Abstract

Fly ash from a municipal solid waste (MSW) incinerator is categorized as a hazardous material. Fly ash contains high amounts of heavy metals which can contaminate the environment. For removal of heavy metals (namely Cd, Pb, Cu, Zn, Ni and Cr), MSW fly ash was treated thermally in co-current batch and continuous mode in a lab-scale indirectly heated rotary reactor at temperature range 950 – 1100°C. Prior to that, fly ash was mixed or pelletized with different additives such as chlorinating agents (mainly calcium chloride), sand or reducing agent as coke. Heavy metal compounds evaporated in different ratios while the maximal removal of heavy metals was required. Influence of different additives in different amounts, influence of temperature or different size fractions of fly ash was studied. MSW fly ash originated from the waste-to-energy plant Fernwärme Wien / Spittelau in Vienna, Austria.

Keywords: municipal solid waste (MSW) fly ash, heavy metals, chlorides, removal, volatilization, thermal treatment, rotary reactor, additives.

Abstrakt

Popílek ze spalovny komunálního odpadu je řazen mezi nebezpečný odpad. Popílek obsahuje vysoký obsah těžkých kovů, které se mohou uvolnit do životního prostředí. Pro odstanění těžkých kovů (jmenovitě Cd, Pb, Cu, Zn, Ni a Cr), popílek byl tepelně zpracován v souproudém vsádkovém a kontinuálním rotačním reaktoru v laboratorním měřítku při teplotách v rozmezí 950°C až 1100°C. Tomu předcházelo smíchání nebo peletizace popílku s různými přísadami jako např. chlorační činidla (především chlorid vápenatý), písek nebo redukční činidlo jako koks. Sloučeniny těžkých kovů se vypařily v různém množství, maximální odstranění těžkých kovů bylo přitom vyžadováno. Vliv různých přísad v různém množství, vliv teploty nebo různých frakcí popílku podle velikosti zm bylo studováno. Popílek pocházel ze spalovny komunálního odpadu a teplárny Spittelau ve Vídni, v Rakousku.

Klíčová slova: popílek ze spalovny komunálního odpadu, těžké kovy, chloridy, odstranění, vypařování, tepelné zpracování, rotační pec, přísady.
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Introduction

Production of municipal solid waste (MSW) has been increasing in many countries. On the other hand capacities of landfill sites are not unlimited. Therefore incineration of municipal solid waste has been applied, even in such country as Switzerland or Austria, untreated municipal solid waste must not be landfilled directly.

Fly ash originated from municipal solid waste incinerators is classified as a hazardous material. Fly ash contains high amounts of heavy metals which can contaminate soil and water by leaching. Therefore fly ash is usually stored in underground or in specially designed landfill sites. However high concentrations of heavy metals make fly ash as a potential source compared with raw materials such as ores.

Thermal treatment of fly ash at temperatures below its melting is most effective in separating the heavy metals from the fly ash by evaporation. Effect of temperature, residence time, type and velocity of carrier gas, different conditions such as oxidizing or reducing and other parameters can influence the thermal treatment of fly ash. Volatilized heavy metal compounds are captured and recovered in the flue gas cleaning system. Solid residues can be used as an additive for cement.

In previous study, the influence of temperature, residence time, gas velocity and additives such as chloride (calcium chloride) and an organic material was studied and described in detail. On basis of these results, fly ash was mixed or pelletized with other additives such as chlorinating agents (calcium chloride, magnesium chloride or PVC), sand, coke or another organic material for maximal removal of heavy metals (namely Cd, Pb, Cu, Zn, Ni and Cr). The effect of different size fractions of fly ash was also investigated. Mixtures or pellets were treated in a lab-scale indirectly heated rotary reactor at temperature range 950 – 1100°C, in batch and continuous modes. The main interest was to understand the chemical processes and changes during thermal treatment of fly ash. Samples of pure fly ash and pellets were also treated at the constant temperature for longer time (24 hours) in a muffle oven and further phase changes were analyzed.

This work is part of the Vienna Spots of Excellence (VSoE) Project “Urban Mining”. The aim of the project is the recycling of nutrients and heavy metals from incineration residues of the city of Vienna. The project is in cooperation with the working group of Prof. Franz Winter of the Institute of Chemical Engineering, Vienna University of Technology, the working group of Prof. Helmut Rechberger of the Institute for Water Quality, Resource and Waste Management, Vienna University of Technology and the company ASH DEC Umwelt.
AG, with a headquarter in Vienna and a branch office in Leoben. This diploma thesis was financially supported by the project AKTION.
1. Municipal solid waste (MSW)

1.1. Characteristics, treatment and utilization of MSW

Municipal waste is defined as “waste from households, as well as other waste, which, because of its nature or composition, is similar to waste from households”, according to [12].

Waste management system defines utilization of MSW which includes material reuse and recycling, anaerobic digestion, composting, combustion with energy recovery or landfilling of MSW. [46]

The composition of MSW can be divided into:

1) Combustible waste (72 %): various inorganic wastes (e.g. paper, paperboard and plastics), wet organic waste (e.g. wood, yard waste and food waste); bulk waste shredding and/or refuse derived fuels (RDF) production. Energetic properties of combustible fraction of MSW are moisture content, ash content, volatile matter, coal content, sulphur content, chlorine content, and gross and net calorific value.

2) Others (18 %): recyclable waste (e.g. cans, PET and glass bottles), bulk waste (electric and electrical appliances) and incombustible waste. MSW does not include industrial waste, agricultural waste, sewage sludge and hazardous waste (e.g. batteries and medical waste). [27]

The recent trend for utilization of solid wastes is to separate the valuable substances by use of advance separation technologies. Metals are selectively collected and sent to metallurgical plants as raw material with high purity. Plastics and biomass are separated to make so-called refuse derived fuel (RDF) or refuse derived paper-plastics fuel (RPF).

The composition of MSW depends on socio-economic level and climatic conditions of countries. In developed countries, the largest fraction is paper and sorted organic wastes. Compared with developing countries, there is smaller moisture content (20-30 %) and about half more of the calorific values of MSW (in average 10 MJ/kg). [7, 30, 46, 62]
1.2. Characteristics of municipal solid waste incineration (MSWI)

The shortage of available space for landfilling has urged communities to decrease the volume of solid wastes by incineration. See recovery and disposal rates for MSW in European countries in the year 2006 (Figure 2).

Before incineration of MSW, important is a selective collection and a separation of combustible and non-combustible components. The combustion of MSW starts after 30 s. The
weight loss occurs within the first 2 minutes of incineration (water vaporization and a quick release of volatile compounds). The most important reaction in MSW incinerator is the combustion of carbon and its compounds to CO$_2$. For rock-forming elements (Si, Fe, Ca, Al, Mg) and heavy metals (Zn, Cu, Pb, Cd), only their chemical speciation and phase can be influenced by incineration.

**Advantages of incineration** are hygienization, reduction of volume (nearly 90%), environmentally friendly emissions (high destruction of organics and toxic compounds), complete mineralization (about 98% of carbon is transformed to CO$_2$), immobilization of bioavailable inorganic substances, landfill volume conservation, energy utilization and resource recovery. [21, 24, 30, 35, 51, 62]

![Figure 3. Waste-to-energy plant, Spittelau, Vienna.](image)

**1.2.1. Situation in the Czech Republic**

In the year 2008, there are three waste-to-energy plants in the regions of the Czech Republic: the Prague region (Pražské služby, a.s.), the Liberec region (Termizo, a.s.) and the Southern Moravian region (SAKO Brno, a.s.).

The total production of MSW in the Czech Republic is 3176 kt/year in 2008. The amount of 377 kt/year (totally 11.9%) was incinerated in comparison with the total capacity of waste-to-energy plants which is 646 kt. To the future, five other waste-to-energy plants are
planned to be established in the regions: the Plzen region, the Usti region, the Pardubice region, the Vysočina region and the Moravian-Silesian region. [8]

1.3. Types of residues from MSWI

Residues of incineration are exhaust gas, air pollution control (APC) residues such as boiler ash, filter ash, gas cleaning residues, and bottom ash. [35]

![Figure 4. Distribution of mass in wastes (slag, fly ash, clean gas) from MSW incineration.](image)

1.3.1. MSW fly ash

Fly ash from a MSW incinerator is categorized as a hazardous material (19 01 05, 19 01 07, 19 01 13), according to [16]. Fly ash is landfilled into specific landfill sites, due to the possibility of contamination of soil and underground water by leaching and content of high concentration of hazardous heavy metals. [45]

Fly ash has an aluminosilicate structure with alkali and calcium salts (as chlorides, carbonates, sulfates, etc.). Heavy metals are presented mainly as oxides, chlorides, sulfates and silicates. The elements volatilized during combustion condense on the surface of the fly ash particles when the flue gas is cooled down. Residues of air pollution control devices contain a higher proportion of heavy metals and soluble components than bottom ash. Element concentration of several heavy metals contained in MSW fly ash and MSW bottom ash exceed 1 to 4 orders of magnitude from the average earth’s crust (Figure 5). [2, 3, 35]
Figure 5. Comparison of elemental concentrations in the earth’s crust, ores, filter ashes and other materials [35].

