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COOPERATION IN THE FIELD OF EMISSIONS ABATEMENT TECHNOLOGY

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Mutual visits:
Lucie Obalová, Kamila Kočí: 1. – 3. 12. 2010 visit in Vienna
Lukáš Skovranek: 15. 11. - 17. 12. 2010 visit in Vienna

The project was realized according to the original plan, accepted by AKTION foundation. During November 15 – December 17, Lukáš Skovranek, Ph.D. student from VŠB-TUO Ostrava visited chemical engineering laboratory at TU Vienna. He dealt with experimental research of fluidization parameters of different materials (sludge, coal, waste and their mixtures) on cold fluidization model. These data will help to optimize emission from process of waste combustion in fluidized bed reactor.

The aim of experimental works of exchange students, which will visit workplace at VŠB-TU Ostrava in spring 2011, was specified at the visit of Czech partners (L. Obalová, K. Kočí) from 1th December till 3th December 2010 at TU Vienna.

We attach copy of our joint publication supported by Aktion project:

Benedikt Nowak, Libor Perutka, Lenka Kuboňová, Lucie Obalová, Kamila Kočí, Harald Mattenberger, Louis Hermann, Franz Winter: *A Study of Heavy Metal Removal from Sewage Sludge Ash*

presented at 37th International Conference of Slovak Society of Chemical Engineering held in Tatranske Matliare, Slovak Republic on May 24 - 28, 2010.

Unutilized financial money (1 982,20 Kč) was used for consumer goods used for project solution.

Obalvá

Prof. Ing. Lucie Obalová, Ph.D.

Ostrava, 17th January 2011

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Institute of Chemical and Environmental Engineering
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A Study of Heavy Metal Removal from Sewage Sludge Ash

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Key words
Sewage sludge ash, Fluidized bed reactor, Decontamination, Heavy metal

1 Introduction

1.1 Phosphor

The current phosphate reserves are 16 billion tons, in 2008 161 million tons were mined, 3% more than 2007 [1]. So, the reserves-to-production-ratio is about 100 years.

Phosphorous is an essential element and not replaceable. 90% of the mined phosphates are used – after digestion – as fertilizer [13]. When mined as a sedimentary mineral, phosphate rock is often contaminated by Cd and U, i.e. these elements end up in agricultural soils [12]. Fertilizing with sedimentary rock phosphate fertilizer (22 kg P / ha) leads to a concomitant contamination by 17-61 g U / ha [7].

The biggest secondary resource of phosphate is sewage sludge [5], which is polluted by organic [6] and inorganic compounds. Sludge incineration destroys organic pollutants and reduces mass and volume of the sludge. The ash cannot be used as fertilizer because it contains heavy metals: E.g., in a Japanese sewage sludge ash (SSA) the concentrations of Cd, Cu, Ni, Sn, Pb and Zn were about 10 – 200 times higher than the concentrations in soil [14]. So, sewage sludge ash is usually deposited in landfills or used for mine filling.

1.2 Process

A promising approach for heavy metal removal from SSA is mixing of sewage sludge ash with environmentally sound chlorides (e.g. calcium chloride) and water and treating this mixture (possibly after pelletizing to avoid dust) at $1000 \pm 100°C$ in a rotary kiln (ASH DEC process). This leads to the formation and evaporation of volatile heavy metal compounds (mainly chlorides). As 90-99% of heavy metals like Cd, Cu, Pb and Zn can be removed, the solid product from the thermal treatment can be directly used for fertilizer production [9].

1.3 Reactions

On molecular scale, the process can be characterized by three governing reaction steps:

1. Formation of HCl or Cl_2 in dependence of the moisture of the reaction atmosphere according to $CaCl_2 + H_2O \rightarrow CaO + 2\ HCl$ or $CaCl_2 + ½\ O_2 \rightarrow CaO + Cl_2$ [3]. HCl and Cl_2 diffuse inside the particles to heavy metal oxides and to the reactor atmosphere as well.

