kilogramm Asche zugegeben), der Pelletisierung, des Reaktors (Drehrohr, Wirbelschicht), der Behandlungstemperatur (800 bis 1200°C), und der Verweilzeit (1 min bis 20 h) auf die Abtrenneffizienz für verschiedene Schwermetalle (Cd, Cr, Cu, Ni, Pb, Zn) untersucht. Zusätzlich werden spezielle Untersuchungen in Muffelofen und Thermogravimetrie durchgeführt.

Während der thermischen Behandlung werden flüchtige Schwermetallverbindungen gebildet (v. a. Chloride). Schwermetalle können entweder direkt (z. B. $ZnO + 2\,NaCl \longrightarrow ZnCl_2 + Na_2O$) oder indirekt chloriert werden. Bei indirekter Chlorierung reagieren Chloride zuerst mit Wasserdampf oder Sauerstoff zu HCl oder Cl_2 (z. B. $CaCl_2 + H_2O \longrightarrow CaO + 2\,HCl$); diese Gase chlorieren im nächsten Schritt Schwermetallverbindungen. NaCl chloriert direkt; große Mengen verdampfen jedoch ohne zu reagieren. $CaCl_2$ und $MgCl_2$ sind effizienter für die Schwermetallentfrachtung; sie chlorieren indirekt.

Behandelt man Pellets aus Klärschlammasche und $CaCl_2$ (150 g Cl pro Kilogramm Asche zugegeben) in einem Labor-Drehrohrreaktor bei 1050°C, so können nach 25 min mehr als 99% Cd, ca. 97% Cu, 95% Pb, und 95% Zn abgetrennt werden. Mehr als 50% dieser Schwermetalle werden bereits während der Aufheizphase verflüchtigt (d. h. beim Aufheizen von Umgebungstemperatur nach 2 min).

Führt man die gleiche Prozedur für Hausmüllasche durch, so werden signifikant geringere Mengen an Schwermetallen entfrachtet: Werden 230 g Cl pro Kilogramm Asche zugegeben, so können nach 45 min bei 1050°C ca. 95% Cd, 60% Cu, 97% Pb, und 80% Zn abgetrennt werden. Die auftretenden Unterschiede der Abtrenneffizienz liegen an verschiedenen Schwermetallkonzentrationen, Korngrößen und Matrixzusammensetzungen der beiden Aschen.

Ohne Pelletisierung können größere Mengen an Cu und Zn aus Hausmüllasche abgetrennt werden. Mit $CaCl_2$ (150 g Cl pro Kilogramm Asche zugegeben) können bei 1000°C bis zu 80% an Cu und Zn nach 60 min verflüchtigt werden. Pelletiert man vor der thermischen Behandlung, so liegen diese Werte nach 45 min bei 25% Cu und 60% Zn.

Eine weitere Verbesserung der Abtrenneffizienz von Hausmüllasche kann durch Zugabe von organischem Material zu der Asche-Chlorid-Mischung erreicht werden, obwohl laut thermodynamischer Gleichgewichtsberechnungen reduzierende Bedingungen der Verflüchtigung von Cu entgegen wirken. Die vorherige Reduzierung und nachfolgende Oxidierung bei Chlorierungsbedingungen führt auch zu höheren Entfrachtungen von Cu.

Für die Schwermetallentfrachtung von Klärschlammasche können sowohl Drehrohr als auch Wirbelschicht verwendet werden. Vergleicht man die Abtrenneffizienz von Cu, Pb und Zn in beiden Reaktoren, so können die Limitierungen den Stoffübergang betreffend identifiziert werden: Die Cu-Abtrennung wird von der Verdampfung und/oder der Diffusion des Chlorids, die Pb- und Zn-Abtrennung von der Verfügbarkeit von HCl und Cl_2 limitiert.

Contents

1. Introduction

Incineration is a widely used technique for reducing mass and volume of waste such as municipal solid waste (MSW) or sewage sludge. One of the residues of the incineration process is fly ash, which is usually disposed off in a landfill. This fly ash contains valuable substances, but is either contaminated by heavy metals or, if the valuable substances are heavy metals, they are usually present in concentrations too low to be of value.

In the present work, a process for decontamination of fly ash is studied. Originally, the process was developed for heavy metal removal from sewage sludge ash; in this work, investigations focus on the decontamination of both MSW fly ash and sewage sludge ash.

1.1. Project

The present work mainly arose in the framework of the project "Vienna Spot of Excellence (VSoE) Urban Mining", which has been a co-operation between Ash Dec Umwelt AG and two institutes from the Vienna University of Technology (the Institute of Chemical Engineering and the Institute for Water Quality, Resource and Waste Management). Work started officially in July 2007 and has been scheduled until June 2011. It has been co-funded by the Zentrum für Innovation und Technologie of the City of Vienna. The goal of the project was heavy metal recovery from MSW fly ash and sewage sludge ash. Project results are reported in Refs. [1–3].

1.2. Objectives of the present work

Mixing ash with chloride and treating the mixture, eventually after pelletization, at temperatures above 800°C, leads to the volatilization of heavy metals (for a detailed description of the process see Chapter 2.1.3 and Figure 2.3, page 8).

Based on findings from literature (Chapter 2), the objectives of the present work are the following:

- Examine the effect of different ash types. In this work, the process is studied for sewage sludge ash and MSW fly ash.

- Examine how different types of chlorides behave differently in the process studied. Thus, one aim of the work is investigating the influence of type and amount of the chlorine donor, and so the impact of $CaCl_2$, $MgCl_2$, and NaCl on heavy metal removal of MSW fly ash is studied.

- Pelletization of the chloride-ash mixture may leads to differences in heavy metal removal, which is studied for MSW fly ash.
- On molecular scale, the thermal treatment process consists of a set of consecutive gas-solid reactions, which are probably effected by the external mass transfer. Treating ash-chloride pellets in a rotary reactor or a fluidized bed reactor leads to different external mass transfers (i. e. mass transfer from the reactor's atmosphere to the pellet's surface and vice versa), which is another purpose of the present work. For sewage sludge ash, this comparative study is conducted.
- One aim is finding the impact of treatment temperature and residence time.
- Different types of heavy metals behave differently under combustion conditions. It is one goal to find the separation efficiency for different heavy metals.

1.3. Publication overview

For the present work, five papers have been submitted to peer-reviewed journals (ordered according to the date of acceptance):

Paper I: Heavy metal removal from municipal solid waste fly ash by chlorination and thermal treatment. *Journal of Hazardous Materials* 179 (2010) 323-331 [4]

Paper II: Limitations for heavy metal release during thermo-chemical treatment of sewage sludge ash. *Waste Management* 31 (2011) 1285-1291 [5]

Paper III: Heavy metal removal from sewage sludge ash and municipal solid waste fly ash – A comparison. *Fuel Processing Technology* (2011), accepted for publication. [6]

Paper IV: Heavy metal removal from MSW fly ash by means of chlorination and thermal treatment: Influence of the chloride type. *Chemical Engineering Journal* 179 (2012) 178-185. [7]

Paper V: Sewage sludge to phosphate fertilizer by chlorination and thermal treatment: residence time requirements for heavy metal removal. *Environmental Technology* (2012), accepted for publication. [8]

For the fulltext of the articles see Appendix A; for impact factors and category data see Table 1.1.

Table 1.1.: Journal overview with impact factors and number of journal in category

Journal	**IF**[a]	**Subject categories**	**(rank/total number; in %)**[b]
Journal of Hazardous Materials	3.723	Engineering, environmental	(6/45; 13%)
		Engineering, civil	(2/115; 2%)
		Environmental Sciences	(18/193; 9%)
Waste Management	2.358	Engineering, environmental	(11/45; 24%)
		Environmental Sciences	(52/193; 27%)
Fuel Processing Technology	2.781	Chemistry, applied	(9/70; 13%)
		Energy & Fuels	(19/79; 24%)
		Engineering, chemical	(13/135; 10%)
Chemical Engineering Journal	3.074	Engineering, environmental	(8/45; 18%)
		Engineering, chemical	(10/135; 7%)
Environmental Technology	1.007	Environmental Sciences	(143/193; 74%)

[a] Impact factor 2010

[b] {rank of journal in category according to IF}/{total number of journals in category}; {fraction expressed in %}

2. Literature Review

Incineration is considered as an environmentally friendly disposal option for wastes like sewage sludge or municipal solid waste (MSW).

Figure 2.1 displays a scheme of the most important parts of an MSW incinerator concerning ash production. MSW enters the combustor; in case of grate firing, the steps drying, devolatilization, and combustion occur one after the other on the grate; burnt out bottom ash remains and is collected. For fluidized bed combustors, those steps occur at no specific place in the fluidized bed; the bed material is continuously removed and after sieving of coarse particles recycled; in case of sewage sludge incineration, continuous bed recycling is not necessary (but replacement of entrained sand).

Primary air enters the combustor through the grate (grate incineration) or through the gas distributor (fluidized bed incineration). Small waste particles as well as fine grained sand (bed material in fluidized bed incineration) are entrained due the gas velocity (caused by primary air entering the reactor). Furthermore, volatile (but not necessarily combustible) materials, e. g. heavy metals, evaporate. If combustible, they will be oxidized by secondary air entering the combustor in the freeboard. If re-condensible they will condense on ash particles when the flue gas is cooled down, i. e. the boiler (and economizer). The entrained particles form the fly ash, whereas coarser particles

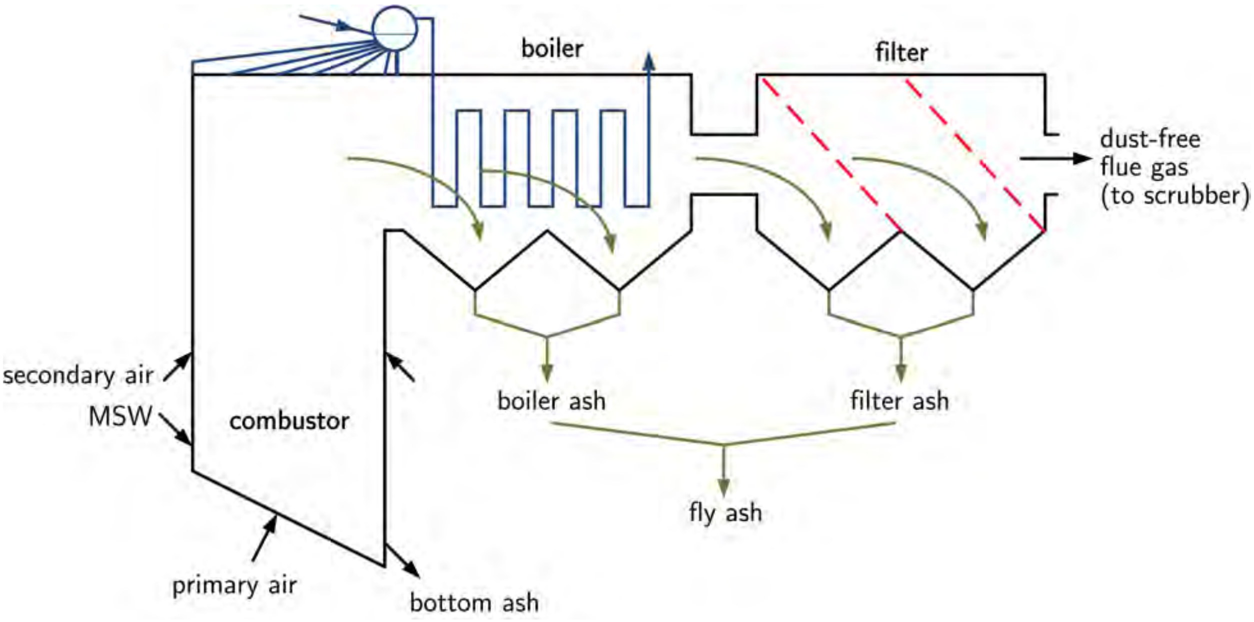


Figure 2.1.: Scheme of an MSW incinerator from combustor via boiler (with steam drum) to filter.

are separated in the boiler forming boiler ash, and finer particles are collected in the filter system (electrostatic precipitator or baghouse filter).

Depending on their volatility, heavy metals are concentrated in fly ash or remain in bottom ash. E. g. Morf et al. [9] reported that 90% of Cd, 6% of Cu, 54% of Pb, and 54% of Zn contained in the waste feed were volatilized and found in the flue gas; the rest remained in the bottom ash. Regarding the total mass flow through an incinerator (approx. 25 wt.-% of the waste entering an MSW incinerator remains as bottom ash, one to 4 wt.-% are entrained as fly ash), especially heavy metals in MSW fly ash are much more concentrated than in waste. Therefore, MSW incineration is an important tool in waste management for waste reduction and concentration of hazardous substances.

Incineration residues from municipal solid waste (MSW) and sewage sludge incineration are mainly disposed off in landfills, although they offer a high potential for recycling of nutrients (especially sewage sludge ash, SSA) and heavy metals [10] (especially MSW fly ash). For both ashes it is necessary to remove heavy metals from the ash for further use of the ash matrix or the heavy metals.

2.1. Sewage sludge ash

Cf. [5, 8].

2.1.1. Phosphorus and phosphate

The current phosphate reserves are 16 billion tons; in 2009 158 million tons were mined (numbers refer to P_2O_5) [11]. This gives a reserves-to-production-ratio of some 100 years. The P consumption in 2050 is estimated to be 1.6-fold to 3.4-fold compared to that one in 2000 [12]. It is estimated that the global phosphorus production reaches its maximum in this century [13]. Phosphorus is an essential element and cannot be substituted. 90% of the mined phosphates are used – after digestion – as fertilizer [14]. Sedimentary reserves of phosphate rock are often contaminated by Cd and U, i. e., these elements end up in agricultural soils if not removed. The quality of mined ore is continuously decreasing resulting in higher concentrations of these elements [15, 16]. Important phosphate reserves are in unstable world regions. Phosphorus is currently used in a linear way and ends up either in soils (biologically not available), in the hydrosphere or in landfills. Thus, phosphorus recycling is necessary [17].

The biggest secondary resource of phosphate is sewage sludge [18], which is polluted by organic [19] and inorganic compounds. Sludge incineration destroys organic pollutants and reduces mass and volume of the sludge. Phosphorus and most heavy metals are concentrated in the ash. Therefore, direct utilization of the ash as fertilizer would lead to long-term contamination of agricultural soils: E. g., in Japanese sewage sludge ash (SSA) the concentrations of Cd, Cu, Ni, Sn, Pb, and Zn were about 10-200 times higher than the concentrations found in soil [20]. So, sewage sludge ash is usually deposited in landfills or used for mine filling.

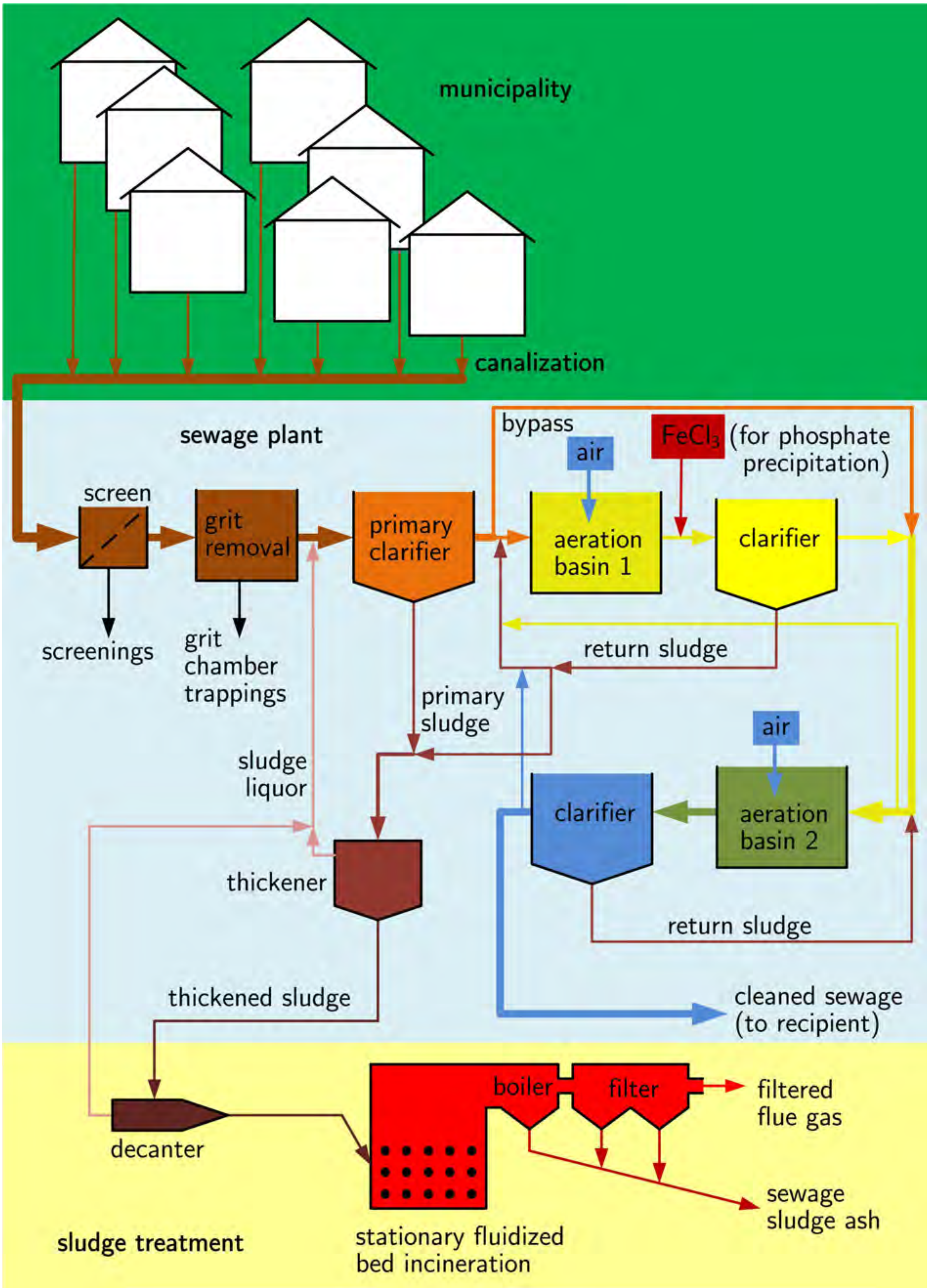


Figure 2.2.: Sewage sludge ash generation: from municipality to sewage sludge ash. Sewage plant: bypass process (as used beside hybrid process in Vienna) [21].

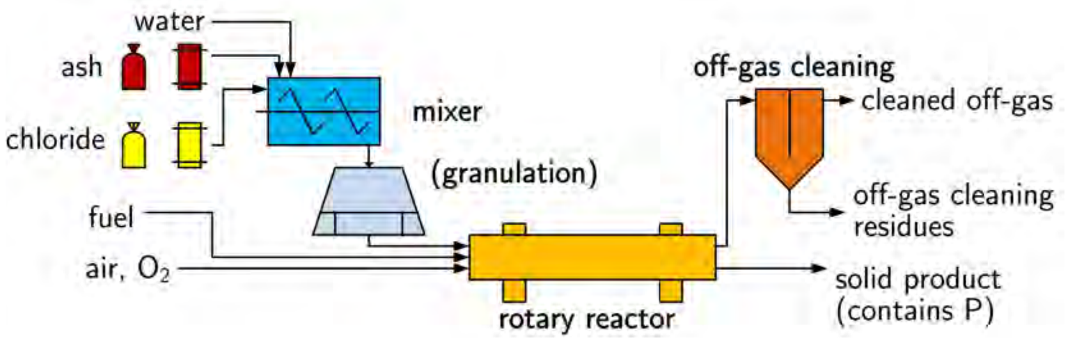


Figure 2.3.: Thermochemical treatment process for heavy metal removal from sewage sludge ash.

Sewage sludge ash (scheme from municipality to ash: Figure 2.2) can be used for P-recovery, but it is only possible if sewage sludge is mono-incinerated [22], or – regarding the work of Petterson et al. [23, 24] – co-incinerated with other P-containing material or not diluted by other ashes. Nevertheless, regarding all possible secondary phosphorus resources, sewage sludge ash is the one with the highest phosphorus concentration [25].

2.1.2. Recovery of phosphorus wet-chemical processes

Recovery of P from sewage sludge ash can be performed either by leaching processes or by thermochemical treatment. Leaching can be performed with sulfuric acid [18, 23, 26–30], hydrochloric acid [27, 31, 32] or bases (e. g. NaOH) [32]. The leachate is then raffinated (e. g. [31]), heavy metals (e. g. [18]) or P (e. g. [28]) are selectively precipitated.

2.1.3. Recovery of phosphorus by thermo-chemical treatment

Leaching processes extract P whereas thermo-chemical treatment processes extract heavy metals from the phosphorus containing matrix. During the past few years, the following process has been developed [33–36] (Figure 2.3):

Sewage sludge ash is mixed with environmentally compatible chlorides (e. g. calcium chloride, magnesium chloride) as well as with water and treated (eventually after granulation to avoid dust) at temperatures between 900 and 1100°C in a rotary kiln. This leads to the formation and evaporation of volatile heavy metal compounds (mainly chlorides). As 90-99% of heavy metals like Cd, Cu, Pb and Zn can be removed, the solid product from the thermal treatment process can be directly used for fertilizer production [33, 35–37]. The P-availability of the product is higher than of the ash because of the formation of new mineral phases leading to a higher solubility in citric acid [34]. When using $CaCl_2$ as chlorination agent, the major P-bearing phase is chlorapatite $Ca_5(PO_4)_3Cl$ (in equilibrium it would be hydroxyapatite $Ca_5(PO_4)_3(OH)$ [38]); for $MgCl_2$ the most important P-phases in the product are stanfieldite $Ca_4Mg_5(PO_4)_6$, chlorapatite and farringtonite $Mg_3(PO_4)_2$ [34, 39, 40].

Contrary to hydrometallurgical processes, organic residues (soot) from the ash are destroyed due to the temperature [41].

Compared to the direct use of sludge on agricultural land, co-incineration in cement kilns or in coal-fired power plants or mono-incineration and the disposal of the ashes in landfills or on soil, the described process (including mono-incineration) performs well with regard to P recycling from sewage sludge and environmental protection. However, this technology has to be improved to reduce the energy consumption [17].

Since chlorine as well as heavy metals are available in the process, one has to discuss the problem of the formation of polychlorinated dibenzodioxins and dibenzofurans. In the solid product, they will be of minor importance because they will be destructed at temperatures above 450°C [42]. In the gas phase of the reactor, the formation can be hindered by a high gas temperature, a sufficiently high turbulence and a rapid off-gas cooling [43, 44].

2.2. Municipal solid waste fly ash

Cf. [4, 7].

Since January 2009, untreated municipal solid waste (MSW) must not be landfilled directly in Austria [45, 46]. MSW incineration is regarded as an environmentally friendly disposal option for MSW. Thus, aside from bio-mechanical treatment, nearly the entire amount of waste is burned in waste-to-energy (WTE) plants. This situation is similar to many other European countries.

One of the residues of MSW incineration is (beside cleaned flue gas, bottom ash, iron scrap, air pollution control ash from gas desulfurization, and filter cake from the wastewater treatment) MSW fly ash, which requires special handling and disposal because of its leaching behavior. It is mainly landfilled (in underground disposal facilities) or it is used in combination with cement, sand, bottom ash, sewage sludge ash and water as a sort of concrete in landfill construction ("slag-ash-concrete", e. g. in Vienna).

2.2.1. Treatment of MSW fly ash

In the past, treatment of MSW fly ash has often been discussed. There are a lot of patented processes concerning the use or disposal of MSW fly ash. These processes can be classified as followed:

- MSW fly ash is mixed with a binder (e. g. inertization in a cement matrix),
- MSW fly ash is treated hydrometallurgically for heavy metal removal and
- MSW fly ash is treated thermally with the objective of inertization and/or heavy metal removal (e. g. melting, vitrification).

Many of these processes have disadvantages, e. g. ash melting requires high energy consumption and produces a secondary fly ash [47]. Once MSW fly ash is hardened with

e. g. cement, heavy metals are diluted. Hence, it would be more difficult and costly to recover them at a later stage.

A detailed literature study (including patents) about treatment of MSW fly ash can be found in [48].

2.2.2. Thermal treatment and heavy metal recovery

The removal of heavy metals from MSW fly ash could lead (1) to the recycling or at least simpler disposal of the ash matrix (having similar properties as cement [49] and (2) to the production of a heavy metals concentrate, which could be recycled. Especially thermal processes are promising as organic residues are destroyed.

A process, which separates heavy metals from MSW fly ash at temperatures below the melting point of the ash mixture used, is the CT-Fluapur®-process [50, 51], Figure 2.4. The process is well described in the literature, but has not been realized on industrial scale yet. MSW fly ash is mixed with 10% carbon and is granulated subsequently. In a fluidized bed reactor the pellets are treated at about 900°C. Hot flue gas from an adjacent

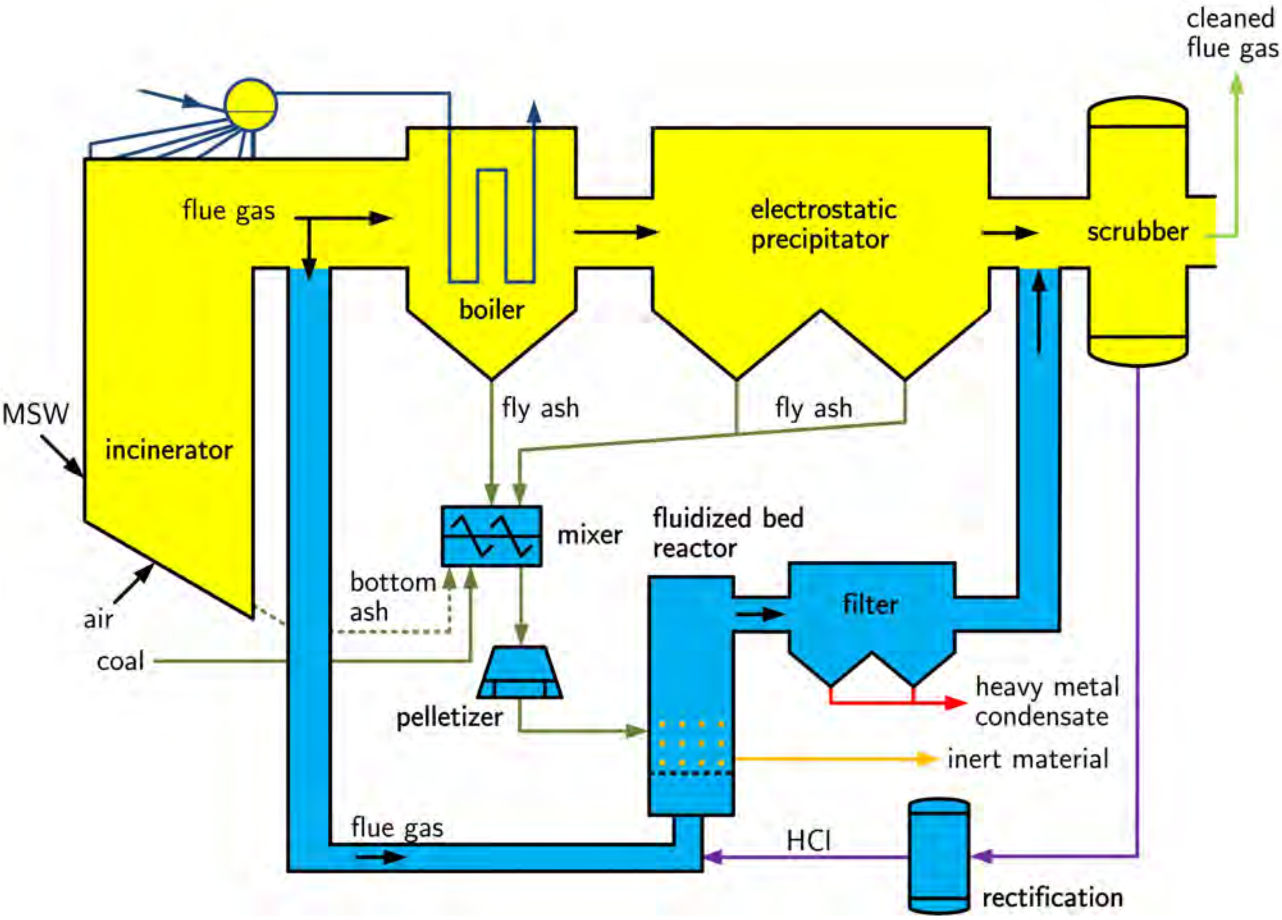


Figure 2.4.: The CT-Fluapur®-process. Standard MSW incinerator equipment marked yellow; additional equipment for CT-Fluapur® in turquois. After [50].

waste incinerator is mixed with HCl from the incinerator's acid scrubber. The gas serves as a heat source and reactant. The off-gas from the fluidized bed reactor is cooled and filtered for separating heavy metals. The filtered gas is recycled to the incineration facility where it is washed in the same scrubber as the main flue gas stream of the incinerator. Cd, Cu, Pb, and Zn are nearly completely (99.8% Cd, 99.5% Cu, 99.5% Pb, 98.5% Zn) removed in the CT-Fluapur®-process within two hours in the fluidized bed reactor. The evaporation of Cr and Ni is incomplete (28 and 57%, respectively) [50, 51]. The disadvantage of the process is the fact that the process cannot be realized in a stand-alone plant but has to be mounted at a waste incinerator. Thus, the complexity of controlling the system increases. Due to the long residence time and costly equipment (rectification for HCl) the costs of the CT-Fluapur®-process are estimated to be 150 to 200 EUR per ton of ash.

