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Waste Materials in Construction: Putting Theory into Practice

Investigation of Sintering Processes in Bottom Ash to Promote the Reuse in Civil Construction (Part 2) - Long Term Behavior

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Abstract

Bottom ashes from two MSWI characterized by different discharge technologies were annealed at temperatures of about 700 °C up to1065 °C under reducing and oxidizing atmosphere, respectively. All products were tested for their leaching stability. Investigations of the mineralogical composition were carried out additionally. The following main conclusion can be drawn from these experiments. Mineral composition is influenced by sintering with respect to the decomposition of $Ca(OH)_2$ and $CaCO_3$ at temperatures above 950 °C and formation of less soluble Ca-silicates. This results in different pH values and acid neutralization capacity compared to the original materials. The effect of sintering on the availability and release of heavy metals under the applied conditions is weak.

1 Introduction

Former investigations carried out in our laboratory [Schneider 1994, Vehlow 1995] showed that sintering of bottom ash is a promising way to receive a construction material with leaching behavior required in the German technical guideline residential waste [TA Siedlungsabfall, Bundesministerium 1993]. In the recent investigation sintering experiments were conducted in a rotary kiln. The material used was either bottom ash from a municipal solid waste incinerator with a wet discharge system or material received from the InRec^{TM} process developed by ABB. The first material, named "wet ash", was annealed at different temperatures under a slightly reducing atmosphere while the second material, named "dry ash", was annealed under oxidizing atmosphere.

"Part 1" of this work discussed the experiments and the effect on the quality of the products. In "Part 2" the influence of sintering processes on mineralogy, alkalinity and availability of harmful elements are summarized. These parameters help to evaluate the behavior of bottom ash with respect to long term leaching. Additionally the chemical reactions during sintering can be estimated by considering the variations of all those parameters.

2 Methods

2.1 Sample Preparation

Since all analytical methods applied use liquid samples and all leaching tests ask for different grain sizes all solid materials require some pretreatment. At first they were subdivided to an appropriate sample size using a riffle box. One subsample was sieved and the material > 3 mm crushed in a jawbreaker for the column tests. Another subsample was crushed and milled for analytical purposes and for the availability test.

2.2 Mineralogical Investigations

The ground samples were examined by X-ray diffractometry to identify the mineral composition. In two sintering tests samples were obtained with larger grainsizes than the original material. These larger pieces were used to get thin sections for microscopy.

2.3 Leaching Tests and Acid Neutralization Capacity (ANC)

The German DEV S4 test [DIN 38414] has been applied to judge the quality in accordance to the German regulations (see part 1).

These data do not allow any conclusion in which way the sintering process influenced the leaching mechanism due to modifications of crystal structures and mineralogy. To obtain more detailed information about these parameters the Dutch test NEN 7341, which includes a column leaching test and availability test, was conducted.

The alkalinity and the acid neutralization capacity (ANC) are also important factors which influence the leaching behavior. Additionally the titration curves of the bottom ash samples allow an estimation of the chemical species of some elements. For most of the samples a titration with HNO_3 was carried out with an automated titration setup. Following the method described in Johnson et al. (1995) a liquid to solid ratio of 100 was chosen in order to avoid the supersaturation of Ca with respect to gypsum. The titration was carried out under nitrogen gas to prevent CO_2 entering the system.

2.4 Digestion and Analytical Method

For the analyses of heavy metals about 100-300 mg of each ground sample was digested using a HNO_3/HCl/HF mixture in a teflon bomb heated in a microwave oven. The halogenides were extracted by superheated steam in a glass set-up.

Total Reflecting X-Ray Fluorescence Analysis (TRFA) was used for metal analysis. The anions were analyzed by Ion Chromatography (IC).

3 Test Results

3.1 Mineralogy

Table 1 depicts the phase composition of some samples analyzed by X-Ray diffractometry.

Quartz is the main constituent in all samples. The mineralogical composition of the original materials varies mainly relating to the calcite content - in the materials "wet ash 1" and "dry ash" calcite exists only as an accessory constituent.