2. Reaction of the intermediates HCl and Cl_2 with heavy metal compounds from the ash, e.g. $2\ HCl + ZnO \rightarrow H_2O + ZnCl_2$ and $Cl_2 + ZnO \rightarrow ½\ O_2 + ZnCl_2$ [4]. Heavy metal chlorides evaporate due to their low boiling points (e.g. boiling point of $ZnCl_2$ is 732°C [8]).

3. Heavy metal chlorides can be adsorbed on matrix material and may react with matrix material (for Zn) according to $ZnCl_2 + SiO_2 + H_2O \rightarrow ZnSiO_3 + 2\ HCl$ [2]. Heavy metal compounds from the ash may also react with matrix material forming stable silicates and aluminates, e.g. $ZnO + SiO_2 \rightarrow ZnSiO_3$ and $ZnO + Al_2O_3 \rightarrow ZnAl_2O_4$ [11]. These reactions reduce the maximum amount removable.
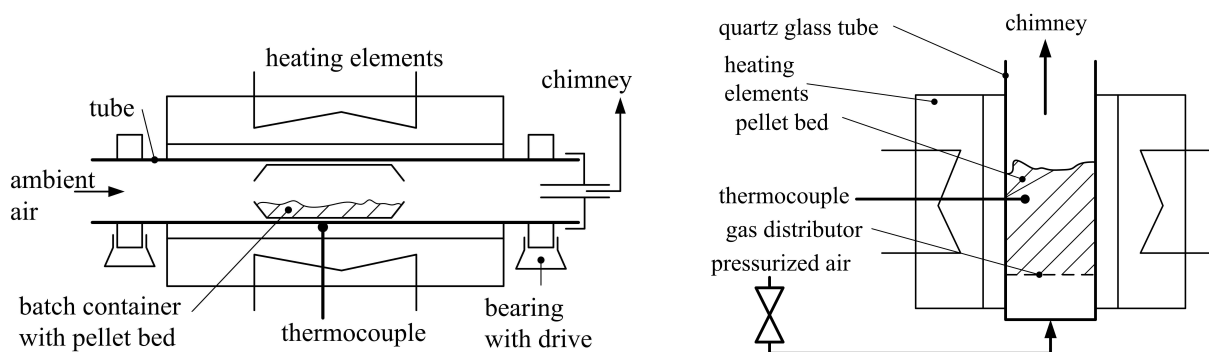
Figure 1: Rotary reactor (left hand side) and fluidized bed reactor (right hand side) used

1.4 Specific objectives

Contrary to rotary kilns fluidized bed reactors (FBR) generally can be characterized by a high heat and mass transfer. So, using a FBR promises the saving of thermal energy and the increase of material throughput. A higher heat and mass transfer will accelerate the steps 1 and 2 from the listing above thus leading to an increase in heavy metal removal.

The aim of this study is to test the described process in a laboratory-scale fluidized bed reactor at different gas velocities and temperatures (850 - 950°C) and to compare the achieved results with those obtained in a laboratory-scale rotary kiln at similar conditions.

2 Experimental Setup

A mixture of sewage sludge ash (from Fernwärme Wien, Vienna, Austria), $CaCl_2$ and water is granulated. The chloride content of the pellets is 150 g per kg ash; the grain size is between 1.4 and 4 mm. The pellets are treated in a laboratory-scale rotary kiln and in a laboratory-scale fluidized bed reactor, see below. After the treatment the sample is milled, digested and analyzed with ICP-OES for the elements Cd, Cu, Pb and Zn.

2.1 Fluidized bed reactor

The stationary (bubbling) laboratory-scale FBR unit (see **Chyba! Nenalezen zdroj odkazů.**) consists of an indirectly heated quartz-glass tube (inner diameter approx. 35 mm). The bed temperature is measured by a thermocouple type K, for fluidization preheated pressurized air is used. The volume flow of the air is indicated by an area flow meter, temperature and pressure are measured as well. Pellets are fed to the preheated reactor. After the treatment, they are removed pneumatically. Particles in the off-gas of the reactor are separated by a cyclone and returned to the reactor.

