

Investigation of Sintering Processes in Bottom Ash to Promote the Reuse in Civil Construction (Part 1) - Element Balance and Leaching

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Abstract

Two types of bottom ash from MSWI, wet and dry discharged, were annealed in a temperature range from 700 °C to 1065 °C under reducing and oxidizing conditions, using a small rotary kiln. The products of these experiments were characterized in respect to their composition and their performance in Swiss and German leaching tests. The results lead to an improved understanding of the ash formation process on the incineration grate. Increasing ash temperatures on the grate result in a better ash burnout, transfer of some components to the flue gas and reduced leaching in the German DEV-S4 test. However, improvements in the Swiss leaching test are not to be expected.

1 Introduction

Bottom ash from municipal solid waste incineration (MSWI) has proven to be a suitable civil construction material in many applications [1-3]. Recently, even a quality certificate was established in Germany [4]. However, bottom ash is by no means a chemically inert material, and its composition and properties may vary in a wide range [5]. To prevent any contamination of ground and surface waters, an ash material usually has to pass a standard leaching test prior to its use. Different opinions on the long term risks of such ash applications unfortunately led to a great variety of tests and leaching limits in the various countries [6]. In an overall view, the most critical ash components are heavy metals, namely lead, zinc and copper, further chloride and organic carbon.

Besides the composition of the municipal waste itself, four major processes define the final quality of the bottom ash:

- the incineration process
- the ash discharge (dry or wet)
- treatment of the ash (sorting)
- aging

The benefits of aging [7, 8] are established and therefore many regulations require a storage of the ash for three month or so [9-11]. Ash discharge and treatment is discussed somewhere else [12, 13].

Concerning the incineration process, little quantitative work has been published on the ash properties as a function of the ash temperature during incineration [14, 15]. This is not surprising, as mass burning of waste, i. e. on a grate system, is a quite variable process due to permanent changes of the waste fuel. In addition, the temperature profile of a given ash volume is very difficult to track.

In an effort to fill this gap, a rotary kiln was used to treat bottom ash at different temperatures similar to conditions present on the incineration grate. Annealing at rising temperatures should lead to microscopic and macroscopic sintering of the ash which is reflected in changes of the mineralogical composition and the leaching behavior.

"Part 1" of this work discusses the experiment and the effect of the annealing temperature on the composition and the leaching behavior in the German standard leaching test DEV-S4 and the Swiss TVA test. In "Part 2", the influence of those sintering processes on the mineralogy, alkalinity and availability of harmful elements are described.

2 Experimental Setup

The experiments were performed in 1996 during two weeks, kindly hosted by a German incineration plant. A total of 30 ash samples of some 15 kg each were treated.

2.1 Ash material

Two types of bottom ash were used for the annealing and sintering experiments. Both originated from combustion of municipal solid waste on a modern grate system. The first material was sampled from a German plant with a standard wet ash discharge system (chain conveyor). It will be referred to as "wet ash". The second material was produced at a pilot installation in Switzerland, where ABB demonstrated the dry extraction of bottom ash as part of the InRec™ process. It will be referred to as "dry ash". Ash particles of larger than 32 mm diameter were not considered. The ash was not further pre-treated, except that it was carefully mixed to get similar samples for each experiment. Both ashes were not allowed to age. The wet ash was taken just before the experiments, while the dry ash does not age due to the lack of water.

2.2 Rotary kiln

Ash on an incineration grate passes a temperature profile, while being transported and slowly mixed by the movement of the grate bars. To offer a somewhat equivalent environment, a rotary kiln was used for the experiments. If not agitated, the ash would bake at temperatures below 1000 °C, as seen in earlier lab experiments. This is not representative for the real process and can be prevented by moving the ash slowly.

We used an electrically heated laboratory rotary kiln of Mannesmann Demag (formerly PLEQ). The model HT 11 had an inner diameter of 0.4 m and a volume of 0.11 m³, was rotated twice per minute and could be heated up to 1100 °C. The kiln was charged and

discharged at experiment temperatures and could accommodate up to 20 kg of material. Gas mixtures could be added into the hot zone.

