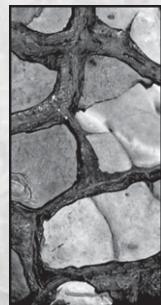# Leaching from Municipal Solid Waste Incineration Residues

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Preface

This thesis is the result of a Ph.D. study carried out at DTU Environment (former E&R). The study was jointly funded by I/S Vestforbrænding, I/S Amagerforbrænding, Aarhus Kommunale Værker, and DONG Energy A/S. Professor Dr. Agro Thomas H. Christensen and Associate Professor Ph.D. Thomas Astrup acted as supervisors.

Journal manuscripts prepared during the course of the study are enclosed:

I. **Hyks, J.**; Astrup, T. & Christensen, T.H. Influence of test conditions on solubility controlled leaching predictions from air-pollution-control residues. *Waste Management & Research 2007, 25 (5), p. 457-466.*

II. Hu, Y.; **Hyks, J.**; Astrup, T. & Christensen, T.H. Effect of drying on leaching testing of treated municipal solid waste incineration APC-residues. *Accepted in Waste Management & Research 2008.*

III. **Hyks, J.**; Astrup, T. & Christensen, T.H. Leaching from MSWI bottom ash: Effects of non-equilibrium during column experiments. *Submitted to Waste Management.*

IV. **Hyks, J.**; Astrup, T. & Christensen, T.H. Long-term leaching from MSWI air-pollution-control residues. *Submitted to Journal of Hazardous Materials.*

The above manuscripts are referred to in the thesis by their roman numerals. In addition to these, two publications in proceedings have been accomplished during the study but they are not enclosed:

Hyks, J., Astrup, T. & Christensen, T.H. (2007): Prediction of leaching from air pollution control residues. In: Cossu, R., Diaz, L. F. & Stegmann, R. (eds.): *Sardinia 2007*, Eleventh International Waste Management and Landfill Symposium, 1-5 October, Sardinia, Italy. Proceedings. CD-ROM, CISA - Environmental Sanitary Engineering Centre, Cagliari, Italy.

Hyks, J., Astrup, T. & Christensen, T.H. (2006): Removal of readily soluble compounds prior to pH-static leaching experiments: effects on leaching predictions. In: Ilic, M.; Goumans, J.J.J.M.; Miletic, S.; Heynen, J.J.M. & Senden, G.J. (eds): *WASCON 2006*. Sixth International Conference on the Environmental and Technical Implications of Construction with Alternative Materials, May 30 - June 2, 2006, Belgrade.

Acknowledgements

Jirka

Summary

Leaching of pollutants from Municipal Solid Waste Incineration (MSWI) residues has been investigated combining a range of laboratory leaching experiments with geochemical modeling. Special attention was paid to assessing the applicability of laboratory data for subsequent modeling with respect to presumed full-scale conditions; both sample pretreatment and actual influence of leaching conditions on the results of laboratory experiments were considered.

It was shown that sample pretreatment may have large impact on leaching test data. In particular, a significant fraction of Pb was shown mobile during the washing of residues with water. In addition, drying of residues (i.e. slow oxidation) prior to leaching experiments increased the leaching of Cr significantly.

Significant differences regarding the leaching behavior of individual elements with respect to (non)equilibrium conditions in column percolation experiments were observed in the study. As a result, three groups of elements were identified based on the predominant leaching control and the influence of (non)equilibrium on the results of the laboratory column experiments:

I.   Predominantly availability-controlled elements (e.g. Na, K, Cl)
II.   Solubility-controlled elements (e.g. Ca, S, Si, Al, Ba, and Zn)
III.   Complexation-controlled elements (e.g. Cu and Ni)

With respect to the above groups it was suggested that results of laboratory column experiments can, with consideration, be used to estimate full-scale leaching of elements from Group I and II. However, in order to avoid large underestimations in the assessment of leaching from Group III, it is imperative to describe the time-dependent transport of dissolved organic carbon (DOC) in the tested system or to minimize the physical non-equilibrium during laboratory experiments (e.g. bigger column, slower flow velocity).

