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Waste Materials in Construction: Putting Theory into Practice

Organic substances in leachates from combustion residues

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Abstract

The release of water soluble organic substances from combustion residues (bottom ashes from municipal solid wastes and from wood) has been followed in laboratory batch leaching experiments. Leachates have been sampled during 70 days (single-step procedure) or frequently during first 24 hours (starting after 10 min), followed by a change of leachate solution and continued sampling during 70 days (two-step procedure). The leachates were analysed for conductivity, pH, Eh, TOC and metals (Cu and Cr). High concentrations of dissolved organic matter were obtained already within 24 hours (up to 30 mg/l of TOC for the solid waste bottom ash). However, a rapid loss of the TOC from the solution (half-life of 50 days) was also observed. The release of copper appeared to be governed by the simultaneous release of organic carbon, while the release of chromium was independent of TOC.

1. INTRODUCTION

The technical use of ashes and slags from combustion of various materials (municipal solid waste, wood etc.) is limited by the potential environmental effects due to releases of harmful components from these products as a result of leaching by percolating precipitation. Most efforts to characterize and quantify the leaching properties of ashes and slags have been focussed on the release of inorganic components under various conditions, not considering the simultaneous release of soluble organic agents. However, the total contents of organic carbon in solid ashes from combustion of e.g. mixed municipal wastes and wood are usually several percent, assessed from measurements of loss of ignition. Total concentrations of organics in leachates in the 10-100 mg/l range have been reported [1, 2]. There are also reports on the composition of the *hydrophobic* fraction, leached by organic solvents [3].

The aim of the present study is to assess concentrations and eventually metal complexing properties of readily soluble *hydrophilic* organics in leachates from combustion residues (municipal solid wastes and wood). Effects on the release of copper and chromium related to the simultaneous release of organic matter will be quantified.

2. MATERIALS AND METHODS

2.1. Materials

Bottom ash from municipal solid waste incineration (BA) and wood (primary wood chips and secondary wood materials) firing (WA) were obtained from energy production plants at Linköping, Sweden. All ash samples were dried at 50°C and crushed to a size of <1 mm prior to storage and laboratory testing. The total element composition was analysed by ICP-AES or ICP-MS (samples digested in lithium borate or nitric acid; see Table 1). The organic carbon content was assessed from the measurements of the loss on ignition (LOI) at 550°C.

Table 1
Elemental composition of the ash samples [4]

	Bottom ash	Wood ash		Bottom ash	Wood ash
Element	g/kg	g/kg	Element	mg/kg	mg/kg
Si	209	222	Pb	737	253
Fe	108	28.3	Sr	285	407
Ca	87.9	82.5	Cr	274	94.5
Al	56.9	48.6	Zr	200	168
Na	26.4	12.2	Ni	138	40.0
K	14.3	40.3	Sn	130	64.7
Mg	11.3	10.9	V	58.7	53.9
S	8.56	5.44	W	33.9	<14
Ti	6.20	2.90	Co	19.1	11.1
P	4.50	5.00	As	16.0	38.2
Cu	3.40	0.089	Mo	16.0	<6
Zn	3.08	1.84	Nb	13.1	13.5
Ba	1.66	1.32	Cd	5.80	4.50
Mn	1.36	4.80	Be	1.78	2.30
LOI	43	170	Hg	<0.4	<0.4

2.2. Leaching procedures

Approximately 400 g of dried and crushed ash samples and appropriate amounts of MilliQ-water (liquid/solid (L/S) ratio of 5) were put into 2 l Duran glass flasks. Two different leaching procedures were followed. In the *single-step* procedure the flask containing ash sample and MilliQ-water was agitated for 24 hours (end over end rotation) after which the first sample was taken. The bottle was put on an oscillating shaking table, and sampling was continued with logarithmic time intervals for 70 days. In the *two-step* procedure the first leachate sample was taken already after 10 min, and sampling then continued with logarithmic time intervals for 24 hours. The leachate was removed after 24 hours by centrifugation at 3000 rpm for 0.5 h and replaced with fresh leaching solution (MilliQ-water). Leaching and sampling continued as in the single-step procedure for 70 days. Two replicates were measured. In addition, a blank sample (without ash) was included in the single-step series.

