

Factors and Technical Methods Influencing the Quality of MSWI Bottom Ash

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0 Abstract

The quality of MSWI bottom ash is decisively determined by its content of leachable salts and of heavy metals. For utilising MSWI bottom ash as a constituent of construction materials, a certain reduction of its hazard potential is urgently required. The state of the art is characterised by various technical processes improving the quality of ashes and slags. These processes can be divided into thermal (melting and sintering) and chemical-physical methods (leaching and ageing). All of these processes exhibit different effects on the hazardous potential of MSWI bottom ash. For an evaluation of the efficiency of these treatments, economic as well as ecological criteria have to be taken into consideration.

The study presents different treatment processes changing the quality of the ash, and the chemical and physical effects they are based on. An innovative process called "rapid ageing" is described. This treatment involves elements of a process-integrated approach. The carbonatisation of the ash is performed by using carbon dioxide containing media.

The technical processes involved in the study are evaluated with respect to the attainable ash quality, the technical feasibility, and the costs. Data taken from the literature as well as data derived from experimental investigations were used for comparison.

Key words: MSWI bottom ash; heavy metals; ageing; rapid ageing; carbonatisation; solubility; sulfate; pH value; carbon dioxide.

1 Background and objectives

In Germany the incineration of municipal solid waste (MSW) results in the production of approximately 3 Mio. t of bottom ash yearly. At present a large amount of bottom ash is disposed of in landfills (nearly 23 %) and utilized in road construction (Krass et al. 1997). Compared to other construction materials, bottom ash is characterized by higher concentration of inorganic salts and heavy metals. Other constituents are silicates, compounds of heavy metals as well as incompletely burned carbon substances.

To compare the MSWI residues with commonly construction materials, the quality of solid residues is characterized by the leaching behaviour under standardized conditions (DEV S4 leaching test). Regulatory limits for landfilling are given by the German Regulation for Waste Deposits, the so-called »TA Siedlungsabfall (TASi)«. If MSWI bottom ash will be utilized in road construction as a granular base material, it has to comply with the structural engineering requirements, and its environmental compatibility has to be ensured. Limits are given by the Federal Work Group »Waste« (LAGA) or by regional laws. Fig. 1 shows the results of leaching data under standardized conditions. The basis of this data set is non-treated MSWI bottom ash available in Germany (Mast 1996). Regarding the average values, most of these parameters fulfill the regulatory limits for landfilling (TASi DK I). However, a few values do not comply with the limits set by LAGA (LAGA Z2). The most critical parameter is lead (Pb), a toxic heavy metal forming an amphoteric hydroxide.

Consequently, there is a certain demand to reduce the potential hazards of MSWI bottom ash. Up to now various technical processes to improve the leaching quality of the ash have been known. These processes can be divided into thermal (melting, sintering) and physico-chemical (leaching, ageing) processes. The various processes have different effects on the content and the potential solubility and mobility of harmful substances in bottom ashes and slags. Thermal processes are expected to produce a rather homogeneous material. New mineral phases will be formed (e. g. Gehlenit), and volatile compounds of heavy metals will evaporate from the solid mixture (Gohlke 1993, Pfrang-Strotz/Reichelt 1996). These thermal processes are characterized by a high energy demand. Physico-chemical processes such as leaching in a quench tank reduce only the amount of soluble salts in the ash but not the total amount of heavy metals. Another process proposed by the LAGA is to store the ash for at least three months. Due to the low costs of the storing technology, this procedure is currently the common treatment method for bottom ash in Germany.