Forward geochemical modeling was applied to simulate long-term release of elements from a MSWI air-pollution-control residue. Leaching of a range of elements was adequately predicted over a liquid-to-solid ratio of 250 L kg^{-1} corresponding to more than 10,000 years in a typical landfill. Notably, based on the modeling it is suggested that removal of Ca and S due to dissolution of portlandite and gypsum could cause increased dissolution of mineral phases like ettringite. Dissolution of ettringite could cause a late increase in concentrations of elements that are substituting sulfate in the ettringite structure; e.g. Sb, As, V, and Cr. Note that such increase in leaching at high L/S ratios is obviously not covered by typical leaching tests and may therefore be underestimated.

Overall, only a minor fraction of many potential pollutants (e.g. heavy metals) present in MSWI residues have been shown leachable even during long-term

percolation experiments; typically, less than 1% of initially present As, Cr, Sb, Cu, Cd, and Pb has leached.

Dansk resumé

I dette studie er udvaskning af farlige stoffer fra restprodukter fra affaldsforbrænding blevet undersøgt ved at kombinere udvaskningstests i laboratoriet med geokemisk modellering. Der blev lagt særlig vægt på at undersøge anvendelsen af laboratoriedata i forhold til efterfølgende modellering af de forventede forhold for udvaskning i fuld skala. Både forbehandling af prøver og indflydelse fra betingelserne i udvaskningsforsøgene på resultaterne blev vurderet.

Det blev vist, at forhandling af prøverne kan have stor indflydelse på udvaskningsdata, idet en betragtelig del af især Pb viste sig at være mobilt når restprodukterne blev vasket med vand. Desuden medførte tørring af restprodukterne (dvs. langsom oxidering) før udvaskningsforsøgene en øget udvaskning af Cr.

Der blev påvist betydelige forskelle i udvaskningen af individuelle grundstoffer i kolonneudvaskningsforsøg som ikke var i fysisk ligevægt. Som en konsekvens blev tre grupper af grundstoffer identificeret på basis af deres fremherskende udvaskningskontrol og indflydelsen fra fysisk ikke-ligevægt på resultaterne fra udvaskningsforsøgene:

I. Hovedsageligt tilgængelighedskontrollerede grundstoffer (f.eks. Na, K, Cl)
II. Opløselighedskontrollere grundstoffer (f.eks. Ca, S, Si, Al, Ba og Zn)
III. Grundstoffer kontrolleret ved kompleksering (f.eks. Cu and Ni)

Med udgangspunkt i de tre grupper blev det foreslået at resultater fra kolonneforsøg i laboratoriet med et vist forbehold kan anvendes til at estimere fuld-skala udvaskning af stoffer fra gruppe I og II. For at undgå en underestimering af udvaskning fra stoffer i gruppe III er det nødvendigt at beskrive den tidsafhængige transport af opløst organisk kulstof (DOC) i det undersøgte system eller minimere fysisk ikke-ligevægt under laboratorieforsøgene (f.eks. større kolonner, langsommere flowhastighed).

Prædiktiv geokemisk modellering af udvaskningen blev anvendt til at simulere langsigtet udvaskning af uorganiske stoffer fra røggasrensningsprodukter fra affaldsforbrænding. Udvaskning af en række grundstoffer blev bestemt for et væske-faststof forhold på 250 l/kg svarende til mere end 10.000 år udvaskning fra et typisk deponi. Det skal især bemærkes at fjernelse af Ca og S som følge af opløsning af f.eks. portlandit og gips kan forårsage en forsinket frigivelse af mineralfaser som ettringit. Omvendt kan en frigivelse af ettringit forårsage øgede koncentrationer af grundstoffer som substituerer sulfat i ettringits struktur, f.eks. Sb, As, V og Cr. Potentielt kan dette medføre en betragtelig stigning i udvaskningen ved meget høje væske-faststof forhold, hvilket normalt ikke dækkes af de typisk anvendte udvaskningstests.

Samlet set er det kun en meget lille del af forureningskomponenterne (f.eks tungmetaller) i restprodukterne der udvasker i løbet af de langvarende

udvaskningsforsøg; typisk mindre end 1% af indholdet af As, Cr, Sb, Cu, Cd og Pb udvaskes.

