

Influence of different artificial weathering methods on the longterm leaching behaviour of thermal residues from municipal solid waste incineration

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1 INTRODUCTION

2 MATERIALS AND METHODS

3 RESULTS

3.1 Influence of artificial ageing on the emission-behaviour of metals

- 3.1.1 Calcium and Sulfate
- 3.1.2 Aluminium
- 3.1.3 Chromium
- 3.1.4 Zinc
- 3.1.5 Lead
- 3.1.6 Copper
- 3.1.7 Antimony
- 3.1.8 Vanadium

4 DISCUSSION

4.1 Artificial weathering compared to weathering under landfill conditions

- 4.1.1 Major elements
- 4.1.2 Minor elements

4.2 Rating of different ageing-methods

5 CONCLUSIONS

6 REFERENCES

Abstract

This paper contains the results of three studies, which dealt with artificial ageing. Five different types of residues from thermal treatment were exposed to different artificial ageing-methods. The leaching-behaviour after artificial ageing of major elements as well as of trace elements is described in the pH-range 7 to 13. Solubility-controlling phases were identified, supported by geochemical modeling and compared to phases, which occur naturally in landfills. The results show, that most weathering-processes of landfilled inorganic wastes can be reproduced by artificial ageing. The different artificial ageing-methods are then rated and a laboratory procedure for artificial ageing is presented.

Keywords: artificial ageing, inorganic residues, weathering, emission-behaviour, carbonation

1 Introduction

Modern society puts a lot of pollutants into circulation. Most of them are then enriched in artificial created sinks like multibarrier landfills. Due to the fact, that the technical barrier systems will not last forever, it depends on the middle and long term behaviour of the wastes itself („inner chemical and physical barrier“), if the landfills will become a source of contamination again.

Besides the chemical composition, the physical properties and the environmental impacts the mineralogical composition particularly affects the leaching behaviour of inorganic wastes. Especially the mineralogical composition of thermal treated wastes und stabilization products shows metastable phase conditions. During ageing processes thermodynamic equilibrium with the environment is strived for, whereby a sequence of secondary mineral neoformations and transformations (oxide – hydroxide – carbonate – silicate - ...) is passed through. Simultaneously with the mineral alterations the solubility and the physical behaviour of the seepage water is therefore affected.

In an initial period strongly alkaline conditions dominate the landfill-milieu and soluble salts are washed out over a short period. Weathering and changing of the mineralogical composition of the landfilled residues occurs. In a next period the formation of carbonates appears due to the reaction with water and CO₂. This leads to a decrease in pH and to a stabilization of the system at pH 8,3. This period will last 1000 to 10000 years, depending on the carbonate-content. The processes which take place below a pH of 7 are not known very well. BELEVI et al (1992) describes, that Al- and Fe-oxides and silicates are the buffering substances. These processes and periods were not target of this study.

In this work inorganic residues were treated with different ageing-methods. The mineralogical and chemical changes which occur in these materials and the leaching behaviour of metals were characterized supported by geochemical modeling and mineralogical analysis. The data was compared to the processes which take place under landfill conditions. As a last step ageing-methods and ageing-durations were rated, to see how far they can describe natural weathering processes and reactions in landfills.

2 Materials and Methods

In this work five different types of thermal residues were investigated. Experiments were made with:

- 3 bottom ashes from MSWI: Sa, Sb, Sc
- an APC-ash before wet treatment: Aa-ut
- an APC-ash after wet treatment; dried: Aa-dt
- an ash from fluidized bed incineration: FB
- 2 natural weathered bottom ashes: Sn, An (2 different mixtures of bottom ash, Fb-ash, rotary drum killn-slag; An = higher ash-content, Sn = higher slag-content; from a 10 years old landfill)

Representative samples of these materials were exposed to different types of artificial ageing:

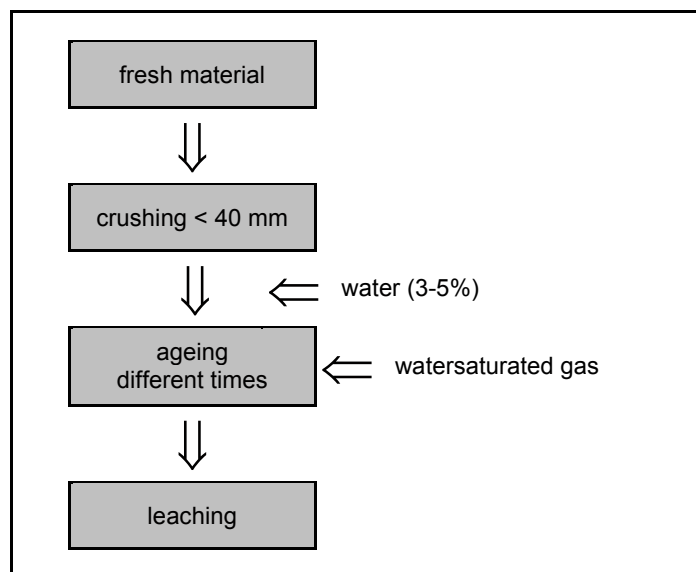
- aeration with watersaturated air
to accelerate oxidation-, hydration- and carbonation-processes
- aeration with watersaturated oxygen
to accelerate oxidation-processes with exclusion of CO₂
- aeration with watersaturated CO₂ (100%)
to accelerate carbonation under anaerobic conditions
- storage in humid anaerobic atmosphere
to simulate anaerobic ageing
- storage in humid anaerobic atmosphere at 80°C (ground material)
to simulate high temperatures in anaerobic landfills