2.3. Leachate analyses

The withdrawn samples were filtered (0.45 μm cellulose acetate filter) and acidified prior to analysis (TOC and metals). Organic carbon was analyzed by high-temperature catalytic combustion (Shimadzu TOC-5000 analyzer). Concentrations of copper and chromium were determined by atomic absorption spectrophotometry (Perkin Elmer 1100B equipped with a HGA700 oven). Conductivity was measured with a Radiometer CDM210 conductivity meter and pH was determined with a Metrom 632 pH-meter. Redox potential was measured with a Pt-calomel electrode combination.

A fractionation procedure was tested on a separate ash system (leaching of BA with 0.1 M NaOH for 24 h) in order to divide the TOC into arbitrarily defined fractions by passage through columns with XAD-8 and XAD-4 in sequence [5]:

- Hydrophobic acids; adsorbed on XAD-8 at pH 2 and desorbed with 0.1 M NaOH
- Other hydrophobic agents; adsorbed on XAD-8 at pH 2, but not desorbed with 0.1 M NaOH
- Hydrophilic acids; adsorbed on XAD-4 at pH 2 but not on XAD-8; desorbed with 0.1 M NaOH
- Other hydrophilic agents; neither adsorbed on XAD-8 nor on XAD-4 at pH 2

3. RESULTS

The 10 dominating elements (besides oxygen) in the ashes account for around 53 and 46% of the mass of BA and WA, respectively. The additional 18 other elements that were determined account for around 10%. LOI indicates maximum organic matter contents of 4.3 and 17% of BA and WA, respectively. This illustrates significant differences between the ashes in terms of the contents of oxygen, as well as organics. The BA generally has higher levels of heavy metals (Fe, Cu, Zn, Pb, Cr, Ni, Sn, Mo etc.) than the WA, while the concentration of alkali and alkaline earth metals are similar in both ashes. Most pronounced are the differences in concentrations of Cu, Fe and Cr (highest in BA), as well as Mn and organic carbon (highest in WA).

3.1. Conductivity

The conductivity reflects the total dissolved solids in the leachate [6]. The increase of the conductivity with time is given in Figure 1. Conductivity in step two (change of leachate after 24 hours in the two-step procedure) is added to the final value after 24 hours in step one. The conductivity after 64 days reached the level 450-500 mS/m for both the BA and WA.

The final conductivities in the single-step procedure would correspond to some 7 and 10% of the total inventory of monovalent cations (K, Na) in BA and WA, respectively, neglecting contributions from other cations.

3.2. pH

Initial pH of 9 was obtained in both the BA and WA systems, Figure 2, however with different developments vs time for the two systems. Both systems exhibited higher pH in the two-step than in the single-step procedure. A maximum pH of 9.8 was obtained during the second step in the WA system, and pH of 9.5 or above was maintained after 64 days. A decrease of pH towards 8.5-8.8 was obtained in the BA system for both procedures.

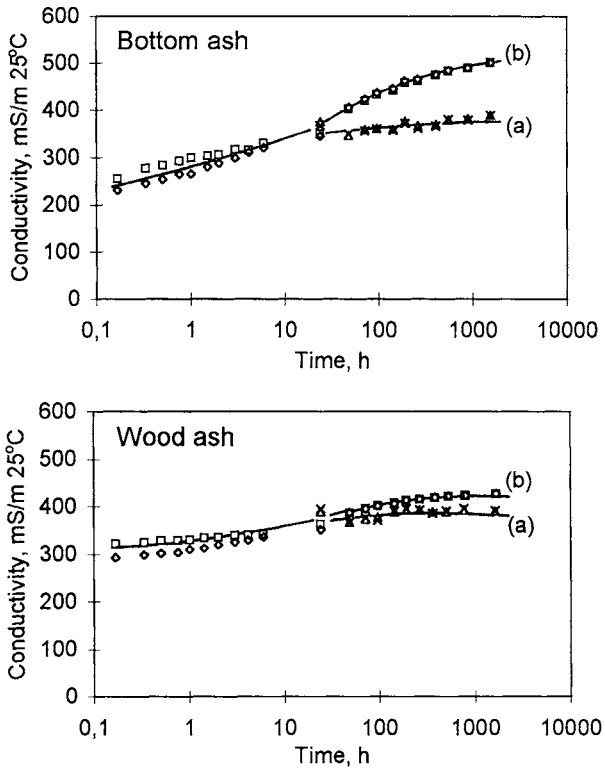

Figure 1. Conductivity as a function of time in BA (top) and WA (bottom) leachates
(a) Single-step leaching (b) Two-step leaching