Note: Numbers are the orders of magnitude of concentrations relative to those in the earth’s crust.

1.3.2. Bottom ash and air pollutants from MSWI

**Bottom ash**

Bottom ash is highly inhomogeneous and difficult to handle. Bottom ash is transported to landfill sites on the results of leaching test and pH and the loss of ignition tests. About 50% or more of treated MSWI bottom ash is used as secondary building material and in other civil engineering applications. [3, 45]

**Air pollutants**

Air pollutants from incineration are: 1) ash, char, tar, soot particles, 2) volatile organic compounds (VOC – PAH, dioxins, furans), 3) gases and acids (HCl, Cl₂, HF, H₂SO₄, SO₂, NOx, H₃PO₄, CO, CO₂, HCN and phosgene), 4) radioactivity and mutagens, and 5) trace elements (Cr, Cu, Ni, Zn, and Cd, Hg, Pb in particular).

Mercury Hg remains in the gas phase because the temperature of the flue gas is too high for mercury to condensate. [9, 30, 51, 52]
The flue gases should reach a temperature of at least 850°C for 2 seconds to ensure the proper destruction of toxic organic substances such as PCDDs/PCDFs. Up-to-date waste-to-energy plants lower PCDDs/PCDFs emissions to tenths of ng/Nm³ [23, 45].

1.4. Origin and distribution of heavy metals in MSW incinerator

Origin of heavy metals

It is necessary to identify the source of each metal to better investigation of the influence of feedstock on metal content in fly ash.

Origin of Pb: accumulators, alloys, paints, pigments, electronics, pipes, gasoline additives, etc. A big contribution rate is in low volume-high concentration items, such as small sealed lead batteries and lead tubes of paint.

Origin of Cd: accumulators, anti-corrosive coatings, paints, pigments, alloys, plastics, etc. A big contribution rate is in low volume-high concentration items, such as in nickel-cadmium batteries, dry batteries.

Origin of Zn: anti-corrosive coating, batteries, alloys, medicine, construction industry and plastics.

Origin of Cu: electric cables, electronics, alloys, colors/pigments, construction industry and herbicides.

The production amount of metals (Cu, Pb, Zn, etc.) has risen with an increase in global population and industrial development. However, the securing of resources is a critical problem to the future. Therefore urban mines could stabilize the supply of rare metals by recovery of end-of-life products (wastes). Fly ash processing in contrast with a source of raw materials such as ores includes savings of investments, operational costs and energy from mining (crushing, screening and grinding). [17, 28, 35, 38, 62]

Distribution of heavy metals in MSW incinerator

The heavy metal concentration in MSW compared to other solid fuels (biomass and coal) is relatively high. Heavy metals in MSW incineration may evaporate or react or show no response. [46]

Categorization according to their volatility (Figure 6):

1) Volatile metals: Heavy metals with a high vapor pressure and a low boiling point are found in the fly ash (such as Pb, Zn, As, in 1/3 from the total amount) and/or in the flue gas (such as Hg, Cd). These metals evaporate as chlorides or gases. The content of heavy metals in fly ash may increase to level possibly comparable with ores.
2) Non-volatile metals: Heavy metals with a low vapor pressure and a high boiling point remain in the bottom ash (such as Fe, Cu, Cr, Ni, and Pb, Zn, As, in 2/3 from the total amount). The quantity of bottom ash is relatively great but the heavy metal content in it is quite low.

3) Other metals: Distribution of heavy metals can vary with the composition (such as content of reactive compounds – chlorine, sulfur, aluminosilicate), the moisture of MSW, and furnace incineration operating conditions (such as temperature, gas composition and residence time). [27, 44, 53, 55, 60, 62, 63]

![Figure 6. Vapor pressure of metals and its dependence on the temperature. [49]](image_url)
2. Characteristics, treatment and utilization of MSW fly ash

To estimate true economic value, all relevant factors for metal recovery as the cost of pretreatment, transfer, the disposal cost of toxic metals from pretreatment should be taken in account. Long-term risk minimization is as the goal of future investors. [27, 35]

2.1. Landfilling

2.1.1. Landfill practices of MSW fly ash

Most fly ash is just landfilled, cemented prior to disposal due to reduction of the heavy metal leachability. The conditioned ashes are stored in controlled locations like specially designed landfills or geologically stable, underground salt mines (e.g. in the northern Germany). Fly ash pretreatment by physical and chemical immobilization or by removal of contaminants as by thermal treatment can simplify landfill design and operation. [27, 35, 42, 44]

Landfilling is the cheapest way of disposing of MSW, as long-term effects and external costs are not considered. Disadvantages of landfilling are possibility of leaching of organic and inorganic pollutants in long-term disposal, limited special resources and emission of greenhouse gases (such as methane). [32, 43]

2.1.2. Standard for landfilling of wastes

A hazardous waste and hazardous properties of waste are characterized according to [1, 13, 15]. Fly ash from municipal solid waste incinerator is classified as hazardous material according to hazardous property of waste H13 – “Substances and preparations capable by any means, after disposal, of yielding another substance, e.g. a leachate, which possesses any of the characteristics listed above”. A significant number of countries use leachate tests as a regular test method however the leachate testing procedures differ from country to country and are not implemented in all countries. Limit concentrations in a leachate see Table 1.

Requirements for landfilling of waste and its use on the surface of the ground are directed in the Czech Republic by [14] according to [12]. Wastes are divided based on the type and the category of wastes, their actual properties, water leaching rate, mutual mixability and content of pollutants in dry matter.

Landfill sites are categorized in accordance with leaching classes as landfill site for inert waste, landfill site for other waste and landfill site for hazardous waste. Hazardous
wastes can be landfilled to the landfill site categorized as other waste if a hazardous waste is stabilized by solidification or if a hazardous waste is placed into close containers or vessels. Otherwise a hazardous waste is landfilled to the landfill site categorized as a hazardous waste. Fly ash from MSW incinerator can be landfilled after stabilization to one-sort landfill site. [12, 14]

Table 1. Limit concentrations in a leachate for evaluation of hazardous property H13, [15].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Limit value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td></td>
<td>5.5 - 13</td>
</tr>
<tr>
<td>Conductivity</td>
<td>mS/m</td>
<td>2000</td>
</tr>
<tr>
<td>Phenol index</td>
<td>mg/l</td>
<td>100,0</td>
</tr>
<tr>
<td>Cyanide (total)</td>
<td>mg/l</td>
<td>20,0</td>
</tr>
<tr>
<td>Cyanide (easy to release)</td>
<td>mg/l</td>
<td>10,0</td>
</tr>
<tr>
<td>As</td>
<td>mg/l</td>
<td>5,0</td>
</tr>
<tr>
<td>Cd</td>
<td>mg/l</td>
<td>0,5</td>
</tr>
<tr>
<td>Cr total</td>
<td>mg/l</td>
<td>50,0</td>
</tr>
<tr>
<td>Hg</td>
<td>mg/l</td>
<td>0,05</td>
</tr>
<tr>
<td>Ni</td>
<td>mg/l</td>
<td>50,0</td>
</tr>
<tr>
<td>Pb</td>
<td>mg/l</td>
<td>10,0</td>
</tr>
<tr>
<td>Se</td>
<td>mg/l</td>
<td>5,0</td>
</tr>
</tbody>
</table>

2.2. Thermal treatment

Thermally treated fly ash could be possibly used in construction industry and heavy metal concentrates as ore sources. A disadvantage of the thermal process is the high-energy cost. An economic efficiency of thermal treatment should include process costs, gate fees for wastes, disposal costs and sale price of secondary materials. [2, 58, 59, 60]

2.2.1. Sintering process

Sintering temperatures are 700-1100°C which is lower than melting point of fly ashes. During sintering process, material is under the influence of excess surface tension and mineral phase reconfiguration. It is leading to a denser product with reduced porosity and enhanced strength. Small ash particles show a higher compressive strength after sintering. [42, 54]

Advantages of sintering process are reduction of weight and volume, encapsulating the hazardous compounds, lower operation cost and lower technological requirement. Application of sintering products is the production of lightweight aggregate, cement or pavements. [56]
2.2.2. Vitrification

During vitrification, residues are mixed with glass precursors and combined at high temperatures (1000–1600°C) into a single-phase amorphous, glassy product. Elements (such as Al, Si, Fe etc.) get enriched in the slag phase due to the reduced total mass of the ash. Heavy metals are immobilized by vitrification. [35, 42, 59]

2.2.3. Melting process

Melting process is similar to vitrification, but does not include the addition of glass-forming materials. It results in a multiple-phased product. Ash melting plants treat MSW incineration residues by direct heating (fuel-burning) or indirect heating (electric). Melting of fly ash or mixture of fly ash and bottom ash at high temperatures (over 1300°C) converts the majority of ash into slag. Melting furnace fly ash (MFA) is also generated which contains evaporated heavy metal compounds. Disadvantage is high energy consumption, a possibility of leaching at a later stage and higher effort for possible recovery. [27, 37, 39, 42]

2.3. Solidification/stabilization

There are several methods such as solidification with cement, stabilization by ferrous sulphate, phosphate or carbonates to decrease a harmful leaching from fly ash.