2.2 Rotary reactor

The rotary reactor (see **Chyba! Nenalezen zdroj odkazů.**) consists of an indirectly heated tube (material: SiC-Si, heat conductivity approx. 100 W m^{-1} K^{-1}) with a rotation speed of 4.2 min^{-1}. The temperature is measured at the outer surface of the tube. At the reactor inlet, ambient air is taken in; the off-gas is cleaned in a venturi-scrubber; volume flow, pressure and temperature are measured in the off-gas which is sucked off by the chimney fan.

The sample is filled into a batch container (quartz glass) which is pushed into the preheated reactor at the start of the treatment. At the end of the treatment, the whole container is pulled out again. A more detailed description of the rotary kiln used can be found in a previous publication [10].

3 Results

Experiments are carried out in the rotary reactor and in the fluidized bed reactor at different gas velocities (6.7, 8.0 and 11 m s^{-1}). The treatment temperature is 850, 900 and 940°C (currently possible maximum temperature in the fluidized bed reactor); the residence time is varied between 10 and 60 min.
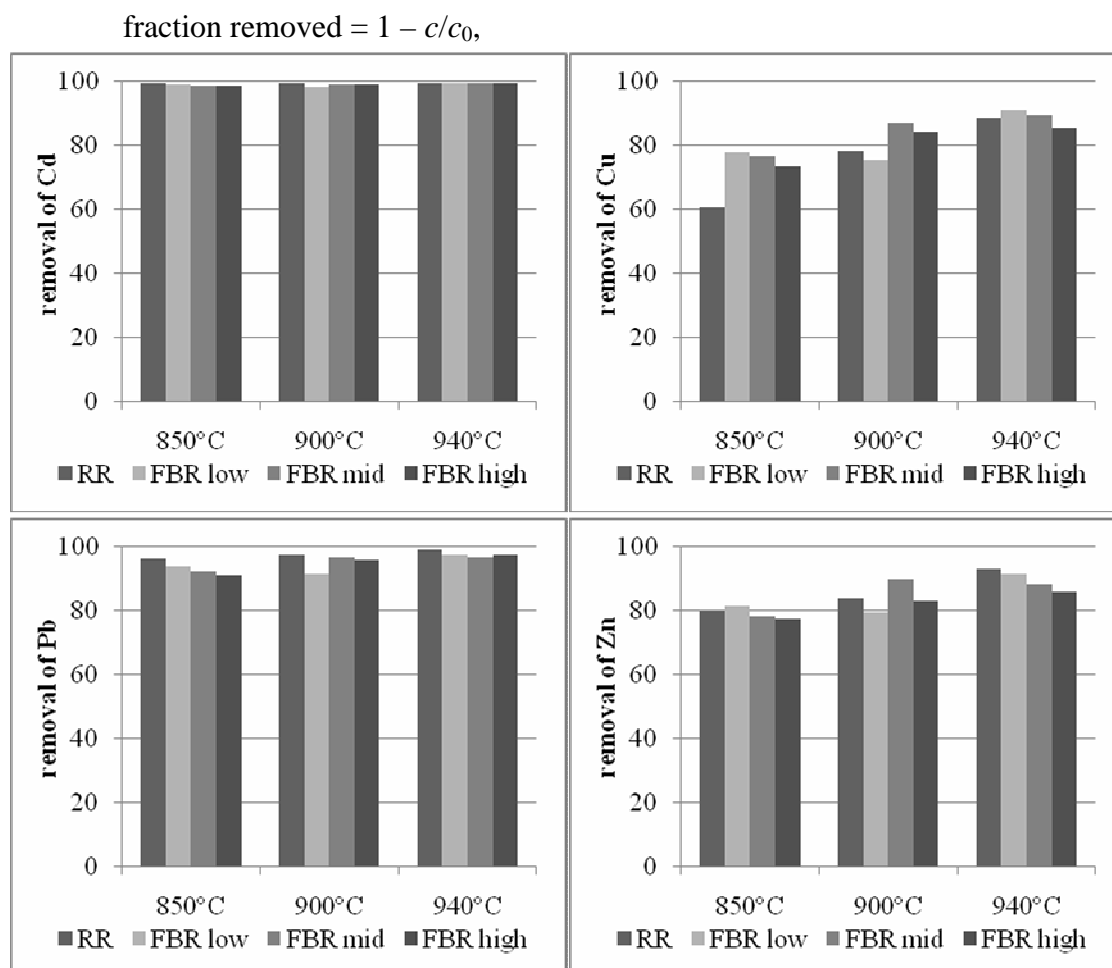
The removal is calculated according to