The effect of sintering can be seen by the decreasing of the calcite content. In the samples "wet ash" which had been annealed by higher temperatures - above 850 °C - calcite is present in lower concentrations than in the other ones. In most samples derived from original materials "wet ash 1" and "dry ash" it could not be determined by X-ray diffractometry. These results are related to the TIC values mentioned in part 1 of this work which proof the destruction of carbonates at temperatures of about 900 °C. But even at high temperatures in the range of 1000 to 1065 °C - the destruction of calcite is not complete, because in the thin section prepared of samples "wet ash 1, 1000°C" and "wet ash 1, 1065°C" calcite can be found in the matrix as a minor component.

Table 1: Phase composition of some original materials and sinter products

Sample	**wet ash**		**wet ash 1**				**dry ash**			
Temperature °C	**untr.**	**950**	**untr.**	**700**	**950**	**1065**	**untr.**	**680**	**955**	**1065**
Quartz SiO_2	xxx	xxx	xxx	xxx	xxx	xxx	xxx	xxx	xxx	xxx
Magnetite Fe_3O_4	x	xx	x	xx	x	x	x	x	x	xx
Gehlenite $Ca_2Al_2SiO_7$ Akermannite $Ca_2MgSi_2O_7$	xx	xx	x	xxx	xx	xxx	xx	xx	xx	xxx
Calcite $CaCO_3$	xx	x		x			x	x		
Dolomite $CaMg(CO_3)_2$	xx									
Feldspar $K[AlSi_3O_8]$ $Na[AlSi_3O_8]$ $Ca[Al_2Si_2O_8]$		x	x		x	x	x	x	x	x
Diopside $Ca(Mg,Fe)[Si_2O_6]$			x			x		x	x	x
Anhydrite $CaSO_4$			(x)			(x)	x		(x)	x

untr. = untreated, xxx = main constituent (>10 %), xx = minor constituent (5-10 %), x = accessories (<5 %), (x) = traces

The formation of gehlenite ($Ca_2Al[(SiAl)_2O_7]$ and akermannite $Ca_2Mg[Si_2O_7]$ gives evidence of mineral reactions, too. These minerals can be found in each sample even in the original material, which itself is a product of combustion in the formation temperature range of these minerals, 700-800 °C (Pfrang-Stotz, 1995). While the X-ray-diffractometry shows only a slight increase of gehlenite and akermannite the thin sections indicate an increase with increasing temperatures.

3.2 Leaching Test Results

3.2.1 Acid Neutralization Capacity

Alkalinity and acid neutralization capacity of bottom ashes depend mainly on the chemical form of the main constituents, i.e. alkali metals, earth alkali metals, silica, aluminum, and iron. Calcium, for example, occurs as hydroxide, carbonate, and bound in silicates. In leachates of bottom ashes the presence of calcium hydroxide and -silicates as well as of alkali metal hydroxides is responsible for pH values of about 11 up to 12.5. pH values of about 10 to 8 are mainly related to Ca CO_3 [Johnson 1994].

The initial pH values measured after ten minutes and the pH obtained by means of the DEV S4 Test of the original materials and the sinter products are shown in table 2.

The initial pH is a hint for the more soluble pH forming fraction. The original material "wet ash 1" and respective sinter products show pH values after 10 minutes in the range of 11.0 - 11.6 while the initial pH values of "dry ash" and its sinter products range between 12.0 - 12.4. This indicates that pH controlling components like $Ca(OH)_2$ of the original materials are responsible for the pH in the sinter products as well. After equilibration the pH values of the original materials and of their sinter products show more variation. All leachates remain in the pH level above 11.0 where Ca-hydroxides and -silicates are responsible for the pH. The equilibrated leachates of original materials are saturated with respect to $Ca(OH)_2$. The leachates of the sinter products of "wet ash 1" still remain undersaturated with respect to this phase. Since $Ca(OH)_2$ was saturated in the leachates of the "dry ash" sinter products after ten minutes, but not after equilibration, some precipitation reactions must have taken place without solution of additional hydroxides. It can be supposed that during annealing parts of the $Ca(OH)_2$ have been decomposed and components with a more "acid" character have been formed, for example $CaCO_3$ or less soluble Ca-silicates. Which reactions have taken place can be investigated by evaluation of the acid titration curves and the acid neutralization capacity. Figure 1 compiles titration curves of the original materials "wet ash 1" and "dry ash" and respective products annealed at 1065 °C.