Different ageing-processes and different-ageing-durations are shown in Table 1

pH/ ageing time	pH fresh	air	pH air	O ₂	pH O ₂	CO ₂	pH CO ₂	an aerob	pH an	80°C	pH 80°C
Sa	12,6	2,4	12,4			1,5	9,6	6,5	12,1	3	10,1
		4	11,5			2,4	8,2	9,3	12,1		
		15	8,6			4	8,3				
Aa ut	11,7			2,4	11,2	1,5	7,6	2	11	3	10,6
Aa td	10	2,4	10,7	2,4	11,4	1,5	8,3	0,9	10,9	3	10,5
Sc	12	3	11,7	3	11,7	1,6	8,1	6,2	11,6	3	10,5
		2,4	11,1					2,4	11,4		
Sb	11,8	1	11,6			1	8,3	2	11,9	2	11,8
								3	11,8		

Table 1: Ageing-durations (months) and the achieved pH

A scheme of the procedure of the experiments is given in Figure 1.



**Fig.1:
Procedure of ageing-
experiments**

The ageing experiments were carried out in ageing-boxes. The boxes, which were made of synthetic material, had an opening at the bottom. A grate made of plastic was fixed 5 cm over the bottom and was covered with a fleece. In each box 15 kg of material (< 40 mm) were put on the fleece. To ensure an atmosphere saturated with water, the boxes were filled with demineralized water from the bottom to the grate. The gas, which was fed through the opening on the bottom, had to bubble through the water. To control the CO₂-concentration after aeration there was a second opening above the material.

A leaching-test, following ÖNORM S2072 (conform to german DIN 38 414), was used to investigate the emission-behaviour of the aged materials. Demineralized water was added to the samples (<40mm) with a liquid to solid-ratio of 10 and the samples were agitated for 24 hours.

The recent version of the geochemical code PHREEQC-2 (PARKHURST & APPELO, 1999) was used for geochemical modelling. Activity coefficients of aqueous species have been calculated with the DAVIES equation. As the ionic strength I of the leachates/eluates are in a range of 0,01 < I < 0,27 the DAVIES equation gives a good approximation. Curves for saturation concentrations in diagrams Nr 2-4, 6-8 have been calculated with a initial Na and Cl concentration of 0,1 m (I=0,10) in most cases. Thermodynamic data were taken from the original PHREEQC-2 database, and in some cases from other sources (APPELO & POSTMA, 1996, CARROLL et al., 1998, PERKINS & PALMER, 1998). For ettringite and gypsum, also the saturation indices have been calculated (not shown in this paper).

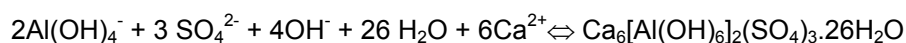
3 Results

3.1 Influence of artificial ageing on the emission-behaviour of metals

Due to varying ageing methods and varying ageing-durations different pH-levels of the investigated materials were reached in the leachates. The concentrations of a selection of the investigated elements are presented versus pH. The covered pH-range is 7 to 13 due to the fact that it is not possible to achieve a pH level lower than 7,5 in the leachate at pCO₂ 0,003 by artificial ageing.

3.1.1 Calcium and Sulfate

Calcium and sulfate show different behaviour in bottom ashes compared to ashes (Fig. 2, 3). As presented in for **bottom ashes** Ca-concentrations at a pH-level higher than 12 remain in equilibrium with respect to gypsum and portlandite. This is also described in MEIMA (1997). The presence of gypsum is also proved by XRD-analysis. With preceding ageing with air and under anaerobic conditions the Ca- and SO₄²⁻-contents of the leachate decrease, because solubilities are controlled by ettringite (fits to the data of aluminium). This is confirmed by geochemical modeling with PHREEQC 2 and by results of XRD-analysis. At the same time pH decreases due to the formation of ettringite (PERKINS, 1998):



At pH-levels lower than 10 ettringite dissolves and the formation of calcite proceeds due to aeration with CO₂. At a pH-level of about 8 Ca-concentrations in the leachates are inbetween the Ca-concentrations, when calcite solely and calcite and gypsum simultaneously are the solubility-controlling phases. The solubility of sulfate in the pH-range of about 8 is controlled by gypsum, which was confirmed by calculations with PHREEQC-2.

Ashes show a different picture. Gypsum seems to be the solubility-controlling phase for Ca on the whole pH-range. In contrast XRD-analysis show, that ettringite is formed with preceding ageing until pH 10. These different results could not be explained up until now. The sulfate-concentrations also correspond to the solubility of gypsum for the pH-range from 12 to 7. FB behaves differently. The fresh sample shows SO₄²⁻-concentration under detection-limit. Simultaneously high Ba-concentration (12 mg/l) appears in the leachate and indicates that sulfate is fixed in BaSO₄. With preceding ageing sulfate is released from gypsum and ettringite. BaSO₄ precipitates and Ba-concentrations decrease.

