Waste Management 78 (2018) 750–762

Contents lists available at ScienceDirect

Waste Management

journal homepage: www.elsevier.com/locate/wasman

Stepwise treatment of ashes and slags by dissolution, precipitation of iron phases and carbonate precipitation for production of raw materials for industrial applications

Daniel Höllen[a,*], Iris Berneder[b], Francesca Capo Tous[b], Markus Stöllner[a], Klaus Philipp Sedlazeck[a], Therese Schwarz[a], Alexia Aldrian[a], Markus Lehner[b]

[a] *Chair of Waste Processing Technology and Waste Management, Montanuniversität Leoben, Franz-Josef-Str. 18, 8700 Leoben, Austria*

[b] *Chair of Process Technology and Industrial Environmental Protection, Montanuniversität Leoben, Franz-Josef-Str. 18, 8700 Leoben, Austria*

ARTICLE INFO

Article history:
Received 30 October 2017
Revised 17 May 2018
Accepted 25 June 2018

Keywords:
Mineral carbonation
Steel slags
MSWI bottom ash
Biomass ash
Carbon capture, utilisation and storage
Precipitated calcium carbonate

ABSTRACT

The purpose of this study was to test the feasibility of a specific mineral carbonation reaction route applied to different types of alkaline industrial residues, i.e. biomass, paper sludge and municipal solid waste incineration bottom ashes and stainless steel slags and dust. This new approach includes the dissolution of industrial residues in hydrochloric acid (HCl), followed by precipitation of iron compounds from the resulting aqueous solutions and the precipitation of calcium carbonates to employ in industrial applications (Carbon Capture, Utilisation and Storage, CCUS). The aim of this work is to apply this stepwise treatment to different types of poorly valorised industrial residues to assess which may be the most promising ones to employ for the process, in terms of total content of specific elements in the obtained products.

Our results clearly indicate that the investigated ashes and slags consist of 20–30 wt% CaO which is bound in a broad variety of mineral phases. Reaction of slags and ashes with HCl leads to the formation of Si-rich solid residues and Ca-rich aqueous solutions. Dissolution residues from ash treatment might be used as lightweight concrete aggregate in case of appropriate mechanical properties, whereas dissolution residues from slag treatment might serve as metallurgical Cr concentrates. Resulting aqueous solutions show high concentrations of Ca (>10 g/L), up to 27 g/L of Fe and significant amounts of heavy metals like Pb, Ba, Zn, Cu, Ni. The concentration of dissolved Fe decreases to 2 mg/L by adding NH_3 which leads to the precipitation of amorphous iron phases. Finally, calcium carbonates with a purity of 79–97% are precipitated by injecting CO_2 at pH 9. These carbonates present lower heavy metal contents than the input materials (e.g. 0.3 wt% ZnO compared to 0.9 wt% for EAF-FD).

1. Introduction

1.1. Recycling of ashes and slags

1.1.1. Recycling of ashes

Ashes represent a huge mineral waste stream, especially in industrialised countries, which is still mostly landfilled due to heavy metal and chloride contents (Austrian Federal Ministry of Agriculture, 2017). The chemical and mineralogical composition of combustion residues as well as the content and availability of heavy metals depend on the feed material and thermal treatment applied (Koukouzas et al., 2006; Ljung and Nordin, 1997; Vassilev et al., 2013a,b; Piantone et al., 2004).

The increase in the energetic use of biomass led to increasing production of biomass ashes from 100.000 t/a in 2004 to 186.000 t/a in 2015 (Austrian Federal Ministry of Agriculture, 2017). Collection logistics are rather difficult as biomass ashes (BA) are produced at more than 1100 different sites in Austria, among which only 10 have a thermal power production of more than 10 MW (Pleßl, 2015). 50% of BA are landfilled in Austria (BMLFUW, 2014a,b), because heavy metals and chloride contents limit their application as soil amendment (Vassilev et al., 2013a,b) and material for cement production (Obernberger and Supancic, 2009).

In 2012, 882.400 t of municipal solid waste incineration (MSWI) ashes were produced in Austria, thereof 579.00 t bottom or bed

---

* Corresponding author.
E-mail address: daniel.hoellen@unileoben.ac.at (D. Höllen).

https://doi.org/10.1016/j.wasman.2018.06.048
0956-053X/

ashes and 303.400 t fly ashes (BMLFUW, 2014a,b). Theoretically, the recycling of MSWI bottom ashes (MSWI-BA) in road construction is possible in Austria (Austrian Federal Ministry of Agriculture, 2017). Due to specific conditions, i.e. the abundance of natural rocks and lack of acceptance of MSWI-BA utilisation (Environmental Agency Austria, 2005) 100% of MSWI ashes are disposed of at landfills in Austria (Bundesministerium für Land- und Forstwirtschaft, Umwelt und Wasserwirtschaft, 2015). Limitations for the recycling of MSWI-BA are mainly due to its content and leaching of soluble components like salts and/or some heavy metals, which might have a negative effect on the environment and/or industrial installations like cement kilns. To avoid these negative effects, washing processes have been successfully conducted to remove chlorides (Pan et al., 2008) and heavy metals like Cd and Zn (Mulder, 1996) from MSWI-BA. However, as leaching depends on the solubility of mineral phases, the mineralogy of ashes must be changed to decrease leaching, e.g. by the incorporation of heavy metals in stable mineral phases (Nzihou and Sharrock, 2002).