Table 2: Initial pH and pH after 24 hours (DEV S4 Test) and ANC at pH 4 (in meq/g)

wet ash	**untreated**	**700 °C**	**850 °C**	**915°C**	**950 °C**	**1000 °C**	**1065 °C**
initial pH	11.4	11.0	11.2	11.4	11.7	11.5	11.6
pH after 24 h	12.4	11.4	11.0	11.0	11.2	11.0	11.6
ANC	2.164	2.244	1.810	1.610	1.982	1.823	1.560

dry ash	**untreated**	**790 °C (O_2, CO_2)**	**955 °C**	**965 °C (O_2, CO_2)**	**1000 °C (O_2, CO_2)**	**1065°C (O_2, CO_2)**
initial pH	12.4	12.4	12.1	12.4	12.0	12.3
pH after 24 h	12.7	11.5	11.4	12.3	11.2	11.5
ANC	3.782	3.907	4.090	3.917	2.799	3.155

The "dry ash" materials have a higher acid consumption than the "wet ash 1" materials. The slope of the original materials` curves varies only slightly with decreasing pH down to pH 5. The constituents which control the respective pH seem to exist in similar amounts in both untreated samples. The slope of the curves of the materials annealed at temperaures higher than 1000 °C is steeper up to a pH of about 5. This fact points out that $Ca(OH)_2$ had disappeared but no carbonate had been formed. At these temperatures Ca has obviously been used up for the formation of silicates like gehlenite, akermannite, and diopside.

Another value derived from the titration curves is the ANC which is depicted in table 2, too. This is an important parameter for the estimation of long term leaching behavior.

There is a slight decomposition of buffering substances in the sinter products of "wet ash 1". A temperature dependence in this case can not be deduced. The sinter products of the "dry ash" obtained at low temperatures show a similar or even slightly increased ANC whereas products of higher temperatures are characterized by lower ANC. The raise of ANC due to annealing processes can be explained by the artificial atmosphere with an excess of oxygen and carbon dioxide. Carbonates are more stable due to higher partial pressure of CO_2 which raises the decomposition temperatures of carbonates [Warne, 1991]. Moreover, the oxidizing atmosphere favors the formation of metal oxides. The raise of ANC can be observed at a pH range of 5-3 where neutralization by metal hydroxides ($Al(OH)_3$, $Fe(OH)_3$) is effective [Scheffer, 1989].

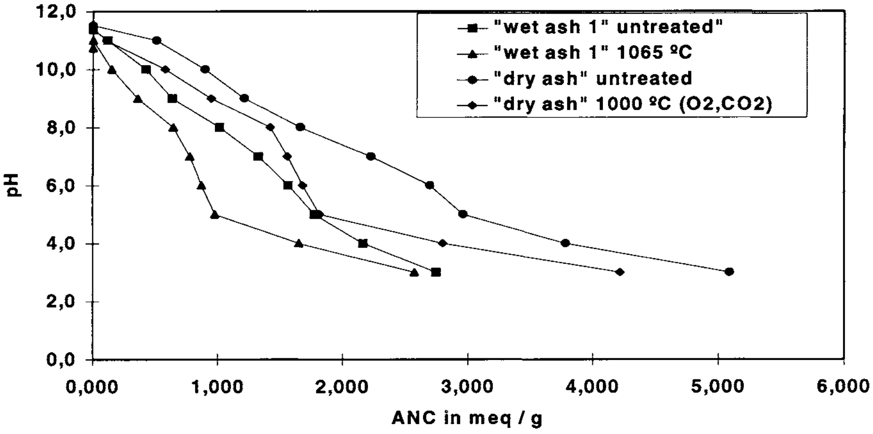

Fig.1: Titration curves of original material from "wet ash 1" and "dry ash" and their products annealed at 1065 °C and 1000 °C

3.2.2 Leaching Test and Availability

Column leaching tests provide information about the time dependent leaching behavior due to varying liquid to solid ratios (0.1 - 10). The pH of the eluent (pH 4) is quickly neutralized in the leachate due to reaction with the solid material (grain size > 3mm). Leaching under these circumstances is evidently controlled by diffusion and sorption processes.