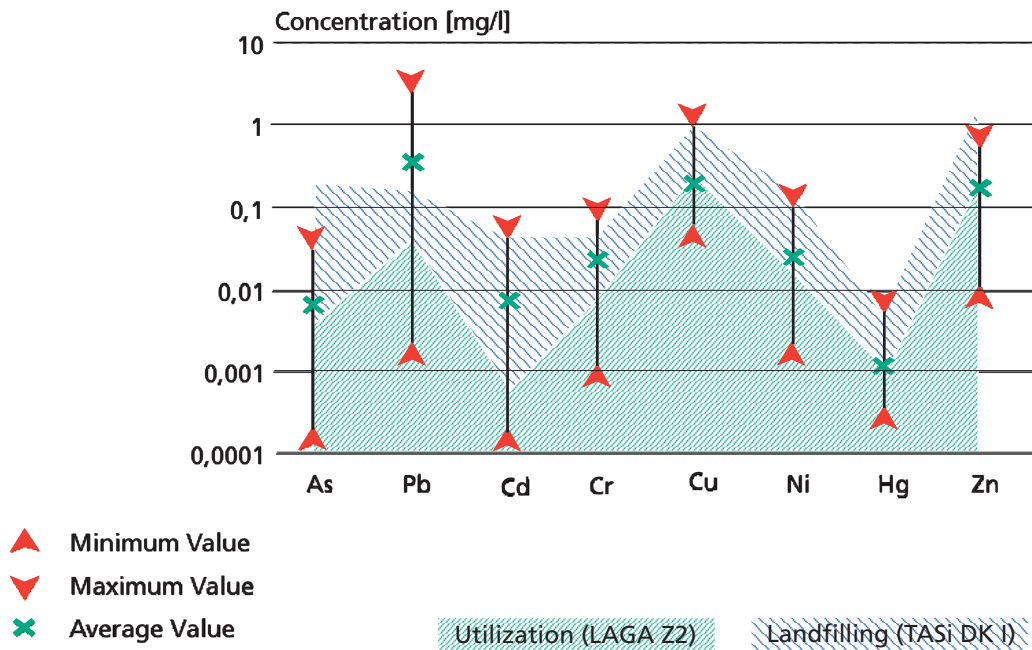


Fig. 1: Average values, maximum values and minimum values in leachates (DEV S4) of non-treated raw bottom ash compared to the regulatory limits (data base: 33 MSWI plants) (Mast 1996)

The primary objective of the present study was to determine the effects which influence the quality of ash, especially the concentration of leachable heavy metals after a three months storage. Another objective was to identify methods for improving the ageing process by technical measures.

2 Procedure

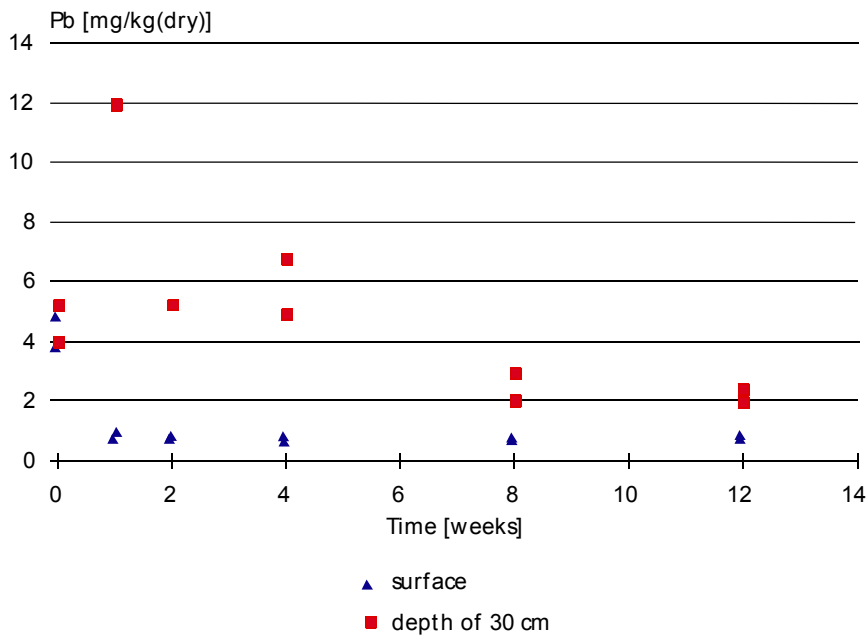
A number of individual chemical reactions which determine the leaching behaviour of ashes were investigated. Approximately 120 tons of raw ash were sampled directly from a quench tank arranged behind a combustion chamber. The ash was divided into grain fractions of 0-6 mm, 0-22 mm and 0-40 mm¹. Ferrous metals were removed by a magnet. These samples were stored in heaps for a period of three months. Regularly samples were taken from the heap surface and from a depth of 30 cm. First tests were carried out to demonstrate the technical feasibility of the carbonization for the improvement of the ageing process.