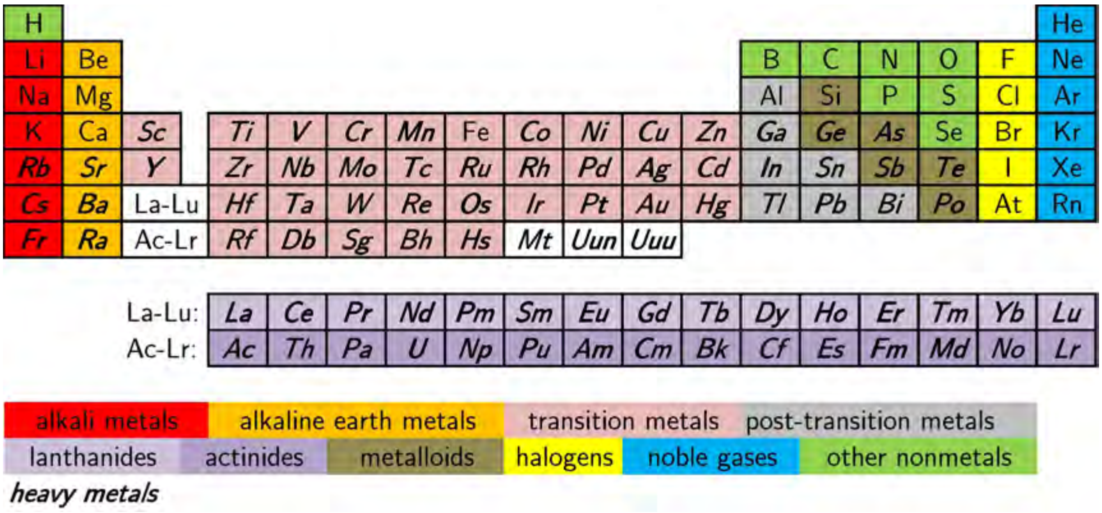
2.3. Heavy metal removal from ash by chlorination and thermal treatment

During combustion processes heavy metal volatilization occurs. Depending on their volatility (Chapter 2.3.1), heavy metals evaporate and recondense in the boiler on ash particles or they are carried by entrainment to the ash (Chapter 2.3.2).

During heat treatment of fly ash, similar processes occur; i. e. heavy metals can be re-volatilized (Chapter 2.3.3); this property can be used for heavy metal recovery from ash.

In recent years, research mainly focused on the heavy metal removal from sewage sludge ash. The volatilization of heavy metals has been studied well (Chapter 2.1.3); a process for industrial scale application has been developed and realized on pilot scale

Table 2.1.: Elements denoted as heavy metals in this work. Periodic table and classification of elements according to [52–55]



H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	*Sc*	*Ti*	*V*	*Cr*	*Mn*	Fe	*Co*	*Ni*	*Cu*	*Zn*	*Ga*	*Ge*	*As*	Se	Br	Kr
Rb	*Sr*	*Y*	*Zr*	*Nb*	*Mo*	*Tc*	*Ru*	*Rh*	*Pd*	*Ag*	*Cd*	*In*	*Sn*	*Sb*	*Te*	I	Xe
Cs	*Ba*	La-Lu	*Hf*	*Ta*	*W*	*Re*	*Os*	*Ir*	*Pt*	*Au*	*Hg*	*Tl*	*Pb*	*Bi*	*Po*	At	Rn
Fr	*Ra*	Ac-Lr	*Rf*	*Db*	*Sg*	*Bh*	*Hs*	*Mt*	*Uun*	*Uuu*							

La-Lu:	*La*	*Ce*	*Pr*	*Nd*	*Pm*	*Sm*	*Eu*	*Gd*	*Tb*	*Dy*	*Ho*	*Er*	*Tm*	*Yb*	*Lu*
Ac-Lr:	*Ac*	*Th*	*Pa*	*U*	*Np*	*Pu*	*Am*	*Cm*	*Bk*	*Cf*	*Es*	*Fm*	*Md*	*No*	*Lr*

alkali metals alkaline earth metals transition metals post-transition metals
lanthanides actinides metalloids halogens noble gases other nonmetals
heavy metals

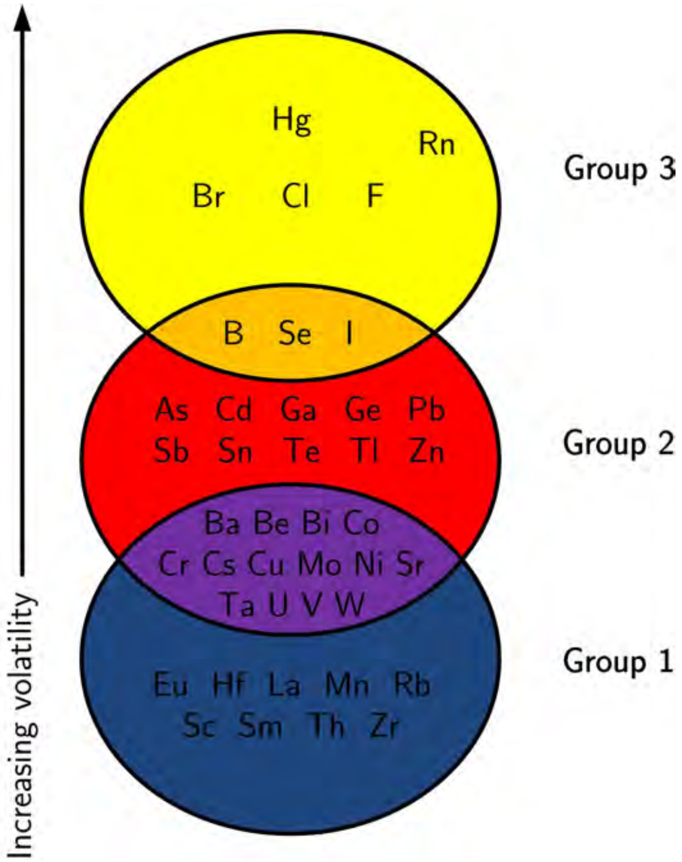


Figure 2.5.: Classification of trace elements in coal combustion according to their volatility. Adapted from [57].

(with a throughput of approx. 500 kg h^{-1}).

Generally, the underlying processes for both types of ashes are similar; therefore they are described here together.

2.3.1. Classification of trace elements regarding their volatility

In combustion processes, trace elements are volatilized in dependency of their property to form compounds with low boiling points. One group of trace elements are heavy metals, whereas it has to be pointed out, that the term "heavy metals" is not well-defined; there are at least 38 definitions [56]. In this work, metals and metalloids with an atomic number ≥ 21 except Fe are denoted as heavy metals in order to distinguish between matrix (Table 4.6 and 4.5) and trace elements in fly ash, Table 2.1.

Based on a literature review, Clarke [57] classified trace elements into three overlapping groups according to their volatilization in coal combustion processes, Figure 2.5:

Group 1 elements hardly volatilize; they are concentrated in particles.

Group 2 elements are volatilized during combustion or gasification but condense especially on surfaces of small particles when the flue gas is cooled down.

Group 3 elements are volatilized as well but are not condensed; they are depleted from all solid phases and may pass the whole plant.

Other authors found similar (but not necessarily the same) volatilization behavior; e. g. Díaz-Somoano and Martínez-Tarazona [58] classified trace elements according to their condensation behavior under coal gasification conditions:

Group A: Mn can probably be condensed under coal gasification conditions.

Group B: As, Be, Cd, Co, Cr, Ni, Pb, Sb, V, and Zn can be condensed under gas cleaning conditions.

Group C: B, Hg, and Se remain in the gas phase.

Differences found in volatilization behavior are caused by different operating conditions and chemical interactions, whereas chlorine is from special importance [59].

For investigating combustion processes, it is often useful to monitor only a few representative elements. E. g. for studying factors affecting the distribution of trace elements, Mn (Clarke's [57] Group 1), Cr (between Group 1 and 2), Cd, Pb, Zn (Group 2), Se (between Group 2 and 3), and Hg (Group 1) have been analyzed [60]; as low volatile heavy metal Ba has been studied in Ref. [61]; Ag, Al,Cu, Fe, Mn, Pb, and Zn were selected in Ref. [62].

However, in coal combustion high temperatures occur; e. g. in typical pulverized coal-fired power stations combustion takes place at temperature > 1400°C [57]. For thermal ash-treatment processes (compare Figure 2.3 and Figure 2.4), temperatures are significantly lower; compared to coal combustion, the atmosphere's chloride concentration is high. Regarding Clarke's [57] classification (Figure 2.5), Group 1 elements will not be volatilized at all; those from Group 3 will be hardly present in fly ash. Thus, only elements with a generally average volatilization behavior, i. e. from Group 2 (including the overlap to Group 1 and 3), have to be studied. Representative Group 2 heavy metals can be furthermore classified into three groups [35, 38]:

low volatile heavy metals are represented by Cr and Ni,

mid volatile heavy metals by Cu and Zn, and

high volatile heavy metals by Cd and Pb.

This classification is also used in the present work.

2.3.2. Fly ash and heavy metals

Cf. [6].

As sewage sludge and municipal solid waste (MSW) contain heavy metals, incineration residues like bottom and fly ash are also contaminated. Volatile heavy metals, e. g. Cd, are concentrated in fly ash more or less independently of temperature, air/fuel and chlorine/metal ratio [63]. Semi-volatile elements, e. g. Cr, Cu, and Ni, remain mostly in

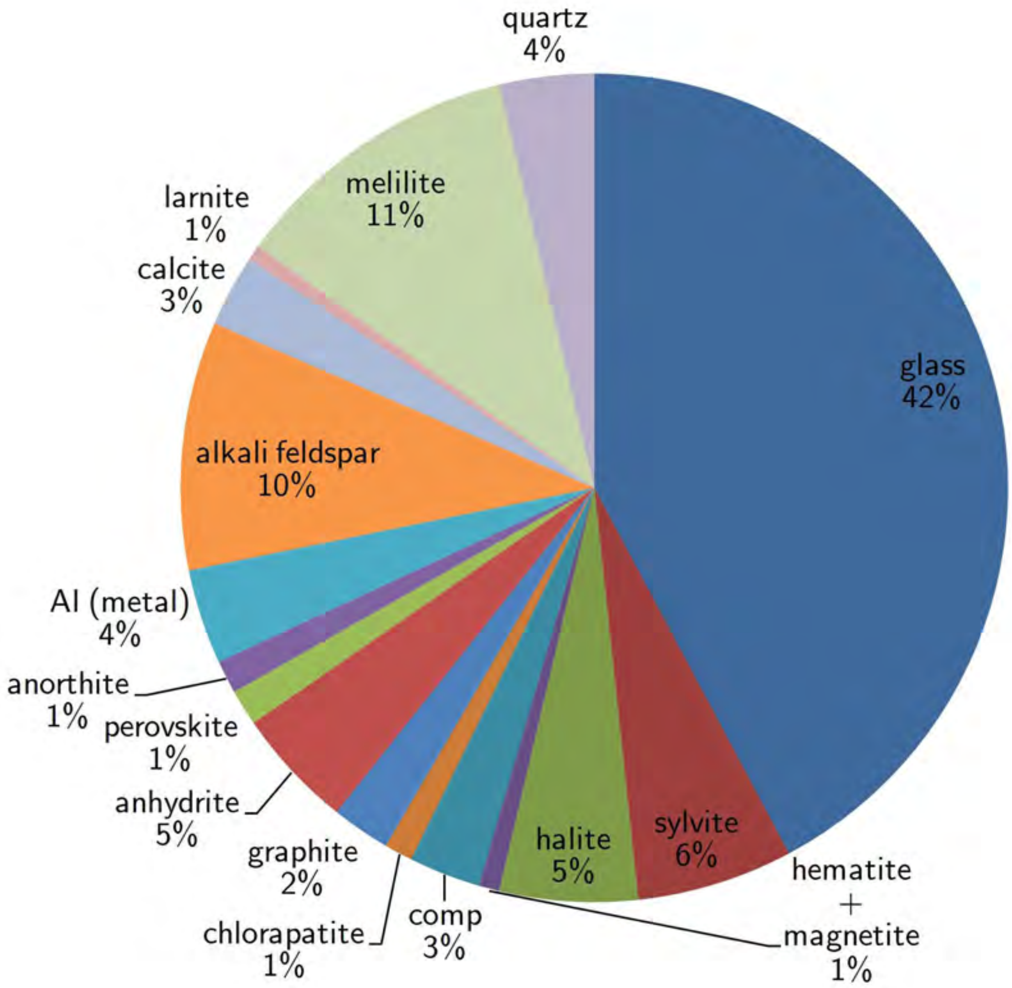


Figure 2.6.: Composition of MSW fly ash analyzed by Forestier and Libourel [82]. Adapted from [82].

bottom ash; they are carried to the fly ash by entrainment and evaporation [64]. The volatility of Cu, Ni, and Zn depends significantly on the parameters mentioned above [63]. Gaseous heavy metal compounds condense in the boiler on ash particles [65] (the lower the temperature the higher the condensed amount [66]). The concentrations of heavy metals and other elements in different types of fly ash are listed in Table 2.2.

The large majority of components in fly ash are nonhazardous compounds: The most important mineralogical fractions in sewage sludge ash (SSA) are silicon oxide, calcium phosphate and iron oxide [34, 68, 69]. The main matrix components of MSW fly ash are chlorides, calcium oxide, silicon oxide and aluminum oxide [76, 77, 82]. A significant quantity of the matrix in sewage sludge ash and MSW fly ash is glass [68, 82], Figure 2.6.

Table 2.2.: Elemental concentrations in sewage sludge ash and MSW fly ash (in ppm).

	Sewage sludge ash[a]			MSW fly ash[b]		
	average	min	max	average	min	max
Ag				410	2.3	1 500
Al	41 000	12 000	110 000	30 000	3 600	90 000
As	80	0.4	730	16	7.5	320
B				140	130	160
Ba	4 200	90	15 000	1 600	330	3 100
Ca	110 000	7 900	290 000	200 000	8 900	310 000
Cd	16	< d.l.	94	440	25	2 300
Cl	1 100	< d.l.	4 300	110 000	29 000	210 000
Co	63	< d.l.	670	280	13	1 100
Cr	430	16	2 600	330	84	1 100
Cu	1 600	200	5 400	1 400	380	4 600
F				7 500	4 100	9 300
Fe	50 000	7 300	160 000	14 000	410	44 000
Hg	0.7	< d.l.	7	5 700	0.7	15 000
K	6 900	420	14 000	37 000	5 700	82 000
Mg	17 000	120	140 000	13 000	1 100	23 000
Mn	1 800	230	7 000	830	77	1 900
Mo	24	5	80		15	150
Na	4 700	37	25 000	56 000	3 400	270 000
Ni	470	40	2 000	260	56	1 300
P	36 000	650	90 000	4 900	1.2	9 600
Pb	510	90	2 100	4 800	1 500	26 000
S	11 000	40	50 000	46 000	11 000	82 000
Sb	37	35	73	1 200	120	3 200
Se					0.4	31
Si	68 000	180	300 000	99 000	20 000	210 000
Sn	68	36	180	690	210	2 000
Sr	540	380	620		40	640
Ti	6 600	1 800	11 000	13 000	720	19 000
V	39	14	66	36	29	150
Zn	2 900	1 100	10 000	17 000	4 600	70 000

[a] [32, 34–36, 38–40, 67–74]

[b] [47, 75–81]

d.l. detection limit

2.3.3. Thermal treatment of fly ash

Cf. [7].

Thermal treatment of MSW fly ash causes both the evaporation [83] and the stabilization [84] of heavy metals depending on the treatment temperature. Cd and Pb are generally volatilized to a high degree [83], whereas the volatilization of Cu and Zn strongly depend on the air ratio [63, 83]. Cr and Ni do not volatilize during heat treatment [85].

As metal chlorides generally have lower boiling points than the corresponding metal oxides [86], chlorination and thermal treatment of the ash is a suitable technology for heavy metal extraction [87, 88]. Chlorine can be either applied as gaseous Cl_2 (e. g. [87, 89]), as gaseous HCl (e.g., [51]) or as solid chloride (e. g. [4, 6, 89, 90]). For industrial processes, solid chlorides (e. g. NaCl, $MgCl_2$, or $CaCl_2$) are advantageous because of (1) the simpler handling compared to gaseous Cl_2 and (2) the fact that Cl_2 also leads to the chlorination of non-hazardous elements like Ca or Fe (i. e., $CaCl_2$, which was used in that study in addition to Cl_2, is more selective for Cd, Cu, Pb, and Zn) [89].

In a quartz-tube furnace between 500 and 1050°C, $CaCl_2$, $FeCl_2$, and $MgCl_2$ are more effective than $AlCl_3$ and NaCl for the removal of Zn from MSW fly ash because $AlCl_3$ releases HCl at temperatures which are too low, and NaCl evaporates without reacting due to its high vapor pressure. For Cu, the effect of the chloride type is not that pronounced. The removal of Cd, Pb, and Zn is finished after 30 min; due to the high boiling point of CuCl, removal of Cu occurs even after 180 min. Up to ca. 95% of Cd, Pb, and Zn and 85% of Cu can be removed from the ash after 60 min at 1000°C, cf. [90].

During the treatment of MSW fly ash-chloride mixtures, mainly Cl salts are released [90]. Zn, which is present in pure MSW fly ash as hydrozincite $Zn_5(OH)_6(CO_3)_2$, willemite Zn_2SiO_4, and gahnite $ZnAl_2O_4$ [91], is found as $Na_2ZnCl_4 \cdot 3\,H_2O$ and K_2ZnCl_4 in re-condensed matter [89]. Cu, present in MSW fly ash as CuO and $CuSO_4 \cdot 5\,H_2O$, forms chlorides ($CuCl_2$, $CuCl_2 \cdot 2\,H_2O$) and CuO in condensate [92]; it is probably released as CuCl(g) [86].

The fraction of heavy metals volatilized can be increased by wetting the mixture with water and drying it afterwards in order to increase the contact area [90]. After heat-treatment of an MSW fly ash-$CaCl_2$ mixture, the solubility of metals, with the exception of Al and Cr, is generally decreased [93]. Cr can be better leached due to the formation of calcium chromate $CaCrO_4$ [94].

Instead of reacting directly with heavy metal compounds to their corresponding chlorides, $CaCl_2$ seems to release Cl_2 (by reacting with oxygen), which subsequently chlorinates [89]. In any case, technical grade $CaCl_2$ reacts with water vapor or oxygen to HCl and Cl_2, respectively [95]. Heavy metals that do not react with chlorine and volatilize are incorporated into the MSW fly ash matrix [88], which has a significant influence on the amount of heavy metals removed [96].

2.3.4. Influencing parameters of the process

Cf. [8].

$CaCl_2$ and $MgCl_2$ are both effective chlorine donors [34]. Highly volatile elements (Cd, Pb) would not require any chlorine addition at all; for semi-and low-volatiles at least 10w-% Cl (about 110 g Cl kg^{-1} ash, which is about a 100-fold molar excess of Cl compared to Zn, 300 to Cu and 2000 to Pb) are necessary [38]. The influence of the ash type and the temperature on the process are bigger than of the granulate type (briquettes vs. rolled pellets are investigated) [36]. The higher the temperature, the higher the removal of heavy metals [34, 35]. A treatment temperature of 1000°C is necessary to remove Cu below the German Fertilizer Ordinance [34]. A residence time of 20 min is sufficient for heavy metal removal [34].

In thermogravimetric experiments, Fraissler et al. [95] investigated the thermal behavior of $CaCl_2$ (technical quality) under different gas atmospheres: Above its melting point (782°C), $CaCl_2$ evaporates and reacts in the gas phase either with oxygen or with water. In a dry flue gas, Cl_2 is formed which kinetics is limited by the gas phase reaction. In humid atmosphere, HCl is released from gaseous $CaCl_2$ which kinetics is limited either by evaporation or diffusion. As the formation of HCl proceeds faster, it is estimated that heavy metal release proceeds faster as well (cf. [95]).

Thermogravimetric experiments revealed that from a mixture of sewage sludge ash with $CaCl_2 \cdot 2\,H_2O$, chlorine is released, whereas HCl is detected between 100 and 450°C when $MgCl_2 \cdot 6\,H_2O$ is added [72].

Cd evaporates as $Cd(OH)_2$ above 700°C, at higher temperatures CdO and elemental Cd^0 are formed as well. Cr is released as oxychloride CrO_2Cl_2; Cu in form of the trimer $(CuCl)_3$ and at higher temperatures also as CuCl. If Cl is available, $PbCl_2$ is formed from Pb; if not and at higher temperatures Pb is released as PbO. Ni and Zn are volatilized in form of their chlorides $NiCl_2$ and $ZnCl_2$. However, the volatilization of low-volatile elements (Cr, Ni) is favored by the absence of H_2O and Fe and a high Si-content. The semi-volatile elements Cu and Zn show the largest deviation between equilibrium calculations and experiments due to kinetic effects (cf. [38]).

Thermogravimetry/differential thermo analysis showed that Cd, Cu, Pb and Zn evaporate above 600°C [72].

2.3.5. Summary of steps leading to heavy metal removal

Cf. [5, 8].

On molecular scale, the process can be summarized by three major reaction steps:

1. Formation of HCl or Cl_2 in dependence of the moisture of the reaction atmosphere according to [95]

$$CaCl_2 + H_2O \longrightarrow CaO + 2\,HCl \tag{2.1}$$

or

$$CaCl_2 + \tfrac{1}{2}O_2 \longrightarrow CaO + Cl_2. \tag{2.2}$$

HCl and Cl_2 diffuse inside the particles and to the reactor atmosphere as well.

2. Reaction of the intermediates HCl and Cl_2 with heavy metal compounds (e. g. oxides) from the ash, e. g.

   $$2\,HCl + ZnO \longrightarrow H_2O + ZnCl_2 \tag{2.3}$$

   and

   $$Cl_2 + ZnO \longrightarrow \tfrac{1}{2}O_2 + ZnCl_2. \tag{2.4}$$

   Volatile heavy metal compounds, mainly chlorides, are formed (e. g. boiling point of $ZnCl_2$: 732°C [52]).

3. Heavy metal chlorides can be adsorbed on matrix material and react with matrix material (for Zn) according to [97]

   $$ZnCl_2 + SiO_2 + H_2O \longrightarrow ZnSiO_3 + 2\,HCl. \tag{2.5}$$

   Heavy metal compounds from the ash may also react directly in solid state with matrix material forming stable silicates and aluminates, e. g. [98]

   $$ZnO + SiO_2 \longrightarrow ZnSiO_3 \tag{2.6}$$

   and

   $$ZnO + Al_2O_3 \longrightarrow ZnAl_2O_4. \tag{2.7}$$

The maximum amount removable is influenced by two factors: First, the availability of HCl and Cl_2 (step 1) as it is possible to achieve in a similar process a heavy metal removal of $> 99\%$ by using gaseous HCl as chlorination agent [51]. Second, side reactions may occur leading to the incorporation of heavy metals into the matrix reduce the maximum amount removable (step 3 from the list above).

3. Methods

During heat treatment of ash (or ash-chloride mixtures) processes occur, which lead to the evaporation of volatile heavy metal compounds, Figure 3.1. Independent of the reactor, a certain amount of heavy metals will migrate to the reactor's atmosphere leaving behind a decontaminated solid product. The quality of treatment can be characterized by the mass of heavy metals migrated to the offgas, i. e.

$$\text{fraction removed} = 1 - \frac{c_\mathrm{e} \cdot M_\mathrm{e}}{c_0 \cdot M_0} \tag{3.1}$$

(mass of solid sample M, heavy metal concentration c, before treatment index 0, after treatment index e); a second definition could be

$$\text{fraction removed} = 1 - \frac{c_\mathrm{e}}{c_0}. \tag{3.2}$$

In Eqn. (3.1), the mass flow of heavy metals is taken into account, i. e. also entrained dust is considered (and increases the amount of heavy metals removed). Eqn. (3.2) is only an approximation (and would be exact for $M_\mathrm{e} = M_0$); if the mass is not well-defined (e. g. due to losses) or if entrainment occurs in higher extents, then Eqn. (3.2) would be the better choice for characterizing the treatment quality.

For the thermal treatment ("Reactor" in Figure 3.1), the following devices are used:

- rotary reactor,
- fluidized bed reactor,
- muffle oven, and
- thermogravimetry.

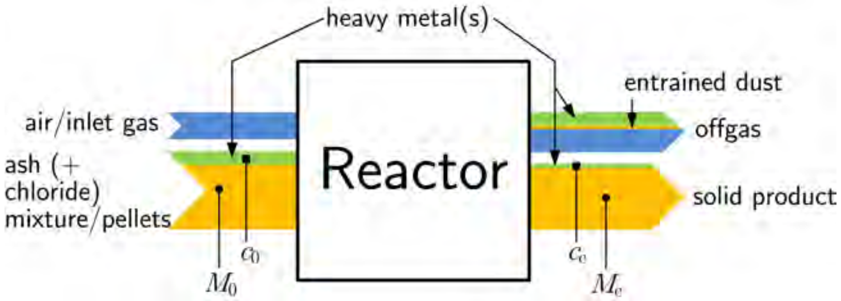


Figure 3.1.: Flows into and out of a reactor

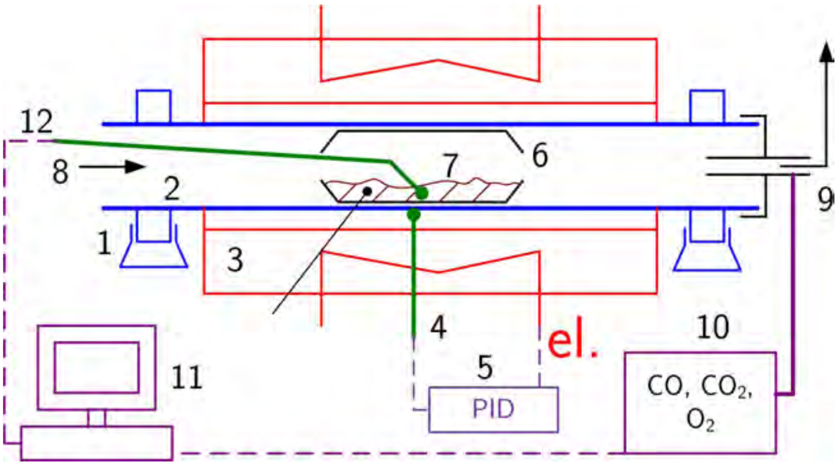


Figure 3.2.: Rotary reactor used. 1 bearing with drive, 2 tube, 3 heating shell (3 heating zones), 4 temperature measurement (perimeter of tube; 3 times), 5 PID controller (3 times), 6 batch container, 7 revolving bed, 8 gas inlet (ambient air), 9 gas offtake and offgas sampling (optional), 10 gas analyzer (optional), 11 data acquisition system (optional), 12 bed temperature measurement (thermocouple type K; optional).

Muffle oven and thermogravimetry used are standard-devices and therefore not explained here; rotary reactor and fluidized bed reactor are explained in Chapter 3.1 and 3.2, respectively.

3.1. Rotary reactor

The rotary reactor, Figure 3.2, consists of an exchangeable tube (length: 1100 mm, inner diameter approx. 75 mm). During the present work, tubes of stainless steel, silicon carbide, and silicon carbide-silicon were used. The rotation speed (regulated by a frequency converter) is 4.2 revolutions per minute. The reactor is indirectly heated by a heating shell covering approx. 70% of the tube. The heating shell consists of three equally spaced zones; in the middle of each of the zones the perimeter temperature is measured and used to regulate the temperature (by three PID controllers).

Experiments can be conducted either continuously (both in co- and counter current gas/solid flow) or in batch mode. The latter's advantage is the well-defined residence time. For batch experiments, a two-side opened quartz glass container is filled with a certain amount of sample and weighed. At the start of the experiment, it is pushed into the preheated reactor and heated together with its content to the envisaged temperature. At the end of the treatment it is pulled out again and cooled in ambient air. When sufficiently cooled, the container is weighed again; the treated sample is removed and stored in plastic bags for analysis.

As the sample bed is good accessible, it is possible to measure directly the bed temperature by inserting a thermocouple. Due to the highly corrosive atmosphere, this leads

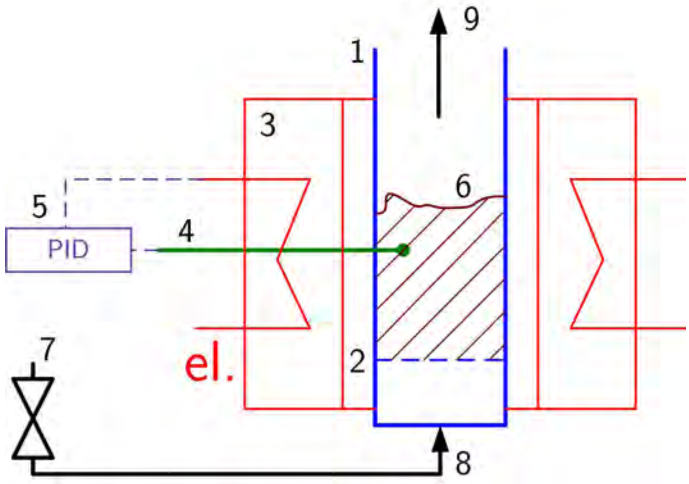


Figure 3.3.: Fluidized bed reactor used. 1 quartz glass tube, 2 gas distributor (quartz glass frit), 3 heating shells, 4 bed temperature measurement (thermocouple type K), 5 PID controller, 6 fluidized bed, 7 pressurized air, 8 inlet in reactor and preheater, 9 offgas outlet (to chimney).

to an enrichment of Cr and Ni in the sample [48]. As the bed temperature is in good agreement with the temperature measured at the perimeter of the tube (high thermal conductivity of the ceramic materials used), the direct measurement is only necessary if the heat-up of the bed is of interest.