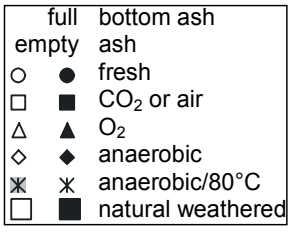
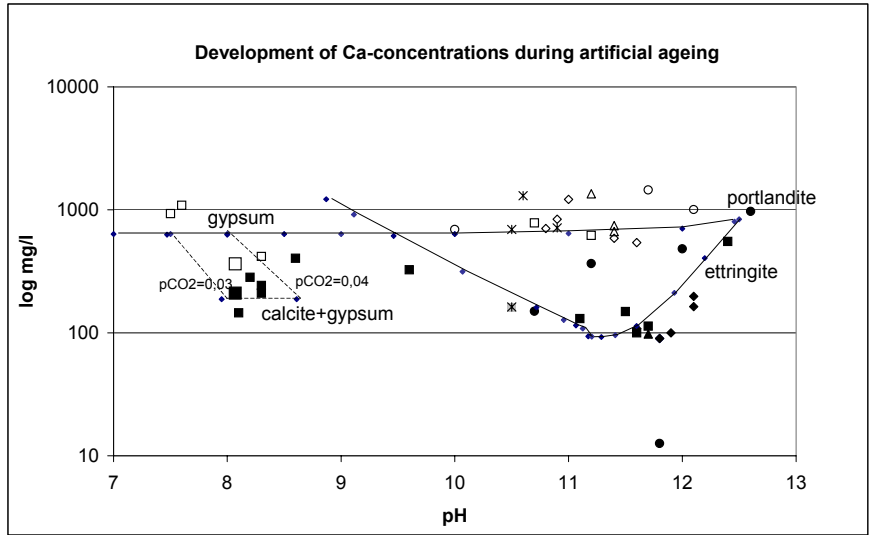


Fig. 2:
Ca-concentrations in leachates of different artificial aged materials

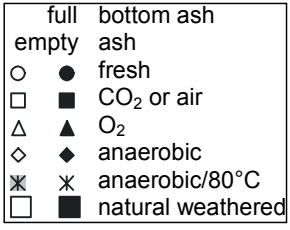
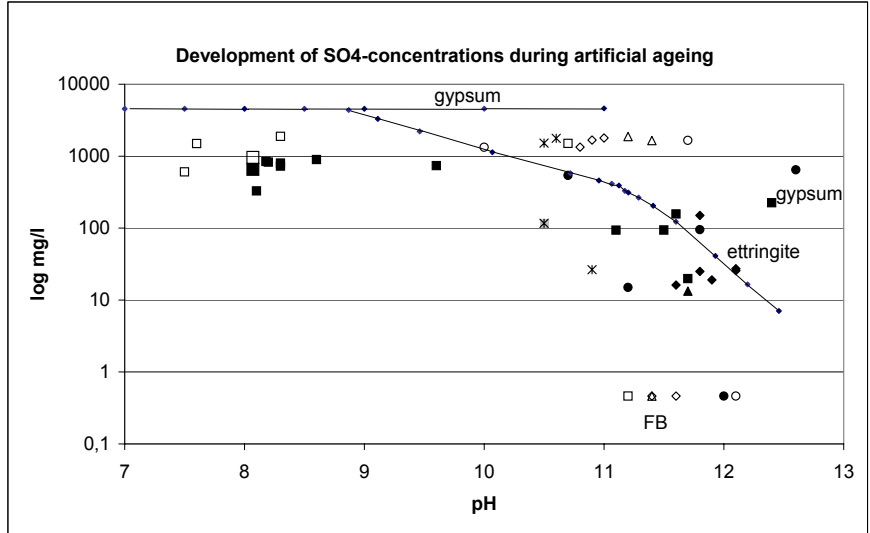


Fig.3:
SO₄-concentrations in leachates of different artificial aged materials

3.1.2 Aluminium

In Fig. 4 the development of Al-concentrations is presented. The concentrations increase in **bottom ashes** at high pH-values due to the oxidation of metallic aluminium under alkaline conditions, whereby $Al(OH)_4^-$ and H_2 are released. This process determines the Al-content in the leachate until a pH of about 11,5 is reached and ettringite is the solubility-controlling phase (see calcium and sulfate). With preceding ageing the pH decreases, ettringite dissolves and amorphous $Al(OH)_3$ precipitates, which controls the Al-concentrations at a pH of about 8. This trend of Al-concentrations agrees with datas which are described in MEIMA (1997), where materials of different ages were investigated. $Al(OH)_3$ besides $Fe(OH)_3$ plays an important part in sorption processes concerning the elements Zn, Pb, Cu. **Ashes** show a different behaviour, since they contain no metallic aluminium. Only FB behaves similar to bottom ashes. Due to the combustion of Al-containing packings, metallic aluminium is found in FB.

