



Heavy metal removal from municipal solid waste fly ash by chlorination and thermal treatment

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ABSTRACT

Municipal solid waste (MSW) fly ash is classified as a hazardous material because it contains high amounts of heavy metals. For decontamination, MSW fly ash is first mixed with alkali or alkaline earth metal chlorides (e.g. calcium chloride) and water, and then the mixture is pelletized and treated in a rotary reactor at about 1000 °C. Volatile heavy metal compounds are formed and evaporate. In this paper, the effect of calcium chloride addition, gas velocity, temperature and residence time on the separation of heavy metals are studied. The fly ash was sampled at the waste-to-energy plant Fernwärme Wien/Spittelau (Vienna, Austria). The results were obtained from batch tests performed in an indirectly heated laboratory-scale rotary reactor. More than 90% of Cd and Pb and about 60% of Cu and 80% of Zn could be removed in the experiments.

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1. Introduction

1.1. Municipal solid waste fly ash

Since January 2009, Untreated municipal solid waste (MSW) must not be landfilled directly in Austria [1,2]. 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. Beside cleaned flue gas and purified wastewater the residues of the incineration process and the (wet) flue gas cleaning are bottom ash, iron scrap, fly ash, Air Pollution Control (APC) ash (from gas desulfurization) and filter cake (from the wastewater treatment). Out of the five solid residues there is only a market for iron scrap and (partly) gypsum; the other residues must be considered as waste without consecutive treatment.

Bottom ash is usually disposed off in landfills. It is also used as construction material (road foundations in Northern Europe coun-

tries). Municipal solid waste fly ash is classified as a hazardous material because it contains high amounts of heavy metals. It is mainly landfilled 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). The production of filter cake is of minor importance due to the small quantities that occur. It is usually stored underground.

Underground disposal of municipal solid waste fly ash is cost-intensive, although reliable figures are not published. Long-term growth in resource pricing and the cost of disposal will lead to processes that will be able to replace primary feed stocks, e.g. ores [3]. Incineration ashes offer a high potential for heavy metal recycling [4].

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).

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Nomenclature

\bar{x}	mean value of the argument x
an	index for analysis
pa	index for parameter
Θ	mass which is contained in the untreated sample (g)
Υ	recovery
ϱ	relative standard deviation
Ξ	mass found in treated pellet, T-junction and scrubber (g)
c	concentration of the treated sample (ppm)
c_0	concentration of the untreated sample (ppm)
c_{Cl}	concentration of chlorine (from $CaCl_2$)
f	function
i	index for element
j	index for batch
k_1	constant (min^{-1})
k_2	constant (K^{-1})
k_3	constant
k_4	constant
M	mass of batch after treatment (g)
m	index for counting
M_0	mass of batch before treatment (g)
R	removal
s	standard deviation
T	temperature (K)
t	time (min)
x	argument
ICP-OES	inductively coupled plasma optical emission spectroscopy
MSW	municipal solid waste
PCDD	polychlorinated dibenzodioxins
PCDF	polychlorinated dibenzofurans
PTFE	polytetrafluoroethylene
RSD	relative standard deviation
tot	total
WTE	waste-to-energy
XRD	X-ray diffraction

Many of these processes have disadvantages. Ash melting requires high energy consumption and produces a secondary fly ash [5]. 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. Binding of heavy metals (hydraulically in a cement matrix or after melting as glass) does not mean complete immobilization: Giergiczny and Król investigated the leaching behavior of concrete made of MSW fly ash. Over 99% of Pb^{2+} , Cu^{2+} , Cd^{2+} , Mn^{2+} , Zn^{2+} were immobilized, but only 91–99% of Cr^{6+} [6].

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 [7,8]. 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 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

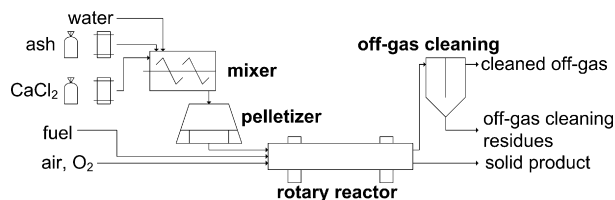


Fig. 1. ASH DEC process.

and 57%, respectively) [7,8]. 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 and if problems in the ash treating facility occur, the whole plant has to be shut down. Due to the long residence time and costly equipment (rectification for HCl) the costs of the CT-Fluapur[®]-process are estimated to be 150–200 EUR per ton of ash.

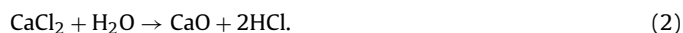
A process quite similar (according to [9]) to the CT-Fluapur[®] process is the following (see Fig. 1), which is already used to recover phosphorus from sewage sludge ash (ASH DEC process [10]): the ash is mixed with an environmentally compatible chloride (e.g. $CaCl_2$) and water. In the next step this mixture is pelletized because of the tendency of fly ash and the mixture to form dust (i.e. more difficult storage and handling and greater losses to the flue gas). These pellets are fed into a rotary reactor. The temperature in the reactor is between 900 and 1100 °C. Organic residues are destroyed because of the high temperature. As the temperature is below the melting point of the ash the energy consumption is comparatively lower than for ash melting processes [11]. Metal chlorides form and evaporate, leaving behind a substantially decontaminated product. The heavy metal chlorides are captured in the flue gas cleaning system (e.g. a scrubber) and can be recovered in an ensuing treatment step [10]. The treatment is estimated to be significantly cheaper than the CT-Fluapur[®] process (which could not be realized so far).