The reactor's offgas is sucked out and cleaned in a wet scrubber (to obtain a closed balance over the reactor; see Chapter 3.3). In experiments with organic material added to the sample, a certain amount of the gas is analyzed by non-dispersive infrared (NDIR) spectroscopy (CO and CO_2) and paramagnetic measurement (for O_2).

3.2. Fluidized bed reactor

The stationary fluidized bed reactor, Figure 3.3, consists of a quartz glass tube (inner diameter approx. 35 mm). Pressurized air is preheated and enters the reactor. At the start of the experiment, pellets are filled into the reactor and remain there for the desired residence time; then they are removed pneumatically (by increasing the air flow). The bed temperature is measured (thermocouple type K, NiCr-Ni) and used as input for the PID controller. Particles from the off-gas are separated in a cyclone and returned to the bed.

3.3. Chemical analysis

Samples are dried, pulverized, and digested in order to dissolve heavy metals. The dilution is then analyzed with ICP-OES for the heavy metals Cd, Cr, Cu, Ni, Pb, and Zn.

Depending on the ash, samples are digested differently:

- Samples based on sewage sludge ash are digested with aqua regia, i. e. a mixture of HCl and HNO_3.
- Samples based on MSW fly ash are totally digested in a mixture of HCl, HNO_3, HF, H_2O_2, and $B(OH)_3$.

The different digestion is due to the properties of the matrix: Experiments revealed that the sewage sludge ash matrix is not as stable as the MSW fly ash matrix; therefore, aqua regia is sufficient [1]. For MSW fly ash matrix it could be shown that total digestion leads to a better reproducibility [2].

The accuracy the chemical analysis can be increased by balancing the reactor (Figure 3.1) and reconciliation of the input and output streams. I. e., beside analysis of the solid input material and the solid output material, also the heavy metal flow in the offgas has to be analyzed. This can be done e. g. by cleaning the gas in a wet scrubber and analyzing the resulting dilution.

4. Results and discussion

4.1. Volatilization of heavy metals in combustion atmospheres

Fuels, e. g. biomass, coal or waste, are often polluted by heavy metals. HCl, which is generated due to the Cl content of fuels, reacts with those heavy metal compounds forming chlorides which evaporate. This process leads to the concentration of heavy metals in fly ash. On the other hand, S, also contained in fuels, could lead to the formation of heavy metal sulfide and sulfate which hardly volatilize. Thus, depending on the Cl, S but also the amount of alkalis in the fuel burnt, the content of heavy metals in bottom ash is low.

In this work, the influence of chlorine, sulfur and potassium on the volatilization under combustion and gasification conditions is studied by thermodynamic equilibrium calculations carried out with FactSage [99].[1]

4.1.1. Method

The aim of the equilibrium calculations is a better understanding of the reactions occurring during combustion and similar processes.

Table 4.1.: Fuel consisting of C, H (ratio similar as MSW [101]) and heavy metals. The molar amounts are the same in all cases considered.

element	concentration	amount[a]
C	90 wt-%	74.9 mol
H	10 wt-%	99.2 mol
Cd	100 ppm	$8.896 \cdot 10^{-4}$ mol
Cr	100 ppm	$1.923 \cdot 10^{-3}$ mol
Cu	100 ppm	$1.574 \cdot 10^{-3}$ mol
Ni	100 ppm	$1.704 \cdot 10^{-3}$ mol
Pb	100 ppm	$4.826 \cdot 10^{-4}$ mol
Zn	100 ppm	$1.529 \cdot 10^{-3}$ mol

[a] used in equilibrium calculations

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[1] This work has been carried out during an author's scientific exchange at Åbo Akademi and has been reported in [100].

Table 4.2.: Overview of the cases # 1 to # 3 calculated (the system consists of the molar amounts from Table 4.1 and one column of molar amounts here). Potassium ration γ according to Equ. (4.1).

case #		1	1	2a	2a	2b	2b	2c	2c
λ		0.8	1.2	0.8	1.2	0.8	1.2	0.8	1.2
w_{Cl}	in wt-%[a]	0	0	2	2	2	2	2	2
w_{S}	in wt-%[a]	0	0	0	0	1	1	5	5
γ		0	0	0	0	0	0	0	0
O_2	in mol	79.8	119.7	79.8	119.7	80	120.1	81	121.6
N_2	in mol	319.2	478.7	319.2	478.7	320.2	480.2	324.2	486.2
Cl	in mol	0	0	0.564	0.564	0.564	0.564	0.564	0.564
S	in mol	0	0	0	0	0.312	0.312	1.559	1.559
K	in mol	0	0	0	0	0	0	0	0

case #		3a	3a	3b	3b	3c	3c
λ		0.8	1.2	0.8	1.2	0.8	1.2
w_{Cl}	in wt-%[a]	2	2	2	2	2	2
w_{S}	in wt-%[a]	0	0	0	0	5	5
γ		0.5	0.5	1.5	1.5	1.5	1.5
O_2	in mol[b]	79.8	119.8	80	119.9	82.1	123.2
N_2	in mol[b]	319.4	479.1	319.8	479.8	328.6	492.9
Cl	in mol[b]	0.564	0.564	0.564	0.564	0.564	0.564
S	in mol[b]	0	0	0	0	1.559	1.559
K	in mol[b]	0.282	0.282	0.846	0.846	5.524	5.524

[a] based on mass of C and H from Table 4.1.

[b] amount added to values from Table 4.1 for equilibrium calculations

The following approach is used:

Fuel Chemistry (case # 1): Fuel consisting of C, H, and heavy metals is converted in air atmosphere. The carbon-to-hydrogen ratio is based on MSW analyzed by Choi et al. [101]; heavy metal concentrations are each 100 ppm; see Table 4.1. The equilibrium is calculated for different air ratios ($\lambda = 0.8$ and 1.2, see Table 4.2) in dependency of temperature (ranging from 200 to 1300°C with a resolution of 25°C).

Influence of S and Cl (cases #2): S and Cl are added to system # 1 in different ratios. In # 2a, only Cl is present; in # 2b and 2c, both Cl and S are present. For the list see Table 4.2.

Interaction with alkalis (cases #3): K is added to some of the cases # 2. # 3a equals

Table 4.3.: Overview of the cases # 4 calculated (the system consists of the molar amounts from Table 4.1 and one column of molar amounts here; values are varied linearly between min and max for equilibrium calculations). Potassium ratio γ according to Equ. (4.1).

case #			4a	4a	4b	4c
λ	min		0.8	1.2	0	0
	max		0.8	1.2	2.5	2.5
γ	min		0	0	0.5	1.5
	max		2.5	2.5	0.5	1.5
w_{Cl}		in wt-%[a]	2	2	2	2
O_2	min	in mol[b]	79.8	119.7	0	0
	max	in mol[b]	80.1	120.1	249.5	249.9
N_2	min	in mol[b]	319.2	478.7	0	0
	max	in mol[b]	320.3	480.4	998.1	999.5
K	min	in mol[b]	0	0	0.282	0.846
	max	in mol[b]	1.41	1.41	0.282	0.846
Cl		in mol[b]	0.564	0.564	0.564	0.564

[a] based on mass of C and H from Table 4.1.

[b] amount added to values from Table 4.1 for equilibrium calculations

2a with a potassium ratio $\gamma < 1$; # 3b is similar with $\gamma > 1$. # 3c equals # 2c with $\gamma > 1$. For the list see Table 4.2.

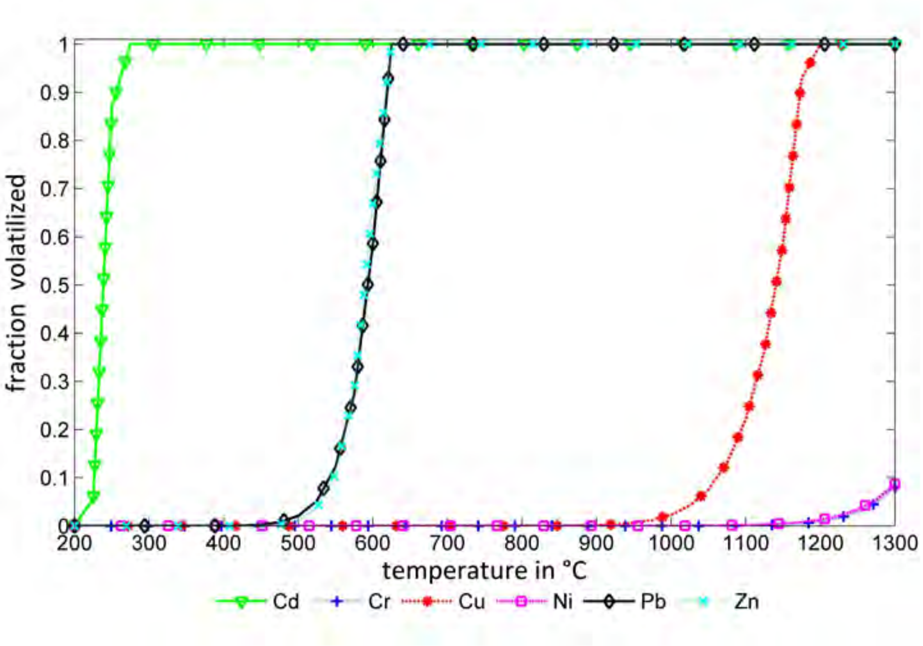
Dependency on potassium ratio and air ratio (cases #4): Instead of calculating the system's equilibrium composition in dependency of temperature, it is calculated as a function of γ or λ. # 4c is similar to the cases # 3a and # 3b, i. e. the potassium ratio is varied here. Case # 4d and # 4e are calculated in dependency of the air ratio λ; they are similar to # 3a and # 3b, respectively. For the list see Table 4.3.

The potassium ratio is calculated according to

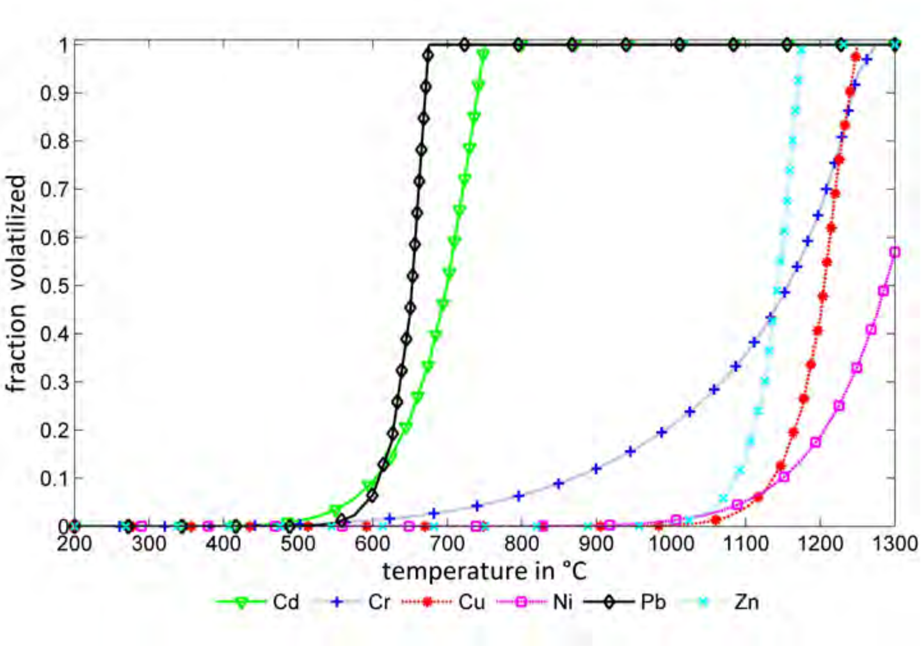
$$\gamma = \frac{x_{\mathrm{K}}}{2x_{\mathrm{S}} + x_{\mathrm{Cl}}}, \tag{4.1}$$

whereas x_i refers to the molar concentration of the element i in 1 kg fuel.

The thermodynamic equilibrium calculations are conducted with FactSage [99]. As long as no K is present, the databases `Elem`, `Fact53` and `Eige` are used. `Eige` is a database containing only $CdCl_2$ (solid, liquid and gaseous; thermodynamic data from [102]) because $CdCl_2(g)$ is omitted in the `Fact53`-database and would thus lead to wrong results. For calculations with K, also solution phases are considered based on the databases `FTpulp` and `FTsalt` (phases considered: `FTpulp`: `MELTA`, `Hexa`, `Ort-B`, `KCO`, `ACL`; `FTsalt`: `CSOB`, `KCO_`, `KCOH`, `KSO_`, `LCSO`, `NHCl`, `SALTA`).



(a) $\lambda = 0.8$



(b) $\lambda = 1.2$

Figure 4.1.: Dependency of the combustion atmosphere on the volatilization of heavy metals (case # 1).

Results from FactSage [99] are exported in `chemsage` format; with a Matlab [103] program, the compounds occurring are re-ordered, summarized, and plotted.

4.1.2. Results

The fraction of each heavy metal i volatilized is calculated according to

$$\text{fraction}_i = \frac{n_{i,\mathrm{g}}}{\sum_i n_i}, \tag{4.2}$$

whereas $n_{i,\mathrm{g}}$ is the concentration of the element i in the gas phase and $\sum_i n_i$ is the total concentration of the element in the system.

Generally, Cd and Pb are easily, i e. already at low temperatures, volatilized. Cu and Zn form, dependent on the conditions, also at rather low temperatures gaseous species. Especially the volatilization behavior of Cu depends strongly on the air ratio λ. Ni and especially Cr are low-volatile. Only at high temperatures and strongly dependent on the system conditions, they will volatilize.

Combustion atmosphere and heavy metals

In a system consisting of carbon, hydrogen, oxygen, nitrogen and heavy metals (case # 1; Figure 4.1), heavy metals are volatilized dependent on the air ratio. At the conditions studied (C, H, N, and O present beside heavy metals), Cd, Cu, Pb and Zn form gaseous compounds at lower temperatures, if reducing conditions occur (i. e. air ratio $\lambda < 1$). The volatilization of Cr and Ni is positively affected by the availability of excess oxygen, i e. $\lambda > 1$.

Cadmium Cd: At $\lambda = 0.8$, Cd is already volatilized at 200°C in elemental form (Cd^0). At oxidizing conditions, evaporation of Cd starts at approx. 500°C; gaseous compounds are $Cd(OH)_2$, CdO and especially at higher temperatures Cd^0 (90% of Cd at 1300°C).

Chrom Cr: Cr is hardly evaporated at reducing conditions; only at temperatures > 1200°C it will form gaseous CrOOH. At $\lambda = 1.2$, volatilization occurs in equilibrium already at 600°C; mainly hydroxides ($CrO_2(OH)_2$, CrO_2OH, $CrO(OH)_2$, and CrOOH) but also the oxide CrO_3 is released, Figure 4.2.

Copper Cu: If no Cl is present, Cu is hardly vaporized at all. At reducing conditions, it forms only elemental Cu^0, whereas Cu^0(g) is partly evaporated at 900°C. At $\lambda = 1.2$, the formation of the oxide shifts the evaporation to higher temperatures. Cu is released elementally from 1000°C; only at temperatures > 1200°C small fractions of gaseous CuO are stable.

Nickel Ni: At reducing conditions, Ni release occurs at similar temperatures as Cr; over 1200°C small fractions evaporate as Ni^0 and $Ni(OH)_2$. At $\lambda = 1.2$, Ni is only released as $Ni(OH)_2$ starting at temperatures over ca. 1000°C.

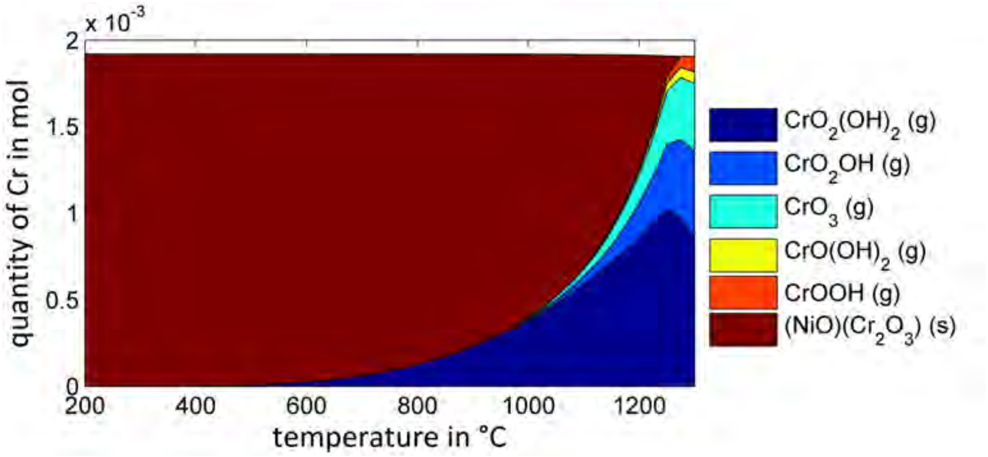


Figure 4.2.: Volatilization behavior of Cr in case # 1 at oxidizing conditions. Compounds displayed result in at least 99% of Cr present in the system for each temperature point.

Lead Pb: The volatilization of Pb starts almost at 400°C at reducing conditions; the gaseous fraction consists mainly of Pb^0. Oxidizing conditions shift the evaporation temperature to ca. 500°C; Pb is then (i. e. from ca. 680°C) completely volatilized as PbO.

Zinc Zn: Independently from the air ratio, only Zn^0(g) and ZnO (zincite) are present in the system studied. At $\lambda = 0.8$, elemental Zn^0(g) is formed at temperatures > 400°C. At oxidizing conditions, Zn^0(g) is released over ca. 1000°C; solid ZnO is stable up to ca. 1180°C.

Influence of sulfur and chlorine

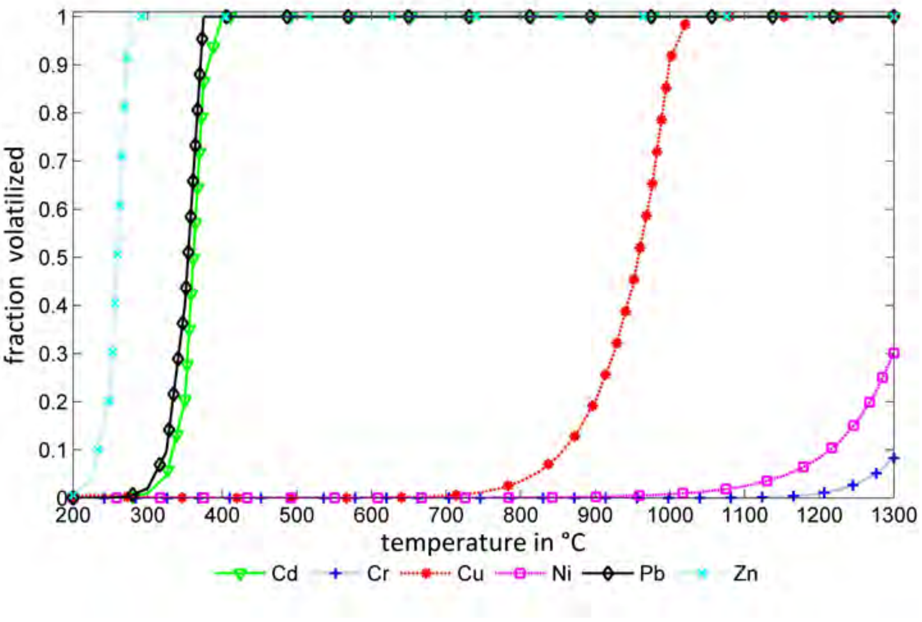
Generally, Cl has a positive (or mostly at least no negative) and S a negative (or at least no positive) effect on the volatilization of heavy metals (Figures 4.3-4.5); case # 2.

Cadmium Cd: Cd is the only element, whose volatilization is negatively affected by the availability of Cl compared to the full absence due to the formation of solid $CdCl_2$ at reducing conditions. However, it is still evaporated at ca. 320°C as $CdCl_2$ and at ca. 400°C as Cd^0 being the only Cd compound > 600°C.

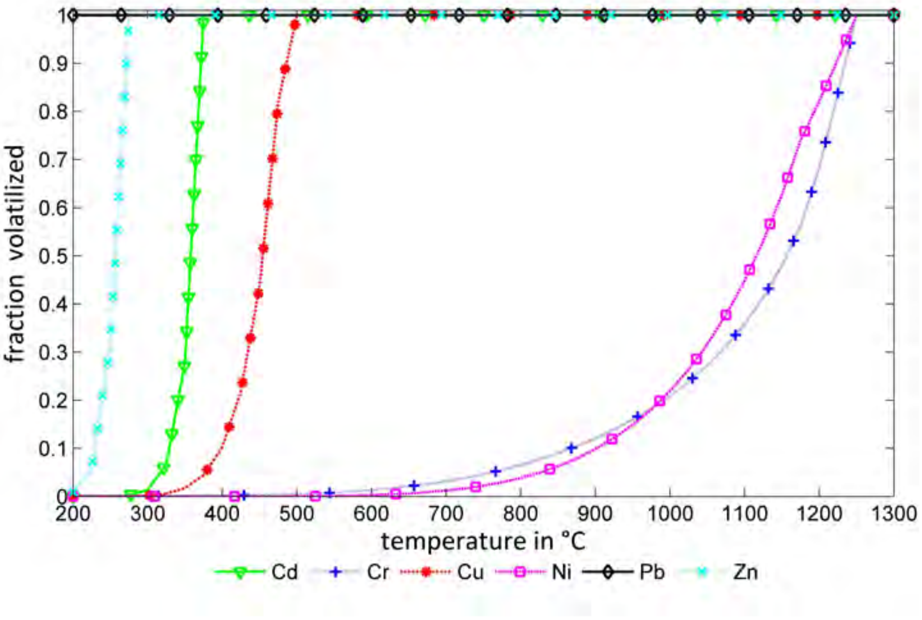
At oxidizing conditions, Cd is already released at ca. 280°C due to the higher vapor pressure of $CdCl_2$ (being the only Cd component up to 800°C) compared to CdO. At higher temperatures, beside $CdCl_2$ also Cd^0, $Cd(OH)_2$ and CdO are present in the gas phase.

The presence of S shifts the evaporation of Cd to higher temperatures due to the formation of solid CdS ($\lambda < 1$) and $CdSO_4$ ($\lambda > 1$).

Chrom Cr: At $\lambda = 0.8$, the volatilization of Cr is generally not affected by Cl or S available in the system; it will be mostly present as solid Cr_2O_3. Even at oxidiz-

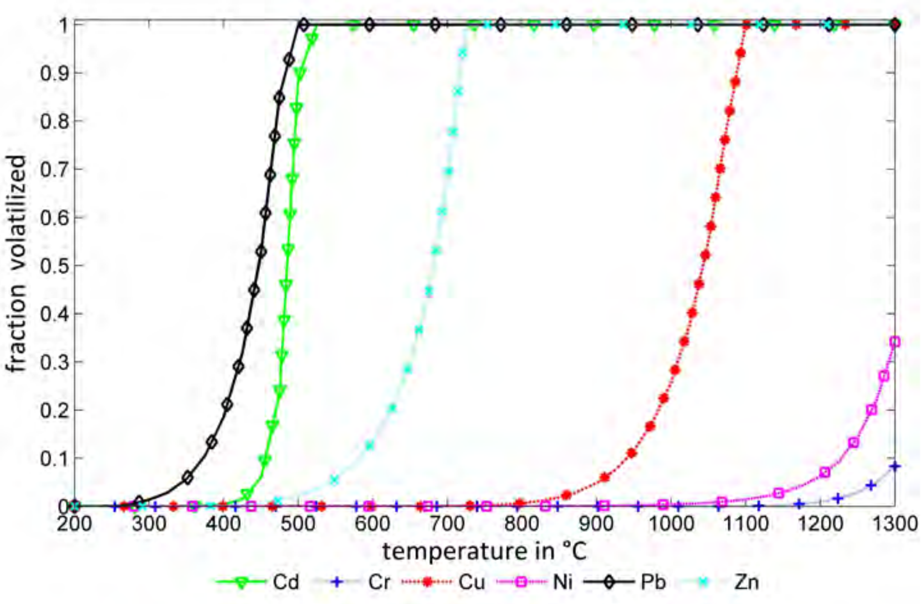


(a) $\lambda = 0.8$

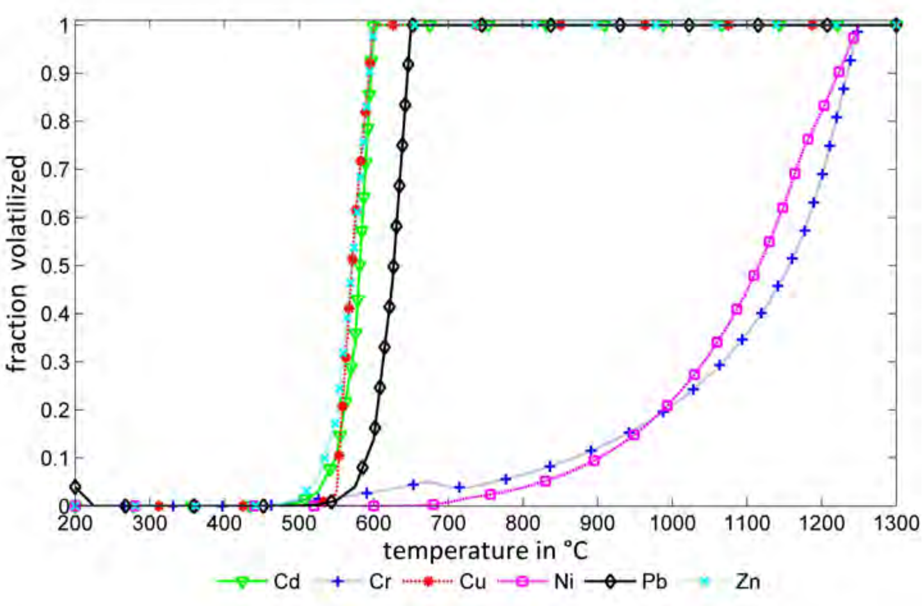


(b) $\lambda = 1.2$

Figure 4.3.: Dependency of the Cl availability (2% Cl) on the volatilization of heavy metals (case # 2a).

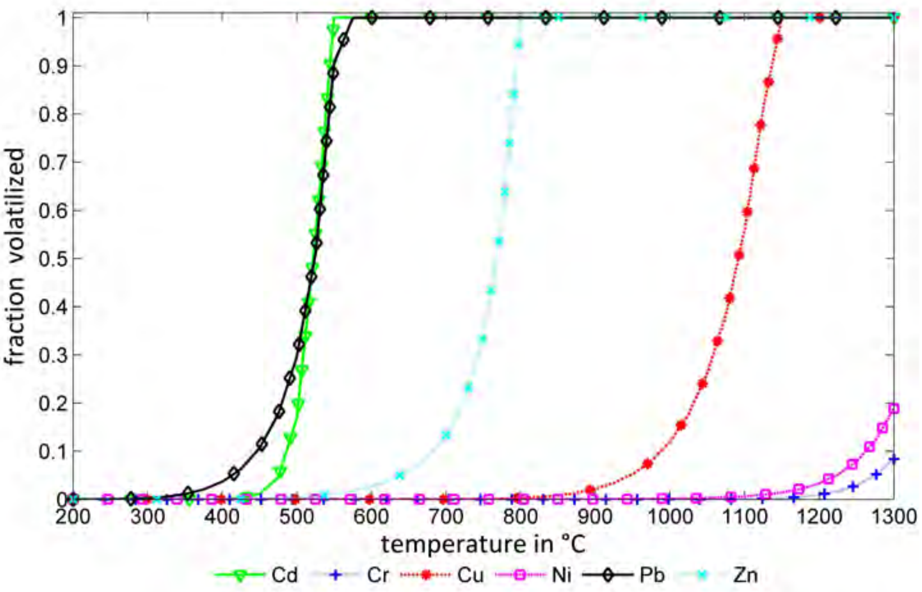


(a) $\lambda = 0.8$

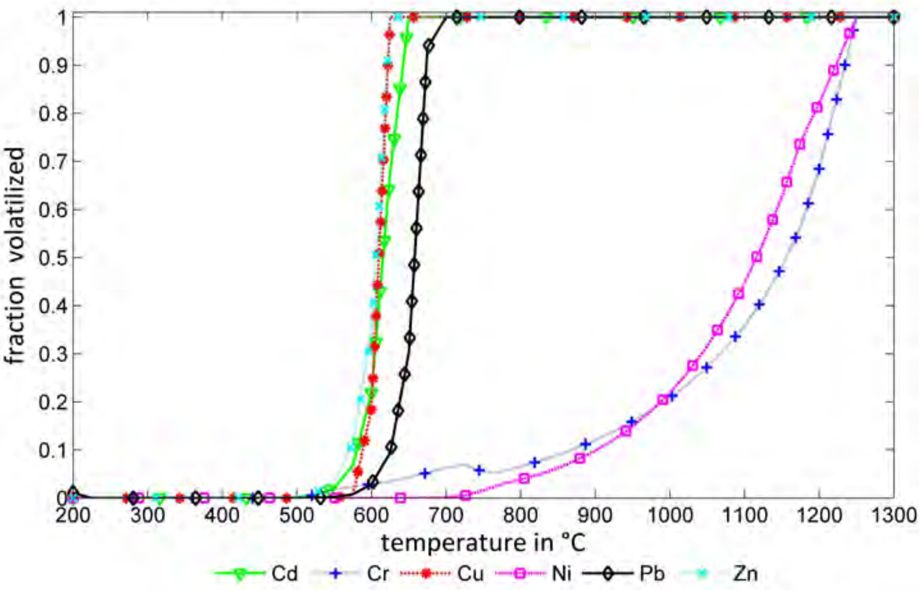


(b) $\lambda = 1.2$

Figure 4.4.: Dependency of the Cl and S availability (2% Cl, 1% S) on the volatilization of heavy metals (case # 2b).