¹ By dividing raw ashes into grain fractions small particles stick to other particles. Therefore, the particle size was not as homogeneous as it was observed with grain-stored ash.

3 Results

3.1 Experimental results regarding the storing processes

As a consequence of the complex mineralogical and chemical composition of MSWI bottom ash numerous chemical and physical processes influencing the leaching behavior of the components can be expected. The course of Pb leaching and the pH values of the leachates (samples of the surface and samples from a depth of 30 cm) versus time are



presented in Figs. 2 and 3.

Fig.2: Change of the Pb concentrations in the leachate of samples from the heap surface and a depth of 30 cm deposited outside (particle size: 0 to 22 mm)

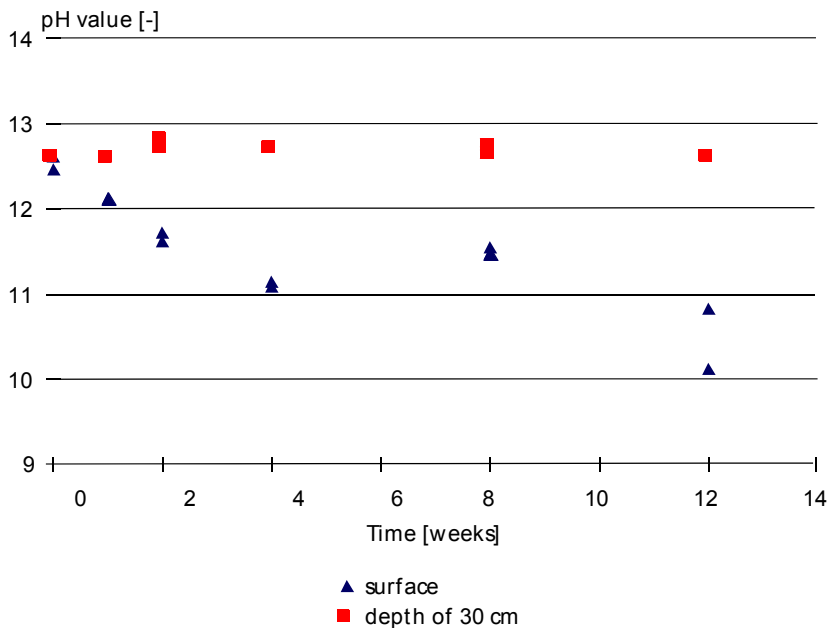


Fig.3: Change of pH in the leachate for samples from the heap surface and a depth of 30 cm deposited outside (particle size: 0 to 22 mm)

There are different processes occurring on the surface and in deeper layers of an ash heap. The Pb concentration in leachate of surface samples is already very low after one week storage. In all cases, the measured concentrations of surface samples were less than the threshold value applicable to lead demanded by TASI. In contrast, the leaching concentration of Pb is clearly lower inside the heap. Even after 12 weeks storage, the value corresponding to the heap surface was not reached.

In Fig. 4, the soluble amount of Pb leached under standardized conditions (DEV S4) depending on the pH value is shown. The data are based on a survey of all MSWI plants in Northrhine-Westphalia. The higher the pH value the higher is the concentration of soluble Pb in the leachates. If the pH value is lower than approximately 11.5, the observed leachate concentration will be low enough as compared to the limiting values given by LAGA for utilization of the ash. If the pH value is higher than 11.5, the leachate concentration will be too high for any kind of utilization.