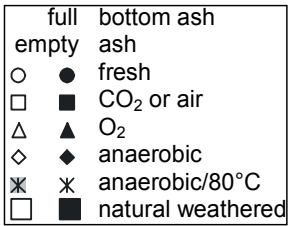
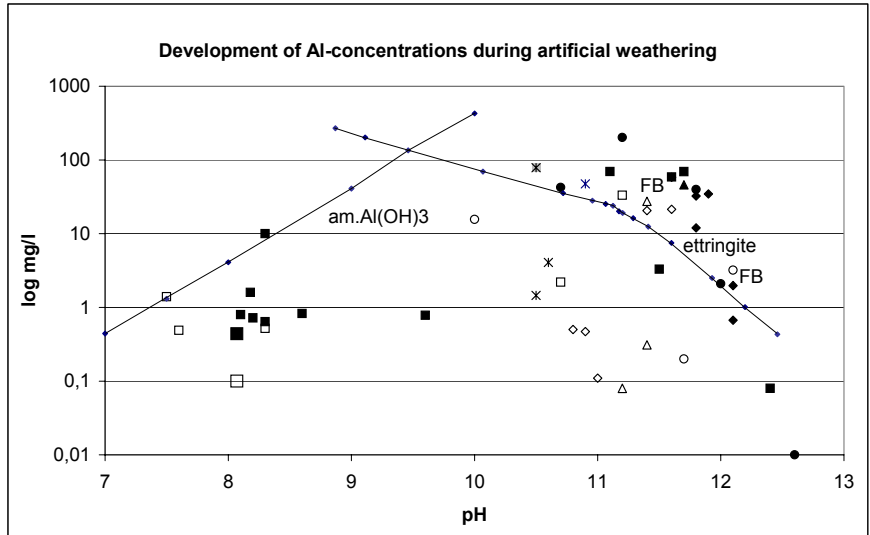


Fig.4:
Al-concentrations in leachates of different artificial aged materials

3.1.3 Chromium

There is an obvious difference in Cr-concentrations between bottom ashes and ashes (Fig.5), although total-contents of chromium are in the same order of magnitude. In bottom-ashes Cr-concentrations are lower, since bottom ashes contain metallic chromium, whereas in ashes chromium occurs in a more available form (maybe BaCrO₄). Material FB shows Cr-concentrations in the range of the bottom ashes, that indicates a differing mineralogical composition. A solubility-controlling phase could neither be identified in bottom ashes nor in ashes.

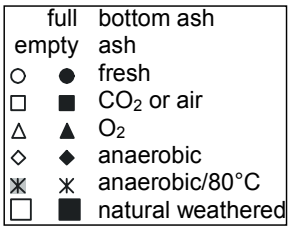
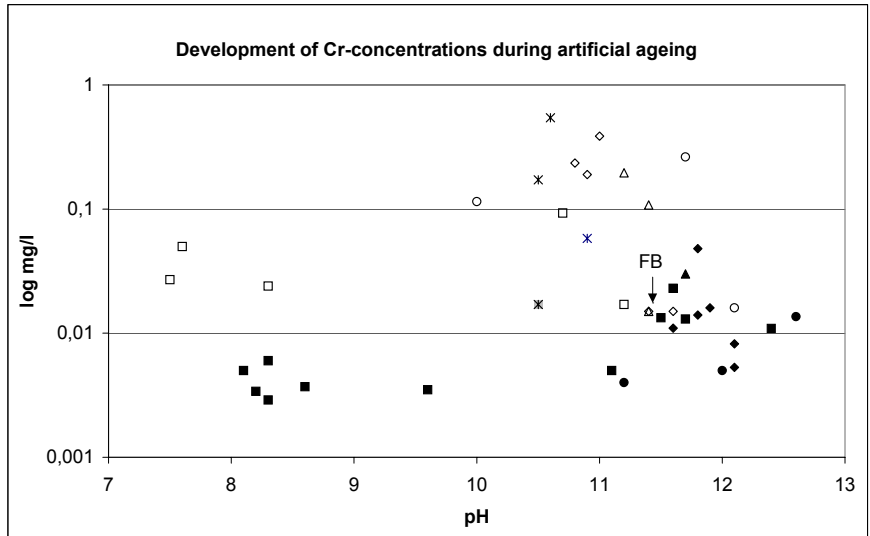


Fig.5:
Cr-concentrations in leachates of different artificial aged materials

3.1.4 Zinc

The behaviour of zinc shows a difference in ashes and bottom ashes (Fig.6). In **ashes** the concentrations of Zn in alkaline conditions are close to concentrations of Zn when Zn(OH)₂ is the solubility-controlling phase. **Bottom ashes** show the same amphotere behaviour, but concentrations are lower and the solubility-controlling phase seems to be willemite (Zn₂SiO₄). In neutral or slightly alkaline conditions the solubility of Zn may be controlled by sorption mechanisms (MEIMA, 1997).