(a) $\lambda = 0.8$



(b) $\lambda = 1.2$

Figure 4.5.: Dependency of the Cl and S availability (2% Cl, 5% S) on the volatilization of heavy metals (case # 2c).

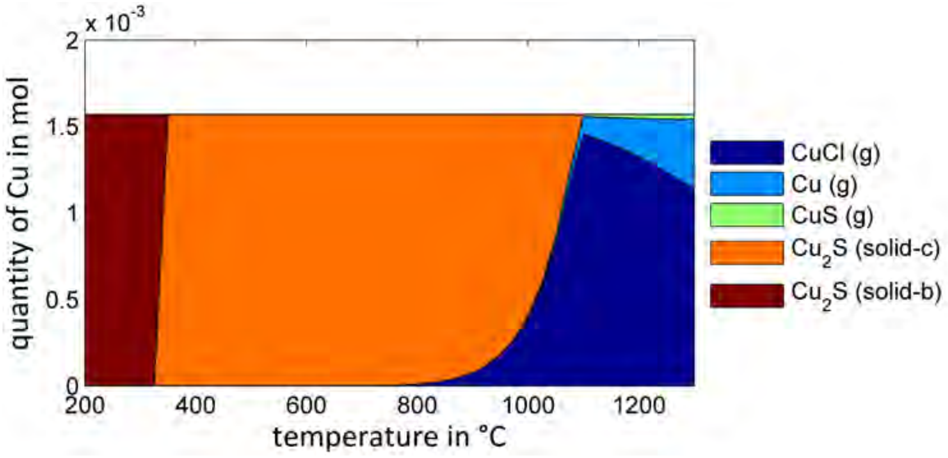


Figure 4.6.: Volatilization behavior of Cu in case # 2b at reducing conditions. Compounds displayed result in at least 99% of Cu present in the system for each temperature point. The phases solid-b and solid-c refer to different solid modifications of Cu_2S.

ing conditions, when solid $Cr_2(SO_4)$ is formed at lower temperatures, the general volatilization behavior and the gaseous Cr compounds are not affected.

Copper Cu: The evaporation behavior of Cu is strongly dependent on the availability of Cl: At reducing conditions, Cu volatilization will start at 700°C due to the formation of gaseous CuCl (without Cl: starting at 900°C). At $\lambda = 1.2$, Cu starts evaporating as $(CuCl)_3$ even at ca. 350°C. On the other hand, the existence of S in the system will lead to Cu evaporation at higher temperatures. At reducing conditions, solid Cu_2S is stable up to 1100°C. Gaseous Cu compounds are CuCl, Cu^0, and also CuS (Figure 4.6). CuS is only at temperatures > 1050°C and over all at high S concentrations of importance. At temperatures < 1100°C, the availability of Cl is always necessary to vaporize Cu at reducing conditions if S is present as well.

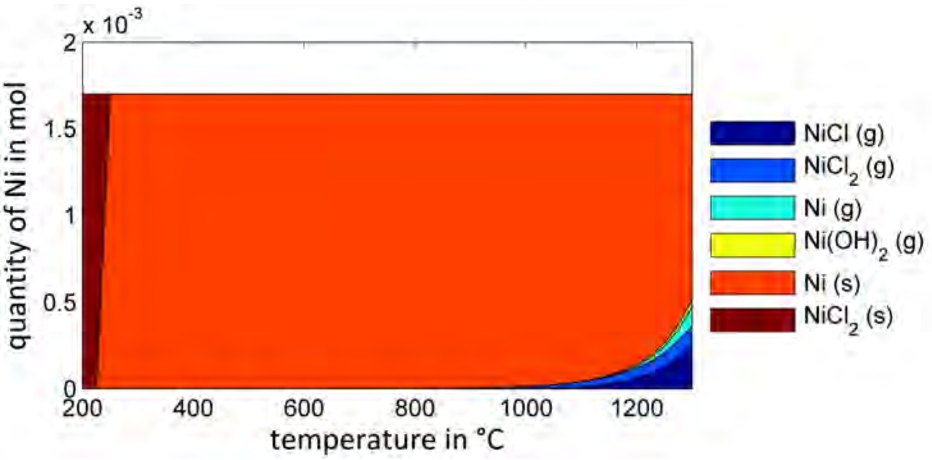
At $\lambda = 1.2$, instead of the sulfide solid $CuSO_4$ is formed which is stable (at the conditions investigated) up to ca. 600°C (depending on the amount of S available). Cu is evaporated as $(CuCl)_3$ at temperatures > 600°C; at higher temperatures CuCl is formed: over 1000°C it is the sole Cu compound. At oxidizing conditions, higher S concentrations are necessary to avoid the volatilization of Cu.

Nickel Ni: The volatilization of Ni is improved by the availability of Cl; in contrast, S has only a small influence (especially at S excess compared to Cl). At $\lambda = 0.8$ with no S present, Ni vaporizes as $NiCl_2$, NiCl, Ni^0 and $Ni(OH)_2$ from 1100°C, Figure 4.7(a). With S present in the system, only the solid components change from chlorides to sulfides.

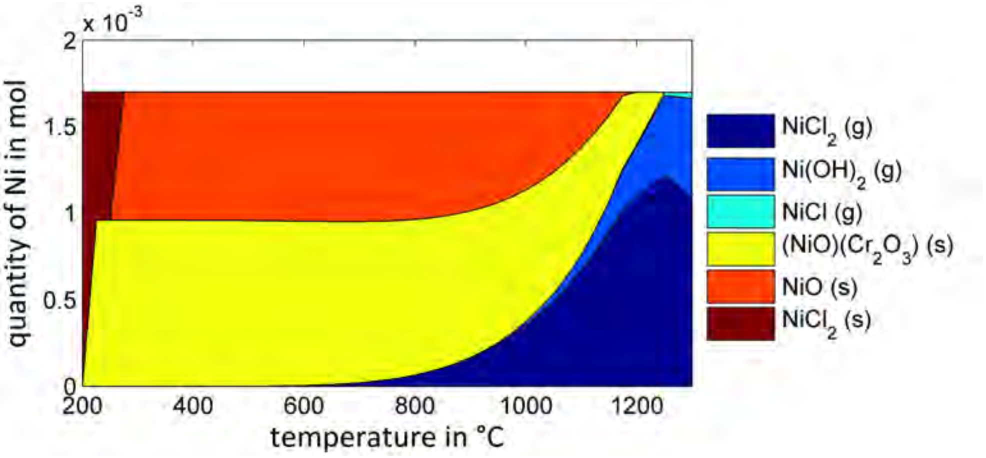
At $\lambda = 1.2$, Ni can be evaporated almost even from 700°C as $NiCl_2$, $Ni(OH)_2$, and NiCl are gaseous and thus volatile, Figure 4.7(b). With no S present, solid

Ni compounds are chlorides and oxides; sulfur leads to the formation of Ni sulfate but has no effect on the volatilization behavior as long as enough Cl is present.

Lead Pb: Pb is strongly affected by the availability of Cl and S. At reducing conditions and no S present, Pb is mainly bound in $PbCl_2$ which starts evaporating in equilibrium at 300°C. Higher temperatures lead to the formation of PbCl (starting from ca. 400°C and being still stable up to 1300°C), elemental Pb^0 (from ca. 600°C being the most important Pb compound at 1300°C) and PbO, which is from minor importance. If S is present in the system as well, solid PbS shifts the evaporation of Pb to higher temperatures. PbS itself evaporates as well at over ca. 500°C being the most important gaseous Pb compound between ca. 1000 and 1200°C (cases # 2b and 2c). PbO does not occur at all at these conditions.



(a) $\lambda = 0.8$



(b) $\lambda = 1.2$

Figure 4.7.: Volatilization behavior of Ni in case # 2a at reducing and oxidizing conditions. Compounds displayed result in at least 99% of Ni present in the system for each temperature point.

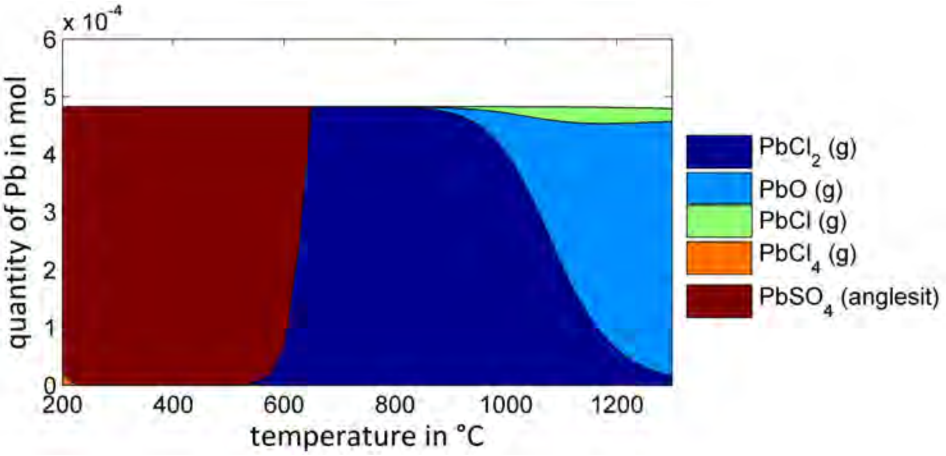
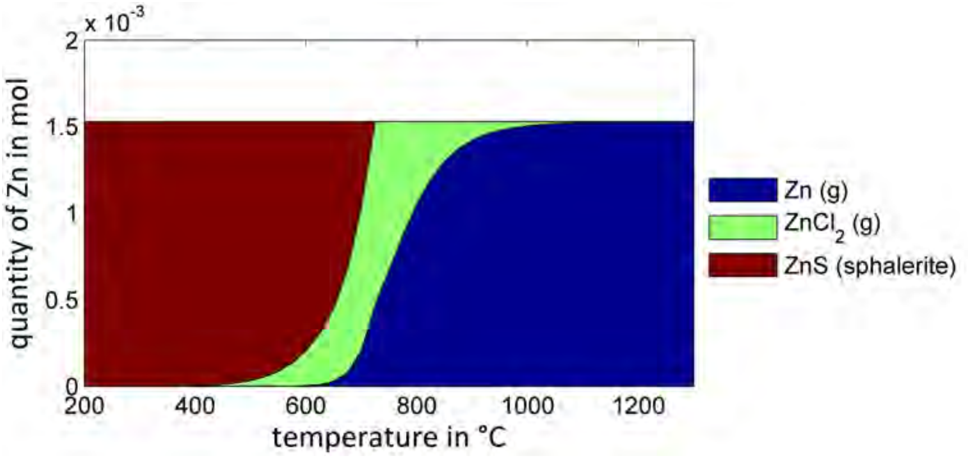


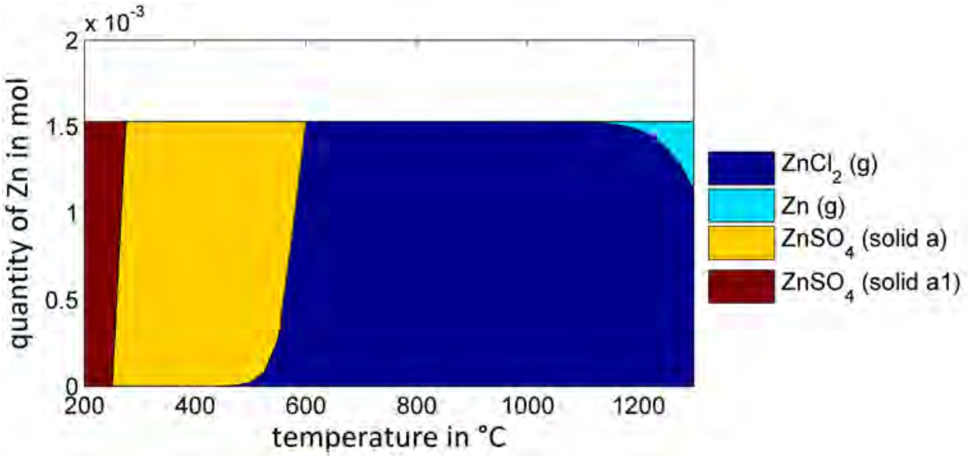
Figure 4.8.: Volatilization behavior of Pb in case # 2b at oxidizing conditions. Compounds displayed result in at least 99% of Pb present in the system for each temperature point.

At an air ratio of $\lambda = 1.2$, Pb is volatilized even at 200°C, as long as only Cl and no S is present. This is due to the formation of $PbCl_4$ (stable up to ca. 500°C). Gaseous $PbCl_2$ occurs from ca. 320 to 1300°C being the sole Pb compound between 500 and 800°C. At 800°C, gaseous PbO and PbCl are formed as well; the latter being only from minor importance. If S is present, the behavior of Pb is hardly not depending on the S amount. Solid Pb is present as sulfate. Pb volatilization starts at ca. 550°C for the cases # 2b and 2c; in the gas phase $PbCl_2$, PbO and PbCl are present. At ca. 200°C, a very small fraction of Pb is present in equilibrium as gaseous $PbCl_4$ causing the decrease at the beginning in Figure 4.4(b); see Figure 4.8.

Zinc Zn: As long as enough Cl is present, the air ratio has no influence on the volatilization temperature of Zn: Without S, Zn volatilization starts from 200°C with $ZnCl_2$ being the most important compound (also in solid state). Up to 400°C, also Zn_2Cl_4 plays a minor role. Depending on the air ratio, elemental gaseous Zn^0 is formed at temperatures over 600°C ($\lambda = 0.8$) or 1100°C ($\lambda = 1.2$). At 1100°C, Zn is only present in elemental form at reducing conditions. Minor amounts of S lead to the formation of solid Zn sulfide ($\lambda = 0.8$) and sulfate ($\lambda = 1.2$). Nevertheless, evaporation of Zn starts then (case # 2b, $\lambda = 0.8$) at 500°C due to the formation of $ZnCl_2$, Figure 4.9(a). At reducing conditions, at 700°C $Zn^0(g)$ is formed as well, being the sole Zn compound at temperatures over 1100°C. At oxidizing conditions, it appears only over 1150°C and binds ca. 25% of Zn at 1300°C, Figure 4.9(b). Higher concentrations of S do not change much of the Zn composition in the gas phase; only the initial vaporization temperature is shifted to ca. 600°C ($\lambda = 0.8$) and ca. 500°C ($\lambda = 1.2$), respectively. Higher S concentrations will only lead to the immobilization of Zn at lower temperatures and at very low Cl concentrations.

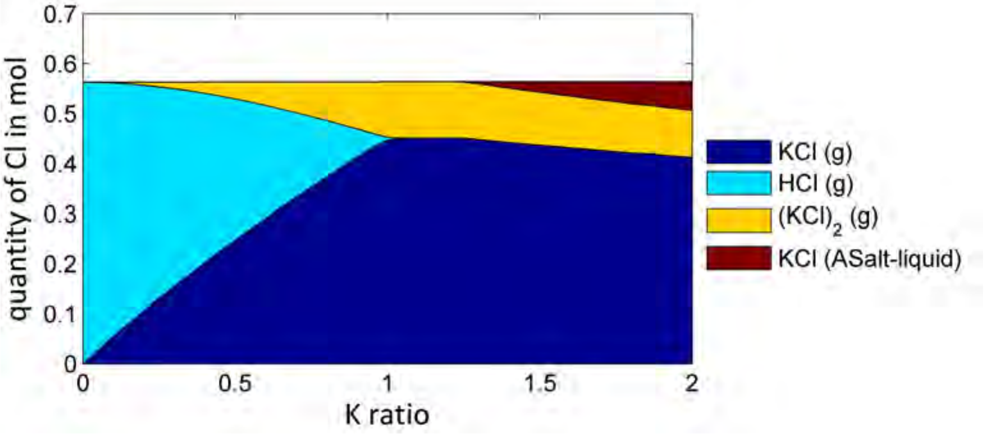


(a) $\lambda = 0.8$

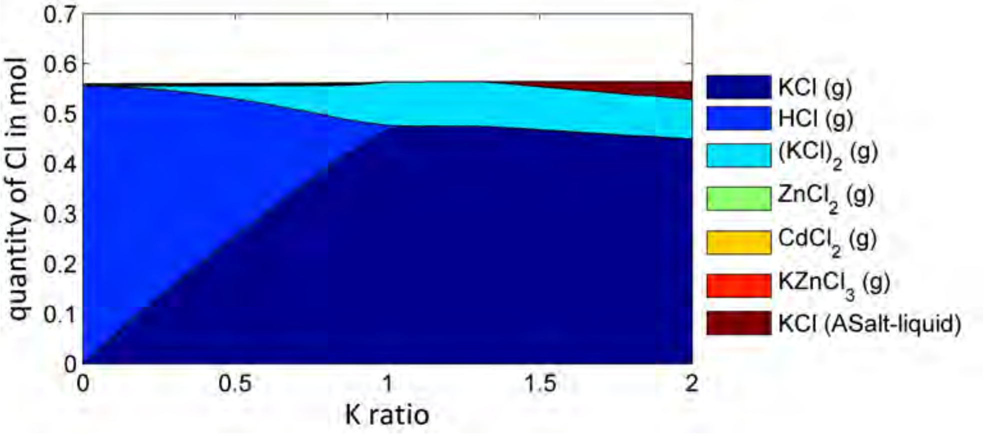


(b) $\lambda = 1.2$

Figure 4.9.: Volatilization behavior of Zn in case # 2b at reducing and oxidizing conditions. Compounds displayed result in at least 99% of Zn present in the system for each temperature point.



(a) $\lambda = 0.8$



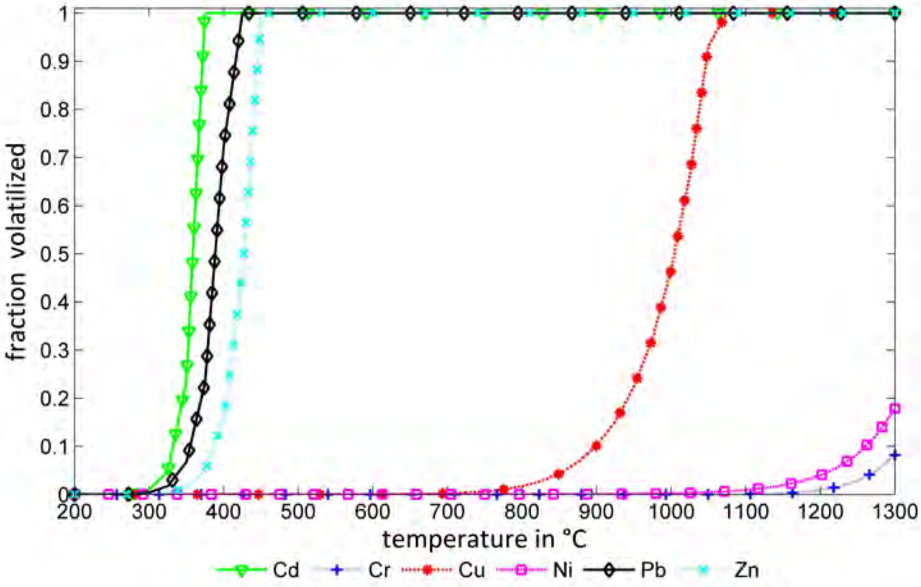
(b) $\lambda = 1.2$

Figure 4.10.: Volatilization behavior of Cl in case # 4a at reducing and oxidizing conditions at 900°C in dependency of the potassium ratio. Compounds displayed result in at least 99% of Cl present in the system for each temperature point. ASalt-liquid refers to a molten halide solution.

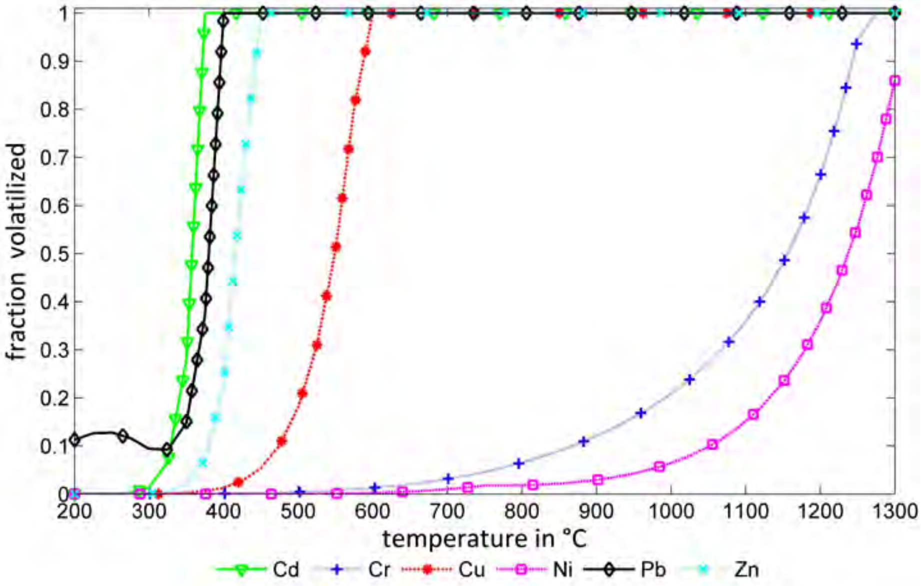
Influence of alkalis (potassium K)

As alkali metal, potassium is chosen, case # 3 and # 4a. Over all, K binds Cl (Figure 4.10) and thus reduces the amount of heavy metals volatilized, Figures 4.11-4.14.

Cadmium Cd: As long as the potassium ratio is low (i. e. $\gamma = 0.5$), Cd is volatilized as if there was no K at all (independent of the air ratio). At $\lambda = 0.8$, Cd is influenced positively by the availability (i. e. $\gamma = 1.5$) of K because the formation of – relatively to Cd^0 – low volatile $CdCl_2$ is avoided. At both S and K excess and an air ratio of $\lambda = 0.8$, Cd behaves as if there was only S excess (i. e. case # 3c is similar to # 2c).

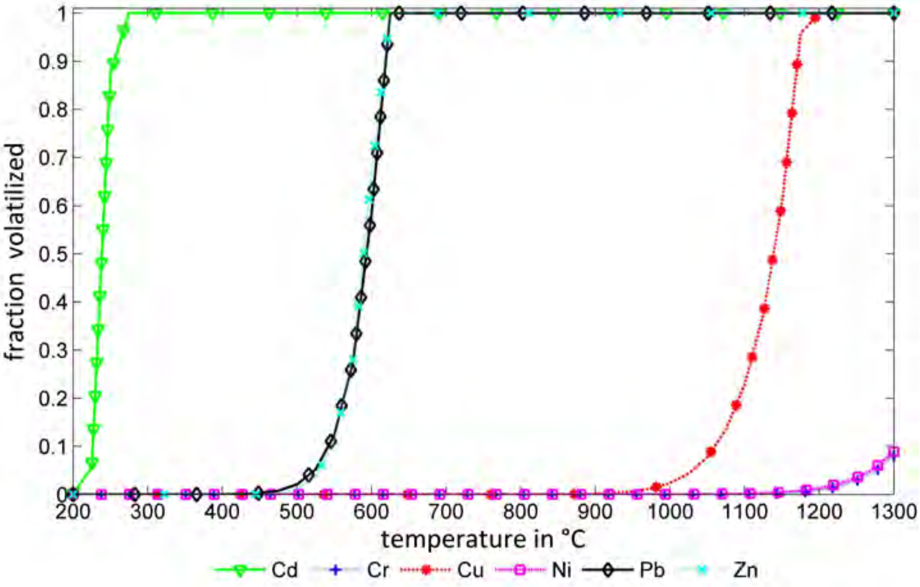


(a) $\lambda = 0.8$

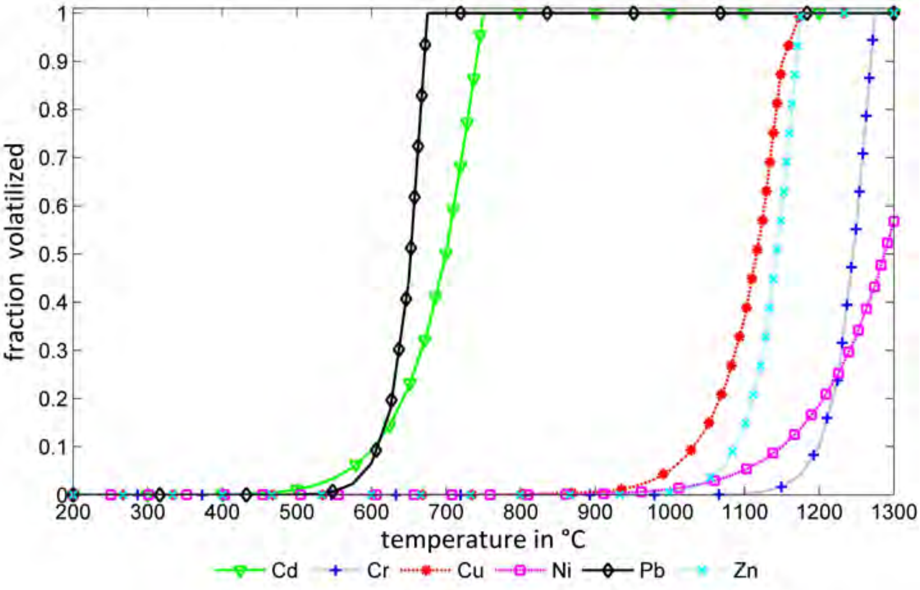


(b) $\lambda = 1.2$

Figure 4.11.: Influence of alkalis (i. e. K; 2% Cl, 0% S, $\gamma < 1$) on the volatilization of heavy metals (case # 3a).

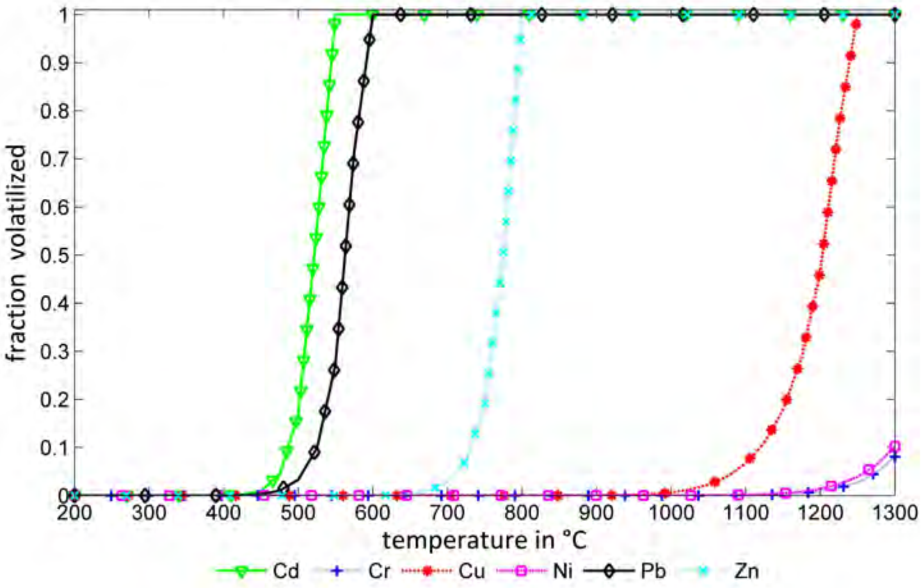


(a) $\lambda = 0.8$

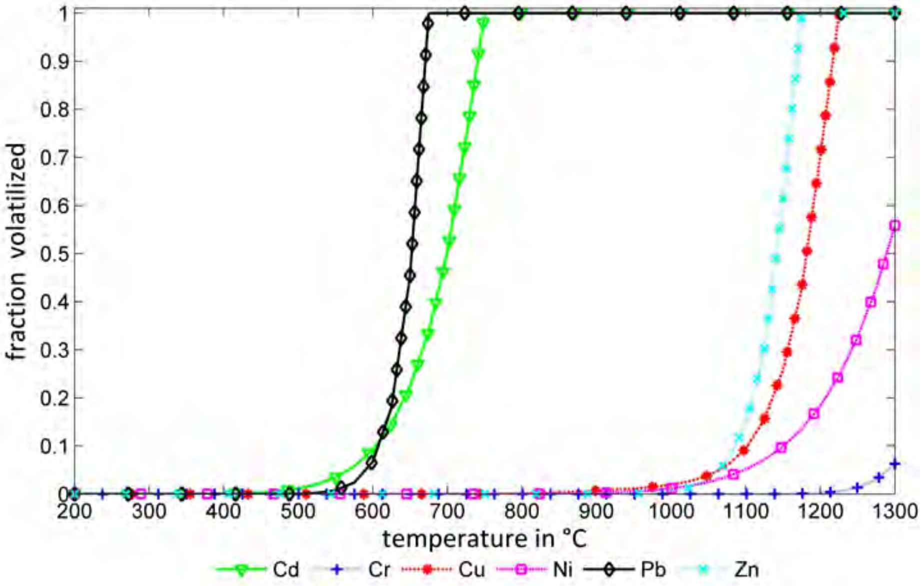


(b) $\lambda = 1.2$

Figure 4.12.: Influence of alkalis (i. e. K; 2% Cl, 0% S, $\gamma > 1$) on the volatilization of heavy metals (case # 3b).