Cement solidification is usually applied for the stabilization treatment of the fly ash. It is an inexpensive and effective method of immobilization using Ordinary Portland Cement (OPC). Materials produced this way are not harmful for environment and can be stored or used in e.g. road construction. However, binding of heavy metals does not have to be permanent. [2, 19, 39, 59]

2.3.1. Standard for concrete production

The concentrations of heavy metals should be in the range of the guidance levels given for pulverized coal ash and blast furnace slag for the production of cement and concrete published by BAFU (Federal Office for the Environment, Swiss Guideline for Reuse as Cement/Concrete Addition). The values for heavy metals are Cd 5ppm, Pb 75ppm, Cu 200 ppm, and Zn 2000 ppm. Austrian regulation on concrete disposals determines the limit values for heavy metals as for Cd 10 ppm, Pb 500 ppm, Cu 500 ppm and Zn 1500 ppm. [35, 39].
2.4. Wet extraction and separation of heavy metals

Wet separation methods extract many toxic and problematic substances from the residue matrix. Leaching is a low cost and easily applied method. Main factors affecting the leaching are temperature, retention time, acid/alkaline concentration and physical characteristics of ash (such as specific surface area, porous size, particle sizes, amount of carbon and buffering capacities of the ash). For acid leaching, sulfuric, hydrochloric and acetic acid can be used. As the disadvantage of this method is that some impurities are also dissolved by acid. For alkaline leaching, sodium hydroxide can be used. [2, 3, 11, 37, 53, 55]

Leaching is a low cost and easily adopted method for removing many toxic and problematic substances from the residue matrix for further recovery and recycling. [60]
3. Separation of heavy metals by thermal treatment

3.1. Heavy metals removal chemistry

3.1.1. General characteristics

The primary factor that determines whether an element is present in the core of the fly ash particles or on their surface is the boiling point. [63]

Class I (e.g. K, Mg, Ca, Al, Si, Sc, Ti, Mn, Fe, Rb, Cs): Elements which have high boiling points and low vapor pressures are not volatilized at the combustion temperature. They form the matrix of fly ash and are only minimally deposited on the surface. They could serve as the nucleation particles.

Class II (Zn, Ga, As, Se, Mo, Cd, Sb, W, Pb): Elements which have low boiling points and high vapor pressures are volatilized during combustion. As temperature of exhaust gas is decreased, their compounds condense on the surface of the fly ash particles.

Class III (Be, Na, V, Cr, Co, Ni, Cu, Sr, Ba): Behaviour of these elements is dependent on the combustion conditions.

Class IV (B, Br, F, Cl, S and Hg): These elements remain in gas phase throughout the process. They undergo volatilization but not condensation. [17, 63]

Factors influencing the vaporization behaviors

1) Effect of temperature: Temperature has an exponential influence on the saturated vapor pressure of most compounds. Generally at higher temperatures, the rate of vaporization increases. In some situations, increased temperature has no effect on the evaporation rate which depends significantly on the mineral matrix.

Thermal treatment of fly ash at temperatures below its melting is most effective in separating the heavy metals from the fly ash by evaporation. [48]

2) Effect of chemical composition: Alkali metals (Na, K) may influence the vaporization because of their affinity for chlorine. Metal sulfates evaporate at low temperature (below 800°C), then metal chlorides which are easily formed than oxides and therefore easily removed. The latest, metal oxides and metallic elements evaporate at higher temperature.

3) Effect of reaction atmosphere: The higher the moisture is the longer time is needed to reach the peak temperature of ignition. The moisture leads to the formation of non-volatile oxides of Zn and Pb (A). It causes the interaction of metal oxides with mineral matrix (e.g. SiO₂, Al₂O₃), which leads to the formation of stable compounds (B, C). Despite of this, an
increase of moisture slightly increases the volatilization of chlorides and metallic form of Cu. [9, 48, 52, 56, 60, 63]

\[
\begin{align*}
\text{ZnCl}_2 + \text{H}_2\text{O} \rightarrow \text{ZnO} + 2\text{HCl} & \quad \text{(A)} \\
2 \text{ZnO} + \text{SiO}_2 \rightarrow \text{Zn}_2\text{SiO}_4 & \quad \text{(B)} \\
2 \text{ZnO} + 2 \text{Al}_2\text{O}_3 \rightarrow 2 \text{ZnAl}_2\text{O}_4 & \quad \text{(C)}
\end{align*}
\]

**Maximum degree of vaporization** is mainly determined by two competing, simultaneous reactions:

1) reaction with some elements (e.g. chlorine) to form more volatilized compounds,
2) interaction between heavy metals with matrix compounds (e.g., Fe$_2$O$_3$, SiO$_2$ or Al$_2$O$_3$), which result in more stable and non-volatile metallic species. In the beginning of vaporization, particles shrink rapidly due to organic matrix burning, so the metallic compounds are released into the gas stream without any limitation. Therefore not only metal vaporization but also explosive fragmentations explain particle formation, so interactions between minerals and metals become important. [62]

**Condensations behaviors:**

1) Heterogeneous condensation takes place on particles surface which result in an enrichment of metals in the fine particulate fractions. Most of volatile elements condense during cooling of combustion products down to 140°C.
2) Homogenous nucleation occurs where not enough particle surfaces are available, or super-saturation of the vapor is sufficiently high. [17, 63]

**3.1.2. Thermodynamics and kinetics**

The total rate of vaporization is controlled by heat and mass transfer rates, reaction kinetics and thermodynamic properties. [46]

In the case of chemical equilibrium, the Gibbs free enthalpy of a reaction at temperature T can be calculated. The more negative the free enthalpy $\Delta G^\circ$, the higher the driving force is for a given chemical reaction. In real situation, the system is chemically and thermally heterogeneous, and the equilibrium is not completely reached. [22, 28]
Relationships between $E$ (recovery efficiency, volatilization efficiency) and $\Delta G^0$

1) Metals with large $E$ (Zn, Cu, Pb, Cd) have a large negative $\Delta G^0$ and form stable chlorides,

2) Metals with very small $E$ (Cr, Fe, Ba, Ti, V, Mg, Al, Sr, Ca) have large positive $\Delta G^0$ and are stable as oxides,

3) Metals in between (Co, Mn, Ni) form oxides or chlorides [9].

See Figure 7, which shows the predictable chemical reactions in pellets and the variation of the Gibbs free energy of these reactions.