Treatment time and rotating speed were kept low enough to prevent substantial grinding of the material.

2.3 Treatment conditions

2.3.1 Temperature

The aim of the study was to investigate changes of the bottom ash properties below the melting temperature. Thus, melting of the ash was not desired. Therefore, the temperature was increased until partial melting led to a rapid growing of the particles. The particle size distribution plot in Fig. 1 shows, that 50% of the wet ash had formed large particles after treatment at 1065 °C. Both materials were treated at temperatures from below 700 °C to 1065 °C, with emphasis of the region between 900 °C and 1000 °C

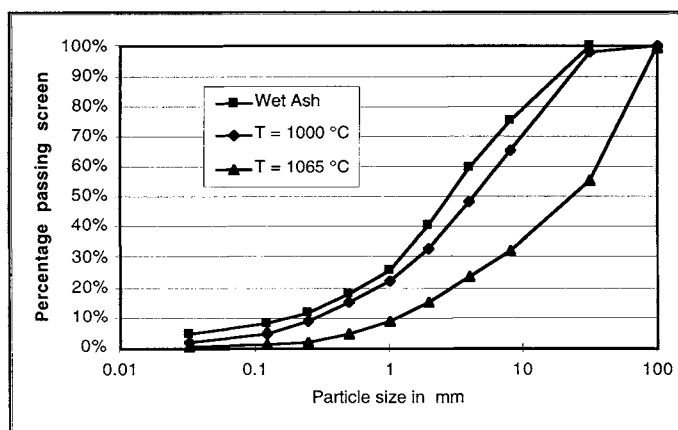


Fig. 1 Ash is forming larger agglomerates at 1000 °C and above

The temperature was measured in the middle of the kiln and verified by measurements directly in the ash and by adding probes with silver and copper shots (melting points of 962 °C and 1085 °C, respectively). The given temperatures are accurate within ± 20 °C.

2.3.2 Time

Each experiment lasted approx. 1 hour, thus the material was kept some 30 min at the desired temperature. This corresponds roughly to the time ash will be at the temperature maximum on the grate. Fig. 2 displays the temperature profile of a wet and a dry sample.

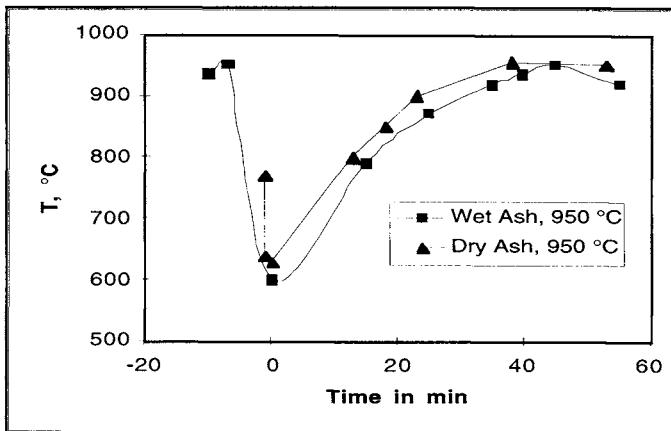


Fig. 2 Temperature in the rotary kiln during sample treatment

2.3.3 Atmosphere

It was seen, that the gas composition of the kiln atmosphere had great influence on the annealing and sintering process. To keep as many parameters constant as possible, only two concepts were applied:

The "wet ash" was kept in its own atmosphere. The water vapor displaced the air from the kiln, so that a reducing wet atmosphere resulted due to reducing ash components like carbon and aluminum. Carbon monoxide (CO) was formed, which was not burned until the kiln was discharged. The "dry ash" was treated in an oxidizing gas mixture of 60% air, 30% H₂O and 10% CO₂ (percentage by volume), according to an estimation of the incinerator gas composition after the main burning zone.

3 Composition and Element Balance

3.1 Composition of the untreated ashes

The following table summarizes the composition of the two ashes, compared to average values from the literature [5] and our own results. The particle size distribution of the wet ash was already shown in Fig. 1. The dry ash distribution is very similar.