$$\text{fraction removed} = 1 - c/c_0,$$

Figure 2: Fraction of Cd, Cu, Pb and Zn removed; residence time 30 min; RR rotary reactor, FBR fluidized bed reactor, low 6.7, mid 8.0 and high 11 m s⁻¹ (superficial velocity)

(concentration of the investigated element in the treated sample c and in the untreated sample c_0). Due to losses of particles during sampling (pneumatically) in the fluidized bed reactor, the total mass of the sample cannot be factored into the equation above. The removal as defined above is thus smaller than the removal regarding element masses.

Generally, Cd and Pb can be removed well (up to >99%, depending on reactor and temperature). The removal of Cu and Zn in all experiments is incomplete; a maximum of 91% of Cu and 93% of Zn can be removed.

3.1 Influence of treatment temperature on heavy metal removal

The influence of the treatment temperature (residence time 30 min) is illustrated in Figure 2. A higher temperature always leads to a higher heavy metal removal in the investigated range.

For Cd, the influence of the temperature on the removal is low as the removal is very high in every case.

The removal of Cu increases from 61% in the rotary reactor (RR) at 850°C to 89% at 940°C, in the fluidized bed reactor (FBR mid) it reaches 77% at 850°C and 89% at 940°C.

For Pb, the removal in the rotary reactor is always > 96%, at 940°C 99% can be achieved. The removal can be improved from 92% (FBR mid) to 97% by changing the temperature from 850 to 940°C.

The removal of Zn is 80-93% in the rotary reactor (850-940°C), in the fluidized bed reactor it reaches 78-88% at similar conditions (the value of Zn removal for FBR mid at 900°C is qualified as an outlier because it does not fit to the trends of the gas velocity and the temperature).