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Appendices

I. **Hyks, J.**; Astrup, T. & Christensen, T.H. Influence of test conditions on solubility controlled leaching predictions from air-pollution-control residues. *Waste Management & Research 25 (5), p. 457-466.*

II. Hu, Y.; **Hyks, J.**; Astrup, T. & Christensen, T.H. Effect of drying on leaching testing of treated municipal solid waste incineration APC-residues. *Accepted in Waste Management & Research, 2008*

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The appendixes are not included in this www-version but may be obtained from the Library at the Department of Environmental Engineering, Bygningstorvet, Building 115, Technical University of Denmark, DK-2800 Kgs. Lyngby (library@env.dtu.dk)

1 Introduction

Municipal solid waste incineration (MSWI) with energy recovery is one of today's major technologies to deal with the increasing amount of municipal solid waste. Although the incineration itself is considered a hygienic way of treatment, the majority of incombustible elements is subsequently concentrated in a relatively small amount of incineration residues which need to be treated further. Two basic types of incineration residues are produced: bottom ashes (BA), and air-pollution-control (APC) residues [1]. In Denmark, about 600,000 tonnes of BA and 90,000 tonnes of APC residues are produced annually from approximately 3,000,0000 tonnes of incinerated municipal solid waste [2].

The main concern regarding future utilization of the residues is possible contamination of the environment due to the release of elements when in contact with water; i.e. leaching. Thus, quantification of leaching of particularly salts and metals prior to utilization and/or landfilling is required [3;4]. Leaching quantification can also be viewed as an important part of a life-cycle-impact-assessment (LCIA) of various waste management scenarios [5-9], since in order to properly assess impacts from these scenarios one must be aware of the emissions (e.g. leaching from BA used in road constructions and/or leaching from landfilled APC residues).

Apart from this environmentally-driven quantification, there may be a certain economical motivation in particular with respect to APC residues. As hazardous waste the APC residues are often landfilled on special landfills; such practice is indeed costly. If one can prove, based on robust experiments and/or modeling, that the leachate concentrations over time comply with legislation regulatory limits then the material categorization may be changed from "hazardous" to "non-hazardous" or even "inert". This would in turn have a significant impact on treatment and disposal costs.

It is necessary to point out that leaching needs to be quantified both in a short- and a long-term perspective. Short term could mean the life-time of a road or landfill (i.e. <100 years), while long-term could mean "forever" (i.e. centuries). Obviously, full-scale data describing long-term leaching from MSWI residues are unavailable. Hence, leaching is usually quantified using laboratory experiments. However, as the lab-scale experiments are by definition only a rough approximation of the full-scale processes that often take decades and centuries to complete, the leaching conditions during lab-scale experiments may not necessarily reflect those in full-scale scenarios (e.g. equilibrium). Thus, the observed concentration levels obtained from the lab-scale leaching experiments may not reflect those which would have been observed in a full-scale leaching scenario with the exact same materials. In other words, use of lab-scale data as input for geochemical modeling of full-scale scenarios cannot be recommended without a careful consideration, as inconsistencies between lab- and full-scale data may significantly affect the leaching predictions.

There are numerous factors that may influence the results of lab-scale experiments. The most important are believed to be: sample pretreatment (e.g. sample storage, sample drying, and sample crushing), kinetics of mineral dissolution/precipitation, equilibrium vs. non-equilibrium conditions during the leaching experiments, chemical retardation, and internal diffusion [10-14]. More specifically, removal of readily soluble salts by percolating water prior to any significant pH change likely occurs in full-scale scenarios [1;15;16], whereas it is not addressed in current batch leaching tests [17;18]. Consequently, rather different solution conditions may be obtained. Mineral dissolution/precipitation, largely depending on kinetics, has been shown the most important process with respect to pH development [11;19;20]. In turn, pH affects the sorption/desorption processes that control release of many metals [21;22]. And although non-equilibrium has been suggested in typical column experiments, these are still considered to provide an adequate input for equilibrium-assuming geochemical modeling of leaching of a number of elements [11;23]. The magnitude of non-equilibrium during the experiments is therefore usually not tested. Hence, the accuracy of the leaching data, which modeling is based on is not assessed, and thus the accuracy of the modeling itself is not assessed. Without such assessment, the implementation of geochemical modeling for risk assessment or environmental impact assessment purposes can not be completed.

