STABILIZATION OF HEAVY METALS IN MSWI BOTTOM ASH BY DYNAMIC CARBONATION

BRENNE T.[1] and WEIGAND H.[1]

[1] THM University of Applied Sciences, ZEuUS
Harald Weigand, Wiesenstr. 14, 35390 Giessen, Germany. Herald.weigand@kmub.thm.de
E-mail: harald.weigand@kmub.thm.de

ABSTRACT

Bottom ash (BA) is the dominant solid residue of municipal solid waste incineration and waste-to-energy (WTE) plants. It is generated as the cinder residue from the combustion process, subjected to wet deslagging and typically left to age for a period of at least three months. Among the mineral transformations taking place during BA ageing, carbonation driven by the access of atmospheric CO_2 is of outstanding importance. Due to the alkaline pH of BA, CO_2 is initially dissolved as carbonate in the pore water of the BA. Together with Ca from the dissolution of Portlandite it precipitates as calcium carbonates. This process eventually transforms the original Portlandite buffer system to a Calcite buffer system and reduces the leachability of heavy metals.

In this study we aimed at enhancing the carbonation process with respect to a reduction of contaminant release from the BA matrix. Asides minimizing the ageing time this could possibly allow for a more economic disposal to landfill (i.e. lower landfill class) and/or geotechnical re-use of the ash as a grounding material.

Dynamic carbonation experiments were performed following a 3^3 randomized factorial design. Varied independent variables were (i) the flow rate of a synthetic flue gas at a fixed CO_2 partial pressure of 6.68×10^4 Pa, (ii) the residence times of the BA in the reactor, and (iii) the reactor loading. The leaching behaviour of the carbonated material was assessed by standardized batch leaching tests with deionized water at liquid/solid-ratio of 10. For both the static and the dynamic tests, conditions of optimum carbonation were reproduced to obtain a sufficient amount of carbonated material for the use in the column tests prescribed for the geotechnical re-use scenario.

In all treatments, depending on the specific CO_2-supply both the pH and the electric conductivity dropped relative to the control. While the decrease in pH is consistent with an increased consumption of the Portlandite buffer the reduction of electric conductivity primarily reflects the precipitation of charged mobile constituents (e.g. metal carbonates). The mobility of amphoteric contaminants (e.g. Pb) was substantially reduced, while the release oxoanion-forming (e.g. Cr) metals was slightly enhanced by carbonation.

Overall, the results show that the ageing of bottom ash may be accelerated by enhanced carbonation. This encompasses a mobility reduction for a series of metals and has consequences for the categorization of the waste in terms of disposal to landfill and geotechnical re-use scenarios. Landfill costs may be significantly cut by enhanced carbonation since reduced leachate concentrations allow for a disposal of carbonated bottom ash on lower category landfills. Geotechnical re-use of carbonated material may even lead to revenues when conventional construction materials are substituted by stabilized bottom ash. Dynamic carbonation will therefore be implemented at full scale into the BA management of the WTE plant under consideration by using flue gas from a biogas co-generation plant next to the incinerator as the CO_2-source.

1. Introduction

Bottom ashes (BA) constitute the dominant solid residue of municipal solid waste incinerators and waste-to-energy (WTE) plants. The ash is generated as the cinder residue from the combustion process which falls into a wet deslagger at the end of the combustion grate. The ash is withdrawn by apron conveyors to containers and typically left to age for a period of at least three months. Among the mineral transformations taking place during BA ageing, carbonation is of outstanding importance [1]. Carbonation is driven by the access of atmospheric carbon dioxide (CO_2) and/or its eventual release induced by microbial respiration under disposal conditions. Due to the alkaline reaction of BA with water, CO_2 is initially dissolved as carbonate in the pore water of the BA. Together with Ca from the dissolution of Portlandite it precipitates as calcium carbonates (see Figure 1).