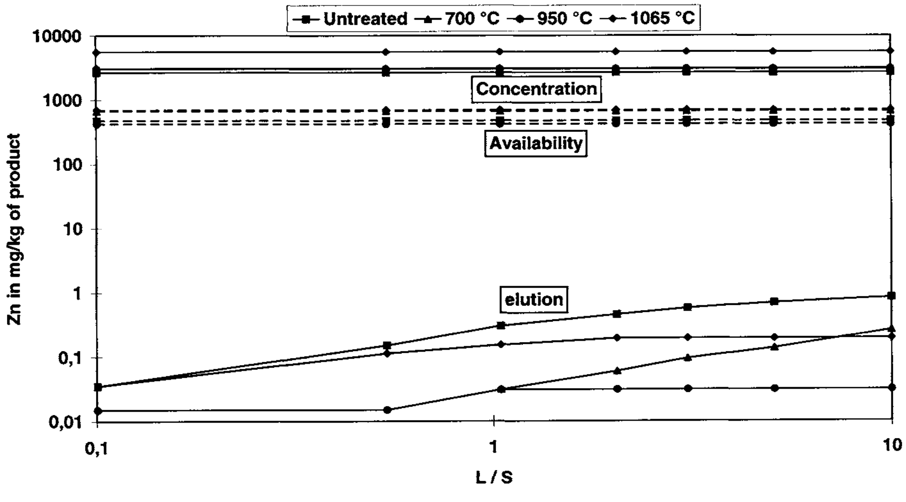

Fig.2: Total concentration, availability, and elution of Zn of "wet ash 1" and sinter products

To evaluate the leaching behavior, which is only controlled by chemical speciation, the Dutch availability test was developed. The test models severe environmental conditions by establishing a L/S 100 and a pH of 4. The release during time and the highest available - but in most cases never reached - amounts of harmful species can be estimated by combining both leaching tests according to NEN 7341.

Figure 2 compiles the elution, availability, and the total concentration of Zn in the "wet ash 1" and in some of the sinter products. The slope of the elution curves of the original material and the material sintered at 700 °C correspond closely though the release of the annealed material is lower. But it seems that leaching of Zn is not complete at a L/S of 10. At contrary the samples annealed at 950 °C and 1065 °C show no further release of Zn after L/S = 1. These similarities between the slopes are not true for other heavy metals, but with the exception of Ni it can be taken as fact that the release from original material is higher than in any annealed material.

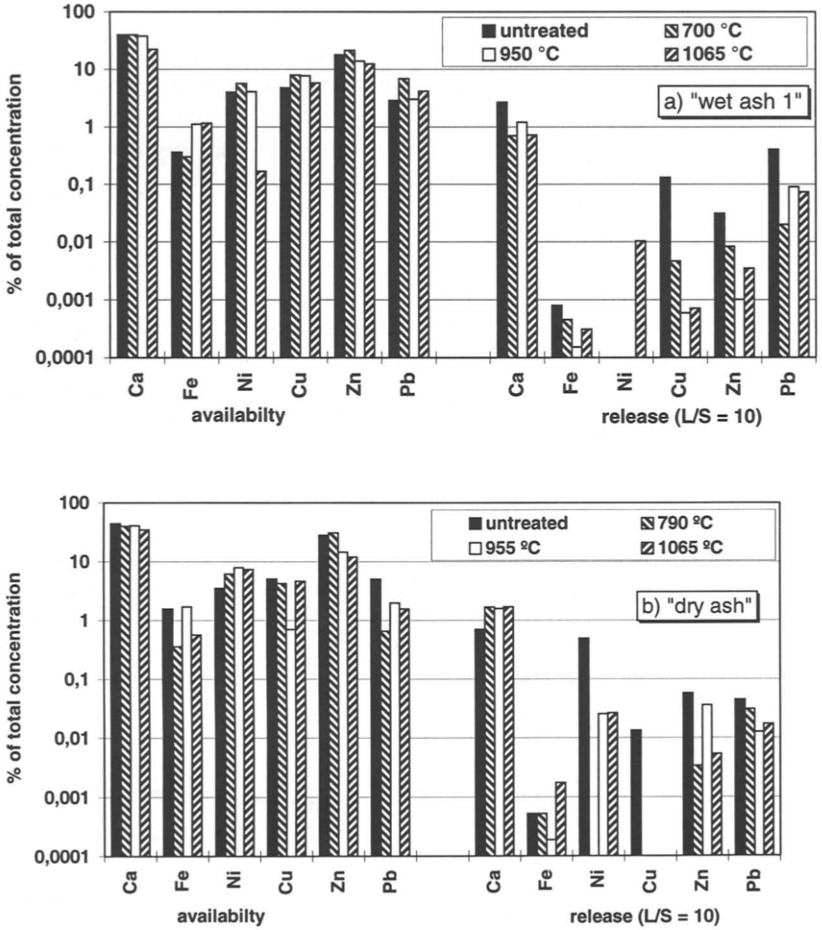

Fig.3: Availability and release of some elements normalized to total concentration a) "wet ash 1", b) "dry ash"