3.3. Redox potential

Redox potentials of -100 to -150 mV corresponding to pe + pH of 6.5 to 7.5 were obtained at the start of the BA leaching, but increased to around 200 mV after 24 hours (pe + pH of 12). A new low level of around -100 mV (pe + pH of 10) was observed after the change of leachate solution in the two-step procedure (see Figure 3). This level increased slowly with time to a stable level of around 400 mV (pe + pH of 15-16).

The redox potential in the closed bottle of the single-step procedure was -450 mV after 24 hours (pe + pH of 2), increasing with time to the same level as in the two-step procedure (pe + pH of 15-16).

Initial potentials around 400 mV were obtained in the WA system with minor changes with time (constant pe + pH of 15-16). Potentials corresponding to pe + pH of 15-16 (in all WA leachates as well as in the BA leachates after a long time) simply reflect a system in contact with the atmosphere (E° of 0.95 V).

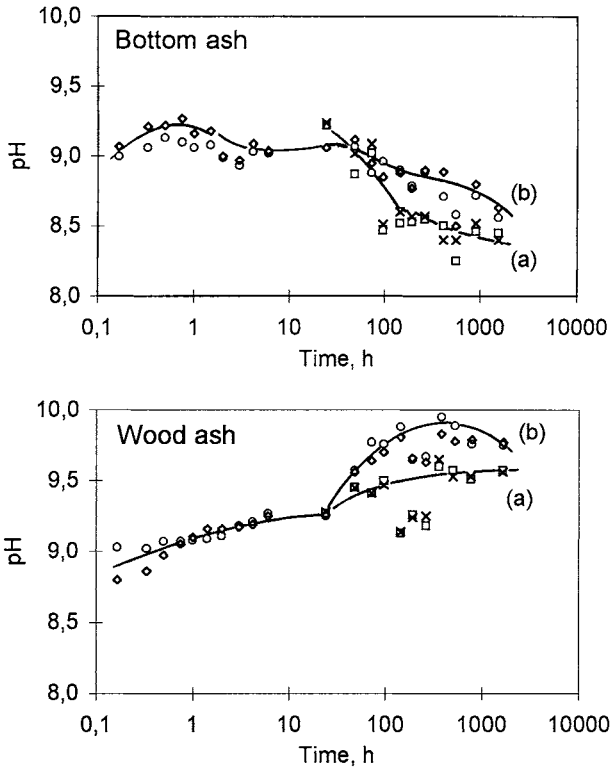

Figure 2. pH as a function of time in BA (top) and WA (bottom) leachates
(a) Single-step leaching (b) Two-step leaching

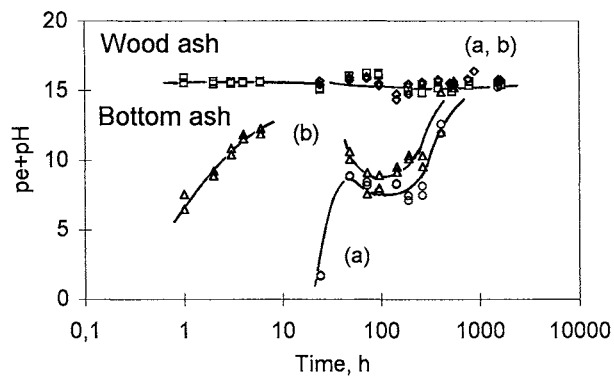

Figure 3. pe + pH as a function of time in BA and WA leachates
(a) Single-step leaching (b) Two-step leaching

3.4. Release of organic carbon

The accumulated release of carbon, determined from the measured TOC-concentration, is given in Figure 4. TOC-concentration in step two (change of leachate after 24 hours in the two-step procedure) is added to the final value after 24 hours in step one.