![Figure 7. Variations of $\Delta G^0$ as the function of temperature. [32]](image)

Rate of heavy metal evaporation can be described by a simple first-order rate low (1), [25]:

$$ M_{m,T}(t) = a_{m,T} (1 - e^{-k_{m,T}t}) \quad [\%] $$  \hspace{1cm} (1)

where  $M_{m,T}$ is  amount of evaporated heavy metal  [\%]

$a_{m,T}$  -  asymptotic value  [-]

$k_{m,T}$  –  rate coefficient  [s$^{-1}$]

$t$  –  time of evaporation  [s]

Arrhenius equation describes the temperature dependence on the evaporation rate coefficient (2):

$$ k_{m,T} = k_{0,m}e^{-E_m/RT} \quad [-] $$  \hspace{1cm} (2)

where  $E_m$ is  constant parameter  [-]
Kinetic limitation of the evaporation is a diffusional resistance inside the pellets. In a porous mineral material, the vaporization is controlled by mass transfer limitations. In an organic matrix, the particles shrink rapidly when the matrix burns, and no internal transfers control the volatilization of metallic compounds. [37, 63]

3.2. Additives

3.2.1. Chlorinating additives

Principle of chlorination

Evaporation of heavy metals is possible if there is a residual chloride present. Interaction of chlorine and heavy metals leads to volatile heavy metal chlorides and to prevention from the transformation and incorporation of volatile heavy metals into the matrix. Metal chlorides are usually more stable than their oxides or sulfides under the same partial pressure because of their lower Gibbs free energy of formation. Chlorides have also lower boiling and melting points and higher vapor pressures compared with the oxides. Added chloride can lower the melting point of some compounds in fly ash and the viscosity of a molten phase, so the rate of diffusion increases. Chlorine also decreases the particle size of fly ash. [10, 25, 63]

Temperature is key factor in chlorination. In the temperature range 100 – 600°C, non-volatile chlorides are formed and the recovery by water leaching is possible. In the range 600 – 1000°C volatile chlorides are formed and the recovery is performed by condensation. [10, 18, 55]

![Figure 8. Evolution of vapor pressure of several chlorides.][21]
Reactions

Direct chlorination as self chlorinating potency (e.g. with CaCl$_2$), (D):

$$ \text{MO (s) + CaCl}_2 (g) \rightarrow \text{MCl}_2 (g) + \text{CaO (s)} \ (\Delta G^o) $$  

Indirect chlorination with chlorinating agent which is more probable (E, F), [9]:

$$ \text{CaCl}_2 (g) + \frac{1}{2} \text{O}_2 (g) \rightarrow \text{CaO (s) + Cl}_2 (g) $$  
$$ \text{MO (s) + Cl}_2 (g) \rightarrow \text{MCl}_2 (g) + \frac{1}{2} \text{O}_2 (g) \ (-\Delta G^o) $$  

The main chlorine release occurs above the melting point of calcium chloride. Tendency of chlorination agents to release chlorine depends on equilibrium partial pressure of chlorine from chlorination agent under a constant partial pressure of oxygen. Metal oxides MO should be stable chemically and have low vapor pressure. In the case of humidity effect, the reactions (G, H) are increasing in importance. [10, 18]

$$ \text{CaCl}_2 (g) + \text{H}_2\text{O (g) \rightarrow CaO (s)+ 2HCl (g) } $$  
$$ \text{MO (s) + 2HCl (g) \rightarrow MCl}_2 (g) + \text{H}_2\text{O} $$  

The results presented in [18] show that below cca.600°C the reactions of the heavy metal oxides with HCl (g) are thermodynamically favored in comparison to reactions with Cl$_2$ (g). Above this temperature the opposite is the case. [4, 9, 52]

Figure 9. Residual Cl in the mixture ash + additive in TGA test (initial amount 10 % of Cl) [41]

Incorporating effect of Cl-donor resulting in metal chloride evaporation, directly (I): [35]

$$ x \text{MO (s) + CaCl}_2 (g) + y \text{SiO}_2 (s) \rightarrow x \text{MCl}_2 (g) + x\text{CaO}$y\text{SiO}_2 (s) $$  

I
Or indirectly in dry conditions (J, K) or in humid conditions (L, M): [35]

\[ 2x \text{CaCl}_2 (g) + y \text{SiO}_2 (s) + x \text{O}_2 (g) \rightarrow 2x \text{CaO}.y \text{SiO}_2 (s) + 2x \text{Cl}_2 (g) \quad (J) \]

\[ 2x \text{MO} (s) + 2x \text{Cl}_2 (g) \rightarrow 2x \text{MCl}_2 (g) + x \text{O}_2 (g) \quad (K) \]

\[ 2x \text{CaCl}_2 (g) + y \text{SiO}_2 (s) + x \text{H}_2\text{O} (g) \rightarrow 2x \text{CaO}.y \text{SiO}_2 (s) + 2x \text{HCl} (g) \quad (L) \]

\[ 2x \text{MO} (s) + 2x \text{HCl} (g) \rightarrow 2x \text{MCl}_2 (g) + x \text{H}_2\text{O} \quad (M) \]

Impact of matrix (such as silica or alumina) with presence of e.g. CaCl₂ results in formation of CaSiO₃ (thermodynamically favored), so the ability of available chlorine from CaCl₂ increases and the evaporation of metal chlorides increases. [24, 35, 62]

However the reactions which lead to the formation of volatile heavy metal compounds are in competition to those with matrix compounds. Mostly silicates and aluminates reduce the maximum amount of heavy metals (N, O). The existence of oxygen shifts the equilibrium of the reactions to form non-volatile compounds, mainly in the case of Zn and Cu. [41, 62]

\[ 2x \text{MCl}_2 + y \text{SiO}_2 (s) + x \text{O}_2 (g) \rightarrow 2x \text{MO} (s) + y \text{SiO}_2 (s) + 2x \text{Cl}_2 (g) \quad (N) \]

\[ x \text{MCl}_2 + y \text{SiO}_2 (s) + x \text{H}_2\text{O} (g) \rightarrow x \text{MO} (s) + y \text{SiO}_2 (s) + 2x \text{HCl} (g) \quad (O) \]

Advantages of the chlorination process are low melting point and boiling points of chlorides, their low cost, easy availability, low toxicity and unproblematic handling of the chlorination process. Disadvantage is that the high concentration of chlorine compounds in the atmosphere of reactor can be extremely corrosive and shorten the life-time of the reactor. [18, 29, 36]

**Chlorination agents**

Gaseous reagents: Chlorine Cl₂ (g) is the best Cl-donor, but require safe handling. Cl₂ evokes total recovery e.g. for Co and Ni. Hydrogen chloride HCl (g) is also superior Cl-donor.

Liquid reagents: e.g. carbon tetrachloride CCl₄

Solid reagents: 1) Inorganic compounds: calcium chloride CaCl₂.xH₂O, magnesium chloride MgCl₂.xH₂O, sodium chloride NaCl, ferrous chloride FeCl₃.xH₂O, aluminium chloride AlCl₃.6H₂O. [10, 35, 39]
Calcium chloride CaCl₂·xH₂O:

Calcium chloride is the most common researched, even in industry for its high efficiency and environmental harmlessness. CaCl₂ is highly hygroscopic, forms hydrates (hexa-, tetra-, di-, mono-). An anhydrous CaCl₂ is formed above the temperature 260°C. [18, 39]

Melting point of CaCl₂ is at temperature 782°C (P), above this temperature CaCl₂ vaporizes (Q). [41]

\[
\begin{align*}
\text{CaCl}_2 (s) & \rightarrow \text{CaCl}_2 (l) \quad 782°C \quad \text{(P)} \\
\text{CaCl}_2 (s) & \rightarrow \text{CaCl}_2 (g) \quad > 782°C \quad \text{(Q)}
\end{align*}
\]

In dry conditions, CaCl₂ (g) releases chlorine according to (R, S), the difference of Gibbs energy is for the comparison with MgCl₂ (V). [9]

\[
\begin{align*}
\text{CaCl}_2 (g) + \frac{1}{2} \text{O}_2 (g) & \rightarrow \text{CaO} (s) + \text{Cl}_2 (g) \quad (\Delta G^\circ = +107kJ) \quad \text{(R)} \\
\text{CaCl}_2 (g) + \text{CO}_2 (g) + \frac{1}{2} \text{O}_2 (g) & \rightarrow \text{CaCO}_3 (s) + \text{Cl}_2 (g) \quad \text{(S)}
\end{align*}
\]

In humid conditions, CaCl₂ (g) releases HCl (g) according to (T, U). The mass decrease is smaller for these conditions. [41]

\[
\begin{align*}
\text{CaCl}_2 (g) + \text{H}_2\text{O} (g) & \rightarrow \text{CaO} (s) + 2 \text{HCl} (g) \quad \text{(T)} \\
\text{CaCl}_2 (g) + \text{CO}_2 (g) + \text{H}_2\text{O} (g) & \rightarrow \text{CaCO}_3 (s) + 2 \text{HCl} (g) \quad \text{(U)}
\end{align*}
\]

Magnesium chloride MgCl₂·xH₂O:

Magnesium chloride is a dust suppressant on roads due to its hygroscopicity. MgCl₂ is similar to CaCl₂, in comparison with KCl, is better for Zn-oxide but worse for Cu-oxide, as described for removal of heavy metals from sewage sludge [36]. In dry conditions, MgCl₂ releases chlorine according to (V), the volatilization of MgCl₂ is preferable in comparison with the reaction of CaCl₂ (R). In humid conditions, MgCl₂ is capable of forming HCl (g) at lower temperatures (110°C) according to (W). [10, 18, 41]

\[
\begin{align*}
\text{MgCl}_2 (g) + \frac{1}{2} \text{O}_2 (g) & \rightarrow \text{MgO} (s) + \text{Cl}_2 (g) \quad (\Delta G^\circ = -9,38kJ) \quad \text{(V)} \\
\text{MgCl}_2 (g) + \text{H}_2\text{O} (g) & \rightarrow \text{MgO} (s) + 2 \text{HCl} (g) \quad \text{(W)}
\end{align*}
\]
2) Organic compounds: polyvinyl chloride PVC, tetrachloroethylene \( \text{C}_2\text{Cl}_4 \).
Increase in the organic bound chlorine (PVC, \( \text{C}_2\text{Cl}_4 \)) led to higher heavy metal volatility (for Pb, Zn, Cu, Cr and Cd). [63]

**Polyvinyl chloride PVC:**

PVC is the second largest volume thermoplastic (up to 30 mil. tons). PVC is an universal polymer with many applications, e.g. for pipes, floor coverings, cable insulation, roofing sheets, packaging foils, bottles and medical products. Advantages of PVC are easy bonding with many additives, low cost, processability, good physical, chemical and weathering properties. [6]

PVC contains a lot of different additives and stabilizer systems. Examples of PVC stabilizers: lead stabilizers, metal carboxylate soaps (barium-cadmium: cadmium in stabilizers under increasing control, barium-zinc, calcium-zinc) or organotin compounds (sulfur-containing organotin stabilizers). The quantitative analysis and characterization of the PVC as a waste is necessary to obtain information such as the residual stability, molecular weight and the content of additives. [6]

PVC decomposition is connected with the elimination of HCl at low temperature (about 100°C) or under the influence of light (Figure 10).

![Figure 10. Scheme of dehydrochlorination of PVC. [5]](image)

**Time of induction** \( t_i \) gives important information about remaining stability of PVC specimen. According to this, a decision whether an additional stabilization is necessary for the material recycling should be made (Figure 11).
Effectiveness of chlorination agents

From the highest to the lowest is MgCl$_2$ > CaCl$_2$, FeCl$_2$ >> NaCl > KCl, AlCl$_3$. The energy of the molecular bonding (e.g. PVC, C$_2$Cl$_4$, FeCl$_3$) is lower than of ionic bonding (e.g. NaCl and KCl), so the release capacity of chlorine ions should be higher than of other inorganic chlorides. [9, 35, 53]

3.2.2. Oxidizing additives

Effect of Oxygen

Basic knowledge such as the activity, vapor pressure and interaction mechanism in oxygen-chlorine system is important. Oxidation could have a harmful effect on heavy metal evaporation. On the other hand, an oxidizing atmosphere carries chlorine (as HCl), and solid chlorides presented in the ash are activated directly or indirectly via oxygen. [35]

For heavy metals Pb and Zn with increase of the oxygen partial pressure, the vapor pressure of PbCl$_2$ and ZnCl$_2$ decrease. Oxychloride of Pb and Zn is formed. ((X), where M = Pb, Zn) [62]

\[
\text{MCl}_2 (l) + \frac{1}{2} \text{O}_2 (g) \rightarrow \text{MOCl} (l) + \frac{1}{2} \text{Cl}_2 (g) \quad (X)
\]

3.2.3. Reducing additives

Evaporation of metallic species by reduction

Reducing agent like carbon C (s) and hydrogen H$_2$ (g), which create locally reducing conditions, can reduce heavy metal species. It is beneficial for Zn (Y, Z) and especially for Cd, but has no advantage or even a disadvantage for Pb and Cu (AA, BB). [35]
\[
\text{ZnO (s) + C (s) } \rightarrow \text{Zn}^0 (g) + \text{CO (g)} \quad \text{(Y)}
\]

\[
\text{ZnCl}_2 + \text{H}_2 (g) \rightarrow \text{Zn}^0 (g) + 2 \text{HCl (g)} \quad \text{(Z)}
\]

\[
\text{CuO (s) + C (s) } \rightarrow \text{Cu}^0 (s) + \text{CO (g)} \quad \text{(AA)}
\]

\[
\text{CuCl}_2 + \text{H}_2 (g) \rightarrow \text{Cu}^0 (s) + 2 \text{HCl (g)} \quad \text{(BB)}
\]

### Types of reducing additives

Gaseous reducing additives: Electrochemical potential is one of factors influencing the redox processes, heavy metals get nobler in the order: \( \text{Zn} < \text{Cd} < \text{Pb} < \text{Cu} \). Reducing agents like CO and \( \text{H}_2 \) are thermodynamically quite similar while in above 700°C carbon C is a more powerful reducing agent. \( \text{H}_2 \) would be a costly additive for an industrial application. [35]

Solid reducing additives: Lignite coke powder is an efficient but an expensive additive, containing about 87% of carbon. Activated charcoal is well-defined and has a high purity, containing above 99% of carbon. Sewage sludge is a waste containing heavy metals and without additional expenses, containing only 19% of carbon. The organic part of additives should be removed to ensure the influence of the inorganic part of organic additives. [35, 60]

### 3.2.4. Sorbents on the basis of matrix composition

**Silica effect on chlorination:** Chlorination of metal oxides by chlorides can be supported by the addition of an acid oxide (such as SiO\(_2\)), (CC). [9]

\[
\text{MO (s) + CaCl}_2 + \text{SiO}_2 (s) \rightarrow \text{MCl}_2 (g) + \text{CaSiO}_3(s) \quad \text{(CC)}
\]

In dry conditions, release of chlorine can be supported by silicate formation (DD). In humid conditions, release of hydrogen chloride can be supported (FF). The reaction with MgCl\(_2\) is preferable in comparison to the reaction with CaCl\(_2\) (EE). [9]

\[
\text{CaCl}_2 + \text{SiO}_2 (s) + \frac{1}{2} \text{O}_2 (g) \rightarrow \text{CaSiO}_3 (s) + \text{Cl}_2 (g) \quad (\Delta G^o = +23,1kJ) \quad \text{(DD)}
\]

\[
\text{MgCl}_2 + \text{SiO}_2 (s) + \frac{1}{2} \text{O}_2 (g) \rightarrow \text{MgSiO}_3 (s) + \text{Cl}_2 (g) \quad (\Delta G^o = -41,4kJ) \quad \text{(EE)}
\]

\[
\text{CaCl}_2 + \text{SiO}_2 (s) + \text{H}_2\text{O (g)} \rightarrow \text{CaSiO}_3 (s) + \text{HCl (g)} \quad \text{(FF)}
\]

The effect of silica is larger for more basic oxides (Na\(_2\)O, K\(_2\)O). [9, 35]

Competing reactions limit the evaporation by incorporating the oxides or chlorides of heavy metals into the matrix of ash. (GG, HH, II). [35]
The formation of stable salts as ferrites, silicates or aluminates (ZnFe$_2$O$_4$, Zn$_2$SiO$_4$, and ZnAl$_2$O$_4$) suppresses the vaporization of heavy metals. They may reduce the chloride salt layer. They can be used for capturing, solidification and inertization of the most volatile elements. Perspective sorbents and inertants could be kaolinite (Al$_2$Si$_2$O$_5$(OH)$_4$), montmorillonite, zeolite, lignite (enriched in calcite) and coals (enriched in kaolinite). [17, 35, 48, 51, 59, 62, 63]

3.3. Carrier gas

Type of carrier gas

Carrier gas by its different composition could be an inert, reducing or oxidizing. Reducing and oxidizing conditions can be considered by varying the air excess ratio.