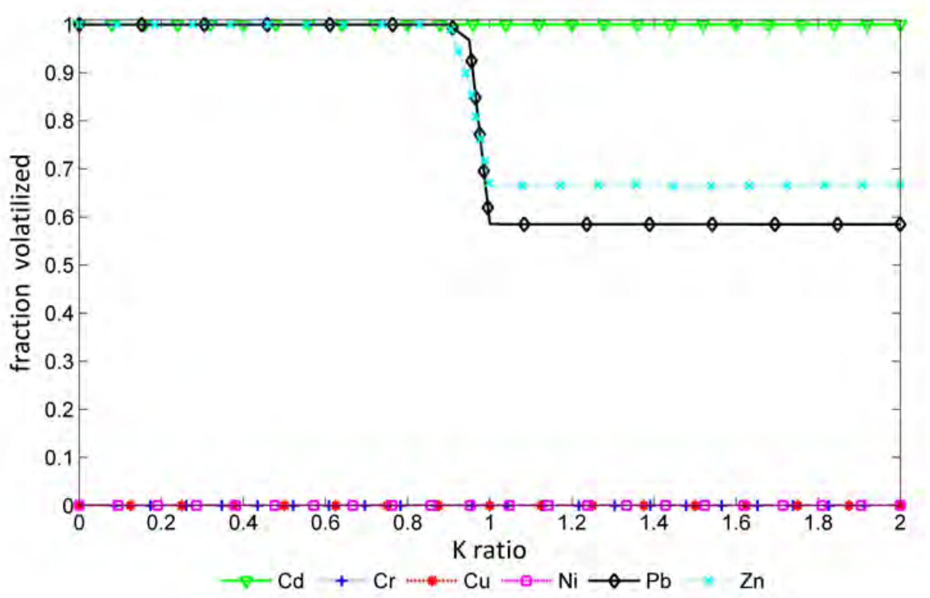


(a) $\lambda = 0.8$

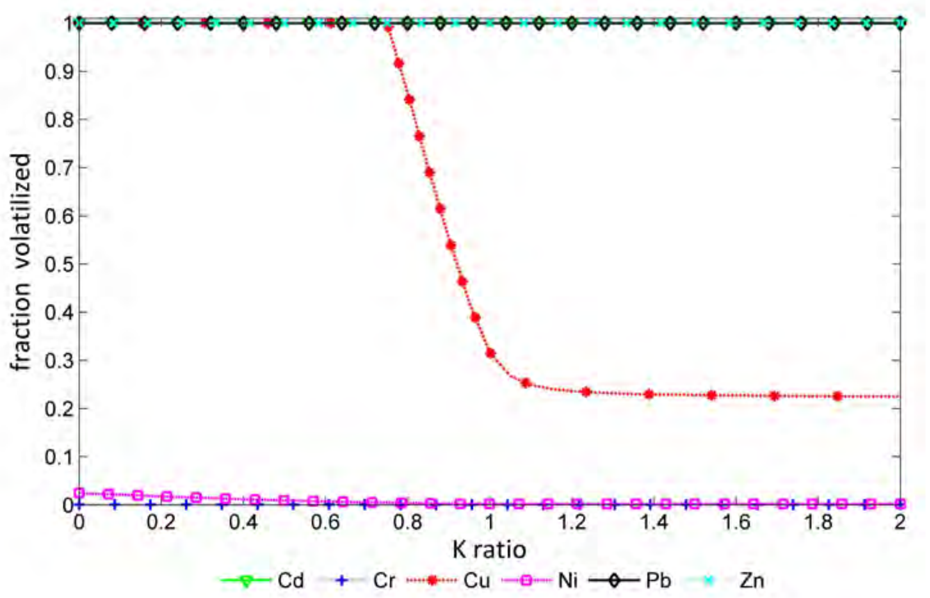


(b) $\lambda = 1.2$

Figure 4.13.: Influence of alkalis (i. e. K; 2% Cl, 5% S, $\gamma > 1$) on the volatilization of heavy metals (case # 3c).

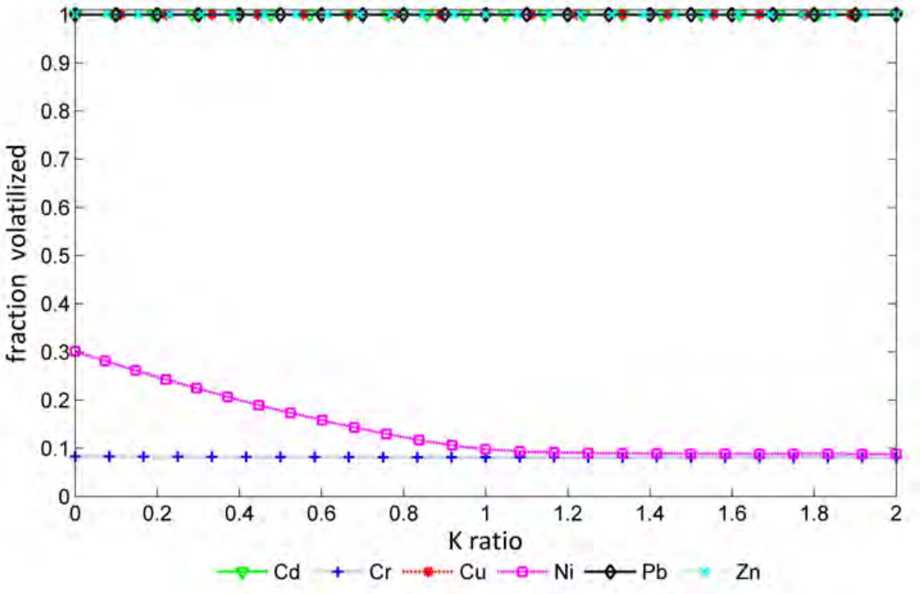


(a) 600°C, $\lambda = 0.8$

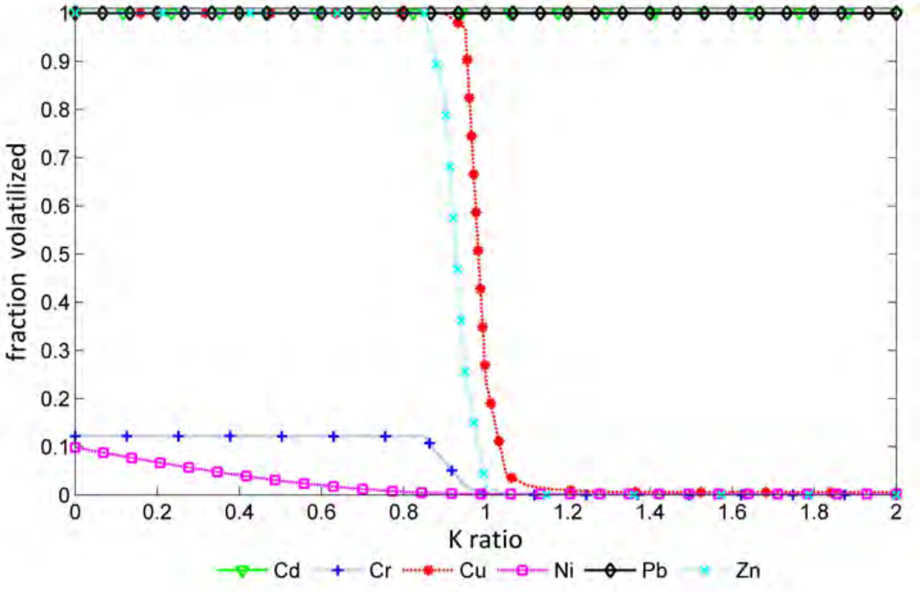


(b) 1100°C, $\lambda = 0.8$

Figure 4.14.: Influence of potassium ratio γ (case # 4a); 2% Cl and 0% S present. *Continued on page 41.*



(c) 1300°C, $\lambda = 0.8$



(d) 900°C, $\lambda = 1.2$

Figure 4.14.: Influence of potassium ratio γ (case # 4a); 2% Cl and 0% S present. *Continued from page 40.*

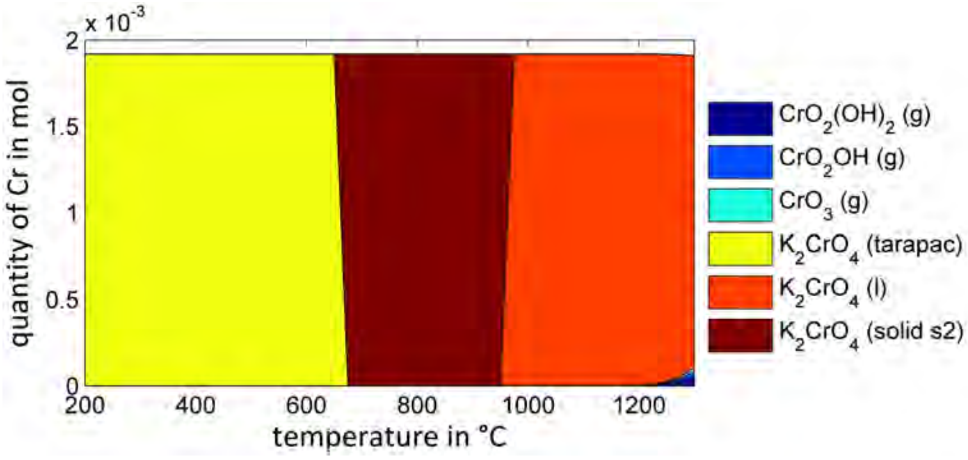


Figure 4.15.: Volatilization behavior of Cr in case # 3c at oxidizing conditions. Compounds displayed result in at least 99% of Cr present in the system for each temperature point. solid s2 and tarapac are modifications of K_2CrO_4.

At an air ratio $\lambda = 1.2$, with or without S present, Cd behaves at K excess ($\gamma > 1$) as if there was also no Cl present (compare case # 1).

Chrom Cr: At reducing conditions, Cr is always very low volatile and also not influenced by the amount of K in the system (Figure 4.14).

At oxidizing conditions, K has hardly any influence on the volatilization behavior of Cr, as long as the potassium ratio is $\gamma < 1$, see Figure 4.14(d). At higher amounts of K, Cr is bound to solid K_2CrO_4 (instead to Cr oxide), which melts somewhat below 1000°C. Volatilization starts then from ca. 1100°C with a similar gas phase composition as if no K was available. With K excess and S present, the start of volatilization is shifted to higher temperatures. In the solid phase, liquid K_2CrO_4 is then the sole Cr compound up to 1200°C. The gas phase is still similar to the case with no K present, except that gaseous Cr oxides are not that likely to occur, Figure 4.15.

Copper Cu: Due to the facts, that K captures Cl and that Cu requires Cl for volatilization, the appearance of K negatively affects the volatilization behavior of Cu. At $\lambda = 0.8$ and no S present, one has to distinguish between $\gamma < 1$ and $\gamma > 1$: At small K ratios, the gas phase is the same as with $\gamma = 0$; the lower amount of available Cl will lead to volatilization at higher temperatures (in the calculations presented at ca. 100°C higher in case # 3a compared to # 2a). K ratios $\gamma > 1$ will lead to a similar behavior of Cu as if no Cl was present at all (compare also Figure 4.14(b)); only at temperatures > 1100°C small fractions of CuCl appear in the gas phase. With S and K both in excess compared to Cl available, Cu volatilization will start not until 1000°C. Even the formation of gaseous CuCl is hindered then; Cu will volatilize as Cu and CuS.

At oxidizing conditions and $\gamma = 0.5$, Cu behaves similar as if no K was present;

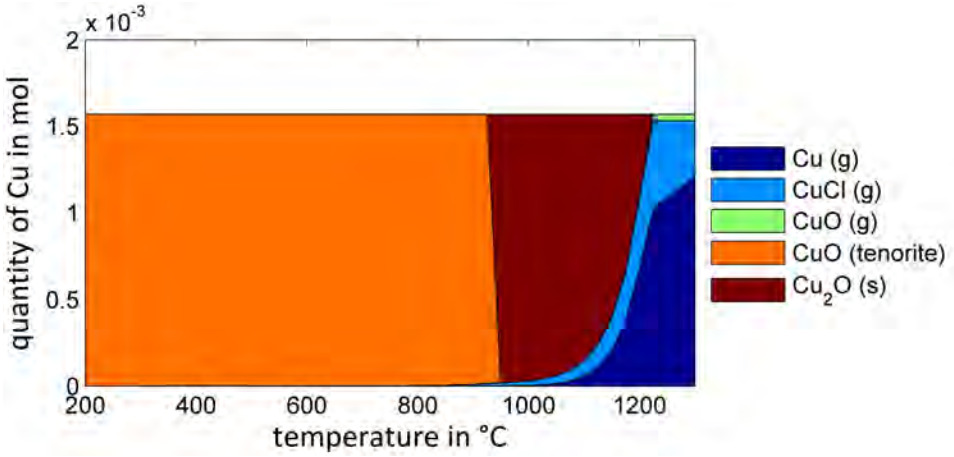


Figure 4.16.: Volatilization behavior of Cu in case # 3c at oxidizing conditions. Compounds displayed result in at least 99% of Cu present in the system for each temperature point.

except that volatilization starts some 150°C later. With $\gamma > 1$, it is more likely that CuO and Cu_2O appear in the solid and thus volatilization starts not before 950°C (case # 3b); in the gas phase, CuCl, Cu and negligible amounts of CuO appear, Figure 4.16. Passing $\gamma = 1$ at 900°C causes immediately the immobilization of Cu, Figure 4.14(d). Oxidizing conditions, high amounts of both K and S lead to a similar volatilization behavior of Cu as if no S was present (compare cases # 3b and 3c at $\lambda = 1.2$).

Nickel Ni: As potassium reduces the availability of Cl for Ni, this heavy metal is strongly affected by the K amount. At $\lambda = 0.8$ and $\gamma < 1$, the reduced availability of Cl does not change the volatilization behavior, but leads to an almost 100°C higher start of volatilization. With $\gamma > 1$, there is no Cl available for Ni at all and thus it has the same behavior as in case # 1. Figure 4.14(c) shows this dependency quite clear. Due to the absence of Cl, the addition of S causes only the formation of Ni sulfides. Thus, Ni will evaporate only as NiS or Ni^0 in small quantities over 1200°C.

At oxidizing conditions, the general behavior of Ni is similar as at reducing conditions: As long as the amount of K is low (or even $\gamma = 0$), it is possible to volatilize Ni even from 700°C. Increasing γ reduces the amount of Ni volatilized (Figure 4.14(d)), i. e. the necessary temperature for vaporization is increased by, e. g. case # 3a, some 200°C. With excess of K, the amount of S does not influence volatilization. That means that cases # 3b and 3c are both equal and very similar to case # 1 (except that solid $(NiO)(Cr_2O_3)$ is not formed at all).

Lead Pb: At $\lambda = 0.8$, the volatilization behavior of Pb is hardly influenced as long as $\gamma < 1$, especially at higher temperatures (i. e., for example, 600°C, see Figure 4.14(a)). Below these temperatures, volatilization will occur some 100°C later than

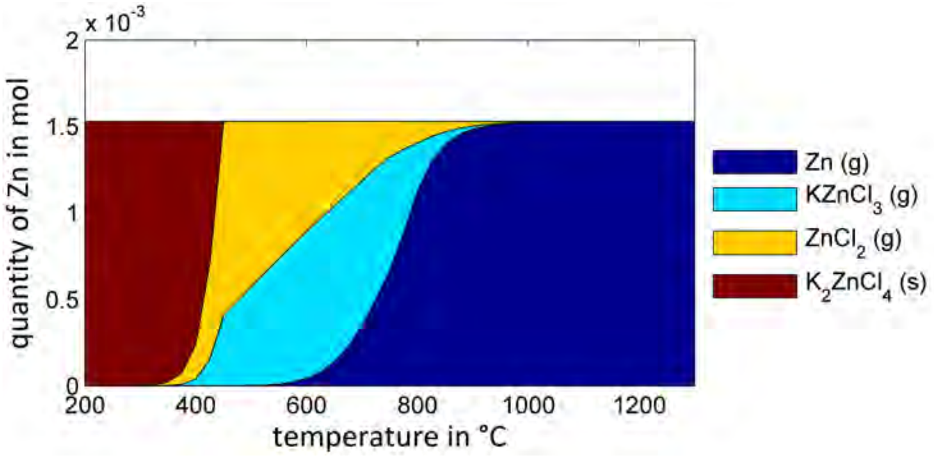


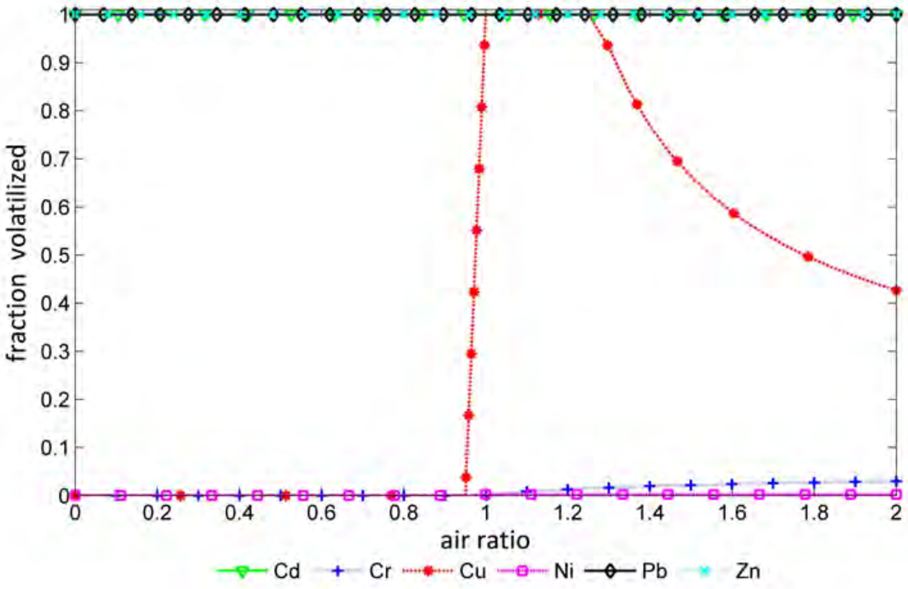
Figure 4.17.: Volatilization behavior of Zn in case # 3a at reducing conditions. Compounds displayed result in at least 99% of Zn present in the system for each temperature point.

with $\gamma = 0$. With $\gamma > 1$, the behavior of Pb is exactly the same, as if no Cl was present at all (compare case # 1). With S available and $\gamma > 1$, Cl will not appear together with Pb; but due to the higher volatility of PbS, volatilization will start already at lower temperatures (ca. 450 instead of 500°C).

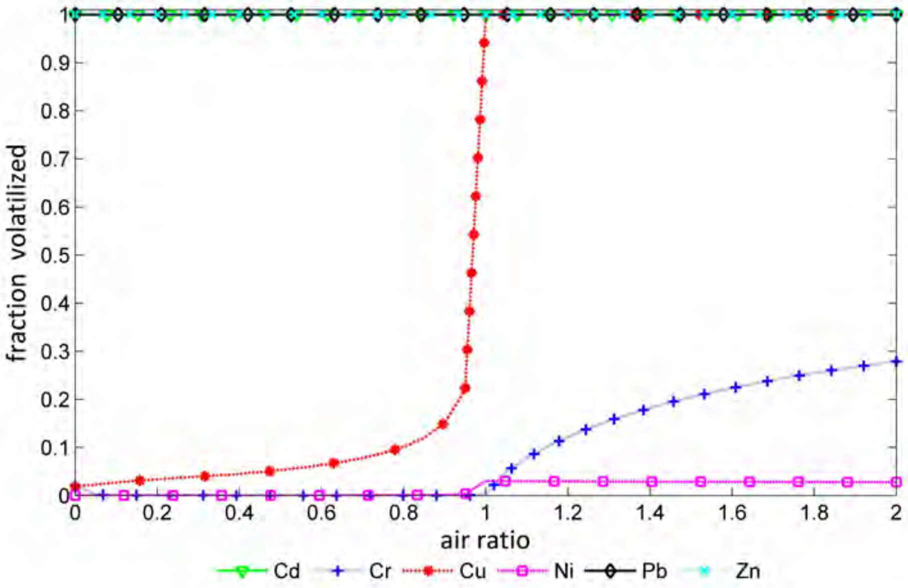
Due to the formation of solid KPb_2Cl_5 and K_2PbCl_4 at the expense of gaseous $PbCl_4$ < 400°C (which still binds ca. 10% Pb) at $\lambda > 1$, significant volatilization will not start below 300°C. At temperatures > 450°C, the composition of the gas phase is the same for $\gamma = 0$ and $\gamma = 0.5$. Increasing the K ratio from $\gamma = 0.5$ to 1.5 causes a much higher vaporization temperature, i. e. > 550°C. Pb will evaporate then only as PbO (being the sole Pb compound over 600°C). There is – similar to the case with $\lambda = 0.8$ – no common appearance of Pb and Cl. The availability of S (case # 3c) does not change anything on the volatilization behavior or the Pb composition.

Zinc Zn: At reducing conditions and $\gamma = 0.5$ (no S present), solid K_2ZnCl_4 (stable up to 450°C) is formed; volatilization starts at ca. 350°C as $ZnCl_2$ and $KZnCl_3$ (in approx. same fractions), Figure 4.17. At 600°C, elemental Zn^0 is getting important being the sole Zn compound over 1000°C. Passing $\gamma = 1$, Figure 4.14(a), the amount volatilized decreases; the Zn behavior and its compounds formed are exactly the same as if no Cl was present (i. e. similar to case # 1). Including S does not affect anything in the calculations carried out. In that sense, Zn behaves similarly as Pb.

At $\lambda = 1.2$ and $\gamma < 1$, Zn volatilizes at temperatures above 400°C (i. e. 200°C more, as if no K was present). Below that temperature, Zn is bound in solid K_2ZnCl_4. Zn evaporates as $ZnCl_2$ and $KZnCl_3$; at > 1100°C also Zn^0 is formed. If more K is in the system, i. e. $\gamma > 1$, again Zn behaves the same way as in case

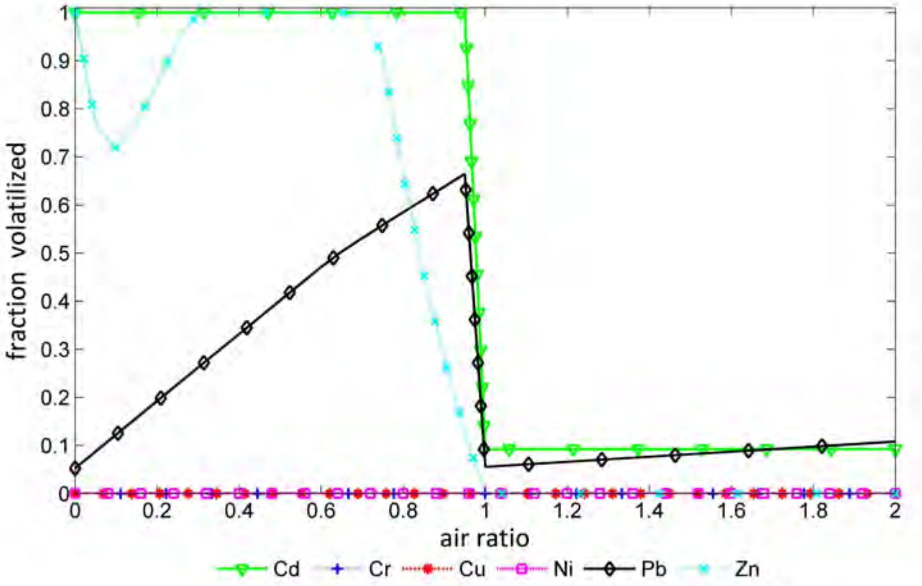


(a) 600°C, $\gamma < 1$

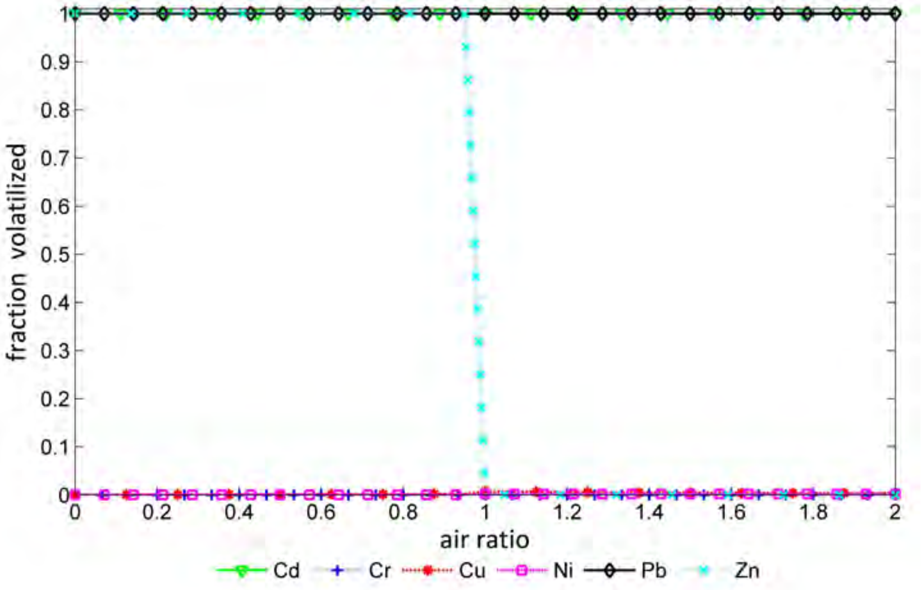


(b) 900°C, $\gamma < 1$

Figure 4.18.: Influence of the air ratio λ (case # 4b); 2% Cl and 0% S present.

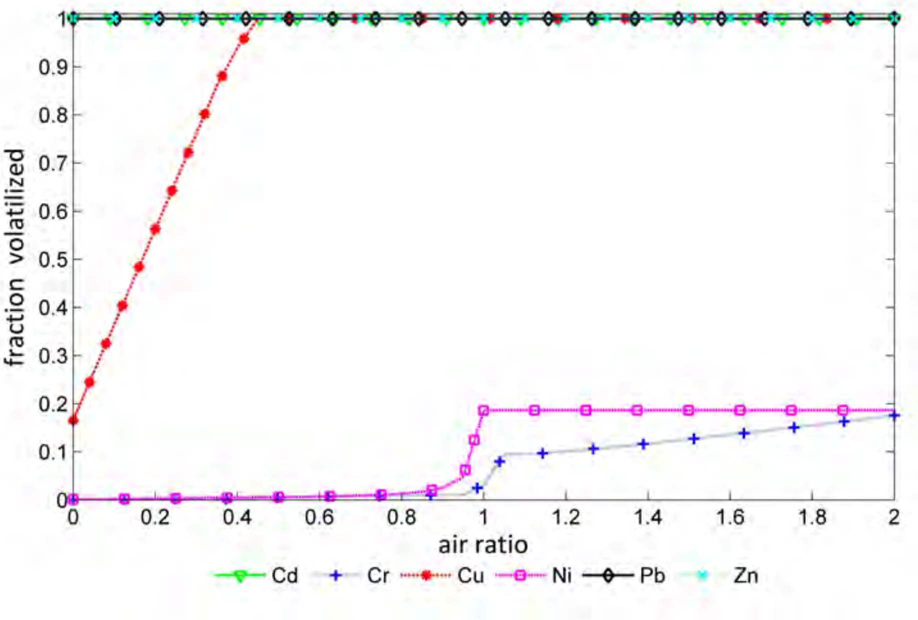


(a) 600°C, $\gamma > 1$



(b) 900°C, $\gamma > 1$

Figure 4.19.: Influence of the air ratio λ (case # 4c); 2% Cl and 0% S present. *Continued on page 47.*



(c) 1200°C, $\gamma > 1$

Figure 4.19.: Influence of the air ratio λ (case # 4c); 2% Cl and 0% S present. *Continued from page 46.*

1 (no Cl present). It is then not even affected by the appearance of S (case # 3c).

Influence of the air ratio λ

The influence of the air ratio has already been discussed above; here it shall be shown exemplary that the volatilization behavior of heavy metals is hardly affected by the air ratio as long as the air ratio is $\lambda < 1$ or $\lambda > 1$; but increasing the ratio from $\lambda < 1$ to $\lambda > 1$ will change the behavior completely at $\lambda = 1$. Figures 4.18 and 4.19 display this for the cases # 3a and 3b; i. e. Cl and K but no S is available.

E. g., at 600°C and $\gamma = 0.5$, Cu volatilization occurs only at oxidizing conditions due to the formation of $(CuCl)_3$, Figure 4.20. At higher air ratios, solid CuO is more stable and thus decreasing the amount volatilized, Figure 4.18(a). Figure 4.18(b) shows clearly, that the volatilization of Cr and Ni requires the availability of excess oxygen; Cu evaporation occurs at 900°C more likely at $\lambda > 1$. Also at $\gamma = 1.5$ and at higher temperatures, these trends can be observed, Figure 4.19(c).