Paper sludge incineration ashes (PSI-A) result from the combustion of fibre residues from waste paper recycling. Their annual production is significantly smaller than that of MSWI-BA and there are already existing recycling opportunities like amendment for soil improvement (Muse and Mitchell, 1995).

1.1.2. Recycling of slags

In Austria, 94.000 t electric arc furnace slags (EAF-S) are produced yearly. Mineralogically, stainless steel slags from EAF processes are composed of Ca-, Al- and Mg-silicates, Ca-, Mg- and Fe-oxides, Ca-ferrites, spinels, aluminates and fluorides (Drissen, 2004). Road construction is the main application of EAF-S (Engström et al., 2014), but the Austrian legislation (Republik Österreich, 2015) sets strict limit values for both total and leachable contents of environmentally relevant elements. Consequently, even advanced methods to reduce the leachability of steel slags (Cabrera-Real et al., 2012) will not allow increased slag recycling under present legal framework conditions. To solve this problem a pyrometallurgical reduction of the slag followed by magnetic separation of the produced zero-valent metals has been suggested (Adamcyzk et al., 2010).

Aside from slags, which account for 75% of all metallurgical residues, dusts and sludges represent a smaller group of materials (7%, (Gara and Schrimpf, 1998)). Steel dusts, which are also considered in this study, can partly be internally recycled (Chairaksa-Fujimoto et al., 2015), but in 2015, 25% were still landfilled in Austria (Austrian Federal Ministry of Agriculture, 2017).

1.2. Mineral carbonation

Mineral carbonation is the exothermic reaction of carbon dioxide with metal oxides or silicates to form carbonates according to the general formula:

$$Me^{2+}O(s) + CO_2(g) \rightarrow MeCO_3(s)\Delta H_R^0 < 0 \tag{1}$$

The theoretical CO_2 uptake, T_{CO2}, is defined as the maximum amount of CO_2 that can be bound in a material, expressed as percentage referred to the mass of the input material (Sanna et al., 2012):

$$T_{CO2} = 0.79 \times (\%CaO - 0.56 \times CaCO_3) + 1.09 \times \%MgO \tag{2}$$

Carbonation of alkaline residues is well known and an important factor in the long-term behaviour of ashes (Meima et al., 2002) and slags (Suer et al., 2009). However, in natural environments, ashes and slags carbonate only at the surface even after 10 years of ageing in a road (Suer et al., 2009). This is due to the lower reactivity of silicates and complex oxides compared to free lime (Costa et al., 2007; Sanna et al., 2014) and due to the clogging effect of the formed carbonates. The following equation summarizes the carbonation reaction of larnite, a calcium silicate:

$$Ca_2SiO_4{+}2CO_2{\rightarrow}2CaCO_3{+}SiO_2 \tag{3}$$

In order to effectively employ carbonation for carbon capture, utilisation and storage (CCUS) an indirect process route may be applied. This process is made up by a first stepaimed at the dissolution of the primary silicate mineral phase (4) followed by the precipitation of the carbonate mineral phases (5).

$$Ca_2SiO_4(s){+}H_2O(l){+}4H^+{\rightarrow}H_4SiO_4(aq){+}H_2O(l){+}2Ca^{2+}(aq) \tag{4}$$

$$Ca^{2+}(aq){+}CO_2(aq){\rightarrow}CaCO_3(s) \tag{5}$$

This decoupling of the reactions allows for inserting an additional reaction in the aqueous solution to precipitate metals which would decrease the purity of the desired carbonate product:

$$Fe^{3+}(aq){+}3OH^-{\rightarrow}Fe(OH)_3(s) \tag{6}$$

1.3. Objectives of the work

Carbon dioxide is the fifth most abundant gas in the atmosphere and its emission is the main cause for global warming, whereas slags and ashes are significant waste streams in Europe. In this study we present an approach for achieving a substantial conversion of ashes and slags into carbonates via dissolution and precipitation, which aims to trap CO_2 and to recover metals in different insoluble mineral phases via a multi-step reaction route.

The aim of this work is to apply this stepwise treatment to different types of poorly valorised industrial residues to assess which may be the most promising ones to employ for the process, in terms of total content of specific elements in the obtained products. All the newly produced side and end products from this process should be utilised in various industrial applications. The proposed stepwise treatment aims to achieve the following objectives:

1. Recycling of those ashes and slags which are currently disposed of in landfills due to their high total and/or leachable heavy metal concentrations and/or due to their poor mechanical properties.
2. Reduction of the CO_2 emissions of Waste-to-Energy plants and other energy-intensive industrial plants by carbon capture, utilisation and storage (CCUS).
3. Production of precipitated calcium carbonate (PCC) as a substitute for primary resources as building material and filler (e.g. in paper industry).
4. Production of a SiO_2 concentrate to be used as an aggregate for building materials.
5. Hydrometallurgical recovery of ferrous metals for the steel industry.

This approach is based on an indirect process where dissolution and precipitation reactions are decoupled (Eloneva et al., 2012) in order to enable faster reaction kinetics, as the release of Ca into the solution is the rate-limiting reaction step (Huijgen et al., 2005) and without decoupling the surface would be passivated by the reaction products.