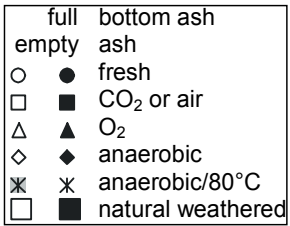
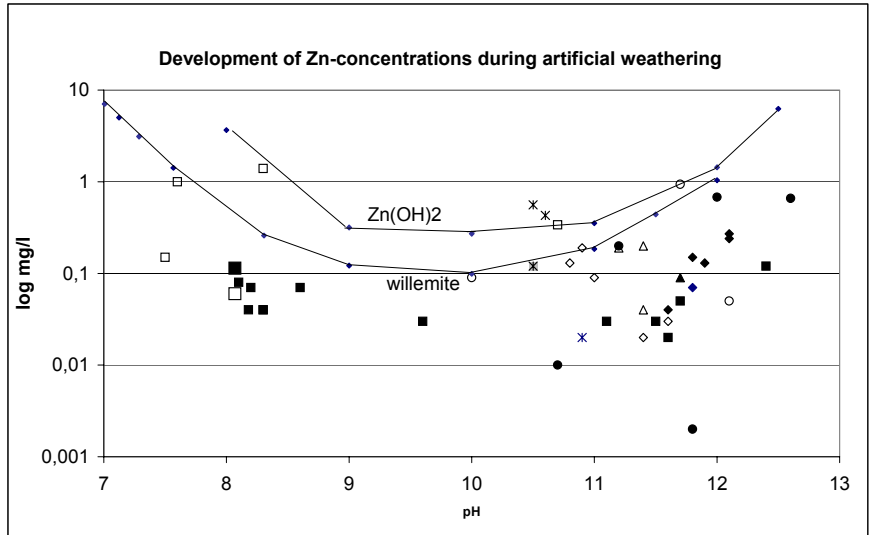


Fig.6:
Zn-concentrations in leachates of different artificial aged materials

3.1.5 Lead

The concentrations of lead, depending on the pH show the typical amphotere behaviour (Fig.7). The leachate-concentrations of **bottom ashes** are close to concentrations in equilibrium with $Pb(OH)_2$ on the whole pH-range. MEIMA (1997) and JOHNSON (1998) describe the behaviour of Pb in neutral conditions by using sorption models. The datas from our investigations could not be explained by surface complexation models using $Fe(OH)_3$ - or $Al(OH)_3$ -sorption data (DZOMBAK and MOREL, 1990). A possibility could be the absence of a sufficient quantity of strongly adsorbent sites. Only the Pb-concentration of sample An is in the concentration-range, which can be described by sorption-processes. This material contains ten times more iron, which can be converted to adsorber phases. For **ashes** larnacite, $PbO \cdot PbSO_4$ seems to be the solubility controlling phase in alkaline conditions.

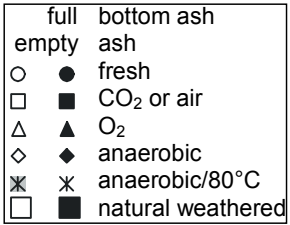
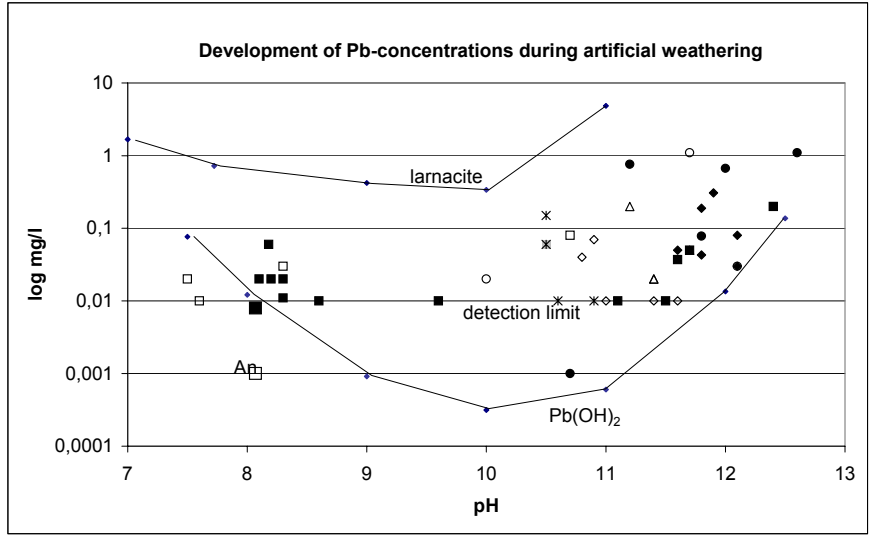


Fig. 7:
Pb-concentrations in leachates of different artificial aged materials

3.1.6 Copper

For **bottom ashes** there is nearly no influence on Cu-concentrations in the leachates with decreasing pH (Fig. 8). Cu-concentrations are close to concentrations in equilibrium with tenorite (CuO) on the whole pH-range. An exception is material Sb, in which all Cu-concentrations are one magnitude higher (0,1 mg/l compared to 1 mg/l) although total-contents are the same. It was not possible for Sb to

identify a phase, which controls solubility for this bottom ash. Also for **ashes** a solubility-controlling phase could not be identified.