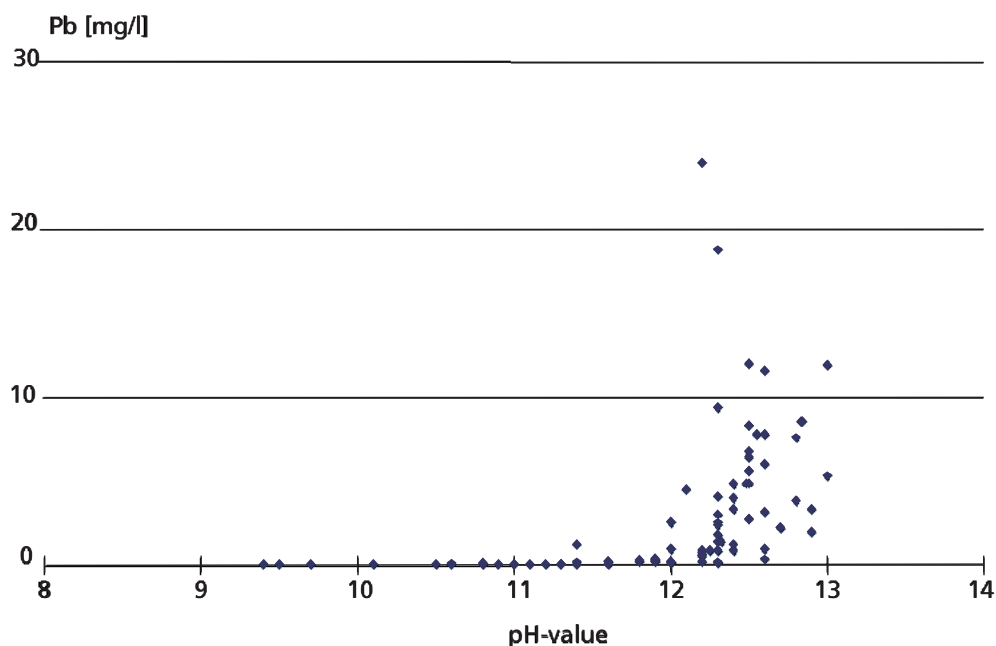
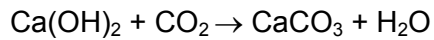


Fig. 4: Concentration of lead in leachates of ashes as a function of pH value (data-base: 16 plants in Northrhine-Westphalia)

Furthermore, Ca concentrations in leachate decrease at the surface. While remaining constant in deeper layers of the heap (Fig. 5). The ageing process at the surface layer is determined by the contact with CO₂ from air or rain water. CO₂ reacts with the calcium-hydroxide of the ash to calcium carbonate.



This solid carbonate layer prevents the additional diffusion of CO₂ into the heap. At the beginning of the tests pH values were measured to be about 12. This corresponds reasonably well with the pH value of a saturated solution of Ca(OH)₂ (12.4). After a short time, the pH values readily decline to approximately 10. The concentration of calcium in the leachates decreases simultaneously since calcium carbonate is only sparingly soluble.

The formation of CaCO₃ is confined to a rather thin surface layer. It is known from examinations of mortar from roman-gallic buildings that a carbonate layer on a surface protects inner layers against further CO₂ access (Hollemann-Wiberg 1976). The complete carbonatization of ash, however, is estimated to take decades or even centuries (Kersten1996). In addition, rough calculations of the mass transport in the heap were performed. In this regard the process was assumed to be diffusion-controlled. It can be assumed that the reaction will be proceeding down depth of 50 cm within one year.