1.2. Removal of heavy metals

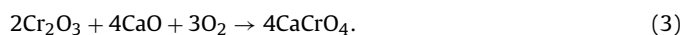
Many studies concerning the chlorine donor have been published [7,12–17]. The best chlorine donor is Cl_2 , which would require expensive equipment for safe handling. Using Cl_2 , even As, Cr and Ni can be removed from sewage sludge ash [13]. Gaseous HCl is also an effective Cl donor, but it is hardly possible to remove Cr and Ni [7,17]. Depending on the water content in the atmosphere, HCl or Cl_2 is also formed as intermediate if $CaCl_2$ is used as chlorine donor [18]: in an oxidizing, dry surrounding $CaCl_2$ forms Cl_2 according to



in a humidified atmosphere, HCl is formed:



In thermodynamic equilibrium calculations Fraissler et al. [19] showed that water has a negative effect on the removal of Cr, Ni and Zn from sewage sludge ash. In turns, CaO can react with Cr forming calcium chromate [20],



$MgCl_2$ reacts similarly to $CaCl_2$ [12]. The difference between $MgCl_2$ and KCl with respect to the removal of heavy metals from sewage sludge ash was investigated by Mattenberger et al. [15]: for highly volatile Cd and Pb, KCl and $MgCl_2$ are equivalent. For Cu, KCl is the better chlorine donor, for Zn higher removal rates are feasible using $MgCl_2$. Cr and Ni are generally little volatile [15].

Table 1

Heavy metal concentrations in the MSW fly ash. 16 samples were analyzed. RSD relative standard deviation between the samples. Elements (except C, N, S) were analyzed with total digestion and ICP-OES. C, N and S were analyzed with a CHNSO elemental analyzer. The values of pulverized coal ash and blast furnace slag are guidance levels published by BAFU [24]. Concentrations in ppm.

Element	Concentration	RSD	Pulverized coal ash [24]	Blast furnace slag [24]
Al	41,000	6.4%		
C	26,000	7.4%		
Ca	190,000	3.1%		
Cd	350	4.6%	2	1
Cl ^a	115,000			
Cr(tot)	500	8.7%	300	200
Cr(VI)			2	2
Cu	890	2.0%	200	200
Fe	9800	15%		
H ₂ O ^b	2400	9.6%		
K	50,000	4.5%		
Mg	11,000	10%		
N	830	13%		
Na	49,000	3.8%		
Ni	94	15%	200	200
P	8000	25%		
Pb	4500	6.5%	300	75
S	26,000	2.7%		
Zn	19,000	4.9%	1000	400

^a Hot-water soluble.

^b Calculated from the dry matter.

The reactions which lead to the formation of volatile heavy metal compounds (e.g. Cd(OH)₂, CdO, CrO₂Cl₂, (CuCl)₃, CuCl, NiCl₂, PbO, PbCl₂, ZnCl₂ [19]) are in competition with those where heavy metals react with matrix compounds (namely those based on SiO₂ and Al₂O₃). For example, ZnO and SiO₂ form ZnSiO₃, while ZnO and Al₂O₃ react to ZnAl₂O₄. Those silicates and aluminates reduce the maximum amount of evaporated Zn [21], whereas aluminates are more stable than silicates [19]. In the ash, heavy metals are present in a variety of speciations, e.g. Forestier and Libourel [22] found Zn in metallic form, as chloride, in alloys, spinels and calcium-bearing aluminosilicate glass. Zn is – beside several other Zn compounds – also present as hydrozincite Zn₅(OH)₆(CO₃)₂, willemite Zn₂SiO₄ and gahnite ZnAl₂O₄ [23]. Stable compounds such as silicates and aluminates in the ash also decrease the maximum evaporable amount of heavy metals.

1.3. Specific objectives

The aim of this study is to examine the behavior of MSW fly ash in the ASH DEC process using an indirectly heated lab-scale furnace. The ASH DEC process is well researched and established for the decontamination of sewage sludge ash [12,15,16].

It is expected that unburned particles (e.g. soot) and organic materials in the ash will be destroyed because of the high temperatures. Heavy metal oxides react with chlorine and form heavy metal chlorides and other compounds which evaporate. The influence of the treatment temperature (950–1050 °C), the residence time (10–45 min), the chloride addition (0.12 and 0.17 kg Cl kg⁻¹ ash) and the gas velocity are examined.

After the heavy metal removal, the ash is expected to be usable as an additive for cement, thus 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, Switzerland) [24] (see Table 1). If the concentration values cannot be met, the landfill in a cheaper dump category than underground disposal is another possibility for the application of the process.

2. Material

2.1. Municipal solid waste fly ash

Municipal solid waste fly ash is taken from the waste-to-energy plant Fernwärme Wien/Spittelau (Vienna). It is a mixture of ashes from both incineration lines which are collected in the vessels and the electrostatic precipitators. For elemental characterization the ash is digested with a mixture of HCl, HNO₃, HF, H₂O₂ and B(OH)₃ (total digestion) and analyzed with ICP-OES for the elements Al, Ca, Cd, Cr, Cu, Fe, K, Mg, Na, Ni, P, Pb and Zn; C, N and S are analyzed with a CHNSO analyzer; hot water-soluble Cl is analyzed titrimetrically; for mean values of the concentrations and relative standard deviations (RSD) (see Table 1). The values are within the given range from Wiles [25].

The main crystalline species in the MSW fly ash used were detected by XRD; they are calcium aluminate, halite and sylvine. The matrix of MSW ashes is complex, amorphous and heterogeneous [26]. Heavy metals cannot be detected by XRD because they are either impure, bound in complexes or amorphous [27]. The fusibility of fuel ash (DIN 51730) is also investigated, the softening temperature (A) is at 1280 °C, the spherical temperature (B) does not appear, the hemispherical temperature (C) is at 1330 °C and the flow temperature (D) is at 1340 °C.

2.2. Calcium chloride

The used calcium chloride is of technical quality. It contains about 20 wt% water.