3.2 Influence of residence time on heavy metal removal

The longer the residence time in the reactor, the higher is the heavy metal removal (Figure 3) whereas removal rates are higher at low residence times.
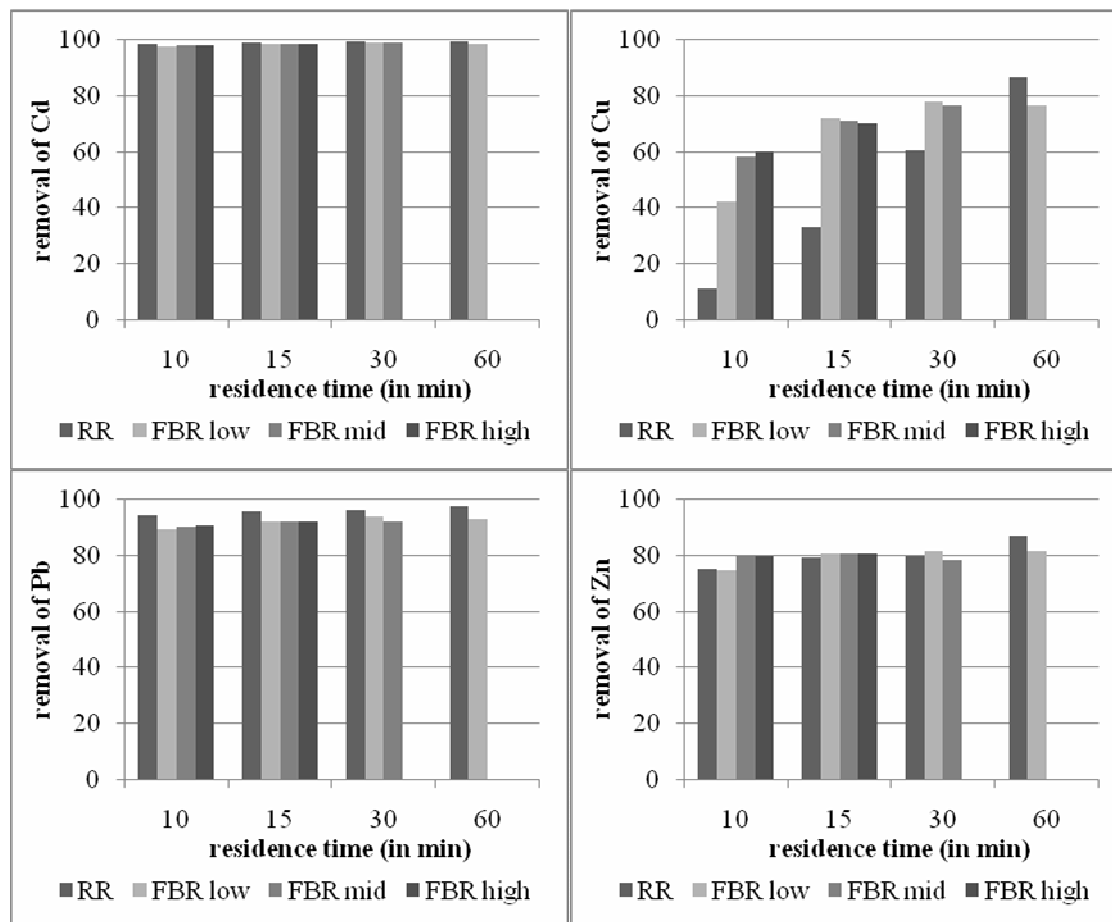

Figure 3: Fraction of Cd, Cu, Pb and Zn removed; temperature 850°C; RR rotary reactor, FBR fluidized bed reactor, low 6.7, mid 8.0 and high 11 m s^{-1} (superficial velocity)

The removal of Cd is always > 98% in the experiments at 850°C.

In the rotary kiln, the removal of Cu increases from 11% after 10 min to 60% after 30 min (87% after 60 min). In the fluidized bed reactor, the initial removal is higher (59% after 10 min), after 30 min 77% can be evaporated.

For Pb, the maximum amount which can be evaporated at 850°C is achieved after 10-15 min; after 15 min it is for FBR low, mid and high 92%, for the rotary reactor it is 96%. A longer residence time than 15 min (e.g. 60 min) increases the removal by no more than 2% additionally.

The removal of Zn is hardly affected by the residence time; it is always in the range of 75-87%. In the fluidized bed reactor, after 15 min the maximum of ca. 81-82% is achieved, in the rotary reactor it is nearly the same, whereas it is not clear if the value after 60 min has to be qualified as an outlier.

3.3 Influence of mass transfer on heavy metal removal

It can generally be assumed that the heat and mass transfer coefficients increase with RR < FBR low < FBR mid < FBR high, whereas reaction rates and diffusion coefficients (in solid and gas) depend on the reactor temperature. In the experiments performed, the influence of mass transfer (or in general the mass transfer by convective transport) is not that consecutive.

Cd does not show an influence of the mass transfer due to its good removal.

For Cu, the maximum amount can be evaporated in the fluidized bed reactor. Depending on the temperature, the maximum amount is found at FBR low or FBR mid. Depending on the residence

time, the maximum amount of evaporated Cu can clearly be found after 10 min at FBR high, after a longer treatment it can be found at lower gas velocities, but differences are minute.

The removal of Pb is more or less affected negatively by a higher mass transfer as the removal is always higher in the rotary reactor than in the fluidized bed.

Zn behaves similarly (Figure 2) even though the trend cannot be distinguished so far.