Due to the potassium ratio $\gamma = 1.5$, hardly any Cl is available for volatilizing heavy metals. At 600°C, $Cd^0(g)$ is stable as long as $\lambda < 1$. At $\lambda > 1$, $Cd(OH)_2$ causes a ca. 10% fraction of Cd to be gaseous, Figure 4.19(a). At the same conditions, at $\lambda < 1$, Pb is completely present as liquid and gaseous metal Pb^0, whereas an increasing air ratio increases the gaseous amount. Passing $\lambda = 1$ results in 90% immobilization of

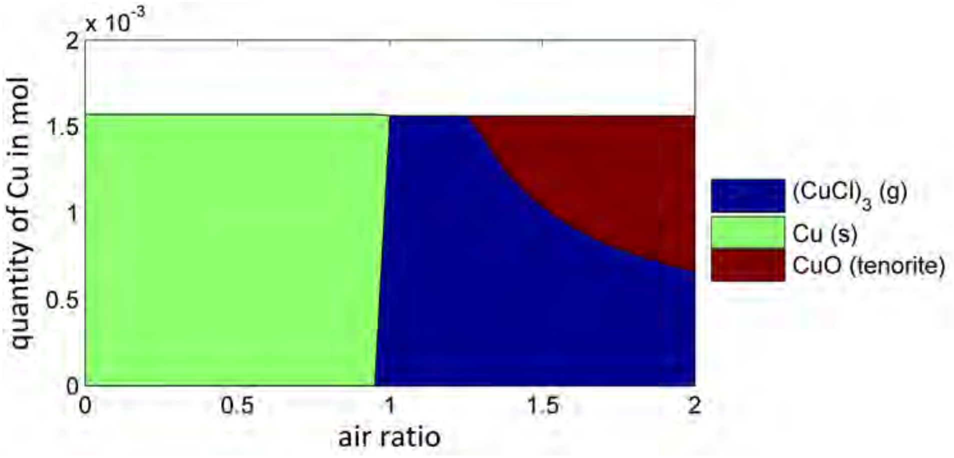


Figure 4.20.: Volatilization behavior of Cu in case # 4b at 600°C in dependency of the air ratio. Compounds displayed result in at least 99% of Cu present in the system for each temperature point.

Pb; only a small fraction (ca. 10%) PbO will volatilize (Figure 4.21). Also at 600°C, solid ZnO is stable at small air ratios ($0 < \lambda < 0.4$) and at air ratios $\lambda > 0.8$. Higher temperatures, Figure 4.19(b), will shift the boarder of stability between Zn^0(g) and ZnO towards $\lambda = 1$.

4.1.3. Discussion

Here, the limitations of the calculations carried out shall be discussed.

On the one hand, chosen concentrations differ to those found in real systems. Other elements are neglected as well. On the other one, the explanatory power of equilibrium calculations is always limited: In real systems, equilibrium is not necessarily reached (especially not at low temperatures). Kinetics and physical processes (e. g., adsorption and agglomeration [86]) as well as open systems cannot be considered in equilibrium calculations; only those compounds, which are selected for the calculation, can be formed [104]. Equilibrium calculations are an useful tool for investigating processes, where kinetics have the same order of magnitude for all major reactions taking place. If co-processes with different kinetic scales are considered, results may be misleading if used to predict real systems (e. g., heavy metal chemistry and glass chemistry [105] in one calculation). Diffusional limited processes cannot be taken into account: E. g., sulfur can be captured with limestone (or other Ca bearing compounds) during combustion [106], but the process' efficiency is limited [107] as formed $CaSO_4$ on limestone particles avoids further reaction [108]. If modeled in equilibrium, the efficiency of sulfur capture with Ca would be close to 100%. Thus, for obtaining reasonable results, only the amount of limestone which is probably reacting has to be taken into account. For studying the general behavior, Ca (and the corresponding amount of S) can be omitted in the calculations if molar excess of S occurs, as these elements will always be situated together in equilibrium [105] (at least at temperatures < 1200°C; above this temperature $CaSO_4$

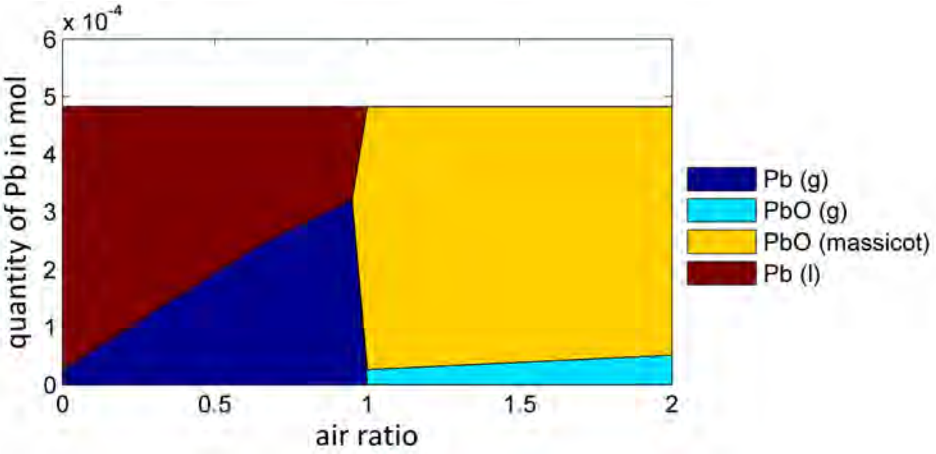


Figure 4.21.: Volatilization behavior of Pb in case # 4c at 600°C in dependency of the air ratio. Compounds displayed result in at least 99% of Pb present in the system for each temperature point.

starts decomposing [109]).

Due to its complexity, the equilibrium composition of a system is calculated numerically. Therefore, numerical uncertainties occur. Especially, discretization errors are from importance: E. g. the compound Cu_2S in Figure 4.6 exists in two modifications called solid-b and solid-c. Due to the resolution of the x-axis (25°C), the transition appears to be within a range. However, there is a well-defined transition temperature, i. e. the boundary line between Cu_2S (solid-b) and Cu_2S (solid-c) should be vertical.

4.1.4. Conclusions

The evaporation of heavy metals is strongly influenced by the air ratio, the appearance of Cl, S and of alkalis (K investigated). Thermodynamic equilibrium calculations were carried out in order to study these influences.

Generally, Cl enhances the amount of heavy metals volatilized mostly due to the formation of heavy metal chlorides. On the other hand, due to the formation of stable sulfides (at air ratios $\lambda < 1$) or sulfates (at air ratios $\lambda > 1$) S leads to the immobilization of heavy metals.

K hardly affects heavy metals directly, but as it is reacting with Cl, the amount of heavy metals volatilized decreases with the amount of K present in the system.

Oxidizing conditions, i. e. air ratios $\lambda > 1$, will enhance the volatilization of Cr, Cu and Ni. A reducing atmosphere leads to a higher amount of Cd, Pb and Zn in the gas phase.

4.2. Sewage sludge ash to P-fertilizer by chlorination and thermal treatment: residence time requirements

Cf. [8] (Paper V, page 119).

4.2.1. Methods

Sewage sludge ash is mixed with $CaCl_2$ (150 g Cl per kg ash added) and water and subsequently pelletized with a die press.

The pellets are treated batch-wise in a rotary reactor (Figure 3.2) at different residence times and temperatures. The treated samples are milled, digested and analyzed for the elements Cu, Pb, and Zn.

Thermogravimetric analysis is (coupled with mass spectroscopy) is carried out as well.

4.2.2. Results and discussion

Thermogravimetric analysis of the pellets reveals that HCl is formed at temperatures over 400°C, whereas the Cl release is maximum between 540 and 660°C, Figure 4.22.

Figure 4.23 shows the concentration decrease of Cu, Pb, and Zn during the first ten minutes in rotary reactor experiments. It is described by

$$\frac{\mathrm{d}c}{\mathrm{d}t} = -k \cdot (c - c_\infty) \tag{4.3}$$

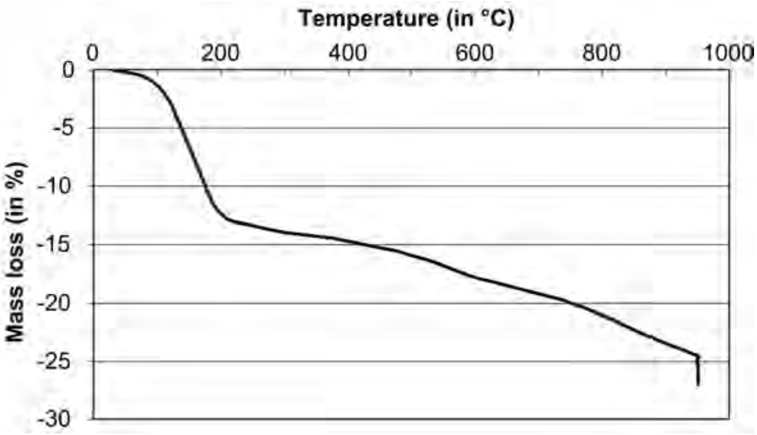
(concentration c, time t, apparent reaction rate constant k, remaining concentration in the sample c_∞), whereas only data points at $t \geq 2\,\mathrm{min}$ are considered (to avoid the influence of the initial heat-up). For Pb and Zn, the final concentration seems to be reached already after approx. 5 min. Apparently, these elements have similar removal mechanisms (apparent reaction rate constant k is $2.4 \cdot 10^{-2}\,\mathrm{s}^{-1}$ for Pb and $2.0 \cdot 10^{-2}\,\mathrm{s}^{-1}$ for Zn) supporting the limiting steps published in [5]. The final concentration of Cu is not reached in the investigated range (apparent reaction rate constant $k = 8.2 \cdot 10^{-3}$); longer residence times ($> 10\,\mathrm{min}$) are required.

Already at 400-500°C, heavy metal removal can be observed: At 470°C, more than 40% of Cu and Pb and more than 30% of Zn are removed. However, these values differ to those found in [72] (heavy metal release starts not below 600°C), probably due to different heating rates and different ashes used.

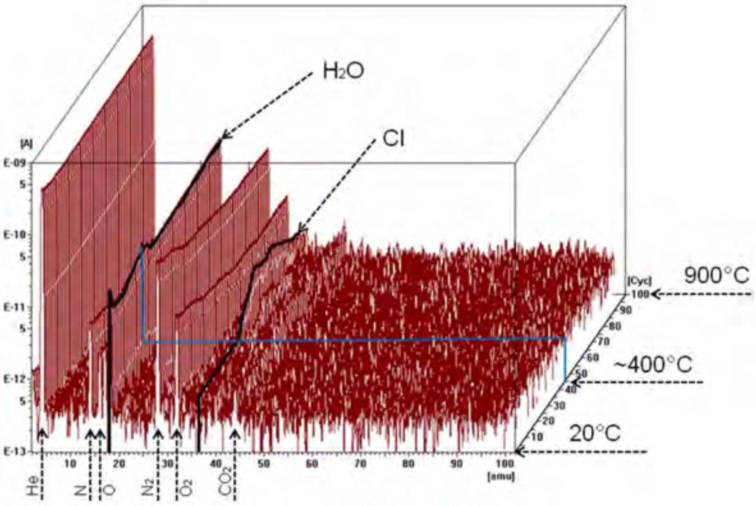
The only relevant limit value of heavy metals according to the Austrian [110] and the German [111] ordinance on fertilizers is the one of Pb (100 ppm in Austria, 150 ppm in Germany). Within 2 min, i. e. already during the heat-up period this value is reached.

4.2.3. Conclusions

Already during the heat-up period, a significant amount of heavy metals is removed; approx. 50% of Cu, Pb, and Zn are volatilized as chloride is released at temperatures



(a) Mass loss in dependency of temperature

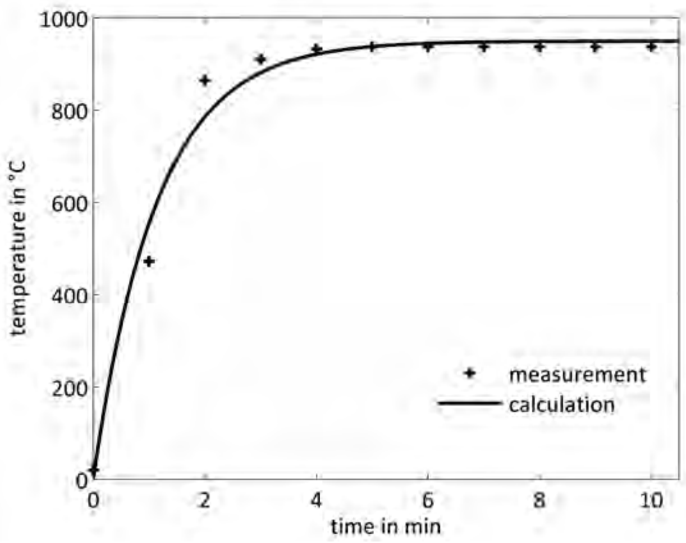


(b) Mass-spectroscopic analysis of the off-gas released

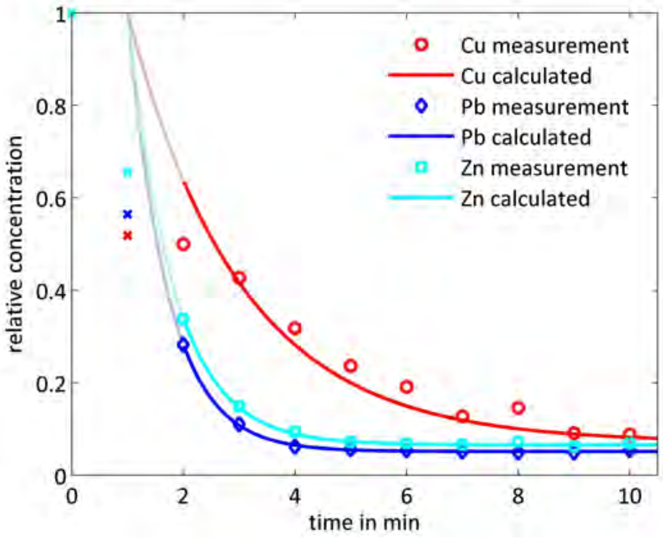
Figure 4.22.: Thermogravimetric analysis of sewage sludge ash-$CaCl_2$-pellets (air atmosphere, constant heating rate 50 K min^{-1}). From [8].

> 400°C. After 25 min it is possible to remove at 1050°C up to 97% Cu, 95% Pb, and 95% Zn.

Pb and Zn have similar removal mechanisms differing to the one of Cu.



(a) Temperature



(b) Concentration decrease

Figure 4.23.: Heat-up and concentration decrease in the rotary reactor during the first 10 min. × marks measured points not used for the calculation. From [8].

4.3. Heavy metal removal from sewage sludge ash in a fluidized bed reactor

Cf. [5] (Paper II, page 89).

The technology for phosphorus recovery from sewage sludge ash (described in Chapter 2.1.3 and Figure 2.3, page 8) has to be improved to reduce the energy consumption [17]. In recent years, research in this field mainly focused on rotary reactors although this technology shows lower over-all reaction rates compared to fluidized bed reactors. This is mainly due to the fact that gaseous reactants have to diffuse into the moving bed of rotary kilns [112]. Fluidized bed reactors can be generally characterized by a high heat and mass transfer due to the formation of bubbles and the circulation of bed material [113]. Thus, by using a fluidized bed reactor the saving of thermal energy, the acceleration of removal processes and therefore the increase of material throughput can be anticipated.

4.3.1. Methods

Granulates made of sewage sludge ash and $CaCl_2$ are treated in both a rotary reactor and a fluidized bed reactor at different temperatures, residence times and – for the fluidized bed reactor – at different gas velocities. The treated samples are milled, digested and analyzed for Cd, Cu, Pb, and Zn.

4.3.2. Results and discussion

The fluidization behavior is investigated; the granulates' minimum fluidization velocity is approx. $1.1\,\mathrm{m\,s^{-1}}$. At gas velocity $> 4.5\,\mathrm{m\,s^{-1}}$ small particle fractions start entraining. For thermal experiments, the gas velocities used are in the range of bubbling fluidization; heavy metal removals are shown in Figure 4.24.

Cadmium can be removed well and almost independently of the conditions in all experiments.

Copper: The removal of Cu is incomplete in all experiments, ranging from 28% (rotary reactor, 850°C, 10 min) to 80% (fluidized bed reactor at $3.4\,\mathrm{m\,s^{-1}}$, 900°C, 15 min). The influence of treatment temperature is clearly pronounced, especially in rotary reactor experiments. From all elements concerned, the Cu removal shows the biggest influence of the residence time: In rotary reactor experiments, 28% can be removed after 10 min at 850°C, after 30 min 69% are separated. In fluidized bed reactor experiments, tripling the residence time from 10 to 30 min leads to an augmentation from 28 to 78% (at $3.4\,\mathrm{m\,s^{-1}}$) and 60 to 73% (at $4.6\,\mathrm{m\,s^{-1}}$), respectively.

Lead can be removed well with both technologies; it exceeds always 90% and reaches its maximum (98%) in the rotary reactor at 900°C. Removal processes are apparently finished after 10 to 15 min as longer residence times do not lead to higher removals.

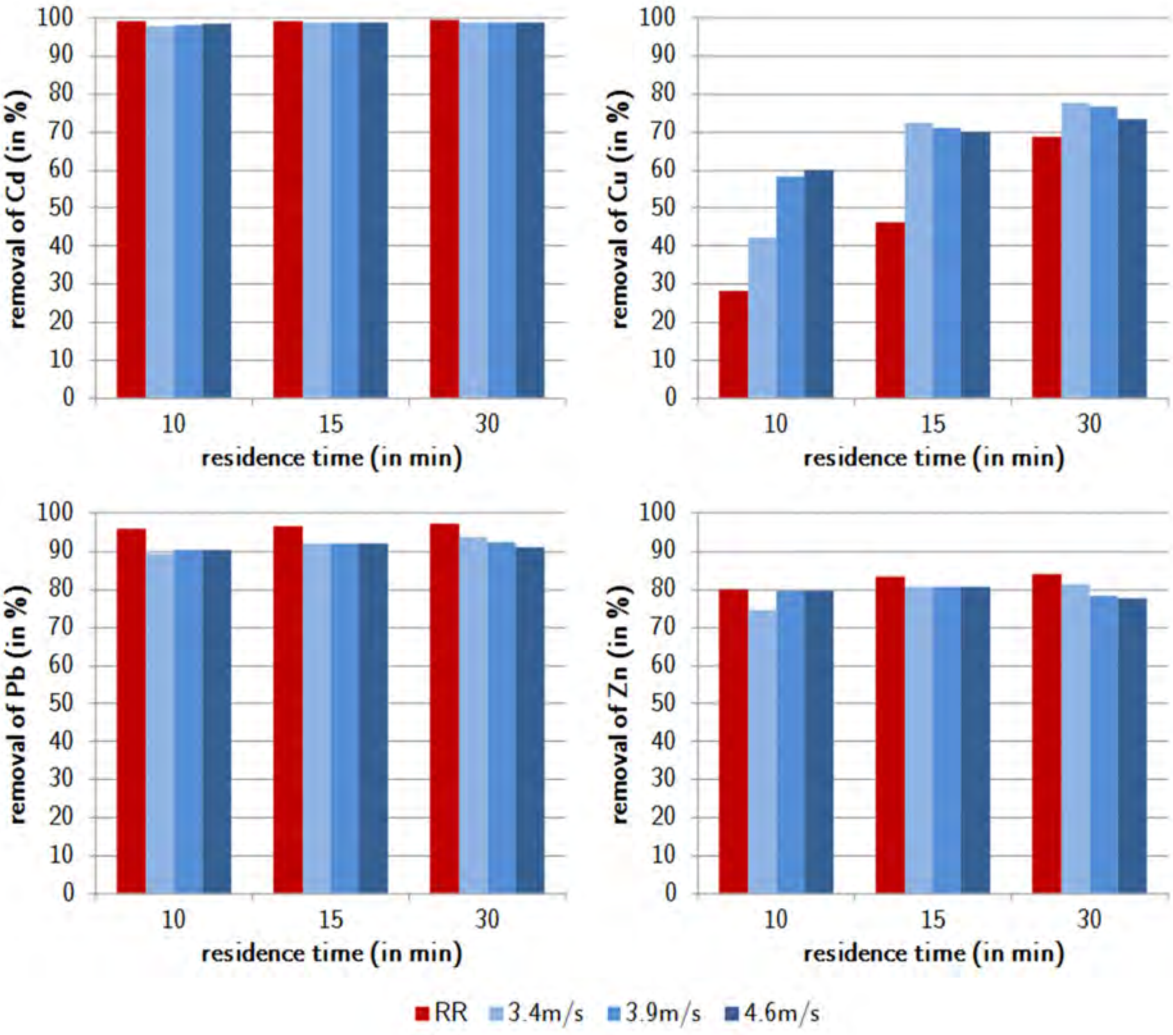


Figure 4.24.: Heavy metal removal in rotary reactor (RR) and fluidized bed reactor (superficial velocity given) at 850°C in dependency of the residence time. Adapted from [5].

Zinc shows a small dependency on the temperature and almost no dependency on the residence time; it is at 850°C always approx. 80±5%. By changing the temperature from 800 to 900°C, it can be increased from 79 to 90% in rotary reactor experiments; in fluidized bed reactor experiments these values are ca. 75 and 84-86%, respectively.

Only the removal of Cu is increased in the fluidized bed reactor experiments; for Pb and Zn it is always somewhat higher in the rotary reactor.

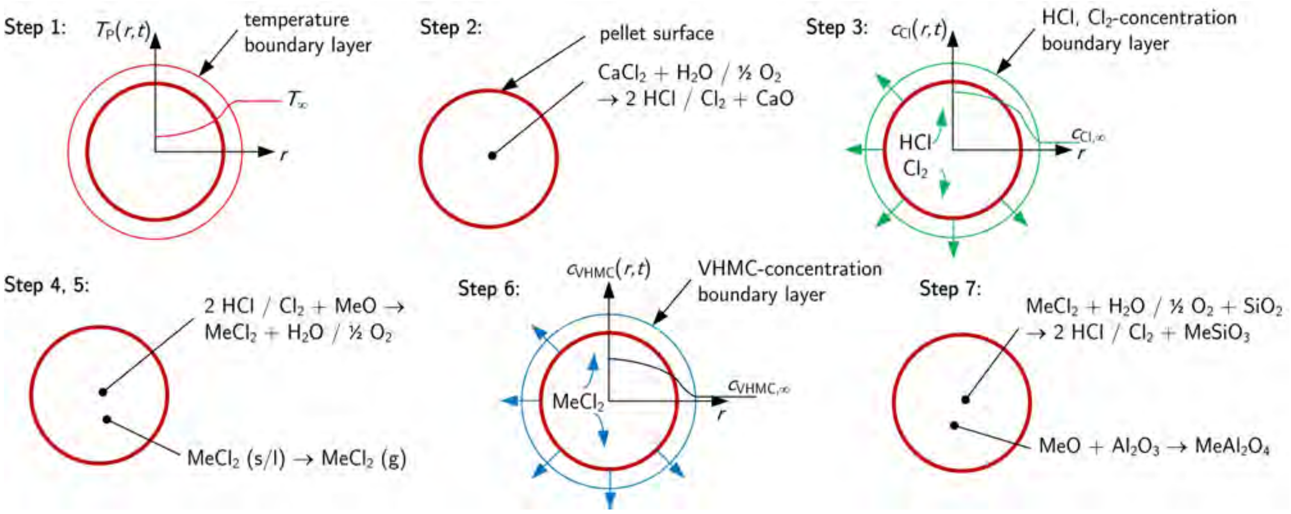


Figure 4.25.: Possible limiting steps in the reaction scheme leading to the evaporation of volatile heavy metal compounds (VHMC). Adapted from [5].

As the external mass transfer is different in both technologies, the limitations of the removal can be identified. Possible limiting steps could be (Figure 4.25):

1. the particle heating rate;
2. reaction kinetics of the formation of HCl and Cl_2;
3. diffusion rates of these gases in the pellet;
4. reaction kinetics of heavy metal compound chlorination;
5. evaporation of formed heavy metal chlorides;
6. diffusion rates of those chlorides;
7. reaction kinetics of matrix reactions.

The removal of Pb and Zn is high already after short residence times; higher mass transfers (in the fluidized bed reactor) lead to lower removals. Thus, these elements are limited by the availability of HCl and Cl_2 (step 3 is hindering step 4: either HCl and Cl_2 migrate to the atmosphere or they react).

Steps 2 and 3 are not limiting the Cu removal as they are formed within a short time (compare Pb and Zn). As higher mass transfers enhance the Cu removal, apparently it is limited by step 5 or 6, i. e. the evaporation (boiling point of CuCl approx. 1400°C [52]) and/or the diffusion of its chloride CuCl. Higher heating rates (step 1) enhances due to the high boiling point of CuCl its removal as well.

4.3.3. Conclusions

Although the mass transfer is higher in the fluidized bed reactor, the removal especially of Pb and Zn are slightly higher in the rotary reactor; up to 95% Pb and 90% Zn could be removed at 900°C after 15 min. In the fluidized bed reactor, these values are somewhat ($< 5\%$) smaller. Higher mass transfers enhance the migration of formed HCl and Cl_2 out of the particles into the reactor atmosphere which decreases the availability of these gases in the pellet and limits the removal of Pb and Zn.

The Cu removal is higher in the fluidized bed reactor as it is apparently limited by the evaporation and/or the diffusion of its chloride; it reached 80% in the fluidized bed reactor and ca. 60% in the rotary reactor at 900°C.

4.4. Heavy metal removal from MSW fly ash by chlorination and thermal treatment

Cf. [4] (Paper I, page 77).

The aim of the work is testing the behavior of MSW fly ash in the process described in Chapter 2.1.3 and Figure 2.3 (page 8), which has been developed for sewage sludge (especially when including the granulation step).

4.4.1. Methods

Municipal solid waste fly ash is mixed with $CaCl_2$ and water and subsequently pelletized. The influence of $CaCl_2$ addition (150 or 230 g Cl added per kg ash), temperature (950 to 1050°C), residence time (10 to 45 min), and gas velocity in the rotary reactor (0.5 to $4\,m\,s^{-1}$) on the removal of Cd, Cu, Pb, and Zn are investigated, Figure 4.26.

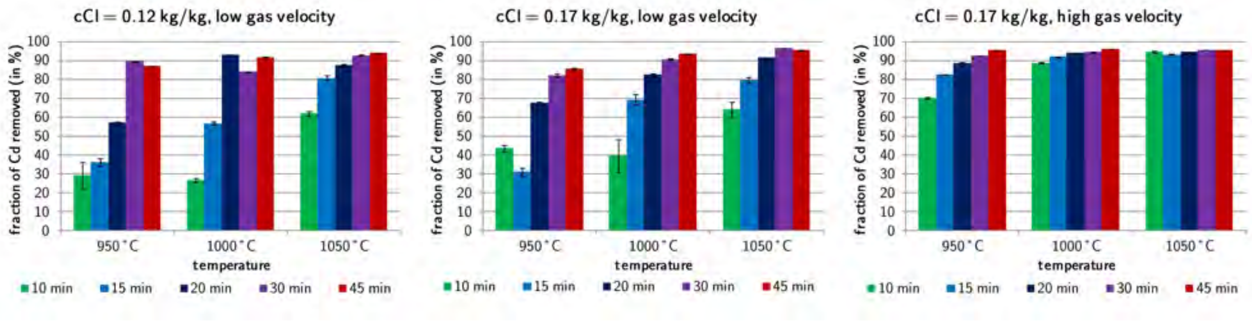
4.4.2. Results and discussion

Generally, higher values of these parameters cause higher removals, whereas the effect depends on the specific heavy metal: For the high volatile elements Cd and Pb, the influence of chloride added to ash is low in the investigated range; for Cu and Zn, which are generally recognized as mid volatile, the increase from 150 to 230 g Cl added per kg ash leads after 45 min to an approx. 10-25% (dependent on the temperature) higher removal of Cu and to an approx. 10% higher removal of Zn.

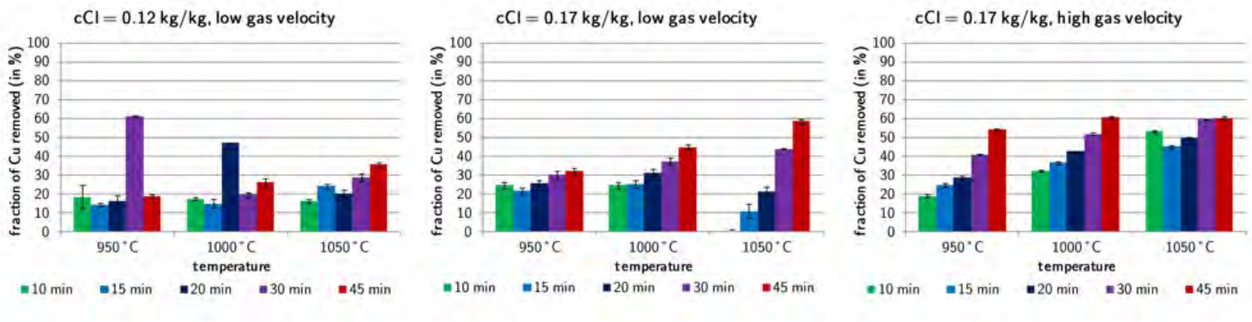
Regarding treatment temperature and residence time, one find that for the high volatile elements Cd and Pb the influence of the residence time is more pronounced at lower temperatures. As longer residence times (i. e., 30 and 45 min, especially at 1050°C) do not enhance the removal of these elements, it can be assumed that maximum amount removed is reached. In contrast, evaporation processes of Cu and Zn seem not to be finished after 45 min. Due to the low volatility of CuCl (boiling point approx. 1400°C [52] higher treatment temperatures significantly affect the Cu removal. For Zn, the residence time has a higher influence on the removal than an increase of the temperature (in the investigated range).