As outlined above, long-term leaching data are often unavailable. Nevertheless, leaching of many elements is usually expected to decrease with time. This assumption is largely based on observations from relatively short-term leaching experiments with bottom ashes [16;23]. However, some potentially important processes (e.g. depletion of controlling mineral phase) may well be overlooked in these observations. In other words, the leaching behavior of only a minor fraction of the total pollution potential has been described by current research. Such limited knowledge is insufficient for evaluation of the long-term environmental consequences of utilizing or landfilling these residues. This being said the aim of this thesis is to:

i)   Investigate the influence of sample handling on the results of laboratory leaching experiments
ii) Evaluate the effects of non-equilibrium conditions on the results of laboratory percolation experiments
iii) Describe long-term leaching behavior of various MSWI residues by means of laboratory experiments and geochemical modeling.

These points were discussed with respect to the air-pollution-control (APC) residues and/or the bottom ashes (BA). In total, two different APC residues were used: a "pure"

fly-ash (FA-residue) and a semi-dry APC residue (SD-residue). Also, BA from five different Danish incinerators were used. In spite of certain differences in chemical composition, all residues were treated similarly in this study as it was assumed that the basic geochemical principles apply to both APC residues and bottom ashes. If necessary, it is explicitly stated when to distinguish between the two types of residues.

2 MSWI residues

2.1 Origin of MSWI residues

Despite the significant reduction in mass and volume of the incinerated waste, several streams of incineration residues are generated partly from the combustion part of the process and partly from the subsequent cleaning of flue gas. The first part includes bottom ash and grate siftings which are usually collected together as "bottom ash" as outlined in Figure 1. The second part includes for instance boiler ash, heat-recovery (economizer) ash, ash collected in an electrostatic precipitator, scrubber residues, etc. [1]. Although generated separately, in reality these separate streams are often mixed depending on further treatment options and/or current legislation. This mixture is often referred to as air-pollution-control (APC) residues. As mentioned in Introduction, for the needs of this thesis "APC residues" refers to both "pure" fly-ash and actual APC residues (i.e. a mixture of fly-ash, unreacted lime, and acid-gas neutralization products) unless noted otherwise.

Typically, about 20-30 % of the initial mass of incinerated waste is converted into bottom ash. Air-pollution-control residues represent about 2-6 % of the initial mass of incinerated waste [1].
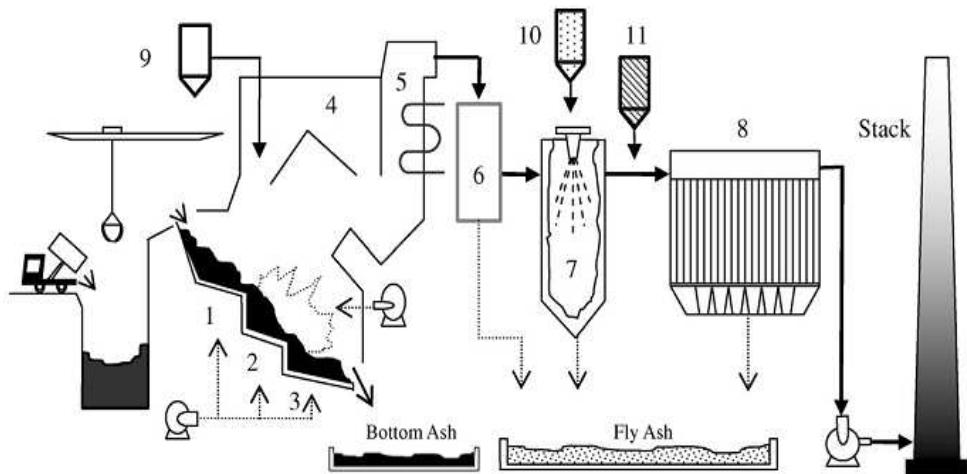

Figure 1. Sketch of an incinerator (mass-burning; semi-dry APC system): (1-3) moving grate, (4) boiler, (5) superheater, (6) heat exchanger, (7) semi-dry reactor, (8) baghouse filter, (9) urea (NO$_x$ control), (10) lime, (11) activated carbon; source: Chang and Wey [24].