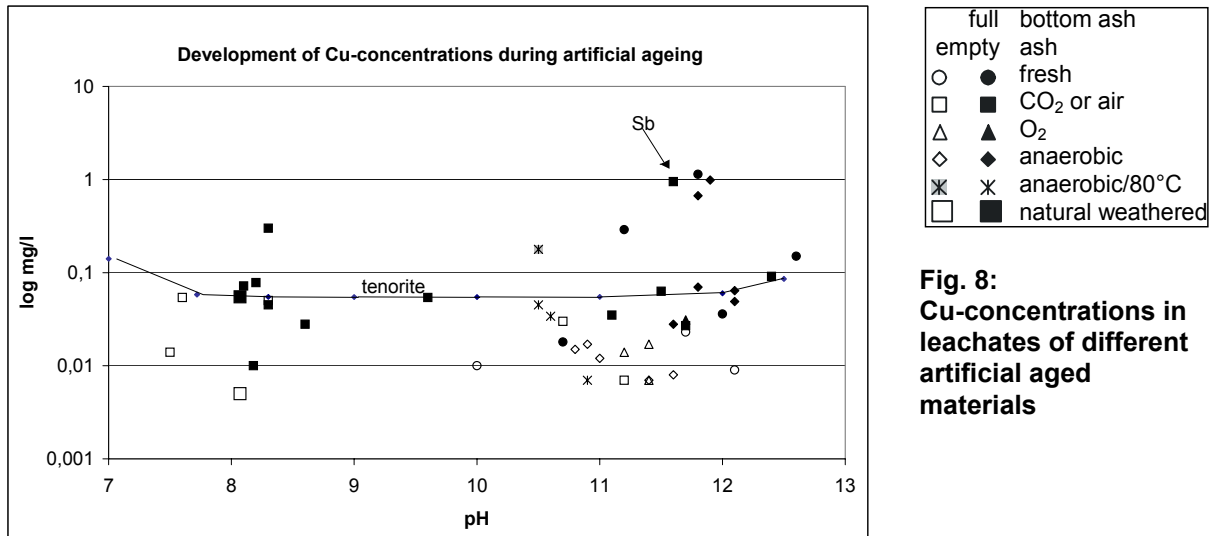


Fig. 8:
Cu-concentrations in leachates of different artificial aged materials

3.1.7 Antimony

Although antimony often show relatively high leachate-concentrations for MSWI-bottom-ashes there are no literature datas available of the leaching-behaviour in thermal residues. As shown in Fig. 9 Sb-concentrations increase with decreasing pH, independent of ageing-method and material. MERIAN (1991) describes this behaviour in seawater by formation of HSbO_2 . The saturation-concentration of Sb_2O_3 (about 13 mg/l) is not reached, maybe due to oxidation of HSbO_2 and adsorption of SbO_2^+ on Fe/Al-hydroxides.

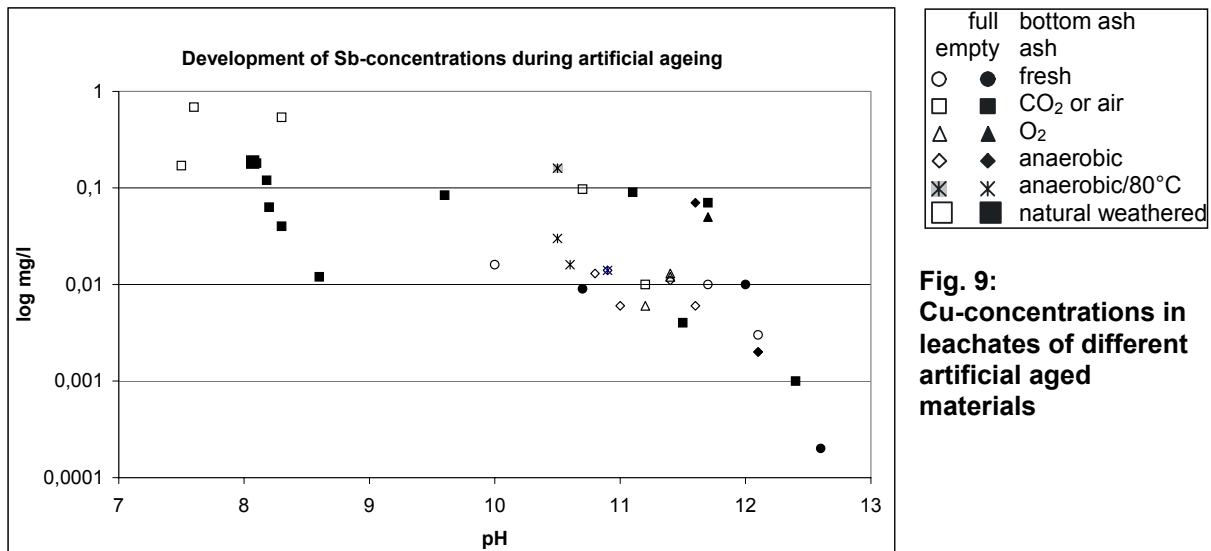


Fig. 9:
Cu-concentrations in leachates of different artificial aged materials

3.1.8 Vanadium

In strongly alkaline conditions V-concentrations (Fig. 10) are very low and increase with decreasing pH. In slightly alkaline conditions highest concentrations are reached in bottom ashes (0,01 mg/l). Concentrations in ash-leachates are all higher. At a pH of about 8 V-concentrations show a indifferent behaviour.