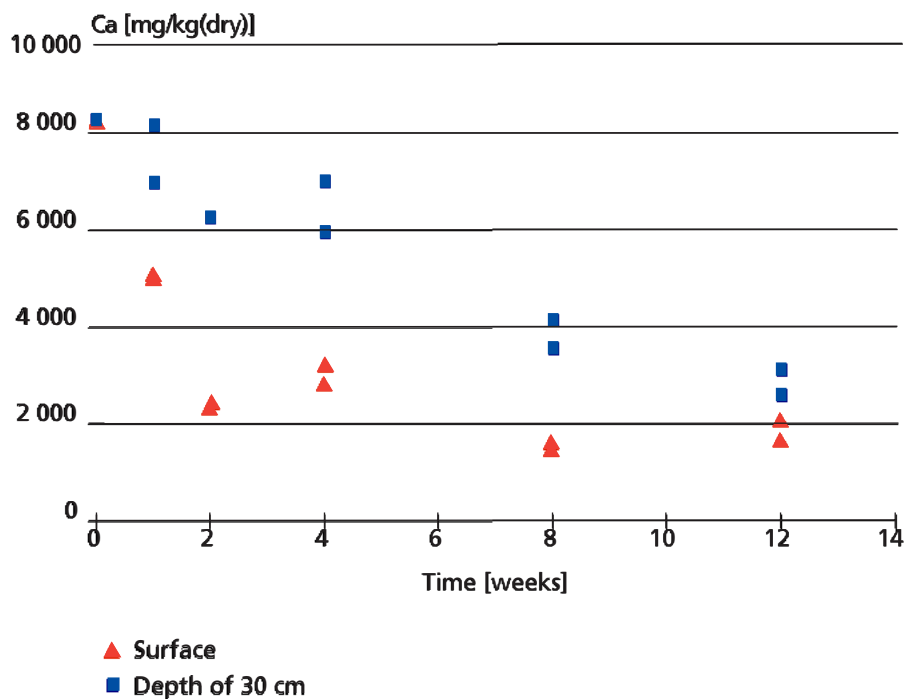
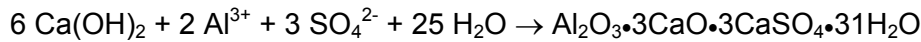


Fig. 5: Changes of Ca concentration in leachates of ash samples (surface and depth of 30 cm, particle size: 0 to 22 mm)

During the time period examined, no reaction to calcium carbonate was observed in deeper layers of a heap. This is due to a limited transport of CO₂ within the heap, which also explains why the pH value of the leachate remains almost constant. Instead, other processes occur which cause a clear reduction of the leachable amounts of sulfate. A decrease of leachable lead and other metal concentrations was also observed. But this reduction is not as explicit as on the heap surface, though.

A possible explanation for the observations mentioned above the formation of springly readily soluble sulfate phases in the ash. A typical phase may be ettringite (Hinz 1970). The reaction to ettringite is formally described by the following reaction:



Presumably, processes are taking place in the examined heaps which are similar to the formation of ettringite in concrete and are leading to the immobilization of sulfate. The leachable amount of sulfate only decreases in deeper layers, while it remains constant on the heap surface. The removal of the leachable sulfate cannot be caused by leaching. If this were the case, one would notice a reduction of the leachable sulfate primarily on the heap surfaces. As Fig. 6 points out, however, this was not the case. Maybe, the carbonate layer on the surface prevents a leaching of sulfate.