Table 1 Ash composition

Ash material	Wet Ash	Dry Ash	Literature Ave.
Water Content	17.4 %	0 %	15 - 20 %
Melting Temp.	1205 °C	1200 °C	1150 - 1200 °C
All values given in mg/g			
Total Carbon (TC)	16.4	12.9	28
Organic Carbon (TOC)	11.0	9.3	10
Lead (Pb)	1.5	1.89	2
Zinc (Zn)	2.7	3.2	4.7
Copper (Cu)	3.46	4.83	2.1
Chromium (Cr)	0.253	0.197	1.2
Nickel (Ni)	0.19	0.097	0.21
Cadmium (Cd)	0.079	0.037	0.021
Calcium (Ca)	93.0	130.0	76.8
Potassium (K)	4.73	6.07	9.6
Sodium (Na)	7.89	10.63	23.4
Chloride (Cl)	6.41	4.9	2.8
Sulfate (SO ₄ ²⁻)	8.11	11.19	10

3.2 Element Balance after Treatment

After thermal treatment, a weight loss is observed. For the dry ash, this is mainly due to organic carbon and carbonate destruction plus evaporation of volatile compounds. The same applies to wet ash, in addition to the loss of the water content. For the highest treatment temperatures, the weight loss value was an average 2% higher than for the lowest ones.

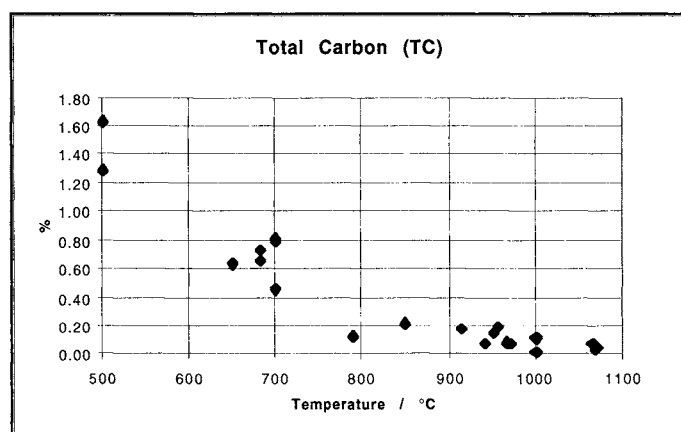


Fig. 4 Total carbon content vs. treatment temperature. TC of untreated ash is plotted on the ordinate ("500 °C").

Carbon

In Figure 4, the total carbon content of 19 treated samples is summarized. Up to 700 °C, mainly the organic carbon (TOC) is destroyed while above 800 °C, also the carbonates are decomposed. Oxidizing conditions (dry ash) yielded the lowest TOC values of less than 0.05% above 800 °C.

Metals

Lead, cadmium and potassium contents decreased by some 20% in the tested temperature range. Those metals are found enriched in fly ashes due to the higher vapor pressure of their compounds (Chlorides). For the other investigated metals (see Fig. 3) no pronounced change was found. Some heavy metals even showed somewhat higher values after annealing, which we explain by an improved availability of the new phases in the analytical procedure (grinding plus digestion).

Anions

Above 800 °C, about half of the Sulfate content was destroyed, with or without oxidizing conditions. Chloride content, in contrast, remained constant at reducing conditions (wet ash), while decreasing by some 30% if air was added at high temperatures.

4 Leaching Behavior

4.1 German Standard Leaching Test DEV-S4

In this leaching test, as described in DIN 31414-S4, the sample is agitated with a water/sample ratio of 10 for 24 hours. Thus, the pH value of the leachate is controlled by the amount of available and soluble alkali, mainly calcium oxide, in the sample. As a consequence, the leachate concentration of a heavy metal is rather independent from its total content. More important is the availability of the metal, which is influenced by the particle surface area, the mineralogical environment of the metal and the mechanical stability of the particles. However, the most important factor is the pH value of the leachate, as the solubility of many metals, namely the heavy metals, depends strongly on the pH. If the pH value is lower than 12, the formation of soluble lead hydroxo complexes is usually low enough to pass, i. e. the requirements for reuse according to the German LAGA Z2 class [8, 9].

pH Value and Conductivity

For both types of ash, the pH was lowered by an average of 1.2 units after treatment, independent from the actual treatment temperature. With a few exceptions, the pH values resulting from the annealed samples were found to be below 11.5, which led to the expected low lead and zinc concentrations. Obviously, the decomposition product of CaCO₃ is not free CaO, but is directly integrated in less soluble mineral matrices (see part 2). The electrolytic conductivity of the leachates is basically caused by the anions hydroxide, chloride and sulfate and is therefore directly correlated to the pH value.