4 Discussion

4.1 Experimental setup

The setup in **Chyba! Nenalezen zdroj odkazů.** indicates two different temperature measuring methods: for the fluidized bed reactor, the temperature of the bed is measured; for the rotary reactor the temperature is measured at the outer diameter of the tube. Thus, the temperature for FBR-experiments which is indicated in Figure 2 and Figure 3 is the *real* bed temperature. The measured bed temperature of the rotary reactor is about 30°C lower than the temperature at the outer diameter of the tube (measurement not shown). I.e. the bars for the rotary reactor in Figure 2 and Figure 3 can be shifted for 30°C to the left.

Nevertheless, the measuring method *defines* the indicated temperature.

4.2 Influence of temperature and residence time

An increasing temperature always leads to a higher removal because mainly reactions, but also mass transfer processes (as diffusion) are accelerated. For Cu, this trend is most pronounced, for Cd and Pb it is less pronounced (due to their good removal).

Longer residence times also lead to a better heavy metal removal. Especially the removal of Cu proceeds slowly; long residence times are necessary to achieve maximum evaporation.

Regarding the boiling points of the heavy metal chlorides ($CdCl_2$: 960°C, CuCl: 1400°C, $PbCl_2$: 951°C, $ZnCl_2$: 732°C [8]), the behavior of Cu can be explained by the relatively high boiling point of its chloride.

4.3 Influence of mass transfer

In the experiments shown, a higher mass transfer does not necessarily lead to a higher removal. Depending on treatment temperature and residence time, the maximum amount evaporated of Cd, Cu, Pb or Zn occurs at different conditions (in Figure 2 and Figure 3 illustrated as RR and FBR low, FBR mid and FBR high).

This can be explained by the three governing reaction steps described in section 1.3. Possible limiting steps in this reaction scheme could be

1. the heating rate of the particles in the reactor;
2. reaction kinetics of the decomposition of $CaCl_2$ (temperature dependent);
3. diffusion rates of HCl and Cl_2 in the pellet (temperature dependent);
4. reaction kinetics of the reaction of HCl and Cl_2 with heavy metal compounds (temperature dependent);
5. diffusion rates of formed heavy metal chlorides (temperature dependent);
6. reaction kinetics of matrix reactions (temperature dependent).

The limiting step may differ for every single heavy metals.

The removal of Cu is superior in the fluidized bed reactor. Regarding the experiments on the influence of residence time (Figure 3), one limiting step is the heating rate of the particle: In the rotary reactor, the heat-up time is about 4-5 min, which is almost 50% of the residence time of the shortest experiment (10 min). This fits also to the relatively high boiling point of CuCl (see above). Apparently, HCl and Cl_2 are formed within a short time (as can be seen by the high removal of Pb and Zn after only short treatment times). Thus, steps 2 and 3 from the list above are not limiting the removal of Cu. Step 4 is also not limiting because it is competing with step 3: HCl and Cl_2 either diffuse to the particle surface and migrate to the reactor atmosphere (where they are more or less lost for further reactions) or they react in the particle. Step 5 and 6 are also competing: heavy metal

chlorides either migrate to the reactor atmosphere (they are removed) or they react with the matrix. Thus, the removal of Cu is limited by the diffusion of CuCl to the reactor atmosphere. I.e. a higher mass transfer will enhance the removal of Cu.

The removal of Pb, which is very high, is limited by the availability of Cl. I.e. the limiting step is step 3 (hindering step 4: once HCl and Cl_2 are migrated to the reactor atmosphere they are lost).

Zn behaves similarly to Pb. Thus, its removal is also limited by the reaction rate of Zn compounds with HCl and Cl_2 and/or the fast diffusion of HCl and Cl_2.

Concerning the defined reactor temperature from section 4.1, the described effects are fleshed out for Pb and Zn; for Cu it is reversed.

Nevertheless, the limiting steps of the removal of a certain heavy metal can be shifted by different reactor temperatures and residence times exceeding the investigated range. Due to the removal mechanism and its kinetic constants which depend on several parameters (e.g. temperature), the removal may be de- or increased in a fluidized bed reactor compared to a rotary kiln at e.g. higher temperatures.