This process eventually transforms the original Portlandite buffer system to a Calcite buffer system [2]. Thereby the pH is shifted from the alkaline towards the circumneutral range. Since especially amphoteric heavy metals exhibit solubility minima at neutral pH, the leachability of BA may be reduced by carbonation [3]. Portlandite solubility (ksp $10^{-5.2}$) is significantly increased with increasing concentration of NaCl [4] also present in the BA matrix. Therefore, diffusion of CO_2 into pore water may be regarded the rate-limiting step of carbonation. The latter is driven by the CO_2 partial pressure in the gas phase and the pH-dependent carbonate species present in the pore solution. Precipitation of calcium carbonates continuously withdraws calcium from the solution causing further dissolution of Portlandite as long as sufficient CO_2 is supplied.

In this study we aimed at enhancing the carbonation process with respect to a reduction of contaminant release from the BA matrix. Asides reducing the ageing time this could possibly allow for a more economic disposal to landfill (i.e. lower landfill class) and/or geotechnical re-use of the ash as a grounding material. Therefore, dynamic carbonation experiments were performed following a 3^3 randomized factorial design. Varied independent variables were (i) the flow rate of a synthetic flue gas at a fixed CO_2 partial pressure of 6.68×10^4 Pa, (ii) the residence times of the BA in the reactor, and (iii) the reactor loading. The leaching behaviour of the carbonated material was assessed by standardized batch leaching tests with deionized water at liquid/solid-ratio of 10. Conditions of optimum carbonation were reproduced to obtain a sufficient amount of carbonated material for the use in the column prescribed for the re-use scenario.

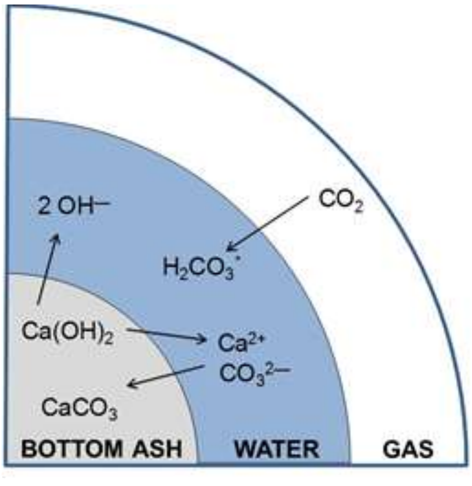

Figure 1: Reactions at the solid-solution interface involved in carbonation of bottom ash.

2. Materials and methods

The BA was sampled at a WTE plant in Hesse, Germany. The sample was collected from the interim storage facility next to the incinerator after 2 days of exposure to the atmosphere. Using a wheel loader approximately 300 L of sample were taken from two distinct positions of the BA pile. The material was thoroughly mixed on-site and stored in 60 L metal clamping ring drums made of high density polyethylene and kept without cooling until used in the experiments.

In the carbonation tests, the BA was exposed in a two phase reactor to a stream of synthetic flue gas. The CO_2 partial pressure of the gas stream was based on measured data of a nearby biogas-fuelled co-generation plant (6.68×10^4 Pa), since for technical reasons the use of the exhaust gas of the incinerator is not viable. Given a BA-output of the incinerator of 5.000 Mg/year and anticipating a CO_2-uptake of 3.5 mass-% [5], the CO_2 demand of the ash amounts to 89.000 m^3/year, approximately. Based on the operation times of the co-generation plant and the CO_2 concentration in the flue gas, the available CO_2-volume amounts to 4.224.000 m^3. This exceeds the demand, even when carbonisation were performed only during labour hours.

The synthetic flue gas was produced from pure CO_2 and synthetic air employing a Gmix gas mixing station [HighTec Zang, Herzogenrath, Germany]. The experiments were conducted according to a randomized 3^3 factorial design that considered the reactor loading, the exposure time, and the volumetric flow rate of the synthetic flue gas as independent variables (=design factors).