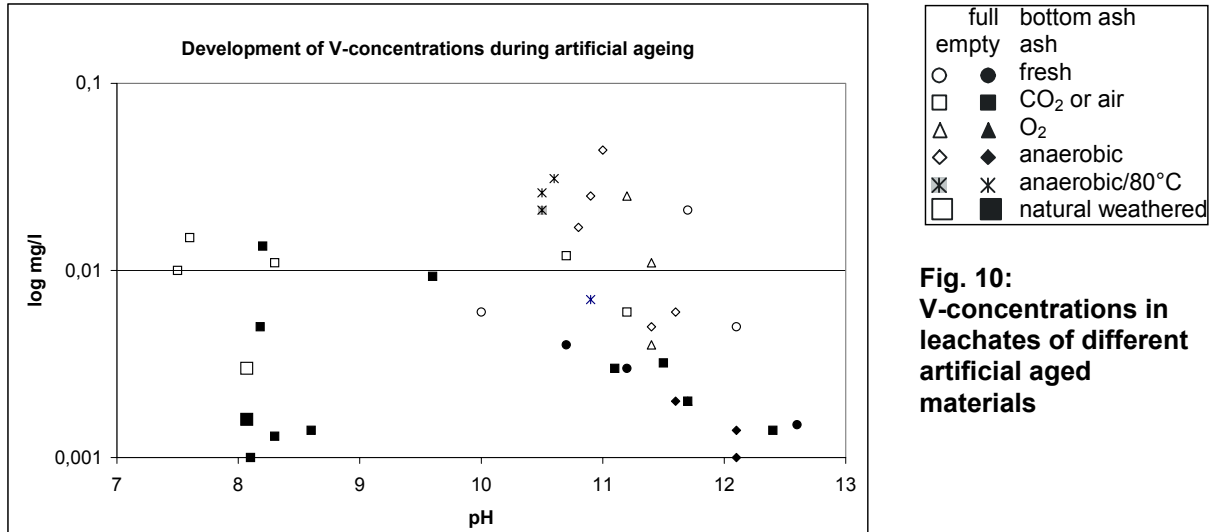


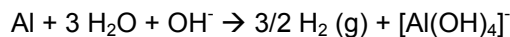
Fig. 10:
V-concentrations in leachates of different artificial aged materials

4 Discussion

4.1 Artificial weathering compared to weathering under landfill conditions

4.1.1 Major elements

In the following, major reactions which occur in landfills are described. The major elements in thermal residues are Si, Ca, Al and Fe. Due to ageing processes the mineralogy of the landfill-system alters. In a first step hydration leads to the formation of hydroxides of Ca, Fe and Al, which results in a strongly alkaline pH. Simultaneously chloride, sulfate and alkali-hydroxides start to wash out. On the one hand calcite is formed due to the reaction of $\text{Ca}(\text{OH})_2$ with CO_2 . On the other hand reaction with SiO_2 leads to the formation of Ca-silicate-hydrates. An other possible Ca-mineral, which can develop in alkaline milieu is ettringite. Oxidation in strongly alkaline conditions play an important part for the solubility of aluminium.



Al is further on precipitated as amorphous $\text{Al}(\text{OH})_3$ or gibbsite.

Investigations of JOHNSON (1998) showed that discharge-concentrations of calcium and sulfate are close to modelled concentrations in equilibrium with gypsum. The solubility of Ca, SO_4 and Al can also be controlled by ettringite. Calcite can also be present in large quantities, but may not be soluble enough or its kinetics are too slow to influence the Ca-concentrations compared to gypsum.

Our results correspond to the findings by JOHNSON (1998). All different ageing – methods lead to leachate-concentrations and pH-values, which are comparable to concentrations and mineral phases presented in other works by MEIMA (1997) or JOHNSON (1998), which have been derived by modeling of natural weathered materials. From the presented results we can deduce, that processes that are forced by artificial ageing are the same, than those that occur naturally in landfills. Our investigations indicate, that for major elements artificial weathering-methods correspond to weathering processes under landfill conditions.

4.1.2 Minor elements

The weathering under landfill conditions, where trace elements are involved are not known very well and cannot be described in particular for most elements. In the following some reactions and processes are presented.

JOHNSON (1998) describes, that the leaching-behaviour of some elements can be partly explained by **precipitation and dissolution**. So Cu, Pb, Cd and Zn precipitate as mixed oxides and carbonates. The solubility of cadmium corresponds to the solubility of CdCO_3 in the pH-range of 8,5 to 11. In the same pH-range CaMoO_4 was identified as solubility controlling phase for Mo, which is also mentioned in MEIMA (1997) and CHANDLER et al. (1997). MEIMA (1997) further identified Pb(OH)_2 as Pb-controlling phase.