3. Experimental

3.1. Preparation of the pelletized material

MSW fly ash is mixed with calcium chloride in an Eirich intensive mixer. During the mixing process, water is added. The mixture is fed to a flat die press (3.25 mm) to form pellets. A die press is used to avoid the addition of excess amounts of water (> 10%) as this needs to be removed before or in the thermal treatment process leading to a larger energy consumption.

3.2. Rotary reactor

The pellets are treated in an indirectly heated lab-scale rotary reactor (length: 1100 mm, inner diameter about 75 mm). As the tube is exchangeable, different materials can be used. The data shown is obtained in a SiC and a steel tube. The rotation speed is regulated by a frequency converter; it is 4.2 rotations per minute in all experiments. The temperature of the reactor is controlled by three PID-controllers (Eurotherm 2132); it is measured at the outer diameter of the tube with three thermocouples. The reactor is heated with electrical heating elements (which cover 730 mm of the tube). The resulting bed temperature in the bed container is also measured with a thermocouple type K (Ni–CrNi). Because of the corrosion of the thermocouple during the measurement, an increase in Cr and Ni concentrations in the samples can be observed. The air which flows into the reactor can be preheated electrically. A flow sheet of the lab-scale plant is presented in Fig. 2.

The experiments are carried out in batch-mode (see Fig. 3). For every experiment, 150 ± 1 g pellets are filled into a bed container made of quartz glass. At the start of the treatment, the container is pushed into the reactor. It takes about 5 min to heat the container with its content to the envisaged treatment temperature. Every 5 min the temperature of the pellet bed is measured. At the end of the treatment, the container is pulled out. After an initial cooling for 5 min inside the bed container the treated pellets are

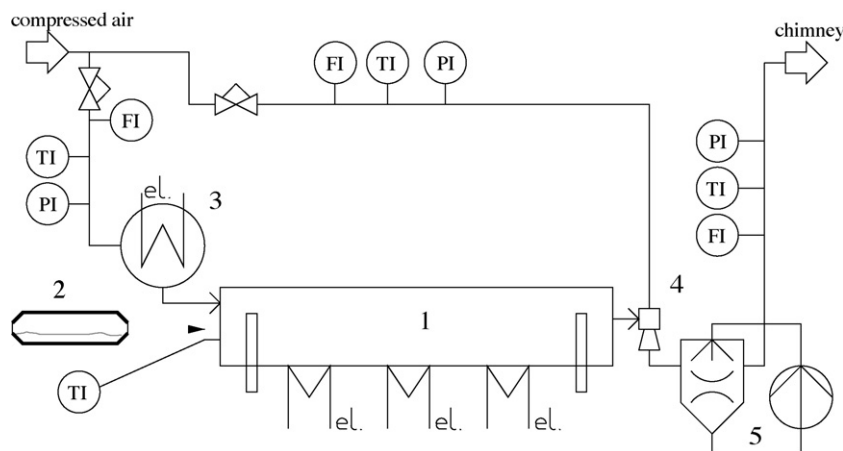


Fig. 2. Flow sheet of the lab-scale rotary reactor and the off-gas cleaning. 1 rotary reactor, 2 bed container (has to be inserted), 3 air preheater, 4 T-junction, 5 scrubber and flue gas cleaning.

filled into a beaker for cooling down to ambient temperature. The cooled, treated pellets are weighed again and stored in plastic bags.

3.3. Scrubber

The off-gas of the reactor is cooled with a stream of excess air (measured by a variable area flow meter) in a T-junction made of quartz glass to achieve temperatures below 260 °C. The gas mixture is washed in a venturi scrubber made of PTFE. The two-phase mixture is separated in a cyclone, the liquid phase is recycled (see Fig. 2). The volume flow (variable area flow meter) and the state of the washed off-gas are measured and then the gas is sucked out by the chimney fan. The gas velocity in the reactor can be varied by regulating the volume flow of the off gas. After several experiments the volume of the washing water is measured, filtered and sampled for heavy metal analysis. The dust in the T-junction is washed with de-ionized water into a beaker; the solution is filtered and also analyzed for heavy metals. For the maximum gas velocity, the scrubber and volume flow measurement can be removed.

3.4. Gas velocity

The experiments with a high gas velocity are carried out in the SiC, those with a low one in the steel tube. The scrubber is removed at experiments with high gas velocity to achieve maximum values. The gas velocity can be measured either by a hot-wire anemometer, which is only applicable up to 100 °C or – in case of using the scrubber – by measuring the volume flow, calculation of mass flows and a balance over the T-junction (see Fig. 2). Because of condensed water in the variable area flow meter, there is a systematic error in measuring the gas velocity; it has to be estimated. It is

about 0.5 m s⁻¹ in case of low gas velocity and 4 m s⁻¹ in case of high gas velocity, respectively (calculated for a gas temperature of 1000 °C).

3.5. Heavy metal analysis

The treated and the untreated pellets are dried, pulverized, digested with a mixture from HCl, HNO₃, HF, H₂O₂ and B(OH)₃ and analyzed twice with ICP-OES for the heavy metals Cd, Cu, Pb and Zn. The average value and the relative standard deviations ($Q_{an,ij}$) are calculated. Liquid samples are also analyzed with ICP-OES.

4. Calculations

4.1. Heavy metal removal

To illustrate the effect of temperature, residence time and chloride addition, the measured concentrations of the heavy metals are used to calculate the removal, which is defined as

$$R_{ij} = 1 - \frac{c_{ij}M_j}{c_{0,ij}M_{0,j}}, \quad (4)$$

where R_{ij} is the degree of removal for the element i in the batch j , $c_{i,j}$ is the concentration of the element i in the batch j in the treated sample, M_j is the mass of the treated sample of batch j , $c_{0,ij}$ is the concentration of the element i in the untreated sample in batch j and $M_{0,j}$ is the mass of the untreated sample of batch j . Another definition would be $1 - (c_{ij}/c_{0,ij})$, which has the disadvantage that no mass flows of heavy metals were considered, only concentrations. On the other hand, if the mass M_j or $M_{0,j}$ is not well defined (e.g. in continuous mode experiments) or if losses occur due to high gas velocities, that formula can be used. Here, the removal will be calculated according to Eq. (4).