2.1.1 Bottom ash

Bottom ash (BA) could be described as a slag-like residue collected from the combustion chamber. As a result of quite similar operational conditions bottom ashes generated in different incinerators (assuming mass combustion) are rather uniform in composition [1;25]. For illustration, composition of 5 different Danish BA is given in Table 1. Lower amount of potential pollutants and rather satisfactory mechanical properties make even untreated BA usable as road-construction material [15]. In addition, weathering of bottom ashes mostly through carbonation (i.e. taking up atmospheric CO_2 thereby changing mineralogy from hydroxides to carbonates) acts as a naturally occurring stabilization process for many metals due to the fact that their carbonates have significantly lower solubility compared with the hydroxides [19;20;26]. Consequently, release of pollutants from weathered BA is generally not considered a major problem and a large fraction of the generated BA is utilized; in Denmark this accounts to more than 90% of annually produced BA [2].

2.1.2 APC residues

APC residues can be described as fine dust-like particles that are carried away from the combustion chamber with the flue-gas. Contrary to mass-combustion technology the flue-gas-cleaning technology is rather plant-specific mostly reflecting legislative requirements and the period of its installation. Consequently, APC residues produced in different incinerators vary in composition, water content, pH, etc. A typical example of such differences is given in Table 1 for two untreated materials collected at different Danish MSWI plants. The so-called "semi-dry residues" is a mixture of the fly ash, unreacted lime and products from acid-gas neutralization; it was collected in baghouse filters. The other material is "pure" fly-ash collected in an electrostatic precipitator. Typically, the mass of pollutants is lower in a semi-dry mixture than in "pure" fly ash due to the dilution with unreacted lime and the neutralization products [1;15;27]. Nevertheless, both materials contain large quantities of readily soluble salts (compare Cl in BA and APC residues) and metals (e.g. Pb, Sb, As) which make them potentially hazardous [28]. Consequently, APC residues should only be landfilled or stored underground after pretreatment [29].

Table 1. *Elemental composition of bottom ashes, semi-dry APC residues, and "pure" fly ash determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) after microwave assisted digestion with HCl/HF/HNO₃.*

Element	unit	Bottom ash [a]	Semi-dry residues (SD) [b]	Fly ash (FA) [b]
Dry matter	%	84.9 – 97.9	95.3	98.8
Ca	g/kg	96.5 – 108	331	181
S	g/kg	3.5 – 5.6	35	57
Al	g/kg	39.1 – 65.6	18.3	35.7
Si	g/kg	198 – 248	63	90
Na	g/kg	23.2 – 29.4	16	42.3
K	g/kg	8.8 – 11.6	17.1	50
Cl	g/kg	3.0 – 9.0	173	122
Mg	g/kg	10.0 – 13.1	7.8	14.1
Fe	g/kg	79.9 – 100	9.7	13.8
As	mg/kg	25.0 – 45.2	80	380
Ba	mg/kg	1360 – 1750	620	1120
Cd	mg/kg	2.6 – 3.7	100	240
Co	mg/kg	20.4 – 26.2	8.9	20.9
Cr	mg/kg	434 – 914	200	700
Cu	mg/kg	2060 – 14300	500	1170
Mo	mg/kg	7.62 – 20.1	9	28
Ni	mg/kg	242 – 526	37.5	67.4
Pb	mg/kg	1080 – 3530	2100	6800
Sr	mg/kg	311 – 634	500	400
V	mg/kg	40.7 – 59.3	19.8	39.7
Zn	mg/kg	2660 – 4230	9100	31700
Sb	mg/kg	51.4 – 105	340	1170
P	mg/kg	3779 – 5237	3400	10000
TOC	g/kg	14.0 – 19.0	2.7	0.7

[a] *Concentration range obtained from 5 bottom ashes collected from 5 different MSWI plants in Denmark*
[b] *Hyks et al [IV]*