Differences in the availability are not noticeable. Results of former experiments carried out in a laboratory oven without motion or control of atmosphere show apparently greater effects caused by annealing of bottom ashes (Schneider, 1994). They show decrease of the availability between the original and the annealed (1000 °C) material in a range of a factor of 10. In order to compare availability and release at L/S 10 of the lithophilic elements Ca, Fe, Ni and the volatile constituents Cu, Zn, and Pb as an effect of different annealing temperatures figure 3 and 4 compile these values. The differences of total concentrations between the samples are taken into account by normalizing the availability and the release to the corresponding total concentration.

The six elements show little modified availability due to the annealing of the "wet ash 1" (fig. 3a). Only Ni shows a decreasing availability after treatment at 1065 °C. The availability of Fe is increased. The effect of annealing on the release at L/S 10 in these samples for the lithophilic elements is not very strong, either. The finding for Ni, which is only detectable in the leachate of the product annealed at 1065 °C, can be explained by the fact that the Ni concentrations in all leachates are near the detection limit of the TRFA. Cu, Zn, and Pb are less leachable after treatment. The explanation for Pb can be found in the lower pH range of the elutes. The lack of differences in the availability show that a incorporation into low soluble compounds did not take place during the annealing process. The difference in release at L/S 10 elucidates the formation of sulfides in the slightly reducing atmosphere at the surface. These compounds are insoluble at this L/S and pH (at about 11) prevent the heavy metals from being leached.

The availability of Ca and Ni in the sinter products of the "dry ash" is nearly the same as in the untreated material (fig 3b). The availability of Cu, Zn, and Pb is slightly more influenced in the "dry ash" sinter products than in the "wet ash 1" products. But again this effect is not very significant. However, the release of Zn and Pb at L/S 10 is less decreased in the "dry ash" sinter products. This can be explained by the slightly higher pH at about pH 11.5 [Schneider 1994]. The release of Ca and Fe is even increased after annealing of "dry ash" due to formation of oxides on the surface in the oxidizing atmosphere. Annealing of "dry ash“ was most effective for release of Cu and Ni. Cu could not be measured in column leachates after thermal treatment, the release of Ni decreases more than 10 % of the release in the untreated "dry ash".

4 Evaluation and Conclusions

In order to compare former investigations of the influence of thermal treatment on the quality and leaching behavior of bottom ashes, carried out in a laboratory oven, to a more realistic scale, with regard to full scale combustion chambers, experiments in a rotary kiln were conducted. Wet bottom ash from an MSWI and dry bottom ash derived from the InRec process was annealed at different temperatures without controlling of atmosphere and under additional O_2 and CO_2, respectively. One goal of this investigation was to find out the best conditions for combustion of waste. The effect of annealing in the rotary kiln can be summarized as follows:

- Analyses of the mineralogical composition proof the formation of Ca-silicates and the decomposition of calcite at high temperatures.
- The pH value found in leachates of the DEV S4 Test is slightly decreased after annealing.
- The ANC after thermal treatment is slightly decreased in products of the "wet ash" and similar to the original material or even higher in products of the "dry ash".
- Considering pH and ANC decomposition of $Ca(OH)_2$ and formation of carbonates (under artificial atmosphere) up to a temperature of 900 °C and Ca-silicates, respectively, has to be supposed.

- The influence of sintering on the availability is insignificant.
- Annealed samples show a decreased release of elements during column tests. Compared to the former laboratory tests the effect on the release is less in products of the rotary kiln sintering.

Evaluation of these results requires that additional modifications of temperatures or atmosphere by supply of oxygen or CO_2 during combustion of waste are not economically due to their weak effect.

The focus for running a MSWI plant should be directed towards a sufficient residence time of the waste at the back end of the grate at temperatures high enough to guarantee a full burnout and some sintering effects on the bottom ash. This should result in a leaching stability sufficient to the German law for deposition.

5 References

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