There were immediate releases of organic carbon into the leachates of both systems, giving TOC-levels of 20 and 4.5 mg/l for BA and WA, respectively, already after 10 minutes of exposure. The TOC-concentrations had reached levels of 30 and 5.5 mg/l after 24 hours, corresponding to a release of around 150 and 30 mg/kg from the BA and WA, respectively.

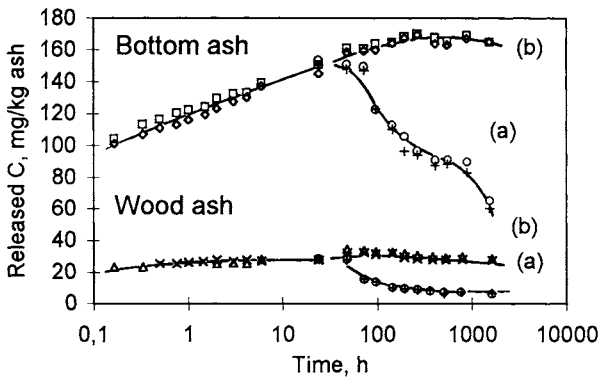

Figure 4. Organic carbon release as a function of time in BA and WA
(a) Single-step leaching (b) Two-step leaching

The carbon release continued after the change of leachate in the two-step procedure, and leveled out at a total release of around 170 mg/kg for the BA system, based on the TOC-concentration. Changes in TOC-concentrations were minor in the WA system in the second step of the two-step procedure.

The high levels of the released organic carbon in the BA system represented only some 0.8% of the maximum organic carbon inventory (assessed from the LOI). The released fraction from the WA system was only some 0.03%, and the concentrations much lower than for the BA system, despite the fact that the carbon content was almost four times higher in the WA.

The TOC-concentration was decreasing with time, after the initial fast in-growth, in the single-step leaching for both the BA and WA systems. Half of the maximum TOC-concentration was lost after about 50 days in the BA leachate, but already after 4 days in the WA leachate.

Preliminary results (BA only) indicate the following distribution of leachable (by 0.1 M NaOH) organic matter: 25-30% hydrophobic acids, 5-10% other hydrophobic agents, 10-15% hydrophilic acids and 45-55% other hydrophilic agents.

3.5. Release of Cu and Cr

The accumulated releases of copper and chromium, determined from the measured concentrations, are given in Figures 5 and 6. The release in step two (after change of leachate after 24 hours in the two-step procedure) are added to the values after 24 hours in step one.

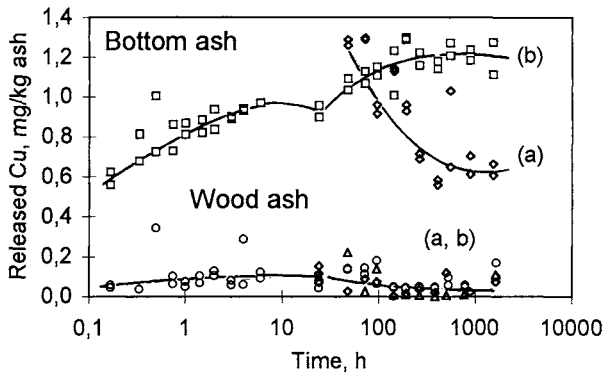

Figure 5. Copper release as a function of time from BA and WA
(a) Single-step leaching (b) Two-step leaching

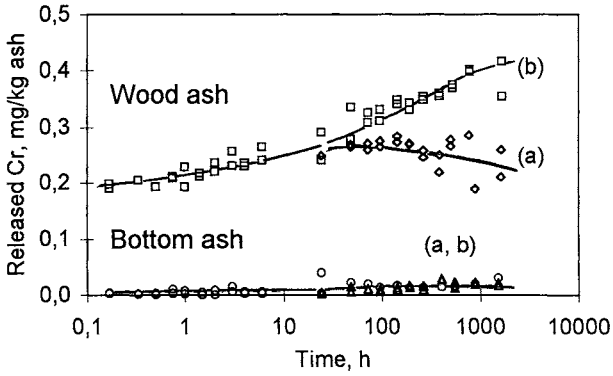

Figure 6. Chromium release as a function of time from BA and WA
(a) Single-step leaching (b) Two-step leaching