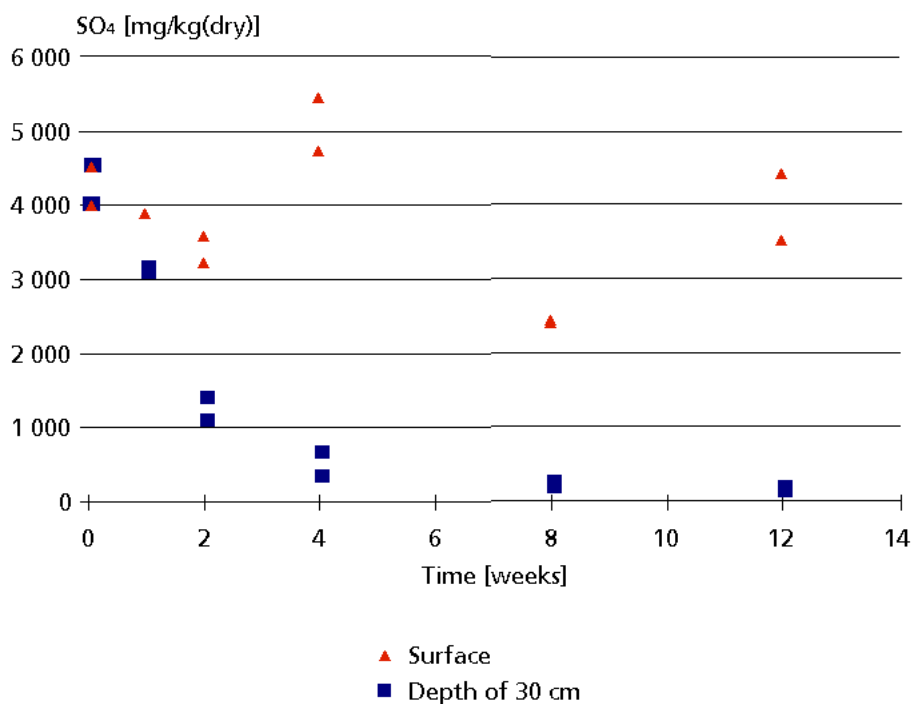


Fig. 6: Changes of sulfate concentration in leachates of ash samples (surface and depth of 30 cm, particle size: 0 to 22 mm)

3.2 Experimental tests to improve the ageing process

Based on theoretical considerations, the concentration of leachable heavy metals is a function of the pH value of the leachate. The pH value in leachates depends on the partial pressure of CO₂. On the other hand, the speed of carbonization is limited by diffusion.

Therefore, the ageing process yielding over pH values in leachates of MSWI bottom ash may be accelerated by contact with CO₂. Laboratory tests have been carried out to check the technical feasibility of such a process.

Spraying CO₂ onto the conveyor-belt is an interesting option, because there is a good heat and mass transfer between the gas and the ash particles (Weyell 1997). Ash for the test was

sampled from the same plant as the ash described in chapter 2. The ash treated with CO₂ was characterized by their leaching behaviour under standardized conditions (DEV S4).

A conveyor-belt was simulated by a laboratory plant which is depicted in Fig. 7. Parameters were varied as indicated in Table 1.

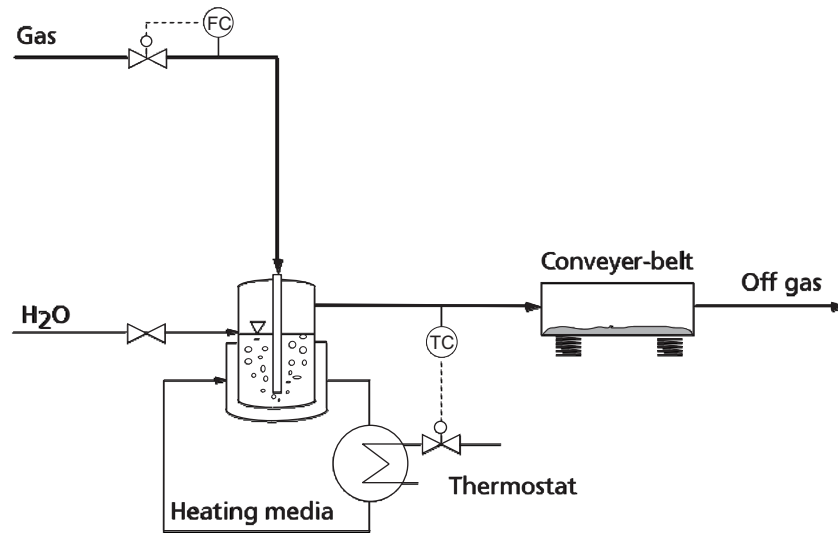


Fig. 7: Laboratory plant for simulation of carbonatization in a conveyor-belt

Table 1: Parameters for laboratory tests for simulating carbonatization in a conveyor-belt

Parameter	Variation
Residence time	2 min, 5 min, 10 min
Concentration of CO ₂ in the gas	10 vol.-% (synthetic flue gas) 100 vol.-%

The leachate pH values of these laboratory tests are shown in Fig. 8. By using synthetic flue gas, the decrease of leachate pH is not enough to reach the threshold values of the German law (Fig. 1). The use of pure CO₂ leads to such pH values in leachates. The threshold values for heavy metals will be reached after 5 minutes residence time (Table 2).