In the air the heavy metals evaporate mainly as chlorides. For Zn in oxidizing conditions, the formation of stable solid compounds (Zn$_2$SiO$_4$, ZnAl$_2$O$_4$) is dominant which limit the release of Zn. Excess chlorine or reducing conditions are necessary to completely volatize Zn which is present in a stable oxide state. Under reducing atmosphere, Zn and Pb exist mainly in metallic form in gaseous state. Cu hardly evaporates under reducing conditions. [24, 47, 57, 63]

Velocity of carrier gas

The gas flow rate together with chlorine content and temperature affect the quantity and size distribution of the input material. High flow rate of gas causes the carry-over or entrainment of fine particles. Material losses with the flue gas negatively influence the output efficiency and cost effectiveness. Minimization of these losses is a main importance. On the other hand higher gas velocity can support mass transfer processes between gas and solid phases. [27, 36, 39, 63]

3.4. Physical properties

Physico-chemical properties are characterized as density, granulometric composition, particle form, porosity, type of phase, form of structure, content of moisture and so on. Physico-chemical properties are generally of high importance for understanding of process.
Particle size

Smaller particles give a larger total surface area, therefore larger change during sintering and larger change of free energy. Fly ash with a smaller particle size has also larger heavy metal content. [54, 63]

Increasing treatment temperature (from 1100 to 1150°C) results in an increase of shrinkage and density. Increasing residence time has an opposite effect. Prolonging the treatment time to 60 min resulted in reducing the shrinkage due to the evolution of gases from inside the material and an increase of closed porosity. [42]

3.5. Characteristics of each heavy metal

In the presence of a sufficiently high concentration of chlorine, each of metals reacts with chlorine as if they were alone in the system. In practice some of the phases may be soluble in each other. [63]

3.5.2. Cadmium Cd

Cd and Pb are easily volatilized as chlorides under oxidizing conditions. CdCl₂ (g) starts to volatilize above 300°C and is the major species between 400°C to 1000°C (JJ). Above this temperature, Cd⁰ (g) becomes the dominant gas species (KK) with a minor amount of CdO (g). No significant variation is observed with an increase of particle size, due to low content of Cd. [46, 52, 54, 62]

\[
\begin{align*}
\text{CdO} + \text{Cl}_2 (g) & \rightarrow \text{CdCl}_2 (g) + \frac{1}{2} \text{O}_2 (g) \quad (JJ) \\
\text{CdO} & \rightarrow \text{Cd}^0 (g) + \frac{1}{2} \text{O}_2 (g) \quad (KK)
\end{align*}
\]

Under reducing conditions, CdO can be reduced to form volatile Cd⁰ (g) (LL). [41]

\[
\text{CdO} + \text{CO} (g) \rightarrow \text{Cd}^0 (g) + \text{CO}_2 (g) \quad (LL)
\]

No significant interaction between ash species and Cd could be detected [46]. However the reaction with the matrix compounds SiO₂ can occur (MM), [41]

\[
\text{CdO} + \text{SiO}_2 (s) \rightarrow \text{CdSiO}_3 (g) \quad (MM)
\]

3.5.3. Lead Pb

Under oxidizing conditions, PbCl₂ (g) volatilizes from 300°C (NN). Above 800°C PbO (g) (OO) with a smaller extent of PbCl (g) increase. A minor amount of Pb⁰ (g) is observed at even higher temperature. The literature shows a large variation in the volatility of
Pb. [46, 52] Pb content decreases with particle size increase at range 400-600°C, while at range 800-1000°C, there is no significant variation with changes in particle size due to low content of Pb. [54]

\[
PbO + Cl_2 (g) \rightarrow PbCl_2 (g) + \frac{1}{2} O_2 (g) \quad \text{(NN)}
\]

\[
PbCl_2 + \frac{1}{2} O_2 (g) \rightarrow PbO (g) + Cl_2 (g) \quad \text{(OO)}
\]

Under reducing conditions, Pb\textsuperscript{0} (g) and Pb chlorides dominate below the temperature 780°C, while above this temperature Pb\textsuperscript{0} (g) gradually increases (PP) and Pb chlorides decrease. [41, 46, 52, 53]

\[
PbO + CO (g) \rightarrow Pb\textsuperscript{0} (g) + CO_2 (g) \quad \text{(PP)}
\]

Pb species can react with matrix slag to form stable compounds (QQ, RR), [63].

\[
2 PbO + SiO_2 (s) \rightarrow Pb_2SiO_4 (s) \quad \text{(QQ)}
\]

\[
PbCl_2 + Al_2O_3:2SiO_2 (s) + H_2O (g) \rightarrow PbO:Al_2O_3:2SiO_2 (s) + 2HCl (g) \quad \text{(RR)}
\]

**3.5.4. Copper Cu**

The amounts of Zn and Cu volatilized depend on the reduction conditions and the amount of Cl present. Locally reducing conditions and the formation of complex oxides (CuO,Fe\textsubscript{2}O\textsubscript{3} and CuO,Al\textsubscript{2}O\textsubscript{3}) or silicates could explain the more limited volatilization.

Under oxidizing conditions, Cu is present only in gas phase. First CuCl\textsubscript{2} (g) is stable up to 200°C, while CuO (g) till 700°C. At higher temperature, the dominant species are Cu\textsubscript{3}Cl\textsubscript{3} (g) till 900°C (TT), followed by CuCl (g) above this temperature (UU). With another increase of temperature, minor amounts of CuO(g) and Cu\textsuperscript{0}(g) are present. Only with fine-grained filter ash, Cu evaporates nearly completely in air. [41, 46, 52]

\[
Cu_2S + 3/2 O_2 (g) \rightarrow Cu_2O (g) + SO_2 (g) \quad \text{(SS)}
\]

\[
3 CuO + 3/2 Cl_2 (g) \rightarrow (CuCl)_3 (g) + 3/2 O_2 (g) \quad \text{(TT)}
\]

\[
Cu_2O + Cl_2 (g) \rightarrow 2 CuCl (g) + \frac{1}{2} O_2 (g) \quad \text{(UU)}
\]

Under reducing conditions, Cu is present as sulphides such as CuS,FeS (cr) and Cu\textsubscript{2}S (cr, l). Then CuCl (g) gradually increase, followed by Cu\textsuperscript{0} (g) and CuH (g). Cu becomes more volatile from reducing to oxidizing conditions and less volatile with increasing sulphur content at reducing conditions. [24, 46, 52]
Carbonate fraction which is a main fraction in raw fly ash partly changes to organic matter (VV). For Cu and Zn, volatilization is reduced by the formation of ZnO,Fe$_2$O$_3$, CuO,Al$_2$O$_3$ and CuO,Fe$_2$O$_3$ (WW). Other elements like silicates, aluminates and silicoaluminates could also decrease volatilization. Total volatilization of Cu$^0$ (g) as CuCl (g) and Cu$_3$Cl$_3$ (g) occurs in oxidizing conditions when no complex oxides are formed. [11, 41, 52].

\[
\text{CuCO}_3 (s) \rightarrow \text{CuO (s) + CO}_2 (g) \quad \text{(VV)}
\]

\[
\text{CuO (s) + Fe}_2\text{O}_3 (s) \rightarrow \text{CuFe}_2\text{O}_4 (s) \quad \text{(WW)}
\]

3.5.5. Zinc Zn

The degree of Zn evaporation depends on the composition of the matrix material, its specific surface, and the total amount of ZnCl$_2$. [48]

**Reaction sequence and explanation of incomplete evaporation of Zn**

1) Reaction of Zn-oxid with chlorine (XX) following by an adsorption of ZnCl$_2$ on a surface site (YY). The reaction rate depends on the vapor pressure of ZnCl$_2$ ($p_{\text{ZnCl}_2}$).

\[
\text{ZnO} + \text{Cl}_2 (g) \rightarrow \text{ZnCl}_2 (g) + \frac{1}{2} \text{O}_2 \quad \text{(XX)}
\]

\[
\text{surface} + \text{ZnCl}_2 (g) \rightarrow \text{ZnCl}_2 (ad) \quad \text{(YY)}
\]

2) Adsorbed ZnCl$_2$ reacts with water vapor (ZZ), the presence of water in moist air decreases Zn volatilization. The rate depends on the partial pressure of water and the surface coverage of ZnCl$_2$ ($\Theta_{\text{ZnCl}_2}$).

\[
\text{ZnCl}_2 (ad) + \text{H}_2\text{O} (g) \rightarrow \text{ZnO (ad) + 2HCl (g)} \quad \text{(ZZ)}
\]

3) Incorporation of ZnO (ad) into the matrix oxide (SiO$_2$, Al$_2$O$_3$ or Fe$_2$O$_3$) leads to the formation of more stable compounds, such as Zn$_2$SiO$_4$ (willemite), ZnAl$_2$O$_4$ (zinc spinell) and ZnO,Fe$_2$O$_3$, (AAA, BBB). The degrees of dispersion of the heavy metals within the matrix cause transport limitations with reaction partners. The rate depends on the surface coverage of ZnO ($\Theta_{\text{ZnO}}$). [48]

\[
2 \text{ZnO (ad) + SiO}_2 (s) \rightarrow \text{Zn}_2\text{SiO}_4 (s) \quad \text{(AAA)}
\]

\[
\text{ZnO (ad) + Al}_2\text{O}_3 (s) \rightarrow \text{ZnAl}_2\text{O}_4 (s) \quad \text{(BBB)}
\]
Under oxidizing conditions, dominant species is $2\text{ZnO}\cdot\text{SiO}_2$ (cr) for whole temperature range. $\text{ZnCl}_2$ (s) is the stable phase at low temperature, which converts to ZnO (s) around 280°C. $\text{ZnCl}_2$ (g) is also formed and increases slowly with temperature. $\text{Zn}^0$ (g) is sharply increasing from 1180 to 1330°C. [24, 46, 52, 63]