There was an immediate release of copper into the leachates of the BA systems, giving concentrations of around 120 mg/l already after 10 minutes and 190 mg/l after 24 hours. Concentrations significantly above the blank values (10-20 mg/l) were not observed in the WA leachates. The copper release continued after the change of leachate in the two-step procedure, and leveled out at a total accumulated release of 1.3 mg/kg for the BA system. This represents around 0.04% of the inventory.

The copper concentration was decreasing with time, after the initial fast in-growth, in the single-step leaching for the BA system. A reduction to half of the maximum copper concentration was observed after about 10 days in the BA leachate.

There was an immediate release of chromium into the leachates of the WA systems, giving concentrations of 40 mg/l already after 10 minutes and 50 mg/l after 24 hours. Concentrations significantly above the blank values (2-4 mg/l) were not observed in the BA leachates. The

chromium release continued after the change of leachate in the two-step procedure, and reached a total release of 0.4 mg/kg for the WA system. This represents around 0.4% of the inventory.

The chromium concentration was decreasing slightly with time, after the initial fast in-growth, in the single-step leaching for the WA system.

4. DISCUSSION

The increase of conductivity with time indicates a similar dissolution process for the two ashes. The high conductivity obtained already after 10 min indicates a rapid release of soluble salts. Notable is the fact that most of these salts were released during the initial 24 hours (above 90% of the conductivity after 64 days in the single-step procedure), in fact, largely within the first 10 minutes (60 and 80% of the final conductivity for BA and WA, respectively).

The pH-development of the WA system indicated a continued release of hydroxide which was not compensated by the generation of acids, including CO_2 contribution from the atmosphere. In the BA system, however, a pH-maximum of 9.2 was obtained already within one hour. A pH decrease towards 8.5 and below in this system after 64 days reflects an inflow of CO_2 from the atmosphere into the system and, probably, also a release of acidic organic material. There is an approach towards a $CaCO_3$-dominated system at constant CO_2-pressure, which would have an equilibrium pH of 8.3 - 8.4. The decrease in pH was more pronounced in the single-step leachate, where the readily released TOC was not removed as in the two-step procedure. The considerably higher release of TOC from the BA in comparison with the WA could be one of the reasons for the different pH-developments. The differences in other pH-controlling systems (Ca, Mg, as well as Na-K) indicate possibly a higher content of alkali hydroxides in the BA-systems, which otherwise would give a higher pH in the BA than in the WA leachates, disregarding the potential effects of organics.

The low redox potential initially obtained in the BA leachate, particularly in the single-step procedure after 24 hours of exposure in a closed system, indicates the presence of elements in their reduced state in the solid BA. The lowest measured potential (-450 mV) corresponds to an E^o-value of around 0.1 V, which could be representative of an Fe(III)/Fe(II)-couple. A significant fraction of the iron in the BA would be Fe(II), while no reducing capacity is indicated for the WA systems (with considerably lower total content of iron than the BA). As a consequence, chromium would be expected to exist primarilly as Cr(III) in the BA, while a significant or dominant fraction of Cr(VI) can not be excluded in the WA.

The reduction of the TOC-concentration in the single-step leaching after the initial fast release of carbon indicates either a loss of volatile organics or adsorption on solid surfaces or possibly a degradation to carbon dioxide. The presence of a large fraction of leachable volatile organics is not likely in high-temperature combustion residues. A substantial adsorption or binding of organic agents directly after a release during the leaching is not probable. A degradation through microbial processes seems to be a likely explanation to the rapid loss of TOC. This degradation would contribute to the pronounced pH-decrease observed in the single-step systems in contrast to the second step in the two-step procedure, where the initially released TOC-fraction is removed by change of leachate solution. It is evident that the organic carbon fraction is of different nature in the two materials, reflected by the differences in leachability and degradation rate. Only a minor fraction of the high organic content of the WA is leachable by water.