4.2. Error bars

The error bars are calculated according to

$$Q_{ij} = \sqrt{Q_{pa,ij}^2 + Q_{an,ij}^2} \quad (5)$$

(Q_{ij} ... relative standard deviation of $c_{ij}/c_{0,ij}$, index pa ... caused by the parameters temperature, residence time and concentration of added Cl; index an ... chemical analysis), because the uncertainty of the analysis and the uncertainty of errors are independent. $Q_{pa,ij}$

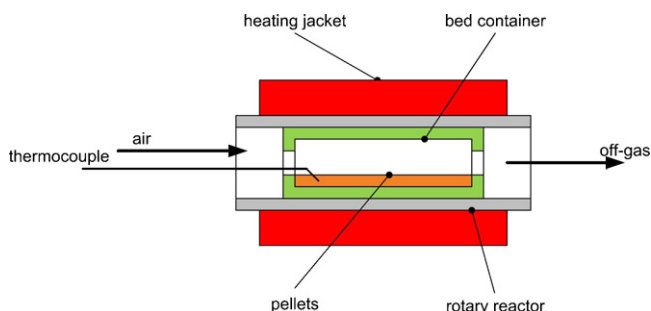


Fig. 3. Principle of the batch experiments.

is obtained by using the Gaussian error propagation, commonly referred to as

$$Q_{pa,ij} := s_f = \sqrt{\sum_{m=1}^n \left(\frac{\partial f}{\partial x_m} \bigg|_{\bar{x}_m} \cdot s_m \right)^2} \quad (6)$$

(standard deviation s_f of the function f with the arguments x_m , the mean values \bar{x}_m and the standard deviation of the arguments s_m) on the regression

$$-\ln \left(\frac{c_i M}{c_{0,i} M_0} \right) = k_{1i} \cdot t + k_{2i} \cdot T + k_{3i} \cdot c_{Cl} + k_{4i}, \quad (7)$$

whereas t is the treatment time (min), T is the operating temperature (K), c_{Cl} is the concentration of chlorine (added as calcium chloride) in the feed material and k_{1i} to k_{4i} are constants. (7) is chosen because of its simplicity. In this way, it is expected that time, temperature and chloride addition affect the removal rate by an exponential function, which is also found in the Arrhenius' law, in the solution of Fick's equation and in the solution for the reaction rates in a first order chemical reaction. The advantage of calculating the error bars according to Eq. (5) is its simplicity: High standard deviations in analysis and due to uncertainties of the parameters can be illustrated quickly. For example, for Cd the values for k_{1Cd} to k_{4Cd} are 0.055 min^{-1} , 0.011 K^{-1} , 4.5 and -14 . The relative standard deviations Q_x for temperature, residence time and chloride concentration are based on the standard deviation of the temperature measurements in the pellet bed, an estimated uncertainty of 20 s in the time measurement (because of the heat-up time and the uncertainty due to manual removal after the treatment) and the discretization error of the digital display of the balance. For example, in the example at a low gas velocity with $c_{Cl} = 0.12 \text{ kg/kg}$, $T = 1000^\circ \text{C}$ and $t = 45 \text{ min}$ the values are $Q_{c_{Cl}} = 0.03\%$, $Q_T = 0.3\%$ and $Q_t = 0.7\%$. With the constants k_{1i} to k_{4i} the derivatives in Eq. (6) describe the influence of certain errors on the relative standard deviation of the parameters. For the example above, $Q_{pa,Cd} = 0.12\%$ is obtained. The relative standard deviation of the analysis is $Q_{an,Cd} = 3.7\%$, this leads to a total standard deviation $Q_{Cd} = 3.7\%$ (relative standard deviation of $c_{ij}/c_{0,ij}$). Usually the influence of the analysis on the total standard deviation is more pronounced (except at low residence times). With respect to the mass loss (about 10%) and its standard deviation, the standard deviation of the removal is 0.28% (standard deviation of R_{ij}). For the example a standard deviation of 0.85% (standard deviation of $1 - M_j c_{ij}/M_{0,j} c_{0,ij}$) is obtained, which is indicated in Figs. 5–8.

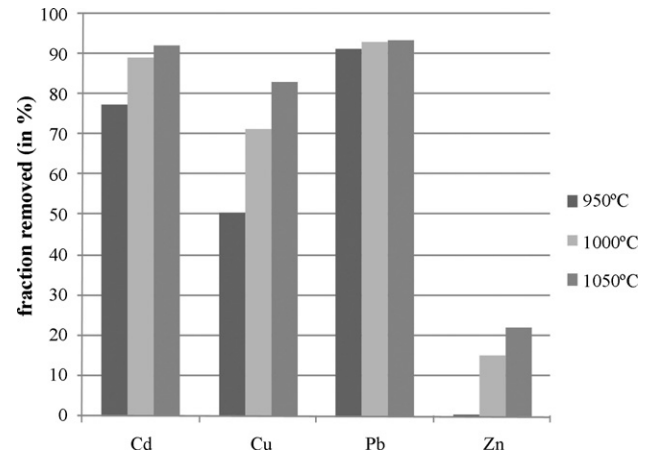


Fig. 4. Reference experiments with pure ash (unpelletized) at a residence time of 45 min. Definition of the removal (see Eq. (4)).