The solubility of some elements are also controlled by **sorption processes**. In general heavy-metal cations are sorbed in alkaline conditions. Me-oxyanions as of the elements Cr, V, Sb and Mo are sorbed in acidic conditions. Following JOHNSON (1998), sorption on reactive surfaces, mainly on Al(OH)_3 and Fe(OH)_3 strongly influences the leaching-behaviour of Pb and Zn. The leaching of Cu can be mainly determined by complexation with organic ligands.

Heavy metals can also be **integrated in newly formed mineral phases**. AUER (1992) describes the integration of chromate, and Cd into ettringite.

Most artificial weathering processes correspond to processes, which can be found also under landfill conditions, e.g. precipitation/dissolution or adsorption. The processes which take place in particular, and the phase which controls the solubility of the element is strongly dependent on the type of material (e.g. difference between bottom ashes and ashes). As shown in Fig. 2-10 leachate concentrations of 10 years old landfill materials (pH about 8) fit the datas of artificial aged materials very well.

4.2 Rating of different ageing-methods

Due to the results from the chapters „Influence of artificial ageing on the emission-behaviour of metals“ and „Artificial weathering compared to weathering under landfill conditions“ the development of the leaching behaviour of inorganic residues can just be simulated by laboratory-tets, when different gases and ageing-durations are applied. Ettringite is formed in all materials independently of the ageing-method, since the phase develops under oxidative as well as under reductive conditions. So aeration with air or O_2 and storage under anaerobic atmosphere can be used to accelerate the formation of ettringite. The oxidation of metallic aluminium is committed to a high pH and the presence of water, which forces the formation of ettringite in the presence of soluble calcium and sulfate. This state can also be achieved by all applied ageing methods. To force carbonation-processes it is necessary to use a CO_2 -containing gas.

In landfills the pH of the system is determined by mineralogical and chemical processes of the residues itself (Fig.11). By the use of different ageing-methods in combination with varying ageing-durations certain mineral associations are achieved. To cover the whole mineral-range various ageing-methods and durations have to be used. If someone wants to describe the whole pH-range by combined ageing- and leaching tests artificial ageing should be slow in the beginning due to the high reactivity of the material to allow the Al-oxidation and the formation of ettringite. This is just possible by the use of a gas with low or zero CO_2 content. Due to ageing with air a pH-level of about 10,5 (ettringite starts to dissolve) can be reached within 4 months. Ageing with O_2 , stored under anaerobic conditions and at 80°C does not lead to different information regarding the leaching-behaviour. To achieve the calcite buffer (pH about 8,5) ageing with air would last at least 15 months. Since this length of time is not workable, the calcite buffer stage has to be covered by ageing with higher CO_2 content. It is possible to reach a pH of 7,5 (presence of gypsum) within 2,4 months. The duration of ageing to achieve a certain mineralogical stage differs between ashes and bottom ashes, whereas the ashes show faster weathering progresses.

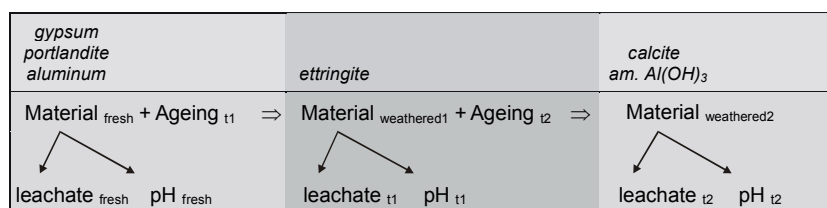


Fig.11:
Scheme of procedures
during ageing

5 Conclusions

This paper focuses on the comparison and rating of different ageing-methods regarding their ability to reproduce processes under landfill conditions.

Artificial ageing of thermal treated residues leads to an acceleration of weathering-processes and allows thus to apply leaching tests to weathered material and makes it possible to predict the longterm behaviour of inorganic wastes.

Most weathering stages between pH 12 and 10, which are characterized by typical mineralogical associations (Al(OH)_4^+ + gypsum + portlandite \Rightarrow ettringite) can be achieved by the use of different ageing methods. To achieve weathering stages, which lead to pH-levels lower than 10 due to the formation of calcite (ettringite \Rightarrow gypsum + calcite + am. Al(OH)_3), it is necessary to use CO_2 as ageing gas.

Particular ageing methods force particular weathering stages. To cover the whole range of the ageing-processes a combination of ageing-methods and durations is necessary. In the following an „artificial ageing procedure“ for thermal residues is presented.

1. ageing with watersaturated air : 3-4 ageing-steps until a pH about 10,5 is reached (covers pH 13 – 10,5)
2. ageing with watersaturated CO_2 : 2-3 ageing-steps until the carbonate-buffer-stage is reached (covers pH 11 – 8,3)

To cover the whole weathering progress about one to six months of artificial weathering is necessary, depending on the type and the grainsize of the investigated material. It is possible to shorten and simplify this procedure by the use of synthetic air containing 30% CO_2 and a smaller grainsize (<20 mm). The advantage of this modified procedure is described elsewhere (SABBAS et al., 2000).

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