The central values of the factorial design were derived from a downscaling of the anticipated full-scale process as follows. An hourly throughput of 2.8 Mg BA is needed for the BA mass annually produced, assuming an 8-hrs-labour-day processing at a residence time of 60 min (central value). The minimum and maximum values of the residence were set to 20 and 100 minutes, respectively. The full-scale reactor capacity is projected to be 35 m^3. A loading of 2.8 Mg would thus result in a density of the gas-solid dispersion of 0.08 Mg/m^3. Downscaled to the laboratory reactor [ecoTech GmbH, Bonn, Germany (void volume 71 L)] the corresponding experimental loading is 6 kg with minimum and maximum values of 4 and 8 kg. The central value of the reactor loading multiplied by the assumed CO_2 uptake (3.5 %-mass) would result a CO_2 demand of 210 g. A factor of 1.5 of this demand was supplied by a flue gas stream with 0.066 vol.-% CO2 at a flow rate of 40 L/min (central value). Minimum and maximum values were set to 20 and 60 L/min, respectively.

Depending on the disposal scenario different compliance tests need to be performed with the carbonated ash. Regarding the option of a disposal to landfill the German landfill ordinance prescribes a batch leaching test with de-ionized water at a liquid to solid ratio of 10 and 24 hrs. of contact time. This was performed according to established standards [6]. If otherwise, the material is to be geotechnically re-used, the German substitute building materials ordinance applies. As required for this scenario, compliance testing involved the use of an upstream percolation column experiment (Ø 9 cm, length 40 cm) with deionized water. The pore water residence time was 5 h and the percolate volume collected corresponded to a liquid to solid ratio of 2 [7].

The output of the dynamic carbonation tests were subjected to either of the above-named test procedures. All aqueos phase analyses were performed after membrane filtration (pore diameter 0.45 µm). Immediately after filtration, the pH, electric conductivity, and redox potential were determined using appropriate electrodes. For the determination of metals and metalloids, samples were stabilized with nitric acid and stored at 4 °C prior to analysis by ICP-MS. In non-stabilised aliquots chloride and sulphate were determined by ion chromatography.

3. Results and discussion

The results of the static carbonation tests [5] were regarded a first indication of the feasibility of the enhanced carbonation in terms of cost reduction. However, the partial pressure of 1 and treatment times of up to 10 d were unrealistically high for a full-scale implementation of the process. Thus, dynamic carbonation tests were conducted to determine whether acceptable results can be obtained with CO_2 concentrations typical of flue and with treatment times that account for the annual BA production at the WTE plant under consideration.

Figure 2 shows selected results of the batch tests performed with the BA from the dynamic carbonation tests together with the corresponding parameters of the untreated control. In all treatments, both the pH and the electric conductivity (Figure 2, left panel) were reduced compared to the control. Neglecting the scatter of the data, both parameters show a tendency to decrease with increasing specific CO_2-supply. The latter summarizes the combined effects of residence time, reactor loading, and volumetric flow rate, i.e. the design factors. The decrease in pH is consistent with an increased consumption of the Portlandite buffer. The reduction of electric conductivity is, to some extent, linked to pH neutralization, but primarily reflects the precipitation of charged mobile constituents (e.g. metal carbonates).

Regarding the mobility of contaminants Figure 2 corroborates the findings from the static carbonation experiments: Compared to the control, Pb was markedly depleted in the batch extracts of all treatments whereas Cr mobility exhibits a tendency to increase with CO_2-supply. The leachate composition as a function of the underlying factor combinations was analysed with the software package Design Expert, version 9.0 [Stat-Ease, Minneapolis, USA]. According to the results, the volumetric flow rate and the residence time had significant effects ($p < 0.05$) on the Pb leachate values, whereas no significant effect was determined for the reactor loading. Thus, regarding Pb mobility, an optimization of the treatment may achieved by a tuning of just two design variables.