4.3. Recovery of heavy metals in the off-gas cleaning system

The recovery Υ_i of the element i is defined as

$$\Upsilon_i = \frac{\Xi_i}{\Theta_i} \quad (8)$$

whereas Ξ_i is the mass of the element i which is found – after several batches – in the three fractions treated pellets, T-junction and scrubber (in dissolved form) and Θ_i is the mass of the element i which is contained in the untreated sample of the same batches mentioned above.

The recovery of experiments at high gas velocities cannot be calculated because of the missing fractions “T-junction” and “scrubber” due to the necessary removal of the gas cleaning system (see Section 3.4).

5. Results

5.1. Reference experiments

Reference experiments with pure ash at 950, 1000 and 1050 °C were carried out (see Fig. 4). Because it is not possible to pelletize pure ash, it is treated “as it is”. Up to 92% Cd, 83% Cu and 22% Zn can be removed at 1050 °C. Regarding concentrations it must be noted that the concentration of Zn does not change at all during the treatment.

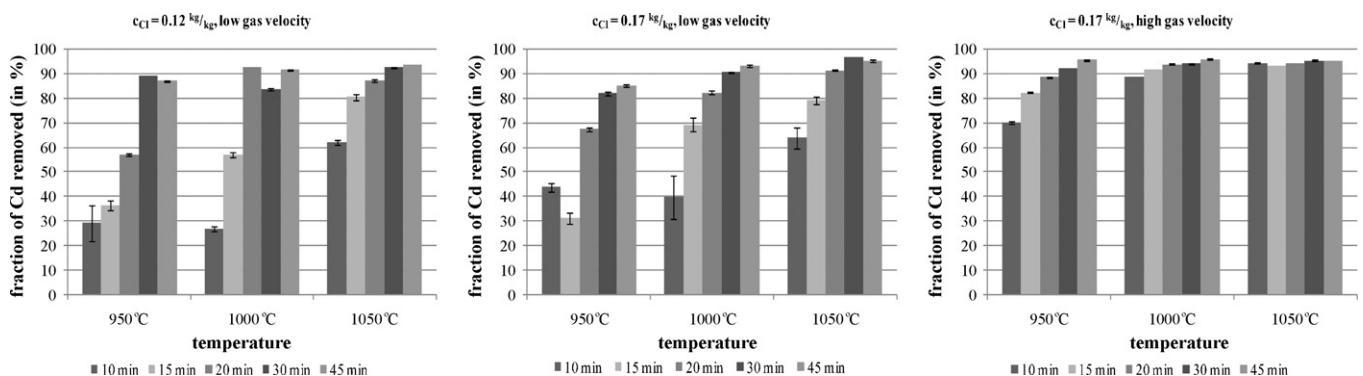


Fig. 5. Removal of cadmium Cd. Definition of the removal (see Eq. (4)), error bars are the standard deviation, calculation (see Eq. (5)). c_{Cl} is the concentration of Cl from the CaCl_2 -addition (kg/kg). Low gas velocity: approximately 0.5 m s^{-1} , high gas velocity: approximately 4 m s^{-1} .

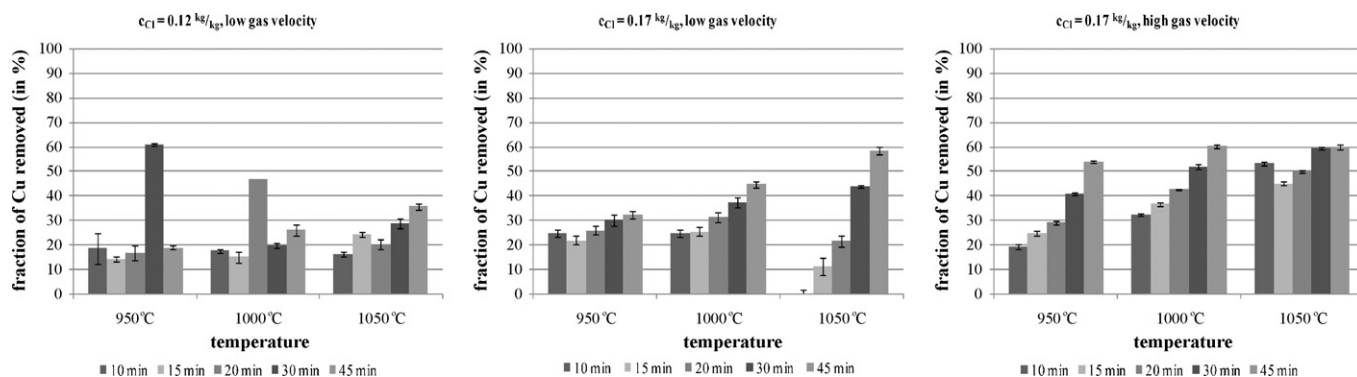


Fig. 6. Removal of copper Cu. Definition of the removal (see Eq. (4)), error bars are the standard deviation, calculation (see Eq. (5)). c_{Cl} is the concentration of Cl from the $CaCl_2$ -addition (kg/kg). Low gas velocity: approximately 0.5 m s^{-1} , high gas velocity: approximately 4 m s^{-1} .