2.2 Mineralogy of MSWI residues

Generally, untreated bottom ash is a remarkably heterogeneous material, the majority of which comprises of calcium-rich minerals and silicates potentially enriched in iron and sodium [30-33]. Numerous studies concluded that a significant fraction of bottom ash consists of melt products such as glass, spinel-group minerals (e.g. magnetite: Fe_3O_4), and melitite-group minerals (e.g. gehlenite: $Ca_2Al_2SiO_7$ and akermanite: $Ca_2(Mg,Fe)Si_2O_7$). In contrast, concentrations of potential pollutants (e.g. heavy metals) are fairly low (Table 1) and it is therefore difficult to identify their mineral phases experimentally by means of for ex. XRD (X-Ray Diffraction) and AES (Auger Electron Spectroscopy), as they are "masked" by the large amounts of major elements (e.g. Ca, Si, Al, and S). Nevertheless, simple metal oxides such as ZnO were both suggested and identified [24;30;31;34]. For illustration, an overview of minerals commonly identified in bottom ash is given in Table 2.

As for the APC residues, their complex mineralogy can be attributed to processes occurring during the combustion and the subsequent flue-gas cleaning, i.e. vaporization, melting, crystallization, vitrification, condensation and precipitation [34]. Consequently, sulfates, carbonates, silicates, phosphates, chlorides, (hydr)oxides, pure metals, and glass were identified in untreated APC residues as outlined in Table 2. Similarly to bottom ash, precise identification of minor compounds is complicated. Metals are likely to be incorporated in both aluminosilicates, present as simple oxides and even in metallic form (e.g. Al and Zn) [13;34]. It can thus be assumed that by dissolving large amounts of soluble salts (e.g. chlorides) metals forming chloro-complexes (e.g. Cd) will be liberated [35]. On the other hand, pollutants captured in glassy phase can be expected to be relatively unleachable as it requires large decrease in pH in order to dissolve glassy phases.

Table 2. *Overview of mineral phases experimentally detected in untreated MSWI residues. Adapted from Astrup [36].*

Bottom ash		APC residues (including fly ashes)	
$CaSO_4$ [a]	$Ca_2Al_2SiO_7$ [a, d]	$Ca(OH)_2$ [b, c, d]	$PbSO_4$ [b, c]
$CaSO_4 \cdot 2H_2O$ [a - d]	$Ca_2(Mg,Fe)Si_2O_7$ [d]	$CaSO_4$ [a, d, f]	PbO [c, d]
$CaCO_3$ [a, c, d, e, f]	$Ca_6Al_2O_6(SO_3)_3 \cdot 32H_2O$ [a]	$CaSO_4 \cdot 2H_2O$ [a - c, f]	$CaCl_2$ [c]
$Ca_2SiO_3Cl_2$ [a]	$Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$ [a, c]	$CaCO_3$ [a - f, i, j]	CaF_2 [c]
SiO_2 [a - e, f]	$(Na,Ca)(Fe,Mn)(Si,Al)_2O_6$ [a]	$CaAl_2Si_2O_8$ [c]	$CdCO_3$ [c, h]
Fe_3O_4 [a, c, d]	$Ca(Mg,Al)(Si,Al)_2O_6$ [a, d]	Ca_2SiO_4 [d]	$CaSiO_3$ [c, d]
Fe_2O_3 [c, d]	$(K,Ca,Na)(Al,Si)_4O_8$ [a, d]	$Ca_2Al_2SiO_7$ [f, j]	$Fe(OH)_3$ [c]
$FeCO_3$ [a]	Al_2O_3 [d]	$NaCl$ [a - f, i, j]	$Fe(0)$ [d]
$FeSO_4 \cdot 7H_2O$ [a]	Na_2O [d]	KCl [a, d, e, f, i, j]	$ZnCl_2$ [c, d]
$FeCr_2O_4$ [b, c]	CaO [d, e, f]	Fe_2O_3 [a, b, d, f, j]	$ZnCO_3$ [c, h]
$Ca_5(PO_4)_3Cl$ [b]	FeO [d]	SiO_2 [a - e, i, j]	ZnO [g]
ZnO [b, d]	$NaCl$ [e]	TiO_2 [a, d, f]	$Zn(0)$ [d]
$CaMoO_4$ [c]		$PbCl_2$ [b, c, d]	$Al(0)$ [d]
$NaAsO_2$ [c]		$PbCO_3$ [b, c]	CuO [g]
		Al_2O_3 [i]	Na_2O [i, j]
		$Ca_2(Mg,Al)(Si,Al)_2O_7$ [d]	
		$Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$ [d, f]	