Table 2: Results of tests for carbonatization of ash on a conveyor-belt (gas: 100 vol.-% CO₂)

Residence time [min]	Threshold value	Leachate concentration [mg/l]		
		Ca	Zn	Pb
0		1 073	0.83	3.7
2		827	0.27	1.4
5		497	0.03	0.2
10		319	0.01	<0.1

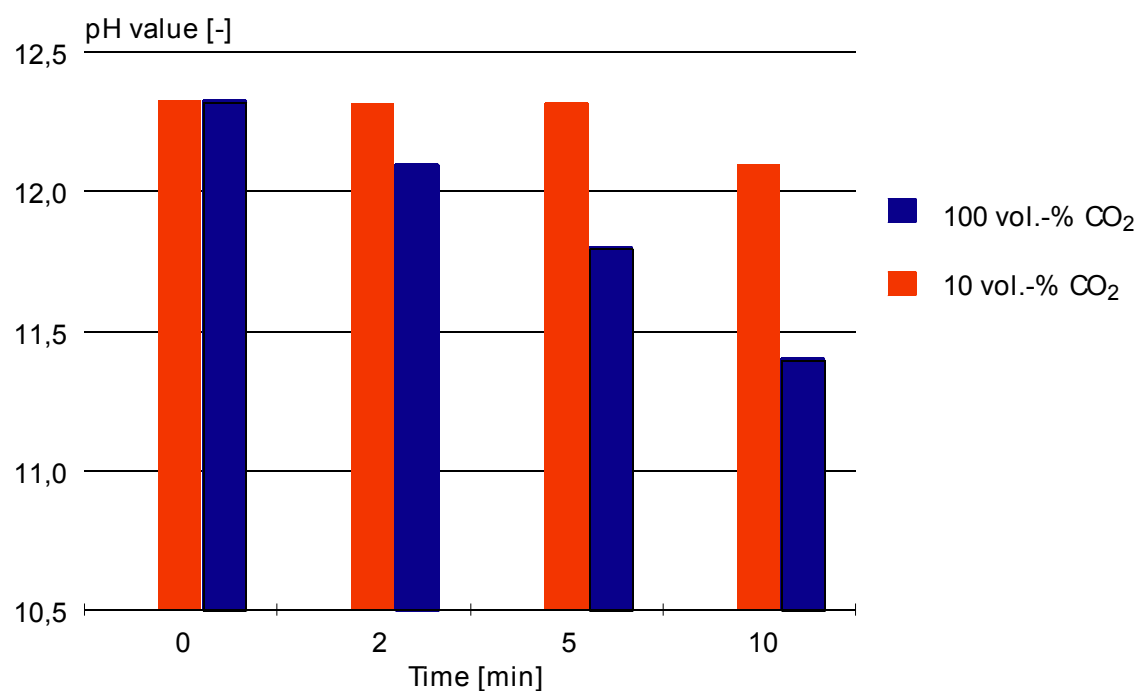


Fig. 8: pH values of ash treated with CO₂ on a conveyor-belt

4 Conclusions

The technical feasibility of a new process to improve the quality of MSWI bottom ash expressed as the stability against leaching of heavy metals was shown. This method is based on a process-integrated treatment of the ash, e. g. by treatment with carbon dioxide on a conveyor-belt.

The results of screening laboratory tests showed that the rate of carbonatization is higher than after a three months aging process by storing the ash in heaps. The residence time for a significant reduction of heavy metal solubility which complies with the regulatory limits for utilization of the ash is approximately 10 minutes.

The costs of this process mainly depend on the amount of carbon dioxide relative to the amount of ash. Assuming a concentration of approximately 3 weight-% of calcium oxide/-hydroxide, almost 25 kg of CO₂/t ash is needed for carbonatization.

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