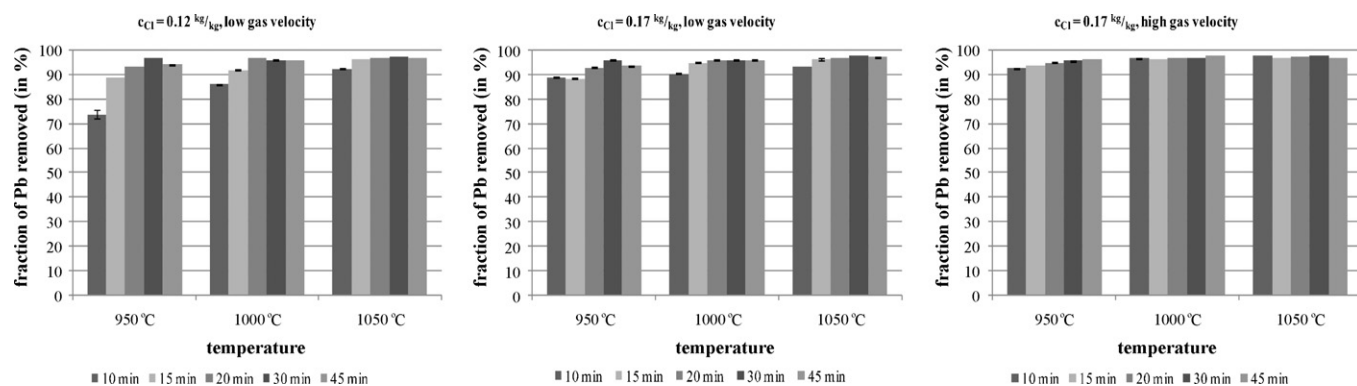


Fig. 7. Removal of lead Pb. Definition of the removal (see Eq. (4)), error bars are the standard deviation, calculation (see Eq. (5)). c_{Cl} is the concentration of Cl from the $CaCl_2$ -addition (kg/kg). Low gas velocity: approximately 0.5 m s^{-1} , high gas velocity: approximately 4 m s^{-1} .

5.2. Influence of calcium chloride addition, temperature and residence time

The results of two experiments ($c_{Cl} = 0.12 \text{ kg/kg}$, 950°C , 30 min; $c_{Cl} = 0.12 \text{ kg/kg}$, 1000°C , 20 min) shown in Figs. 5–8 do not fit the trends depicted by their neighbours. Therefore these results are omitted in the subsequent discussion.

5.2.1. Cadmium Cd

As seen in Fig. 5, a concentration of added chloride $c_{Cl} = 0.17 \text{ kg/kg}$ causes at 950 and 1000°C at residence times below 30 min a removal, which is about 10% higher than in experiments with $c_{Cl} = 0.12 \text{ kg/kg}$ (whereas at 950°C and 10 and 15 min there is no clear statement possible). At residence times of 30 and 45 min, respectively, it seems that a lower concentration of Cl effects a

higher removal. At 1050°C and low gas velocities, there is nearly no effect of the chloride addition detectable in the investigated range.

Generally, higher temperatures and longer residence times cause higher removal rates, whereas the influence of the residence time is more pronounced at lower temperatures and vice versa. It is possible to remove 95% of Cd at 1050°C and 45 min.

5.2.2. Copper Cu

Fig. 6 reveals that a higher addition of $CaCl_2$ improves the removal of Cu: At 45 min, 0.17 kg/kg Cl added and 950°C the evaporated amount is approximately 10%, at 1000°C 20% and at 1050°C approximately 25% higher than in the results with 0.12 kg/kg Cl added. Apparently, the influence of the treatment temperature is more distinctive at higher residence times. At 1050°C , it seems, that at low residence time (10 and 15 min) the removal rate is even

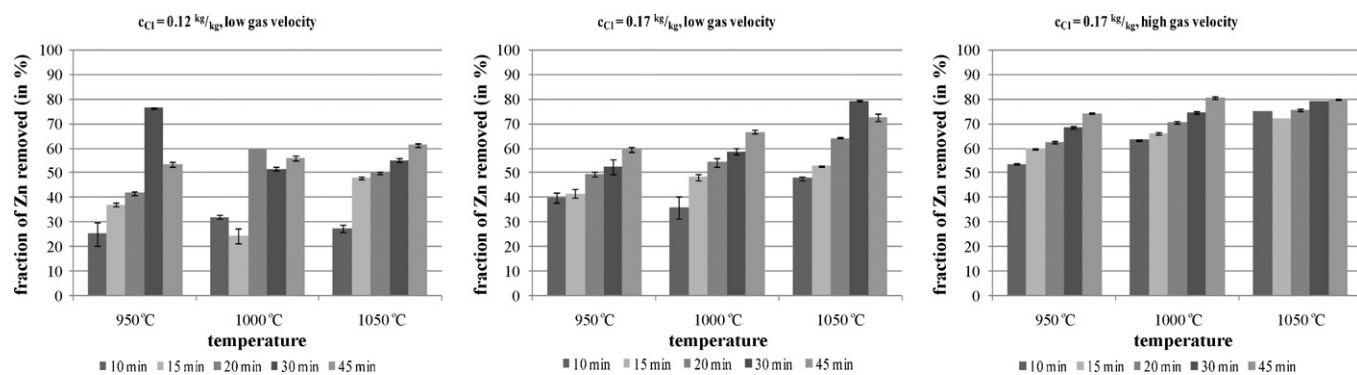


Fig. 8. Removal of zinc Zn. Definition of the removal (see Eq. (4)), error bars are the standard deviation, calculation (see Eq. (5)). c_{Cl} is the concentration of Cl from the $CaCl_2$ -addition (kg/kg). Low gas velocity: approximately 0.5 m s^{-1} , high gas velocity: approximately 4 m s^{-1} .

smaller than at 950 and 1000 °C, above all at $c_{Cl} = 0.17$ kg/kg. Later on it increases more rapidly with an increasing residence time in the experiments at 1050 °C than in the others. The absolute removal of Cu is very low compared to Cd and Pb; in the best case it does not even reach 50%.

5.2.3. Lead Pb

Due to its good removal, Pb does not show a dependency on the chloride addition in the examined range, except at 10 min and 950 °C and 1000 °C, respectively (see Fig. 7). The influence of the residence time is very low, particularly at higher temperatures. Even at 950 °C, $c_{Cl} = 0.12$ kg/kg it is possible to remove more than 90% of Pb at residence times > 20 min. At 1050 °C, up to 97% of Pb can be separated.