Under reducing conditions, silicate $2\text{ZnO}\cdot\text{SiO}_2$ (s) is the dominant species which decreases to about 830°C. Above this temperature, $\text{Zn}^0$ (g) is the dominant stable phase (CCC), also a minor amount of $\text{ZnCl}_2$ (g) is observed. Zn can be volatilized completely with an excess of Cl or under highly reducing conditions, as in Ar and Ar/H$_2$ atmosphere. [46, 48, 63]

$$\text{ZnO (s) + CO (g) \rightarrow Zn}^0\text{ (g)+ CO}_2\text{ (g)} \quad \text{(CCC)}$$

An increase of the mass transfer from particle grain to gas phase and an avoidance of long residence time at low temperatures by rapid heating are necessary to improve the separation of Zn from fly ash. [48]

### 3.5.6. Chromium Cr

Cr is stable in solid phase over the temperature range (680 – 1330°C), only small amount is volatilized at high temperatures. No influence to volatilization of Cr occurs due to changing sulphur or chlorine content, but Cr is slightly more volatile at higher temperatures with decreasing air/fuel ratio. Higher temperature resulted in conversion of Cr compounds from an insoluble form to a soluble form. The content of Cr decreases with increasing particle size.

Under both oxidizing and reducing conditions, $\text{CaO.Cr}_2\text{O}_3$ (s) is a dominant and stable compound, with small amounts of oxides for oxidizing system. [46, 53]. Reaction which may occur under oxidizing conditions (DDD) [41].

$$\text{Cr}_2\text{O}_3 + 2\text{Cl}_2\text{ (g) + }\frac{1}{2}\text{O}_2\text{ (g) \rightarrow 2CrO}_2\text{Cl}_2\text{ (g)} \quad \text{(DDD)}$$

Reaction of Cr-oxide with matrix compounds ($\text{Na}_2\text{O}$, $\text{MgO}$ or $\text{CaO}$) leads to the formation of chromate (EEE), [41]

$$\text{CaO (s) + Cr}_2\text{O}_3\rightarrow \text{CaCr}_2\text{O}_4\text{ (s)} \quad \text{(EEE)}$$
3.5.7. Nickel Ni

Under oxidizing conditions, the dominant species is NiO. SiO$_2$ (cr). Increasing amounts of chlorine (g) reacts with Ni to evaporation of NiCl$_2$ (g) \((\text{FFF})\). Under reducing conditions, Ni is present as the stable condensed element Ni (cr, l) \([41, 46]\).

\[
\text{NiO (s) + Cl}_2 (g) \rightarrow \text{NiCl}_2 (g) + \frac{1}{2} \text{O}_2 (g) \quad (\text{FFF})
\]

Reaction of Ni-oxid with matrix compound Fe$_2$O$_3$ \((\text{GGG})\) \([41]\).

\[
\text{NiO (s) + Fe}_2\text{O}_3 (s) \rightarrow \text{NiFe}_2\text{O}_4 (s) \quad (\text{GGG})
\]

3.6. Types of reactors

3.6.1. Rotary reactor

Rotary kiln is heterogeneous, non-catalytic, gas-solid reactor. It is used for incineration processes, due to simultaneously treated wastes as liquids or solids of various shapes and sizes. It fulfils the complete destruction and detoxification of hazardous wastes and minimizes emissions of dioxins and heavy metals. In an ordinary rotary reactor, the flow pattern of solids at steady state is almost like plug flow.

Major disadvantage is a diffusional resistance of the gaseous reactant within the rotating layer of bulk solids and poor contacting between gas and solids. Therefore a rotary reactor is applied for cases of gas-solid systems where heat transfer and thermal decomposition of solids are the rate controlling step. \([30, 33]\)

Continuous mode

Movements of solids in rotary cylinder (Figure 12)

Solids rotate like a rigid body, and then collapse to slide down along a flat surface and mix into the main body. Result is uniform mixing of solids and uniform temperature. Slipping of solids should be prevented. When solids are coarse, the flow pattern of the gas is similar to an ordinary fixed bed reactor. \([30]\)
Conversion of solids with gaseous reactant

The conversion rate of solids depends upon their physical characteristics (rigid versus porous, crystalline versus amorphous, pure versus catalytic impurities, etc.). Heat transfer is a crucial step for these processes. There is also the radiant heat transfer from its inner surface to the rotating solids.

\[
A \text{(gas)} + bB \text{(solid)} \rightarrow \begin{cases} 
\text{gaseous product} \\
\text{solid product} \\
\text{gaseous and solid products}
\end{cases}
\]

Organic substances are decomposed very quickly at high temperatures. For coarse solids, a longer time is needed to raise the temperature of their centers. [30]

Performance and heat transfer in rotary reactors, indirect heating

Material of the rotary reactor could be stainless steel (700°C), special alloys (1000°C), SiO\(_2\), SiC (1200°C). It is necessary to prevent unexpected destruction of the reactor due to corrosive gas originated during conversion of solids at a high temperature. Thickness of the rotary reactor should be determined to give enough mechanical strength and an uniform temperature. [30]

Electric heating

The heating elements should be divided into 3 or more regions. The input of electric power should be independently controlled. Reduction of cost and electric energy can be done by heat exchange between hot and cold solids, by heat evolution from the oxidation of residual carbon in the fly ash or by installation of tubes to inject the air into the rotating layer of ash. [30]
Mean residence time (MRT)

MRT is one of the most important parameters, it determines the degree of chemical reaction of gas and solid phase. Residence time of solids through rotary kiln is not a constant, but a probability distribution.

Variable parameters are 1) the dimension of the kiln such as diameter D and length L, 2) operational variables such as feed rate m, rotation speed n, and the inclination angle \( \beta \), 3) property of solids such as the angle of repose \( \theta \), and 4) geometry of the dam at the discharge end or feed end of the kiln, internal structures and roughness of kiln wall. [34]

The values have to ensure that the solids motion stays in the rolling mode. However axial cascading velocity of particles increases along the axial direction, because of the decreasing of the bed depth along the kiln axis. [30]

Calculation of MRT (Sullivan et al., 1927) without a discharge dam:

\[
MRT = 1.77 \cdot \frac{L}{D} \cdot \frac{\sqrt{\theta}}{n \cdot \beta} \text{ [min]}
\]

where  
- \( MRT \) is mean residence time [min]  
- \( L \) – length of rotary kiln [m]  
- \( D \) – diameter of rotary kiln [m]  
- \( \theta \) – angle of repose* [°]  
- \( n \) – rotation speed [rpm]  
- \( \beta \) – inclination angle [°]

* Note: The dynamic angle of repose increases with the increasing of wall roughness but is independent of the rotation speed of the kiln.

According to this calculation, the feed rate has no influence on the residence time. Therefore the calculated values are lower than the measurements. This simple empirical equation gives satisfactory results, with a small error (from -10 % to +4 %), at higher feed rates and low rotation speeds the discrepancy is 20 %. However the feed rate definitely influences the residence time. With an increasing feed rate, MRT shows a slight increase which is almost negligibly at high rotation speeds. It is needed to improve the inlet device for preventing solids loss, instead of increase of rotation.

Parameters of testing solid (sand) are particle diameter, bulk density and dynamic angle of repose, which has a significant influence on the transport and mixing of the solids (e.g. sand 29.7 °). [30, 33, 34]
3.6.2. Others

In the CT-Fluapur® - process, a fluidized bed reactor is used for treatment of pellets at temperatures about 900°C. Pellets are composed of MSW fly ash which is mixed with 10 % carbon and granulated. The process has to be placed next to a MSW incinerator. Its hot flue gas, which is mixed with its HCl from the acid scrubber, is used as the carrier gas in CT-Fluapur® - process. The flue gas from the fluidized bed reactor is cooled down and filtered for separation of heavy metals. Disadvantages of this process are capital and process intensity. [39]

3.7. ASH DEC process

ASH DEC process

Similar to CT-Fluapur® - process is ASH DEC process which focuses on recovery of phosphorus as a fertilizer from sewage sludge ash.