Sources:

[a] *Freyssinet et al [31]*

[b] *Krzanowski et al [32]*

[c] *Zevenbergen et al [33]*

[d] *Eusden et al [30]*

[e] *Chang and Wey [24]*

[f] *Saikia et al [34]*

Sources:

[a] *Kirby and Rimstidt [37]*

[b] *Kirby and Rimstidt [38]*

[c] *Eighmy et al [39]*

[d] *Le Forestier and Libourel [40]*

[e] *Li et al [41]*

[f] *Fermo et al [42]*

[g] *Fermo et al [43]*

[h] *Van Herck et al [44]*

[i] *Chang and Wey [24]*

[j] *Saikia et al [34]*

3 Characterization of leaching from MSWI residues

3.1 Introduction to leaching characterization

Leaching can be described as "dissolution of solid material when in contact with water" [1]. Although this may indeed sound primitive that is hardly the truth. In fact, leaching should be perceived as a multi-dimensional process. Particle morphology, kinetics, chemical speciation, influence of pH, inorganic/organic complexation, influence of time, and the leaching-available fraction are the major parameters that must be described in order to accomplish our ultimate goal; i.e. a time-dependent leaching description.

In order to do so, a great amount of preferably full-scale data is required. However, as outlined in Introduction, there are many full-scale scenarios for which the leaching data are either scarce or not available at all. Laboratory leaching experiments are then a valuable tool for obtaining such information. Yet again, due to overall complexity of the leaching process, it is generally presumed that a single leaching test can not provide an adequate description since various combinations of the major controlling processes occur (see BOX 2) and the overall leaching control for a given element can vary in time [23;45;46]. Consequently, several types of leaching tests may be combined to obtain desired information. It is very important though to realize what type of leaching scenario is considered. For instance, there is a significant difference in leaching when comparing (i) a percolation through granular material with (ii) a flow-around type of percolation observed for monolithic materials. Hence, the type of leaching test should fit closely to the scenario it describes. With respect to leaching from granular materials three types of leaching experiments were used in this thesis for leaching characterization: batch experiments with continuous pH control (i.e. pH-static test) [17], up-flow percolation experiments (i.e. column test) [47], and batch experiments without pH-control [18]. For more detailed description of experimental set-ups refer to BOX 1.

An important parameter should be explained here with respect to all leaching tests, i.e. a liquid-to-solid (L/S) ratio. L/S ratio can be defined as a volume of liquid [L] in contact with a dry mass of solid material [kg]. Hence, multiplying the measured solution concentrations [mg L^{-1}] with the L/S ratio of a given test [L kg^{-1}] allows one to express the results of different leaching test as "released mass" [mg kg^{-1}]. Consequently, leaching data for different materials can be subsequently compared. In addition, assuming knowledge of the infiltration rate (e.g. precipitation), any given L/S ratio may ideally be recalculated to leaching time [48].

BOX 1. *Leaching characterization; description of leaching experiments as used in this thesis.*

Batch leaching test with continuous pH-control, i.e. "pH-static test" [*17*]. One-stage batch experiment performed on granular material with particle grain size < 4 mm; material may be subject to drying prior to experiments. Solid material is mixed with distilled water at a liquid-to-solid (L/S) ratio of 10 L kg^{-1}; open-air containers are used. In our set-up, 8 separate batches are operated simultaneously for each tested material. Computer-guided titration system ensures continuous pH control over 48 hours; pH range is maintained between pH ~ 4 and "natural" pH of tested material (often pH > 12). Solution samples are taken at the end of the leaching period.