5.2.4. Zinc Zn

Fig. 8 shows, that the removal of Zn is almost 10% higher in those experiments with $c_{Cl} = 0.17$ kg/kg, independent of residence time and temperature. In the investigated range, the residence time has a higher influence than the temperature. At $c_{Cl} = 0.17$ kg/kg, 1050 °C and 45 min, a maximum amount of 72% of Zn can be removed.

5.3. Influence of gas velocity

The “high” gas velocity is about eight times higher than the “low” gas velocity. In most cases, a higher gas velocity causes a higher removal rate for all elements. It must be noted that in experiments at high gas velocities an additional mass loss occurs due to entrained dust, which positively affects the removal as defined in Eq. (4). However, the greater the removal, the smaller this influence.

5.3.1. Cadmium Cd

The higher the temperature, the smaller is the increase of the removal with the temperature at high gas velocities (see Fig. 5) because of the already high absolute removal level at the shortest residence time. At 1050 °C, a high gas velocity leads to more than 90% removal even at a residence time of 10 min while at low velocities this value is not reached within 20 min. At 950 °C, in both cases the removal rises with the residence time, at high gas velocities this increase is on a higher level (from 70% at 10 min to 95% at 45 min instead of 43% to 84%, respectively).

5.3.2. Copper Cu

For Cu, the removal increases in general with the gas velocity, especially in experiments at 1000 and 1050 °C (see Fig. 6). At 1050 °C, the removal increases with increasing time at low gas velocities, at high ones the increase is less pronounced. At 950 °C, it generally seems for low residence times that a lower gas velocity is better for the removal, at higher residence times the removal behaves as stated above.

5.3.3. Lead Pb

For Pb, the influence of the gas velocity is negligible (see Fig. 7). At high gas velocities, the removal is > 90% in all experiments. It seems that the maximum amount of removed Pb is somewhat higher at high gas velocities.

5.3.4. Zinc Zn

For Zn, the removal rates increase about 10% at a higher gas velocity (Fig. 8). This effect can be observed at almost every treatment temperature and residence time. Only at 1050 °C and at a residence time larger than 30 min is the influence of the gas velocity less pronounced.

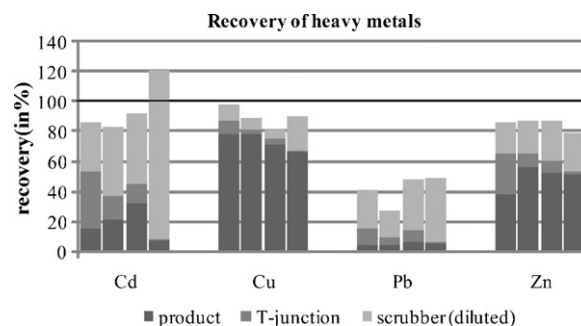


Fig. 9. Recovery of heavy metals in the product, in the T-junction and the scrubber (in diluted form). 100% is the content of the element in the untreated sample.

5.4. Recovery of heavy metals in the off-gas cleaning system

Fig. 9 shows the recovery of heavy metals in the treated product, in the scrubber and in the T-junction for five test series (serial nr. 1: 5 batches, nr. 2: 7, nr. 3: 6, nr. 4: 11 batches). 100% is the amount of the element concerned in the untreated sample. Between 83 and 121% of Cd, 81–98% Cu, 27–49% Pb and 79–87% Zn can be found in different fractions after the experiment. Due to their high degree of removal, Cd and Pb are mainly recovered in the scrubber and in the T-junction, whereas Cu and Zn remain in the solid product.

6. Discussion

6.1. Quality of measured data

The standard deviations of the analyses are relatively small. The chosen method for calculating the total error (analysis and parameter) overstates the error at low residence times (see Section 4.2). The absolute values of the removed fractions are not always conclusive. A different path for obtaining data and relative standard deviation would be to repeat every experiment, e.g. three times and to average the concentrations (like Mattenberger et al. [15]). However, the effort of doing these additional trials would significantly raise costs.

6.2. Reference experiments

Without chloride addition and without pelletizing, quite a high amount of Cd, Cu and Pb can be removed. The observed removal of Zn in Fig. 4 can be ascribed to mass losses due to entrained dust. Apparently, Zn compounds in fly ash are stable, i.e. the amount of evaporable Zn and ZnCl₂ is very low. The removal of Cu is even better than in the experiments with added CaCl₂. Probably the evaporation of Cu is hindered by diffusion in the pellet. Another possible effect is beside the precipitation of stable Cu-compounds the occurrence of secondary reactions in the pelletized ash–CaCl₂–admixture hindering evaporation.

6.3. Influence of calcium chloride addition, residence time and temperature

A higher temperature generally causes a higher removal rate according to literature [3,14,15]. In the data shown, this effect can – more or less – be observed for all heavy metals. A higher temperature facilitates the formation of heavy metal chlorides, their evaporation and their diffusion inside the pellets. As already stated by Jakob and Moergeli [7], the maximum amount removable is nearly independent of the temperature. In the presented data, however, this can only be observed for the highly volatile elements Cd and Pb.

It seems that the removal of Cd and Pb is almost complete, i.e. longer residence times will not increase the evaporated amount of these heavy metals. By contrast, the removal of Cu and Zn in the treated sample might consequently continue to further increase at longer residence times.

As the original ash contains Cl itself (present as NaCl and KCl), heavy metals are removed by Cl from the ash and by added Cl from CaCl₂. Mattenberger et al. [15] found that KCl affects the removal of Cu, which can also be observed in the reference experiments. In the results shown here, added CaCl₂ affects the removal of both Cu and Zn in a positive manner.