The ASH DEC process is described that firstly, sewage sludge ash and harmless chlorine donors (e.g. CaCl$_2$) are mixed and compacted in a pellet press. In the next step, the pellets are fed to a thermal reactor and exposed for about 20 minutes to a temperature of 1000°C. At this temperature, up to 99 % of the monitored metals, such as mercury, cadmium, lead, zinc and copper, react with the additives and evaporate. Treated pellets remain in form of phosphorus-rich product without toxic substances. Metals are captured in the air pollution control system in form of a metal concentrate. [39].
Experimental part

4. Material

4.1. Municipal solid waste fly ash (MSW fly ash)

4.1.1. General characteristics

4.1.2. Chemical composition

According to Material safety data sheet of the waste to energy plant Fernwärme Wien / Spittelau (Vienna), MSW fly ash contains in average 3 940 mg/kg of lead, 246 mg/kg of cadmium, 189 mg/kg of chromium, 669 mg/kg of copper, 66 mg/kg of nickel, 14 300 mg/kg of zinc, see Appendix 1.

4.1.3. Analysis of phases

4.1.4. Thermal analysis (DTA/TG)

4.2. Chlorinating agents

4.2.1. Calcium chloride

4.2.2. Magnesium chloride

4.2.3. PVC granulate

4.3. Additives

The criteria for selection of additives were cost and efficiency and possibility of comparison with additives used in prior experiments.

4.3.1. Organic material

4.3.2. Sand (SiO₂)

4.3.3. Coke (C)

4.4. Preparation of samples

Mixtures of MSW fly ash and pellets with relevant additives were prepared in a pilot plant laboratory of ASHDEC in Leoben, Austria. Prepared samples were used for further experiments in the laboratory of the Institute of Chemical Engineering, Vienna University of Technology.
4.5. *Ash fractioning (sieving)*

5. **Lab-scale thermal treatment (ASH DEC process)**

5.1. **Rotary reactor**

5.1.1. **Batch mode**

Lab-scale rotary reactor was indirectly heated. Material was silicon carbide-silicon (SiC-Si). The rotation speed was regulated by a frequency converter and was same for all batch-mode experiments. The temperature of the reactor was controlled by three PID-controllers.

The parameters of batch-mode trials were distinguished from previous experiments [41].

5.1.2. **Continuous mode**

In continuous mode experiments, pure MSW fly ash or pelletized sample family were mixed with PVC granulate. Treatments were held in the rotary kiln in co-current mode.

5.2. **Flue gas cleaning**

The flue gas of the rotary kiln was cooled down with a water stream from the Venturi scrubber. The gas phase flew to the countercurrent packed column filled with plastic Pall rings. The samples of water solution were taken for ICP-OES analyses.

5.3. **Muffle oven**

Samples of pure fly and pellets were treated in a muffle oven in the Institute of Chemical Engineering. In these experiments the influence of temperature was investigated.

6. **Elemental analysis of sample families**

6.1. **ICP-OES**

Analyses of MSW fly ash

The ICP-OES analyses were made in the Institute for Water Quality, Resource and Waste Management, Vienna University of Technology, Austria.
6.2. XRD

X-ray powder diffraction analysis was used for investigation of phase analysis of samples at the Nanotechnology Centre of VSB – Technical University of Ostrava.
7. Results and discussions

7.1. Thermal analysis DTA/TG

7.2. Removal of heavy metals

7.3. Influence of additives in batch mode

7.4. Continuous mode

7.5. Recovery of heavy metals in the flue gas cleaning system

7.6. Muffle oven

Note: Whole version of diploma thesis can be found at Department of Physical Chemistry and the Theory of Technological Processes and in Central Library of VŠB – Technical University of Ostrava
Conclusion

The aim of this work was to investigate behavior of MSW fly ash with different additives during thermal treatment. Concentrations of heavy metals (Cd, Pb, Cu, Zn, Ni and Cr) were analyzed and their removals were calculated.

Fly ash was pelletized or mixed with additives. Evaporation of heavy metals from pellets could be hindered by diffusion in pellets, so that removals for non-pelletized samples were higher. However pellets are easy to handle during manipulation, transport and experiments. Also mass of pellets can not be easily entrained with a carrier gas as in case of fly ash with fine particles.

Addition of different amounts of sand resulted again in higher removals for non-pelletized samples. Incorporation of Cu and Zn into matrix of ash appeared at 1050°C.

Addition of coke to samples was not contradictory to removals of heavy metals.

Addition of MgCl₂ caused higher removal of heavy metals except for Cu. Again pellets with CaCl₂ showed lower removals than in case of mixtures with CaCl₂.

In experiments with different fractions of ash, influence of time on removals was more significant at lower temperatures of treatment.

Mass flow in continuous mode experiments was not constant; steady state could not be reached due to mass losses by evaporation. In comparison with pure fly ash, pellets were better for maintenance of continuous mode experiments.

Treatment of pure fly ash and pellets in muffle oven showed better removals of heavy metals (Cd, Pb, Zn, Ni) for pellets. Cu was better removed from pellets above 950°C. Results of XRD analyses of samples treated at 800°C and 1000°C and pure fly ash showed that chlorides (such as NaCl, KCl) were removed at temperature 1000°C. Newly formed silicates and aluminates appeared with increase of temperature.

Concentrations of heavy metals in treated samples should be compared with the guidance levels for the production of cement and concrete published by BAFU, Switzerland. However, thermally treated MSW fly ash with different additives can fulfill requirements for disposal of fly ash in comparison with current practices of MSW fly ash landfilling.
List of literature

[1] Act No. 185/2001 Coll., on waste and on amendment to some other laws, as amended.


[40] NOWAK, B.; PESSL, A.; ASCHENBRENNER, P.; MATTENBERGER H.; Friebert, A., RECHBERGER, H., HERMANN, L., and WINTER, F. Thermal processing for heavy


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<td>APC</td>
<td>Air pollution control</td>
</tr>
<tr>
<td>BAFU</td>
<td>Federal Office for the Environment</td>
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<tr>
<td>Coll.</td>
<td>Collection</td>
</tr>
<tr>
<td>cr</td>
<td>Crystal</td>
</tr>
<tr>
<td>DENOX</td>
<td>Conversion of hazardous nitrogen oxides into nitrogen and water</td>
</tr>
<tr>
<td>DTA</td>
<td>Differential thermal analysis</td>
</tr>
<tr>
<td>EC</td>
<td>European Commission</td>
</tr>
<tr>
<td>EU</td>
<td>European Union</td>
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<tr>
<td>g</td>
<td>Gas</td>
</tr>
<tr>
<td>HCB</td>
<td>Hexachlorobenzene</td>
</tr>
<tr>
<td>ICP-OES</td>
<td>Inductively coupled plasma optical emission spectroscopy</td>
</tr>
<tr>
<td>l</td>
<td>Liquid</td>
</tr>
<tr>
<td>MFA</td>
<td>Melting furnace fly ash</td>
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<tr>
<td>MRT</td>
<td>Mean residence time</td>
</tr>
<tr>
<td>MSW</td>
<td>Municipal solid waste</td>
</tr>
<tr>
<td>MSWI</td>
<td>Municipal solid waste incinerator</td>
</tr>
<tr>
<td>No.</td>
<td>Number</td>
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<tr>
<td>OPC</td>
<td>Ordinary Portland Cement</td>
</tr>
<tr>
<td>PAH</td>
<td>Polycyclic aromatic hydrocarbon</td>
</tr>
<tr>
<td>PCB</td>
<td>Polychlorinated biphenyls</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>PCDD</td>
<td>Polychlorinated dibenzodioxin</td>
</tr>
<tr>
<td>PCDF</td>
<td>Polychlorinated dibenzofuran</td>
</tr>
<tr>
<td>PET</td>
<td>Polyethylene</td>
</tr>
<tr>
<td>PID-controller</td>
<td>Proportional integral derivative controller</td>
</tr>
<tr>
<td>ppm</td>
<td>Parts per million</td>
</tr>
<tr>
<td>PVC</td>
<td>Polyvinylchloride</td>
</tr>
<tr>
<td>RDF</td>
<td>Refuse derived fuel</td>
</tr>
<tr>
<td>rpm</td>
<td>Rotations per minute</td>
</tr>
<tr>
<td>RSD</td>
<td>Relative standard deviation</td>
</tr>
<tr>
<td>s</td>
<td>Solid</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
</tr>
<tr>
<td>VOC</td>
<td>Volatile organic compounds</td>
</tr>
<tr>
<td>VSoE</td>
<td>Vienna Spot of Excellence</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
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