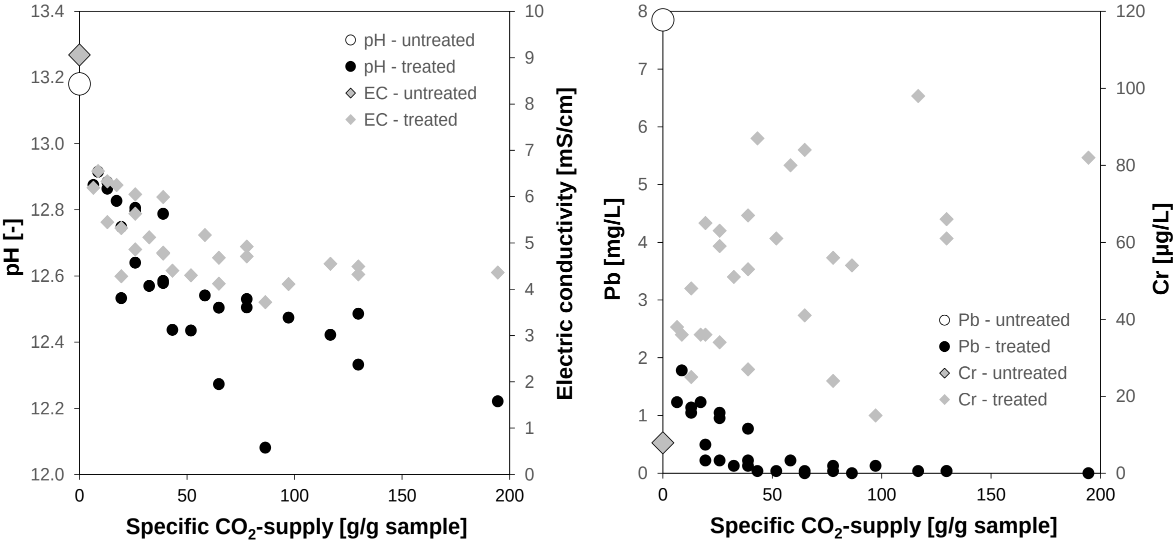

Figure 2: Selected components in batch leachates obtained after carbonation of the BA under dynamic conditions employing a 3^3 factorial design. Large symbols denote the results of the untreated control (zero specific CO_2-supply).

According to the statistical evaluation of the experiments in terms of concentration isolines (not shown) the Pb WACs for the disposal on a class I landfill can be met by employing volumetric flow rates of the flue gas between 20 and 60 standard L/min as long as the corresponding residence times are adjusted to values above 60 and 50 minutes, respectively. Regarding the risk of Cr mobilisation, residence times of to up to 100 minutes would not pose a problem, since all leachate concentrations observed in this study were below the Cr WAC for a class I landfill. However, Cr mobilisation is critical to the disposal of the BA at an inert waste landfill. The fact, that only a few of the treatments complied with both the WAC for Pb (0.05 mg) and the WAC for Cr (0.05 mg) implies that the tuning of treatment conditions for this specific disposal scenario is delicate.

For compliance testing regarding the geotechnical re-use scenario, a further carbonation experiment was undertaken. According to the evaluation of the factorial design study the volumetric flow rate, residence time and reactor loading were adjusted to 40 L/min, 80 min and 8 kg, respectively. The carbonated BA was then subjected to a column leaching test. Analysis of the effluent confirmed that unlike the control the material is to be classified as HMVA-1 allowing for a multi-purpose geotechnical re-use.

4. Conclusions

The ageing of bottom ash may be accelerated by enhanced carbonation. This encompasses a mobility reduction for a series of metals and has consequences for the categorization of the waste in terms of disposal to landfill and geotechnical re-use scenarios. Landfill costs may be significantly cut by enhanced carbonation since reduced leachate concentrations allow for a disposal of carbonated bottom ash on lower category landfills. Geotechnical re-use of carbonated material may even lead to revenues when conventional construction materials are substituted by stabilized bottom ash. Dynamic carbonation tests show that the treatment may be integrated into the BA management of the WTE plant under consideration by using flue gas from a biogas co-generation plant next to the incinerator as the CO_2 source

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