The higher gas velocity enhances removal processes as the boundary layers of the pellets are altered. Additionally, gaseous heavy metal compounds are faster discharged from the reactor which increases the concentration gradient from pellet body to atmosphere. For Cd, this effect can only be detected at low residence times; for Pb due to its high volatility hardly at all. For Cu, especially at high temperatures the increased gas velocity increases the removal; the Zn removal is always approx. 10% higher at higher gas velocity. Highest removals were obtained in these experiments (i. e., high gas velocity at 1050°C and a residence time of 45 min); they were 95% Cd, 60% Cu, 97% Pb, and 80% Zn.

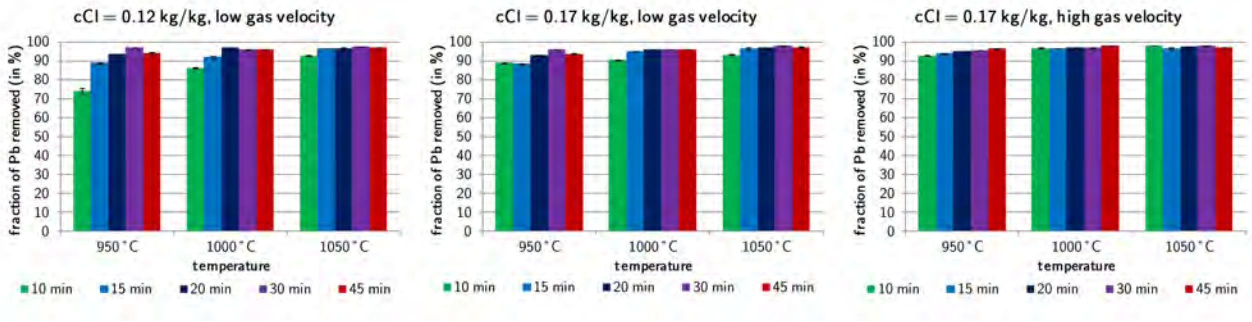
Another part of this study was a mass balance over the reactor, Figure 4.27 (one bar in the diagram refers to 5 to 11 batch experiments): The amount of heavy metals



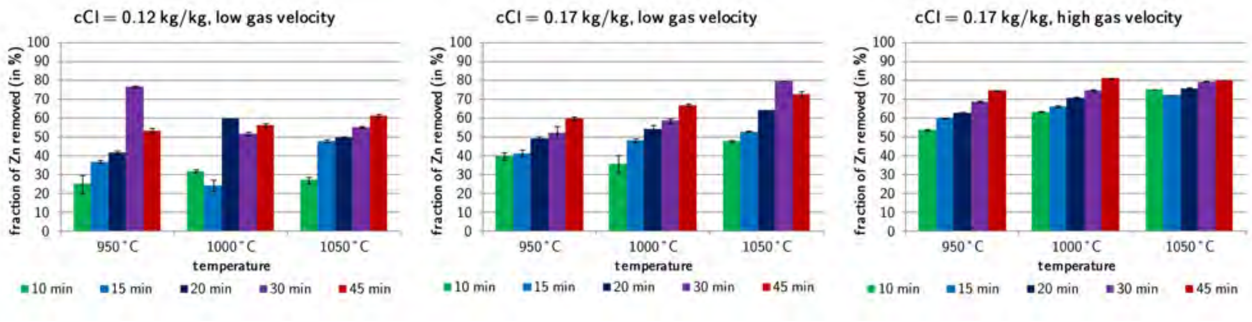
(a) Cadmium Cd



(b) Copper Cu



(c) Lead Pb



(d) Zinc Zn

Figure 4.26.: Heavy metal removal from a pelletized MSW fly ash-$CaCl_2$ mixture. $c_{Cl} = 0.12\,{}^{kg}/_{kg}$ and $c_{Cl} = 0.17\,{}^{kg}/_{kg}$ correspond 150 and 230 g Cl added per kg ash, respectively. Adapted from [4].

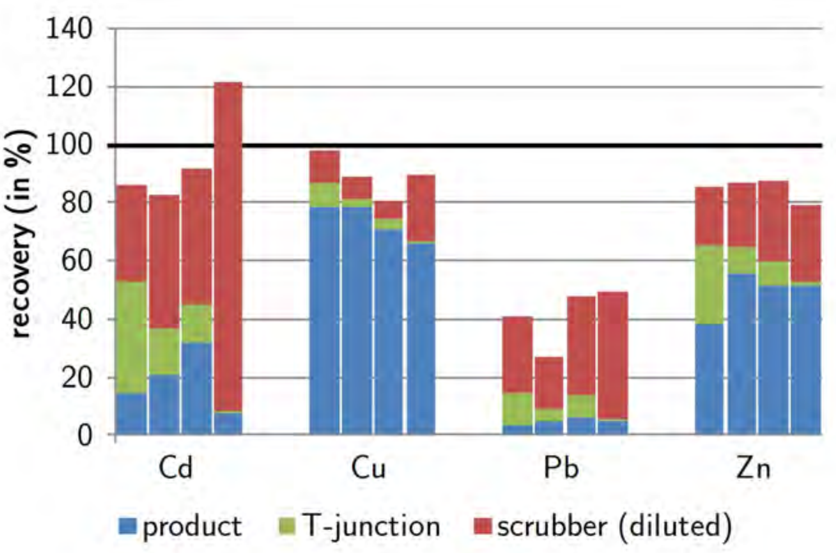


Figure 4.27.: Recovery of heavy metals in the rotary reactor. 100% refers to the amount of heavy metals in the untreated sample. Adapted from [4].

fed into the reactor (with the untreated sample) is compared to the amount found in the treated product and the reactor's off gas cleaning system (the off-gas is cooled with air in a T-junction and then fed to a venturi scrubber). For Cd, Cu, and Zn, mostly above 80% can be recovered. Due to the low solubility of Pb under acidic conditions, its recovery is significantly lower.

4.4.3. Conclusions

In this work it could be shown that the process described in Figure 2.3 (page 8) is principally suitable for heavy metal removal from MSW fly ash, although the amount of heavy metals volatilized is – compared to sewage sludge ash – significantly smaller.

Higher chloride concentrations, higher treatment temperatures, longer residence times, and higher gas velocities lead to higher heavy metal removal. E. g. increasing the temperature from 950 to 1050°C at a residence time of 45 min, the Cu and Zn removal can be increased by approx. 10%. An increase of the amount of chloride added (230 instead of 150 g Cl added per kg ash) leads also to a ca. 10% higher removal.

Highest removals where 95% Cd, 60% Cu, 97% Pb, and 80% Zn.

4.5. Comparison of the heavy metal removal from sewage sludge ash and MSW fly ash

Cf. [6] (Paper III, page 99).

4.5.1. Methods

Sewage sludge ash and MSW fly ash are both treated similarly in the process described in Chapter 2.1.3 and Figure 2.3 (page 8) [4, 8].

4.5.2. Results and discussion

Compared to sewage sludge ash, the removal of heavy metals from MSW fly ash is lower and proceeds slower, over all for Cu and Zn, Figure 4.28. The influence of residence time and treatment temperature is for MSW fly ash more pronounced. E. g., after 10 min at

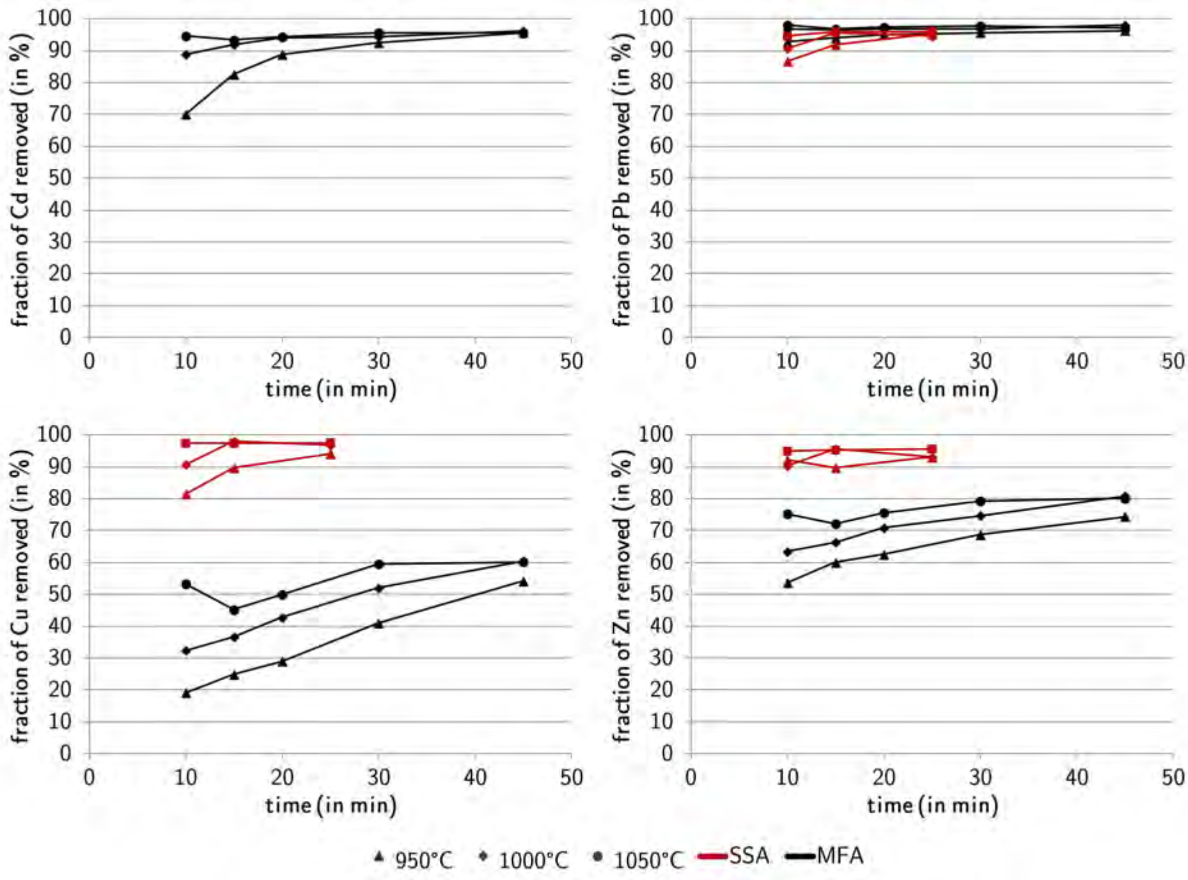


Figure 4.28.: Heavy metal removal from sewage sludge ash (SSA) and municipal solid waste fly ash (MFA). For SSA, Cd was not investigated due its good removal in pre-tests (>99%). Adapted from [6].

Table 4.4.: Heavy metal concentrations in MSW fly ash and sewage sludge ash from Vienna (in ppm). Adapted from [6].

	Cd	Cr	Cu	Ni	Pb	Zn
MSW fly ash	350	500	890	94	4500	19000
Sewage sludge ash	4	160	550	64	260	2000

Table 4.5.: Phase composition of sewage sludge ash used. Adapted from [6].

#	Phase	Formula	Abundance (in wt.%)	Estimated crystallite size (in nm)
1	β-tricalcium phosphate	$\beta\text{-}Ca_3(PO_4)_2$	34.4	61
2	Quartz	SiO_2	28.9	390
3	Hematite	Fe_2O_3	13.3	74
4	Potassium-calcium phosphate	$K_2Ca_2(SO_4)_3$	8.8	
5	Anhydrite	$CaSO_4$	6.8	
6	Magnetite	Fe_3O_4	4.9	
7	Calcite	$CaCO_3$	2.9	
Sum of crystalline phases			100.0	

1000°C, the removal of Cu is about 91% for sewage sludge ash-pellets, but only 32% for MSW fly ash-pellets (compare Chapter 4.4). Best results for the heavy metal removal from MSW fly ash are 95% Cd, 60% Cu, 98% Pb, and 80% Zn (1050°C, 45 min). More than 95% Cu, Pb, and Zn can be removed from SSA at similar conditions.

Because of these significant differences (over all for Cu and Zn) a better understanding of the underlying processes is necessary. Therefore, the following work is carried out:

- Both ashes are characterized by (1) ICP-OES analysis for the heavy metals Cd, Cr, Cu, Ni, Pb, and Zn (Table 4.4); (2) phase analysis is carried out, Table 4.5 and 4.6; and (3) the grain size distribution is measured (average grain size: 75 µm for sewage sludge ash and 150 µm for MSW fly ash).

- Based on ash characterization, thermodynamic equilibrium calculations for possible single reactions are carried out, i. e., the Gibbs free enthalpy is calculated for a set of 27 reactions in dependency of temperature.

It is found that SiO_2, a main component in sewage sludge ash, accelerates the formation of HCl and Cl_2 according to

$$CaCl_2(l) + H_2O(g) + SiO_2(s) \longrightarrow CaSiO_3(s) + 2\,HCl(g) \tag{4.4}$$

$$CaCl_2(l) + \tfrac{1}{2}O_2(g) + SiO_2(s) \longrightarrow CaSiO_3(s) + Cl_2(g) \tag{4.5}$$

because these reactions are thermodynamically favored compared to the analogous re-

Table 4.6.: Phase composition of MSW fly ash used. Adapted from [6].

#	Phase	Formula	Abundance (in wt.%)	Estimated crystallite size (in nm)
1	Calcium aluminate	$Ca_3Al_2O_6$	23.2	11
2	Halite	$NaCl$	13.3	60
3	Sylvite	KCl	10.5	64
4	Calcite	$CaCO_3$	10.3	88
5	Anhydrite	$CaSO_4$	10.2	130
6	Gehlenite	$Ca_2Al_2SiO_7$	9.2	
7	β-tricalcium phosphate	$\beta\text{-}Ca_3(PO_4)_2$	6.4	
8	Lime	CaO	5.2	
9	Quartz	SiO_2	4.0	
10	Siderite	$FeCO_3$	3.2	
11	Periclase	MgO	2.4	
12	Mayenite	$Ca_{12}Al_{14}O_{33}$	2.1	
Sum of crystalline phases			100.0	

actions to CaO,

$$CaCl_2(l) + H_2O(g) \longrightarrow CaO(s) + 2\,HCl(g) \tag{4.6}$$

$$CaCl_2(l) + \tfrac{1}{2}O_2(g) \longrightarrow CaO(s) + Cl_2(g). \tag{4.7}$$

CaO, which is contained is CaO-bearing phases in MSW fly ash, decreases the rate of the reactions in Eqn. (4.6) and (4.6) because of the mass action law. Al_2O_3, also contained in MSW fly ash-phases, leads to the formation of aluminates,

$$CuO(s) + Al_2O_3(s) \longrightarrow CuAl_2O_4(s) \tag{4.8}$$

$$ZnO(s) + Al_2O_3(s) \longrightarrow ZnAl_2O_4(s), \tag{4.9}$$

whereas $CuAl_2O_4$ is stable in both HCl and Cl_2 containing atmospheres, i e. the reactions

$$CuAl_2O_4(s) + 2\,HCl(g) \longrightarrow CuCl_2(g) + Al_2O_3(s) + H_2O(g) \tag{4.10}$$

$$CuAl_2O_4(s) + Cl_2(g) \longrightarrow CuCl_2(g) + Al_2O_3(s) + \tfrac{1}{2}O_2(g) \tag{4.11}$$

will proceed backwards. $ZnAl_2O_4$ is only stable in HCl but can react with Cl_2.

4.5.3. Conclusions

Differences in the removal for different heavy metals are caused by the following reasons:

Cadmium: As highly volatile elements are condensed on the grain surface [65], they are also removed more quickly if the layer thickness is low. The cadmium concentration in MSW fly ash is approx. 100 times higher than in sewage sludge ash, and the specific surface is higher for sewage sludge ash as well.

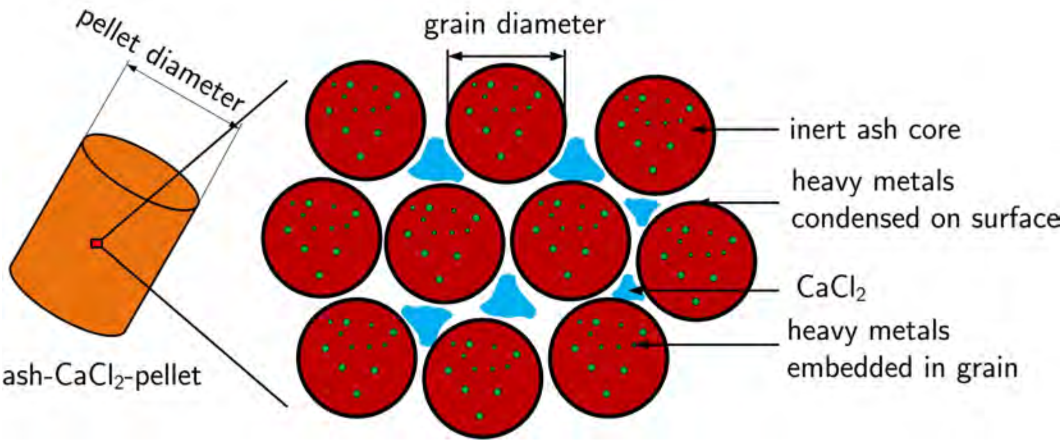


Figure 4.29.: Microstructure of an ash-$CaCl_2$-pellet. Adapted from [6].

Copper, which' concentration is in the same order of magnitude for both ash types, is mainly carried to the fly ash by entrainment [64] and thus not concentrated on the grain surface like highly volatile elements. As the Cu removal is limited by the phase change and/or the diffusion of its chloride CuCl [5], the longer diffusion path through the grain body causes a lower Cu removal from MSW fly ash compared to sewage sludge ash. Additionally, Cu can form stable aluminates in MSW fly ash.

Lead is approx. 10 times more concentrated in MSW fly ash, but its removal is from sewage sludge ash slightly inferior. Probably the formation of Pb silicate is the reason for this behavior. Nevertheless, the removal is in the same order of magnitude and reaches almost 100% in both cases.

Zinc: According to the calculations, it is possible to remove Zn as long as Cl_2 or HCl are available. Thus, different matrix composition might not be the main reason for different removals. The 10-fold Zn concentration in MSW fly ash and the fact that Zn is semi volatile lead to the assumption that physical properties of the ash are more important: Similar effects as for Cd (heavy metal layer on grains) and as for Cu (diffusional effects) occur.

Nevertheless, in both reactors similar results are obtained. Thus it is yet not clear, which technology achieves in larger scales or at different conditions better results.

4.6. Impact of chloride donors for heavy metal removal from MSW fly ash

Cf. [7] (Paper IV, page 109).

4.6.1. Methods

In an indirectly heated laboratory-scale rotary reactor, mixtures of MSW fly ash with different amounts and different types of chlorides are treated batch-wise at 1000°C for 60 min (Figure 4.30). As chlorides, $CaCl_2$ (both in flake form and milled), $MgCl_2$, and NaCl are used; between zero and 200 g Cl per kg ash are added. Similar experiments are conducted in a muffle oven (800 to 1200°C, residence time 20 h).

4.6.2. Results and discussion

$CaCl_2$ and $MgCl_2$ are more effective for most of the heavy metals of concern (Cd, Cr, Cu, Ni, Pb, and Zn) than NaCl, which evaporates in significant amounts without reacting and even decreased the removal of Cd, Cr, Cu, Pb, and Zn in rotary reactor experiments. Thermodynamic equilibrium calculations (Figure 4.31) reveal that NaCl directly chlorinates heavy metals but also vaporizes without reacting in significant amounts; $CaCl_2$ and $MgCl_2$ first form HCl and/or Cl_2 by reacting with H_2O and/or O_2 (indirect chlorination).

With $CaCl_2$ or $MgCl_2$, the removal of Cd and Pb could be insignificantly, and the removal of Ni (only with $CaCl_2$) and Zn significantly increased. Ni removal is apparently limited by the chlorination reaction; only $CaCl_2$ flakes set HCl and Cl_2 free slowly enough for Ni volatilization.

Maximum amounts of heavy metals released are in the rotary reactor: ca. 95-100% Cd and Pb ($MgCl_2$ or $CaCl_2$), more than 80% Cu and Zn ($MgCl_2$), approx. 10% Cr (any Cl donor) and 35% Ni ($CaCl_2$); removals in the muffle oven were generally higher than in the rotary reactor. Depending on the Cl donor, at 1200°C up to 100% Cd, Cu, and Pb, ca. 30% Cr, 75% Ni, and 95% Zn could be vaporized. Higher removals in the muffle oven are found to be due to lower mass transfer into and out of the crucible, increasing the residence time of HCl, Cl_2 or chloride in the crucible which should be taken into account in further research.

4.6.3. Conclusions

During heat treatment, approx. 80-90% Cu and 40% Zn reacted with ash inherent chloride; Cd, Pb, and ca. 10% Cr were either present in ash in volatile form or also reacted with ash inherent Cl.

NaCl directly chlorinates heavy metals. $CaCl_2$ and $MgCl_2$ indirectly chlorinate, i. e. they form first HCl and/or Cl_2 by reacting with H_2O and/or O_2. The latter are generally more effective for heavy metal removal as NaCl evaporates in significant without reacting.

In terms of resource conservation, $MgCl_2$ seems to be the best choice due to high heavy metal removals (especially Zn important) and low remaining chloride, which is necessary for further use of the treated ash.

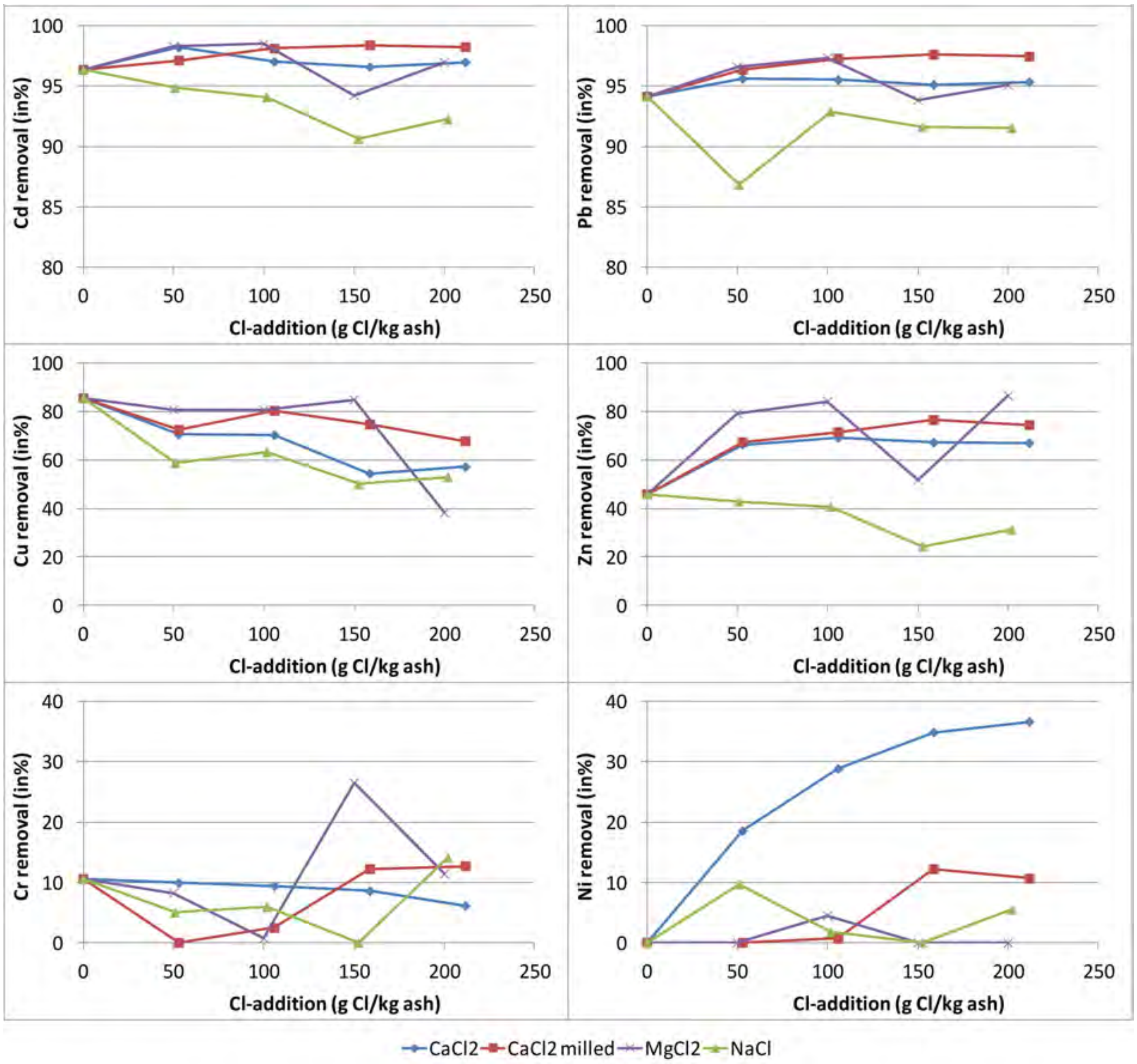


Figure 4.30.: Influence of amount and type of chloride added to MSW fly ash on the removal of heavy metals. From [7].

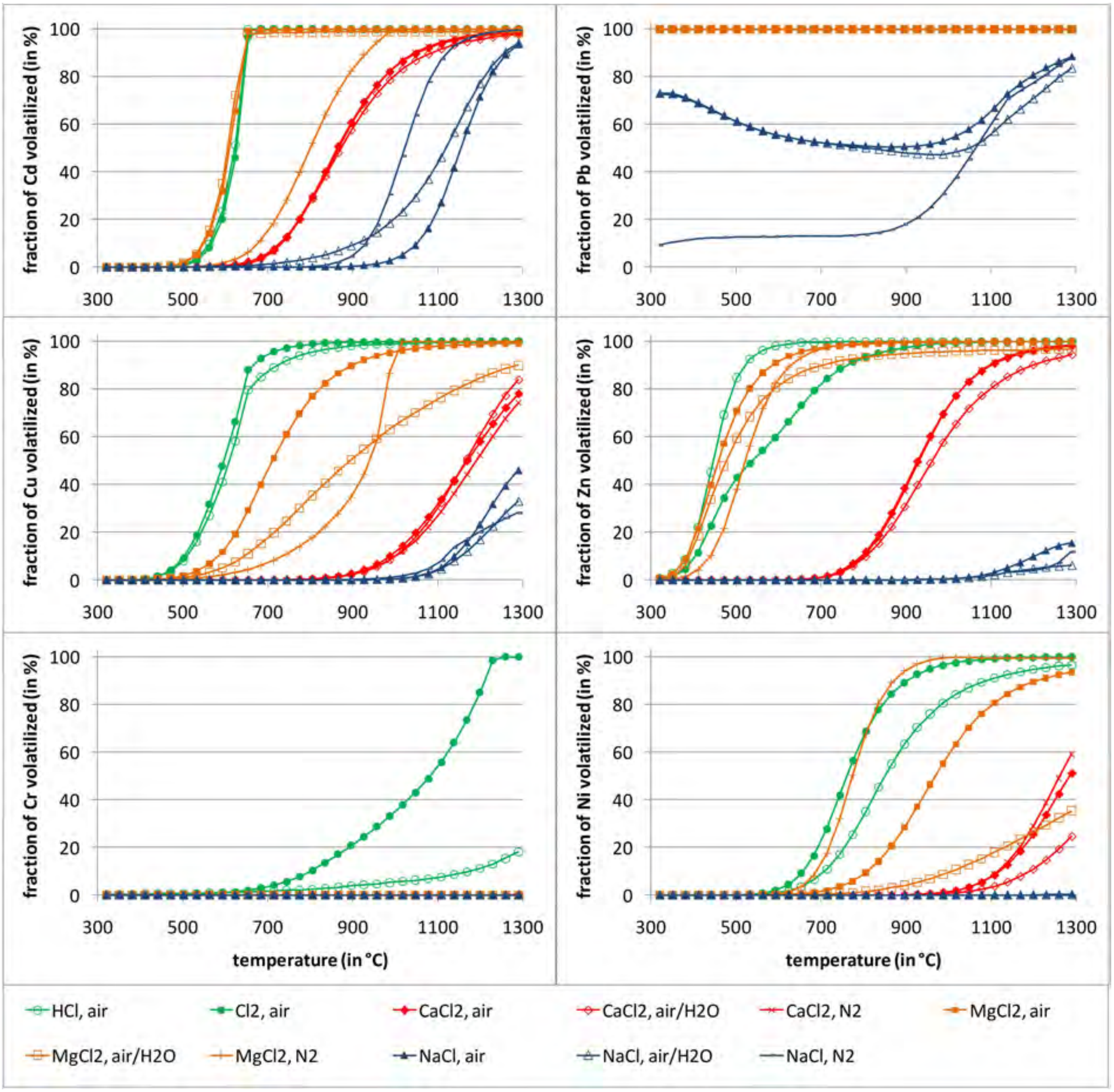


Figure 4.31.: Thermodynamic equilibrium calculations: Influence of atmosphere and chloride donor on the removal of heavy metals. From [7].