Table 2 Leaching in the DEV-S4 Test (Summary)

Treatment	Wet Ash			Dry Ash			LAGA Z2 (Re-use)
	raw	<900 °C	>900 °C	raw	<900 °C	>900 °C	
pH	12.4	11.0	11.2	12.7	11.6	11.6	13
Conduct. mS/cm	5.9	1.8	1.2	9.9	1.7	1.8	6
Pb mg/l	1.08	0.03	0.01	0.21	0.08	0.02	0.05
Zn mg/l	4.24	0.003	0.01	9.65	0.04	0.11	0.30
Cu mg/l	0.43	0.003	0.004	1.81	0.005	0.067	0.3
Cr mg/l	0.03	1.20	0.45	0.07	0.29	0.01	0.3
Cl mg/l	351	231	82	261	108	66	250
SO ₄ mg/l	152	314	170	87	208	36	600

Heavy Metals

Annealing of both types of ash at any temperature significantly reduced the leaching of the main heavy metals lead, zinc and copper. Except for one lead value, even the low LAGA Z2 leaching limits are met - without aging of the ashes. As copper, different from lead and zinc, is not sensitive to high pH-values, the reason for the low leaching after treatment will be the formation of new stable phases. Lead leaching values showed a continuous decreasing trend towards high temperatures, which the others, surprisingly, did not. Chromium showed a different behavior. When there was enough oxygen available, the strongly bound chromate(III) was partially oxidized to chromate(VI), which is soluble and more toxic than its precursor.

Anions

Chloride, while not significantly evaporated, showed nevertheless a rapid decreasing solubility with increasing treatment temperature. In contrast, sulfate became less soluble with air, but quite soluble under reducing conditions (not distinguished in Table 2), despite the decomposition of up to 60% of the sulfate (see 4.2). Again, the chemical context seems more important than the total content.

4.2 Swiss TVA Leaching Test

The Swiss Leaching Test, according to the "Technische Verordnung Abfälle", is performed with carbon dioxide saturated water. At the resulting pH value of about 6, the solubility of lead (-carbonate) is very low, but zinc carbonate is soluble. Annealing at any temperature had no definitive effect in respect to the Swiss test. The leaching values varied statistically, but no trend was found. Only for nickel, an increased elution was found. Summary table 3 gives an impression of the achieved values.

Table 3 Summary of leaching in the Swiss TVA leaching test

CH-TVA Tests		Untreated Ash	Treated Ash	CH-TVA Inert
pH		6.06	6.04	
Conduct.	mS/cm	2.77	2.29	
Pb	mg/l	0.015	0.005	0.1
Zn	mg/l	3.09	4.72	1
Cu	mg/l	0.21	0.20	0.2
Cr	mg/l	1.96	1.88	0.05
Ni	mg/l	0.09	0.32	0.2

5 Conclusions

Although ash on an incineration grate may presently reach temperatures as high as applied in our rotary kiln experiments, this is never true for the whole mass stream. We showed, that annealing changes the ash properties already at temperatures around 700 °C, with a significant step at around 900 °C. New compounds are formed, which feature a higher leaching stability in a basic environment (DEV-S4).

Improved burnout and mass transfer to the flue gas are additional advantages, if a homogenous high temperature can be achieved for the bottom ash. We recommend to aim at an ash temperature of at least 800 °C, better 900 °C for some 20 min. Excess oxygen must be avoided to prevent chromate elution. Good mixing of the ash on the grate is mandatory.

Improvements in the Swiss leaching tests are only to be expected for ash heated up to the melting point. However, an ash quality which is sufficient for construction purposes can be achieved at much lower temperature.

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