5 Conclusions

In a fluidized bed reactor and in a rotary reactor experiments with the aim of heavy metal removal of a granulated mixture of sewage sludge ash and $CaCl_2$ were performed. Although the mass transfer is higher in the fluidized bed reactor, the removal especially of Pb and Zn is not necessarily higher than in the rotary reactor. This was found to be due to the accelerated migration of formed HCl and Cl_2 out of the particles into the reactor atmosphere.

Acknowledgements

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A Study of Heavy Metal Removal from Sewage Sludge Ash

Benedikt Nowak[a], Libor Perutka[b], Lenka Kuboňová[b], Lucie Obalová[b], Kamila Kočí[b], Harald Mattenberger[c], Louis Hermann[c], Franz Winter[a]

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Introduction

Phosphorous is an essential element for plants grow and 90% of the mined phosphates are used – after digestion – as fertilizer. Sewage sludge ash (SSA) is the biggest secondary resource of phosphate. However, the SSA cannot be directly used as fertilizer because it contains heavy metals. A promising approach for heavy metal removal from sewage sludge ash is mixing of sewage sludge ash with environmentally sound chlorides (e.g. calcium chloride) and water and treating this mixture (possibly after pelletizing to avoid dust) at $1000 \pm 100°C$ in a rotary kiln (ASH DEC process). This leads to the formation and evaporation of volatile heavy metal compounds (mainly chlorides). As 90-99% of heavy metals like Cd, Cu, Pb and Zn can be removed, the solid product from the thermal treatment can be directly used for fertilizer production.
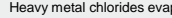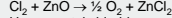
Reactions
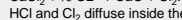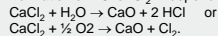
1. Formation of HCl or Cl_2 in dependence of the moisture of the reaction atmosphere:
   $CaCl_2 + H_2O \rightarrow CaO + 2 HCl$ or
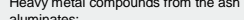 $CaCl_2 + \frac{1}{2} O2 \rightarrow CaO + Cl_2$.
   HCl and Cl_2 diffuse inside the particles to heavy metal oxides and to the reactor atmosphere as well.
2. Reaction of the intermediates HCl and Cl_2 with heavy metal compounds from the ash
   $HCl + ZnO \rightarrow H_2O + ZnCl_2$
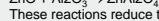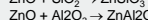 $Cl_2 + ZnO \rightarrow \frac{1}{2} O_2 + ZnCl_2$
   Heavy metal chlorides evaporate due to their low boiling points (e.g. boiling point of $ZnCl_2$ is 732°C).
3. Heavy metal chlorides can be adsorbed on matrix material and may react with matrix material, for Zn:
   $ZnCl_2 + SiO_2 + H_2O \rightarrow ZnSiO_3 + 2 HCl$
   Heavy metal compounds from the ash may also react with matrix material forming stable silicates and aluminates:
   $ZnO + SiO_2 \rightarrow ZnSiO_3$
   $ZnO + Al_2O_3 \rightarrow ZnAl2O_4$
   These reactions reduce the maximum amount removable.

Objectives

Contrary to rotary kilns fluidized bed reactors (FBR) generally can be characterized by a high heat and mass transfer. So, using a FBR promises the saving of thermal energy and the increase of material throughput. A higher heat and mass transfer will accelerate the steps 1 and 2 thus leading to an increase in heavy metal removal.
The aim of this study is to test the described process in a laboratory-scale fluidized bed reactor at different gas velocities and temperatures (850 - 950°C) and to compare the achieved results with those obtained in a laboratory-scale rotary kiln at similar conditions.

Experimental Setup

A mixture of sewage sludge ash (from Fernwärme Wien, Vienna, Austria), $CaCl_2$ and water is granulated. The chloride content of the pellets is 150 g per kg ash; the grain size is between 1.4 and 4 mm. The pellets are treated in a laboratory-scale rotary kiln and in a laboratory-scale fluidized bed reactor, see below. After the treatment the sample is milled, digested and analyzed with ICP-OES for the elements Cd, Cu, Pb and Zn.