The maximum copper concentration (280 mg/l, corresponding to 4.4×10^{-6} M) is 1-2 orders of magnitude above expected total solubility, considering complexation and potentially solubility

limiting secondary solid phases (hydroxide and possibly hydroxy carbonates). The similarity in leaching behaviour and concentration change with time between copper and TOC is striking. The appearent over-saturation can be explained, assuming that around 1% of the TOC represents a strong complexing agent with a complexing capacity of 6-7 meq/g, which is not unreasonable. Similar enhanced releases related to the presence of organics have previously been claimed [7]. The reduction in appearent copper concentration with time in the single-step procedure can either be due to a decreasing solubility or a loss of copper due to adsorption. The decreasing pH (c.f. Figure 2) could actually lead to an enhanced adsorption of an organic complex. The loss of organic carbon assumed to be due to microbial degradation and a related reduced total solubility is, however, more likely as an explanation to the decreasing copper concentration.

The leaching behaviour of chromium in the WA system has some similarity with the behaviour of copper in the BA system. The slightly decreasing concentration of chromium with time in the single-step leaching could be due to interactions with organics analogous to the copper system, although less pronounced. The absence of significant chromium releases from the BA system, however, indicates a predominant dependence on the redox conditions (c.f. Figure 3) and the oxidation state of chromium in the solid matrix. The existence of chromium predominantly as Cr(III) of low solubility in the BA would lead to a slow leaching-rate and low over-all chromium concentrations. In the WA, which apparently has a minor reducing capacity, chromium may exist partly as Cr(VI), which would be more mobile and soluble as compared to Cr(III).

5. CONCLUSIONS

An immidiate release of organic carbon compounds was observed by the exposure of the BA and WA to water. The readily released organic fraction was partly lost from the systems with time, possibly as the result of microbial degradation. The long-term leaching of the organic inventory of the ashes and subsequent TOC-degradation in solution should be further analysed.

The potential metal solubilizing effects of organic matter released from the ashes by leaching has been demonstrated for copper. Further studies of the nature of these organic agents (composition, complexing properties and chemical stability) are required in order to allow an assessment of the over-all importance of the organic fraction for release and mobilization of metals. The possible existence of strong complexing agents that may significantly affect both leaching rates and solubilities of certain metals is of particular interest.

6. ACKNOWLEDGEMENTS

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7. REFERENCES

1 P.H. Brunner, M.D. Mueller, S.R. McDow and H. Moench. Total organic carbon emissions from municipal incinerators. *Waste Management & Research* (1987) 355-365

2 B.S. Shane, C.B. Henry, J.H. Hotchkiss, K.A. Klausner, W H. Gutenmann and D.J. Lisk. Organic toxicants and mutagens in ashes from eighteen municipal refuse incinerators. *Arch. Environ. Contam. Toxicol.* **19** (1990) 665-673

3 H. Belevi, N. Agustoni-Phan and P. Baccini. Influence of organic carbon on the long-term behaviour of bottom ash monofills. In *Proc. Forth International Landfill Symposium*, Cagliari (1993) Environmental Sanitary Engineering Centre, Cagliari

4 A.-M. Fällman and J. Hartlén. Leaching of slags and ashes - controlling factors in field experiments versus in laboratory tests. In J.J.J.M. Goumans, H.A. van der Sloot and T. Aalbers (eds), *Environmental Aspects of Construction with Waste Materials,* Elsevier, Amsterdam, (1994) 39-54

5 I. Pavasars, A.-M. Fällman, B. Allard and H. Borén. Work in progress

6 *Standard Methods for the Examination of Water and Wastewater.* American Public Health Association, American Water Works Association, Water Pollution Control Federation, Washington (1985)

7 R.N.J. Comans, H.A. van der Sloot and P.A. Bonouvrie. Geochemical reactions controlling the solubility of major trace elements during leaching of municipal solid waste incineration residues. In J Kilgroe (ed.), *Municipal Waste Combustion Conference*, Air and Waste Management Association, Pittsburg (1993) 667-679