The low removal of Cu and Zn could be caused by the high content of these elements in the ash or a disadvantageous availability in the ash (either embedded in the matrix or as stable compounds, which are hardly affected by Cl), or by the Cl being available at the wrong time during the experiment. Thus, the reaction and diffusion rate is relatively low. Also, Cl compounds (CaCl₂, KCl, NaCl) react with water and oxygen forming HCl and Cl₂. These gaseous compounds diffuse from the pellet into off-gas already during the heat up phase, so that this Cl is not available for further reactions with Cu and Zn compounds. Probably in a co-current rotary reactor the removal of Cu and Zn will be higher than in the presented batch-experiments. HCl and Cl₂ from the gas atmosphere can react subsequently with Cu and Zn after diffusion into the pellets in the bed because a part of the bed is always in the hottest zone of the reactor downstream of the zone of Cl-release from the pellets.

6.4. Influence of gas velocity

Higher gas velocity causes two effects:

1. Higher gas velocity alters the boundary layers of the pellet (in general they become more narrow) and so heat and mass transfer are increased. That is the initial heating rate of the ash inside the pellet becomes higher; this leads to higher reaction and diffusion rates. The mass transfer from the pellet surface to the reactor atmosphere is also enhanced.
2. Higher flux in the reactor dilutes the heavy metal containing atmosphere and faster discharges gaseous heavy metal compounds: the gradient of the concentration of the heavy metal from pellet body to atmosphere becomes greater which accelerates the diffusion.

In the results presented, both effects play a role. The (slightly higher) concentration of oxygen in the reactor atmosphere at high gas velocities is neglectable: Lutz [14] found, that an increase of the oxygen concentration from 0.4 to 6.0% in the atmosphere does not enhance the removal eminently [14].

It has to be noticed that the amount of entrained dust is higher in experiments at high gas velocities. This apparently enhances the removal according to Eq. (4) of heavy metals, above all if $c_{ij}/c_{0,ij}$ is small.

6.5. Recovery of heavy metals in the off-gas cleaning system

The recovery of Cd, Cu and Zn is mostly above 80%, that one of Pb much lower. This is due to of the low solubility of Pb under acidic conditions (acid scrubber; only diluted compounds were analyzed). Furthermore, low-soluble PbO and PbCl₂ are not removed completely from the T-junction by de-ionized water. Nitric acid would have been a better choice. Apparently, droplets are not totally precipitated after the single-stage venturi scrubber and the mass transfer from the gas to the liquid phase is not complete. A second scrubber (to obtain at least two stages), e.g. a packed column, and

the analysis of undissolved compounds could help to reach about 100% recovery for all heavy metals.

6.6. Concentrations of heavy metals and threshold values

The lowest remaining concentrations of heavy metals could be achieved in the experiments with $c_{Cl} = 0.17$ kg/kg at high gas velocities, 1050 °C treatment temperature and 45 min residence time. The remaining concentration is about 17 ppm for Cd, 390 ppm for Cu, 140 ppm for Pb and 4500 ppm for Zn. So, – contrary to the product of the CT-Fluapur®-process [7,8] – for use as cement admixture, the guidance level for pulverized coal ash and blast furnace slag published by BAFU [24] could not be reached. The limit values from the Austrian regulation on concrete disposals [1] (10 ppm Cd, 500 ppm Cu, 500 ppm Pb and 1500 ppm Zn) are complied with only for Cu and Pb. Anyway, the material complies – depending on individual national legislation – with dump categories where disposal should clearly be less costly than current disposal practices.

6.7. Formation of dioxins and furans (PCDD/PCDF)

Dioxins and furans can be formed in the process if reducing conditions occur because chloride is as well as heavy metals available. On the other hand the temperature, which is necessary for heavy metal removal (> 1000 °C), hinders the formation, if the gas residence time in the (industrial) rotary kiln is long enough (> 1s) and if the turbulence in the kiln is sufficiently high [28]. Additionally, rapid gas cooling of the off-gas (e.g. by water injection [29]) in the range between 400 and 250 °C will inhibit the “de novo synthesis” [28].

7. Conclusions

The objectives were to test the behavior of MSW fly ash in the ASH DEC process. Higher temperatures (950–1050 °C), higher chloride concentrations (0.12–0.17 kg/kg), longer residence times (10–45 min) and higher gas velocities (0.5–4 m s⁻¹) generally cause a higher removal of heavy metals. For example, an increase of the operating temperature from 950 to 1050 °C at a residence time of 45 min leads to an increase in removal of Cu and Zn of about 10% in all experiments. That is about the same as what can be achieved by an increase of the chloride concentration from 0.12 to 0.17 kg/kg. For the highly volatile elements Cd and Pb higher temperatures and higher chloride concentrations do not have such a significant influence. As the occurring mass transfer processes are time-sensitive, changing the residence time from 10 to 45 min, the removal of the elements Cd, Cu and Zn increases by a factor of 1.5–3 (at 1000 °C and low gas velocities). Higher gas velocity enhances mass transfer processes. Mainly at short residence times the removal of Cd and Zn is accelerated. Highest removal rates obtained were 95% of Cd, 60% of Cu, 97% of Pb and 80% of Zn.

The concentrations of heavy metals in the treated samples are still above the guidance level of pulverized coal ash and blast furnace slag published by BAFU [24] to allow usage as a cement admixture in Switzerland. Nevertheless, a better material quality could be reached at this stage of development. The material complies – depending on individual national legislation – with dump categories where disposal should clearly be less costly than current disposal practices.

8. Outlook

Further work is necessary to achieve residual concentrations which are within the range of pulverized coal ash and blast furnace slag. Other reactor types will be studied that offer a better heat

and mass transfer, which should increase the removal rates of Cd, Cu, Pb and Zn. Additionally, reducing conditions offer an additional potential for the removal of Cd, Pb and Zn. Longer residence times will be examined for Cu and Zn because of the time-sensitivity of the removal reactions.

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