Influence of temperature and residence time

An increasing temperature always leads to a higher removal because mainly reactions, but also mass transfer processes (as diffusion) are accelerated. For Cu, this trend is most pronounced, for Cd and Pb it is less pronounced (due to their good removal).
Longer residence times also lead to a better heavy metal removal. Especially the removal of Cu proceeds slowly; long residence times are necessary to achieve maximum evaporation.
Regarding the boiling points of the heavy metal chlorides ($CdCl2$: 960°C, $CuCl$: 1400°C, $PbCl_2$: 951°C, $ZnCl_2$: 732°C), the behavior of Cu can be explained by the relatively high boiling point of its chloride.

Influence of mass transfer

In the experiments shown, a higher mass transfer does not necessarily lead to a higher removal. Depending on treatment temperature and residence time, the maximum amount evaporated of Cd, Cu, Pb or Zn occurs at different conditions (in Figure 3 and Figure 4 illustrated as RR and FBR low, FBR mid and FBR high).
This can be explained by the three governing reaction steps. Possible limiting steps in this reaction scheme could be
• The heating rate of the particles in the reactor;
• Reaction kinetics of the decomposition of $CaCl_2$ (temperature dependent);
• Diffusion rates of HCl and Cl_2 in the pellet (temperature dependent);
• Reaction kinetics of the reaction of HCl and Cl_2 with heavy metal compounds (temperature dependent);
• Diffusion rates of formed heavy metal chlorides (temperature dependent);
• Reaction kinetics of matrix reactions (temperature dependent)

Conclusions

In a fluidized bed reactor and in a rotary reactor experiments with the aim of heavy metal removal of a granulated mixture of sewage sludge ash and CaCl2 were performed. Although the mass transfer is higher in the fluidized bed reactor, the removal especially of Pb and Zn is not necessarily higher than in the rotary reactor. This was found to be due to the accelerated migration of formed HCl and Cl2 out of the particles into the reactor atmosphere.
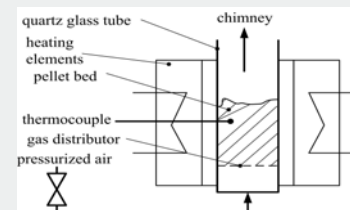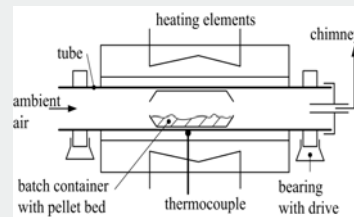

Figure 1. Rotary reactor (left hand side) and fluidized bed reactor (right hand side) used
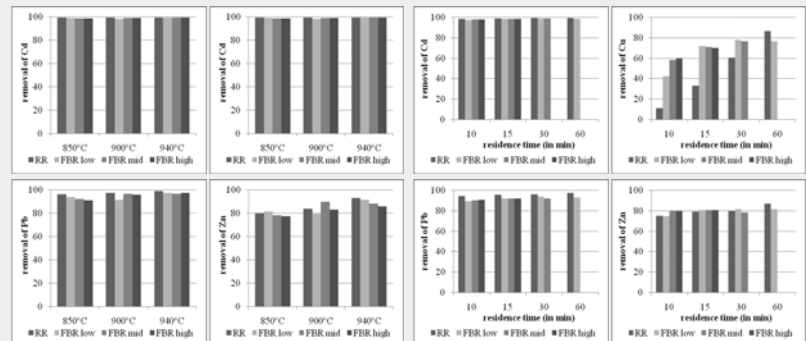

Figure 2. Rotary kiln - air panel system

Figure 3. Fraction of Cd, Cu, Pb and Zn removed; residence time 30 min; RR rotary reactor, FBR fluidized bed reactor, low 6.7, mid 8.0 and high 11 m s^{-1} (superficial velocity)

Figure 4. Fraction of Cd, Cu, Pb and Zn removed; temperature 850°C; RR rotary reactor, FBR fluidized bed reactor, low 6.7, mid 8.0 and high 11 m s$_{-1}$ (superficial velocity)

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