4.7. Heavy metal removal from MSW fly ash by carbochlorination

As reducing conditions improve the volatilization of Zn but decreases the one of Cu [63, 83, 100, 114] (compare Section 4.1), it could be a possibility to treat MSW fly ash first at reducing and then at oxidizing conditions. This would lead first to the evaporation of Pb and Zn; in the second step, reduced Cu^0 would be chlorinated and volatilized. This two-step treatment could be realized by two serial rotary reactors, or with one reactor and an injection lance (Figure 4.32): MSW fly ash mixed with chloride (and eventually organic material) is fed to a rotary reactor. This reactor is heated by a burner, whereas fuel is combusted together with air and/or O_2 at air ratios $\lambda < 1$. This leads to reducing conditions in the first section of the continuous reactor and thus to the volatilization of elements like Pb and Zn. Via a lance, air and/or O_2 and eventually H_2O are induced into the reactor. The amount of oxygen in the induced gas mixture is high enough to obtain air ratios $\lambda > 1$. For limiting the temperature in this part, water droplets could be added into the gas. The produced steam could further lead to the accelerated hydrolysis of chlorides and thus to lower remaining chloride in the solid product.

4.7.1. Methods

Instead of using a continuous reactor, experiments are performed in batch mode. MSW fly ash is mixed with $CaCl_2$ (150 g Cl added per kg ash), organic material (approx. 60 g added per kg ash), and water and subsequently pelletized to 3.25 mm pellets.

The pellets are treated in the rotary reactor from Figure 3.2 at 1000°C at residence times between 10 and 45 min. Air from the ambiance is sucked into the reactor.

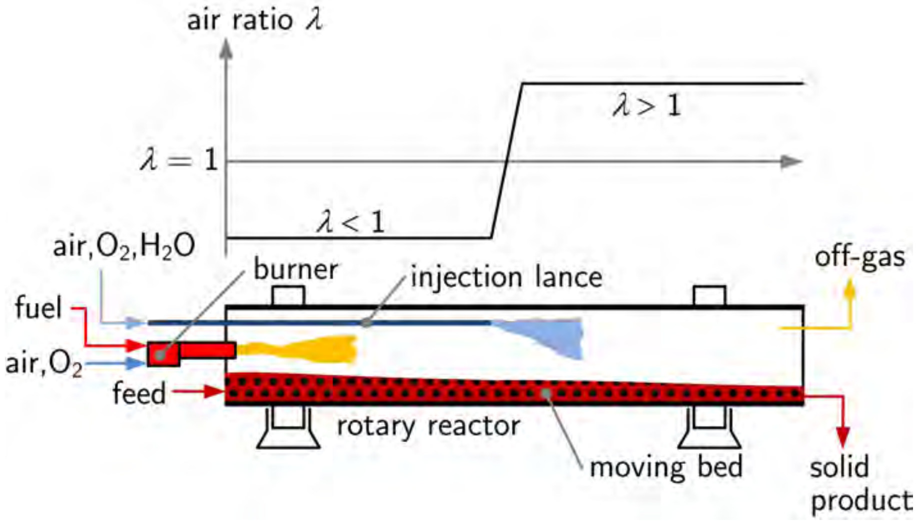


Figure 4.32.: Treatment of an MSW fly ash-chloride mixture (eventually after pelletization) in a rotary reactor at both reducing and oxidizing conditions.

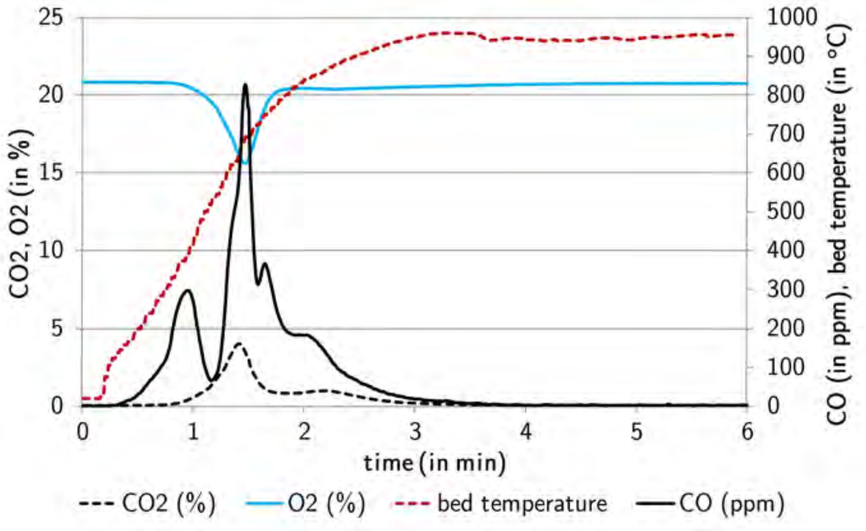


Figure 4.33.: Off-gas analysis of rotary reactor when treating pellets containing organic material. Target temperature 950°C.

4.7.2. Results and discussion

Off-gas analysis

Pellets with organic material added are treated in the rotary reactor. For the latter, the reactor's off-gas is analyzed with NDIR and paramagnetic analysis (Chapter 3.1), see Figure 4.34.

After approx. 3 min, the target temperature is reached in the pellet bed. Already during the heat-up, i. e. after 1.5 min, the oxygen concentration decreases and the CO_2 concentration increases (approx. same amount).

After ca. one minute, a CO concentration of 300 ppm can be detected, which then decreases to ca. 100 ppm before reaching after 3 min (together with CO_2) its maximum (ca. 800 ppm). This two peak behavior reveals that the formation mechanism of CO changes. In fact, it can be visually detected by the flame that after one minute the oxidation of volatilizes from organic material occurs downstream of the batch container; afterwards, the flame moves into the batch container and char is directly combusted in the pellet bed. Char combustion can also be seen from the tailing behavior of the CO_2 concentration (constant in the range from ca. 100 to 140 seconds and then decreasing).

However, with the paramagnetic measurement always $> 15\%$ oxygen can be detected. This is due to the continuous dilution of the reactor's atmosphere by fresh air (and probably by leaks, i. e. air is also sucked in from the off-gas side). Nevertheless, it can bed assumed that for a certain time period, probably two to three minutes, local reducing conditions occur in the bed.

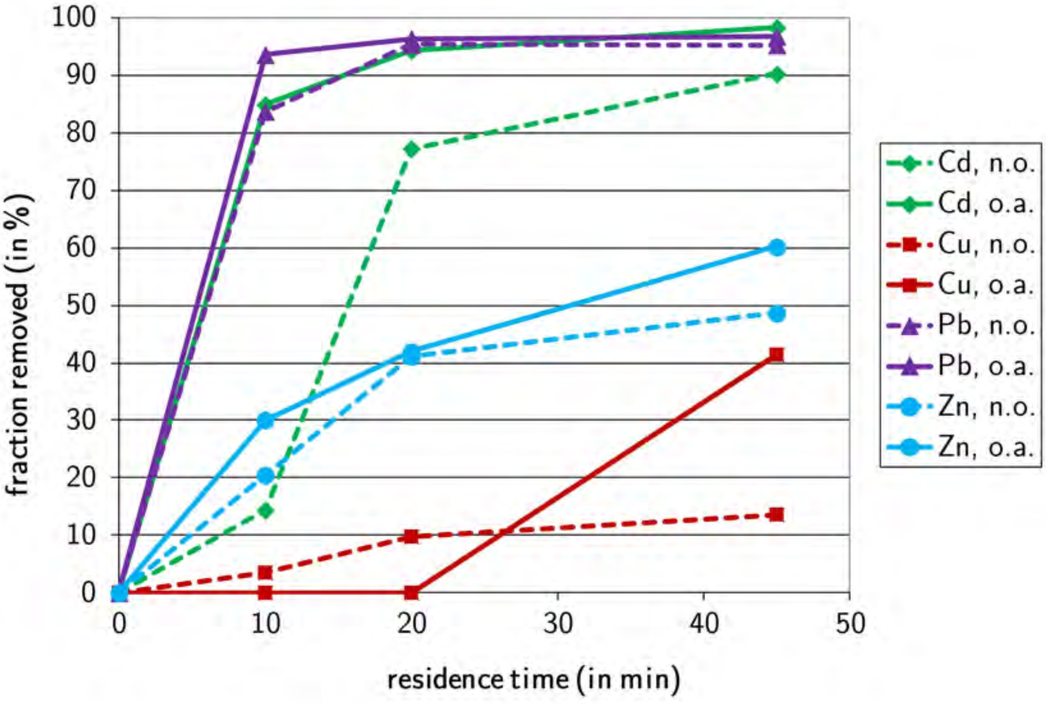


Figure 4.34.: Heavy metal removal from MSW fly ash. Measurements (dots) connected by lines. n.o. = no organic material added, o.a. = organic material added

Heavy metal volatilization

Pellets with and without organic material added are treated in the rotary reactor at 1000°C, see Figure 4.34.

The addition of organic material accelerates removal processes of Cd and Zn. Pb is always removed well, almost independently from the addition of organic material. For Cu, organic material has a negative effect during the first 20 min, after long residence times ($\geq$ 45 min) organic material has a positive effect.

After 45 min, without adding organics, approx. 90% Cd, 15% Cu, 95% Pb, and 50% Zn can be removed in the experiments. With the addition of organic material, these values can be increased to $>$ 95% Cd, approx. 40% Cu, $>$ 95% Pb, and approx. 60% Zn.

Local reducing behavior

Organic material influences the heavy metal removal obviously by its locally reducing behavior. Cd is reduced to elemental Cd^0 (boiling point 767°C; boiling point of $CdCl_2$ 960°C [52]), i. e. volatilization is at lower temperatures possible.

Elemental Cu, which has a boiling point far above its chlorides (CuCl 1400°C, $CuCl_2$ 993°C, Cu^0 2562°C [52]) cannot be removed by reduction. But as the chlorination reaction is thermodynamically favored if heavy metals are present in elemental and not in oxide form, the prior reduction and subsequent chlorination leads to higher fractions volatilized. This is why Cu can be removed well after 45 min.

Pb evaporates at significant higher temperatures then its chloride (Pb^0 1749°C, $PbCl_2$ 949°C [52]), but apparently the reduction to the metal, if it occurs, is not contradictory to its chlorination.

Zn has a similar boiling point as its chloride (Zn^0 907°C, $ZnCl_2$ 726°C [52]). Reduction obviously offers a second pathway for volatilization and therefore improves its removal.

4.7.3. Conclusions

The addition of organic material (60 g per kg ash added) accelerates removal processes of Cd, and Zn. For Cu, organic material has a negative effect during the first 20 min, after long residence times ($\geq$ 45 min) organic material has a positive effect. Pb is always removed well, independently from the addition of organic material.

This behavior is especially for Cu interesting: The reduction to the metal form Cu^0 inhibits its volatilization but enhances the chlorination reaction. Thus, after longer residence times and at oxidizing conditions, the Cu removal can be enhanced as well.

5. Conclusion

The volatilization of heavy metals during combustion processes is strongly influenced by the air ratio and the amount of chlorine, sulfur, and alkalis available (i. e. the composition of the fuel).

Thermodynamic equilibrium calculations revealed that Cl enhances the amount of heavy metals volatilized mostly due to the formation of heavy metal chlorides. On the other hand, due to the formation of stable sulfides (at air ratios $\lambda < 1$) or sulfates (at air ratios $\lambda > 1$) S leads to the immobilization of heavy metals. Alkalis hardly affect heavy metals directly, but due to the reaction with Cl, the amount of heavy metals volatilized decreases with the amount of alkalis in the system. Oxidizing conditions, i. e. air ratios $\lambda > 1$, enhance the volatilization of Cr, Cu and Ni. A reducing atmosphere leads to a higher amount of Cd, Pb and Zn in the gas phase.

Volatilized heavy metals recondense on fly ash particles, which contain heavy metals as well. Heavy metal removal from fly ash can be principally performed by re-volatilizing heavy metals. For example heating, MSW fly ash to approximately 1000°C led to the evaporation of $>$ 95% Cd and Pb, 80-90% Cu, 40% Zn, 10% Cr, and 0% Ni, whereas Cu and Zn reacted with ash-inherent chloride (Cd, Pb and the 10% Cr could also be present in volatile form in the ash). Thus, mid and low volatile heavy metals require extra chloride for their volatilization.

For removing heavy metals from sewage sludge ash or municipal solid waste fly ash, ash was mixed with chlorides (usually 150 g Cl added per kilogram of ash) and treated, eventually after pelletization, thermally at temperatures between 900 and 1100°C. The following conclusions can be drawn:

- Comparing chlorine donors, $CaCl_2$ and $MgCl_2$ are more effective as NaCl. $CaCl_2$ and $MgCl_2$ indirectly chlorinate heavy metals, i. e. they form first HCl and/or Cl_2 by reacting with H_2O and/or O_2. NaCl directly chlorinates heavy metals but evaporates without reacting in significant amounts as well.

- Higher treatment temperatures and longer residence times lead to higher heavy metal removal.

- The ash type has a significant influence on heavy metal removal:

  For sewage sludge ash, already during the heat-up period, a significant amount of heavy metals is removed (more than 50% of Cu, Pb, and Zn were volatilized after 2 min heating from ambient temperature to 950°C in a rotary reactor). After 25 min it is possible to remove at 1050°C up to 97% Cu, 95% Pb, and 95% Zn.

For MSW fly ash, removal processes proceed much more slowly and often less efficiently: At 1050°C after 45 min approximately 95% Cd, 60% Cu, 97% Pb, and 80% Zn can be removed.

Differences in heavy metal removal are caused by different heavy metal concentrations (Cd, Zn), grain size effects (i. e. longer diffusion paths; Cu, Zn), and different matrix compositions leading to different side reactions (Cu, Pb, Zn).

- Pelletizing an MSW fly ash-$CaCl_2$ mixture in order to decrease the amount of entrained particles and treating the pellets in a rotary reactor leads to lower amounts of heavy metals being released; differences are especially significant for Cu and Zn. For example, without pelletization, up to 80% of Cu and Zn can be removed from an MSW fly ash-$CaCl_2$ (150 g Cl added per kilogram of ash) mixture at 1000°C after 60 min. At similar conditions (45 instead 60 min) and pelletizing the mixture, 25% Cu and 60% Zn can be volatilized.

  Chemical analysis of treated unpelletized MSW fly ash-chloride mixtures showed more deviations than the pelletized mixtures. Thus, pellets lead to more reproducible conditions (pellet acting as a microreactor).

- Experiments concerning heavy metal removal from sewage sludge ash-$CaCl_2$-pellets in a rotary reactor revealed that Pb and Zn have similar removal mechanisms. By comparing heavy metal removal in rotary and fluidized bed reactors, it could be shown that both heavy metals are limited by the chlorine availability. Cu is limited by the evaporation and/or the diffusion of its chloride.

- For heavy metal removal from sewage sludge ash, both a fluidized bed reactor and a rotary reactor were found to be suitable reactors. The kinetics of Pb and Zn release were similar in both reactors; Cu removal was significantly higher in the fluidized bed reactor.

- Heavy metal removal from MSW fly ash can be increased by the utilization of $CaCl_2$ or $MgCl_2$ (instead of NaCl) and without pelletization, whereas in terms of resource conservation, $MgCl_2$ seems to be the best choice (high heavy metal removals, low remaining chloride).

  Further enhancement of heavy metal separation is possible by adding organic material to the ash-chloride mixture, which accelerates removal processes. Although thermodynamic equilibrium calculations reveal that reducing conditions decrease the amount of Cu volatilized, prior reduction and subsequent oxidation can also increase the amount of Cu volatilized.

6. Outlook

In this chapter, the author wants to give future researcher some ideas about what to focus on.

6.1. Sewage sludge ash

For sewage sludge ash, it has been demonstrated that heavy metal removal is possible to a very high degree; sufficient amounts of heavy metals can be released after very short residence times [8]. It is also known, that the bio-availability of phosphorus increases during the thermal treatment process due to the formation of new P-bearing phases.

For reducing the energy demand of the thermal treatment process, the formation kinetics of those phases have to be studied. Therefore, high bio-available phases and their formation temperature have to be identified before focusing on the minimum cooling rate for freezing the phase composition at lower temperatures.

6.2. Municipal solid waste fly ash

For MSW fly ash, the heavy metal removing process has to be still improved. Anyway, future work should focus here on reducing conditions (compare Chapter 4.7) and the influence of water vapor on the release of HCl and Cl_2.

As aggregate, probably a tubular furnace could be suitable, as it is possible to seal it completely. For heavy metal analysis, both on-line analysis from the off-gas and the sample could be used. The off-gas analysis would also allow to identify the kinetics.

Focusing on the usage of decontaminated MSW fly ash, one possibility could be the addition to cement due to the hydraulic properties of MSW fly ash. One point to study would be the impact of the addition of water to pure MSW fly ash (before pelletizing for example) on the hydraulic properties of treated ash. Another point would be the addition of certain materials to untreated MSW fly ash (e. g. Al_2O_3, SiO_2, CaO, Fe_2O_3) to improve the hydraulic properties and thus the usage as cement additive.

6.3. Reduction of the energy consumption

The energy demand of the process heavy metal removal from sewage sludge ash or MSW fly ash can be reduced by an optimal process design. When knowing minimum required residence times, the throughput can be optimized which reduces the specific energy

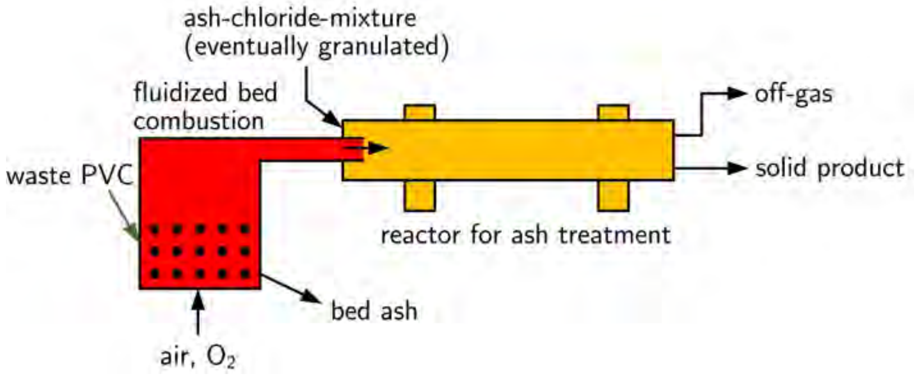


Figure 6.1.: Use of PVC as RDF: Separate combustion of PVC and usage of the off-gas for the thermal treatment process.

consumption. The knowledge of the influence of the external mass transfer allows the usage of a fluidized bed reactor instead of a fluidized bed reactor.

When applying fluidized bed reactor instead of rotary reactor, it is probably necessary to pelletize the ash-chloride mixture before feeding it into the reactor. Pellets have due to their size always the same fluidization behavior (Geldart type D); different types of ashes behave differently. E. g. sewage sludge ash from Vienna seems to fluidize easily (Geldart type A or B); MSW fly ash seems to form channels. Another problem for using fly ash in fluidized beds directly is their grain size and grain size distribution. Pelletizing avoids the entrainment of large amounts of ash.

On the other hand side, pelletization of ash cannot be performed that easily; different ash types behave in this sense different as well. Nevertheless, in a previous work a possibility of improving the compacting process of a die press has been shown [48].

Refuse derived fuels (RDF) can be used to replace the demand of fossil fuels. The usage of especially those RDFs is interesting which do not only substitute energy but also contain important compounds or have other properties. In case of sewage sludge ash, RDFs containing phosphorus are important, e. .g. sewage sludge or meat and bone meal. For heavy metal removal, chlorine bearing RDFs are interesting, e. g. plastic fractions with high amounts of PVC (polyvinyl chloride).

RDFs can either be mixed to the ash-chloride mixture or combusted separately. Adding sewage sludge or meat and bone meal to sewage sludge ash and chloride, mixing and eventually granulating is the best choice. Nevertheless, the resulting phase composition has to be studied. When pelletizing, the resulting pore structure may affect heavy metal removal as diffusion processes could be accelerated.

PVC cannot be pelletized together with ash but it can be added to the ash-chloride mixture or ash-chloride pellets. For the latter, it could be shown that the removal of Cd, Pb, and Zn is improved; Cu has been enriched in the sample [115]. This was due to copper wires sticking at plastic particles of the waste plastic fractions used (cable insulation). Thus, for PVC, separate combustion would be the better choice, e. g. according to Figure 6.1.

A. Papers

The following articles have been published for the present work:

Paper I: Heavy metal removal from municipal solid waste fly ash by chlorination and thermal treatment. *Journal of Hazardous Materials* 179 (2010) 323-331 [4]. For a copy of the manuscript see page 77.

Paper II: Limitations for heavy metal release during thermo-chemical treatment of sewage sludge ash. *Waste Management* 31 (2011) 1285-1291 [5]. For a copy of the manuscript see page 89.

Paper III: Heavy metal removal from sewage sludge ash and municipal solid waste fly ash – A comparison. *Fuel Processing Technology* (2011), accepted for publication [6]. For a copy of the manuscript see page 99.

Paper IV: Heavy metal removal from MSW fly ash by means of chlorination and thermal treatment: Influence of the chloride type. *Chemical Engineering Journal* 179 (2012) 178-185 [7]. For a copy of the manuscript see page 109.

Paper V: Sewage sludge to phosphate fertilizer by chlorination and thermal treatment: residence time requirements for heavy metal removal. *Environmental Technology* (2012), accepted for publication [8]. For a copy of the manuscript see page 119.

Paper I

Journal of Hazardous Materials 179 (2010) 323-331

Visit www.sciencedirect.com for a copy of the article.

Paper II

Waste Management 31 (2011) 1285-1291

Visit www.sciencedirect.com for a copy of the article.

Paper III

Fuel Processing Technology (2011), accepted for publication

Paper IV

Chemical Engineering Journal 179 (2012) 178-185

Visit www.sciencedirect.com for a copy of the article.

Paper V

Environmental Technology (2012), accepted for publication

Visit www.tandfonline.com for a copy of the article.

B. Author's publications

The following pages provide a complete list of the Author's publications.

Publications B. Nowak

page 1/4

Journal publications

B. Nowak, O. Karlström, P. Backman, A. Brink, M. Zevenhoven, S. Voglsam, F. Winter, and M. Hupa. Mass transfer limitations in thermogravimetrical analysis of biomass gasification. *Submitted to Journal of Thermal Analysis and Calorimetry*, 2012.

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B. Nowak, L. Perutka, P. Aschenbrenner, P. Kraus, H. Rechberger, and F. Winter. Limiting steps of heavy metal release during thermochemical treatment of sewage sludge ash. *Waste Management* 31:1285-1291, 2011.

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Conference publications

B. Nowak, S. Frias, F. Winter, P. Aschenbrenner, and H. Rechberger. Thermo-Chemical Heavy Metal Removal from MSW Fly Ash: Influence of Chloride Type and Coke Addition. *Proceedings of International Solid Waste Association World Congress*, Daegu, South Korea, Oct. 17-20, 2011.

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B. Nowak, S. Frias, P. Aschenbrenner, H. Rechberger, and F. Winter. Thermo-chemical heavy metal removal from MSW fly ash: Improvement of the yield. In M. Abián and M.U. Alzueta, editors, *Cleaner Combustion 2011 Scientific Report, 2nd Annual Meeting*, pages 178-179, Zaragoza, Spain, September 7-9, 2011. ISBN: 978-84-615-3062-5. *Poster Presentation.*

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B. Nowak, L. Kubonová, F. Winter, P. Aschenbrenner, and H. Rechberger. Schwermetallabtrennung von Flugasche aus MVAs durch Carbochlorierung. K.E. Lorber et al., editors, *DepoTech 2010 – Abfallwirtschaft, Abfalltechnik, Deponietechnik und Altlasten - Tagungsband zur 10. DepoTech-Konferenz,* pages 739-744, Leoben, Austria, Nov. 3-5, 2010. ISBN: 978-3-200-02018-4. *Poster Presentation.*

B. Nowak, L. Kubonová, F. Winter, P. Aschenbrenner, H. Rechberger, H. Mattenberger, and L. Hermann. Erhöhung der Ausbeute bei der thermochemischen Schwermetallabtrennung von Hausmüllasche. *Chemie-Ingenieur-Technik* 9:1441, *ProcessNet-Jahrestagung 2010 und 28. Jahrestagung der Biotechnologen*, Aachen, Sept 20-23, 2010. ISSN 0009-286-X.

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Publications B. Nowak

Non-scientific publications

Comparing a thermo-chemical process in fluidized bed reactor and rotary reactor. *LOK_MB die Zeitung der Fachschaft Maschinenbau* N. 01a/2011: 14-15

Phosphor aus Klärschlamm. *Nachwachsende Rohstoffe* Nr. 51 – März 2009

B. Nowak S. Voglsam, and N. Zwazl. Factors influencing the release of PVC during combustion – Ein Poster & seine Geschichte. *Der Reaktor (Vereinszeitung des Vereins der StudentInnen und AbsolventInnen der Verfahrenstechnik an der TU Wien)* 95-3/2011: 18-20. ISSN 2070-0873

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C. Author’s curriculum vitae

The following pages provide the author’s curriculum vitae.

Benedikt Nowak

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Education

2009 Apr-2012 Mar	Vienna University of Technology, Vienna, Austria Doctorate in Chemical Engineering • Graduate thesis: Heavy metal separation from incineration ashes by chlorination and thermal treatment • Degree expected March 2012
2011 Mar-May	Stay abroad: Åbo Akademi University, Turku, Finland Research on CO_2 biomass char gasification
2004 Sept-2009 Mar	Vienna University of Technology, Vienna, Austria Process and Chemical Engineering (concentration in Chemical Engineering) • Academic degree Diplom-Ingenieur (Dipl.-Ing.) • Master’s thesis: Heavy metal removal from municpial solid waste fly ash (Schwermetallabtrennung von Hausmüllaschen, in German) • Final examination passed with distinction
2008 Nov-Dez	Stay abroad: VŠB-Technical University of Ostrava, Ostrava, Czech Republic Research on catalytic decomposition of nitric oxides
1995-2003	Secondary school, 2700 Wr. Neustadt, Austria

Military service

2003 Sept-2004 Apr	Austrian Armed Forces, Zwölfaxing, Austria

Professional experience

since 2012 Feb	SMS Siemag Process Technologies GmbH, Vienna, Austria
2006 Jul-2012 Jan	Institute of Chemical Engineering, Vienna, Austria Dissertation, diploma thesis; dust and tar measurements of biomass gasification plants
2007 Aug-Sept	Internship: Scheuch GmbH, Aurolzmünster, Austria Pressure loss calculation of bag house filters
2005 Aug	Internship: Pörner Ingenieurgesellschaft mbH, Vienna, Austria Modeling of the Biturox-process
2004 May-Aug	Materialprüfung G.m.b.H, Gumpoldskirchen, Austria Head of on-site laboratory Fischer-landfill
2003, 2002, 2001 (Aug)	Month-long internships: Materialprüfung G.m.b.H, Gumpoldskirchen Wet chemistry analyses

Awards

2009 Nov	Würdigungspreis 2009 (Appreciation Award 2009), Austrian Federal Minister for Science and Research, 2500 EUR
2009 Nov	Preis für eine hervorragende Leistung (Award for an Excellent Achievement), The Association of German Engineers (VDI), 250 EUR
2009 Oct	Wissenschaftlicher Förderpreis 2009 (Scientific Sponsorship Award 2009), Vienna’s Environmental Department MA 22, 588 EUR
2009, 2008, 2007, 2006, 2005	Merit grants, Deanery for Mechanical Engineering and Science of Management, 1000-1500 EUR

Skills

Languages	• German (native) • English (fluent) • French (basic)
IT Skills	Matlab, FactSage, HSC Chemistry, Latex, Solid Edge
Others	Welder’s qualification test ÖNORM EN 287-1 111 P BW 1.1 RB t6 PA bs (manual arc welding) ÖNORM EN 287-1 135 P BW 1.1 S t10 PA bs (shielded arc welding)

Nomenclature

c	concentration
c_e	heavy metal concentration after treatment
c_0	heavy metal concentration before treatment
c_∞	remaining concentration in the sample
el.	electric
FTIR	fourier transform infrared spectroscopy
g	gaseous
ICP-OES	inductively coupled plasma atomic emission spectroscopy
IF	impact factor
k	apparent reaction rate constant
l	liquid
Me	metal
M_e	mass of solid sample after treatment
M_0	mass of solid sample before treatment
MFA	municipal solid waste fly ash
MSW	municipal solid waste
n. o.	no organic material added
$n_{i,\mathrm{g}}$	concentration of heavy metal i in the gas phase
$\sum_i n_i$	total concentration of heavy metal in the system
NDIR	nondispersive infrared spectroscopy
o. a.	organic material added
PID	proportional-integral-derivative controller
ppm	parts per million
PVC	polyvinyl chloride
r	radius
RDF	refuse-derived fuel
RR	rotary reactor
s	solid
SSA	sewage sludge ash
t	time
T	temperature
VHMC	volatile heavy metal compounds
w_i	mass of element i in 1 kg fuel
WTE	waste-to-energy
x_i	molar concentration of element i in 1 kg fuel
γ	potassium ratio according to Eqn. (4.1)
λ	air ratio

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