Up-flow percolation test, i.e. "column test" [*47*]. Percolation experiment performed on granular material without size-reduction (see CEN procedure for details). Material is packed in a column and percolated with distilled water in an up-flow direction. Two types of columns are used depending on particle size of sample; columns with inner diameter of 50 mm are used for APC residues whereas columns with inner diameter of 100 mm are used for bottom ashes. In either case, length of the column is 300 mm. The flow velocity in the APC column is kept between 10-12 mL h^{-1} while the BA columns are operated at 40-50 mL h^{-1}. Solution samples are taken continuously at pre-defined L/S ratios.

Batch leaching test without pH control [*18*]. One-stage batch test performed on granular material with particle grain size < 4 mm; material may be subject to both crushing and drying prior to the leaching test. Solid material is mixed with distilled water at L/S 2 L kg^{-1} in PTFE bottles equipped with PTFE caps. Bottles with suspensions are then placed in an "end-over-end" rotation device at approximately 5-10 rotations-per-minute for a period of 24 hours. No pH control is applied in this batch test; in addition, headspace is avoided in order to minimize changes in redox potential. Solution samples are taken at the end of the leaching period.

3.1.1 Batch tests with continuous pH-control

Generally, batch tests with continuous pH-control (so-called "pH-static test") can be seen as a material characterization tool since most of the leaching processes depend strongly on pH. Testing the same material at well-defined conditions where only pH is changing allows us to identify the predominant leaching processes at a different stage of leaching (pH value of leached material is expected to change in time). During the last two decades countless studies were performed on different MSWI residues. As a result, three major leaching behaviors were identified and elements were subsequently organized in three groups commonly referred to as: availability-controlled elements, solubility-controlled elements, and elements predominantly controlled by a sorption to

active surfaces and/or complexation with dissolved organic carbon [19;26;39;49-53]. More detailed description of the above "leaching-control" is given in Box 2.

BOX 2. An overview of predominant "leaching-control" usually suggested for MSWI residues [1;11;15;19-21;27;39;52;54-60].

Availability-controlled elements. Their leaching is not limited by the solubility of the source mineral as this is very high (e.g. Cl and NaCl). In other words, they dissolve readily and thus the availability of the source mineral is the limiting factor. Accordingly, only minor differences in solution concentrations are observed at different pH values. In column tests their leaching is characterized by fairly high initial solution concentrations (i.e. tens to hundreds of grams per liter) followed by rather fast decrease as depletion occurs.

Solubility-controlled elements. Their leaching is limited by mineral solubility (e.g. Ca with respect to $CaSO_4$). Consequently, in pH-static test both no and large differences may be observed across the pH range. The first happens in case of a single controlling mineral whose solubility is not affected by changes in pH, e.g. gypsum. The latter can be seen in case of many metals which often show so-called amphoteric behavior also referred to as "V-shape leaching" (i.e. high leaching at both high and low pH levels with a minimum at neutral pH). This is caused by the fact that (i) there are different controlling minerals across the pH range or (ii) solubility of the controlling mineral varies with pH (e.g. ZnO). Consequently, leaching of the solubility-controlled elements in column tests is, contrary to the availability-controlled elements, characterized by rather stable solution concentrations over long periods of time, since pH is not changing. Depletion of one controlling mineral and its substitution by other may lead to changes in solution concentrations. Although mineral depletion has been suggested by geochemical modeling, it has yet to be observed in column leaching experiments.

Sorption/complexation-controlled elements. This type of leaching control is typical for many metals (e.g. Cd, Cu, and Pb). Generally, at high pH levels observed in leachates from MSWI residues, metal cations tend to sorb to negatively charged reactive surfaces such as hydrous ferric (hydr)oxides (HFO) and hydrous aluminum (hydr)oxides (AlO); hence, solution concentrations of these metals decrease with the abundance of the reactive surfaces. As for the complexation, the affinity of metals for complexation with the dissolved organic matter (DOC) is well known and leaching of metals has been shown to vary proportionally to amount of DOC. Nevertheless, DOC complexation and sorption to HFO/AlO may not be the only processes controlling the leaching of metals. It was shown that significant amounts of many metals may be immobilized during the formation of hydrated cement phases such as ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$) and thus become rather solubility-controlled.

3.1.2 Column leaching experiments

Basically, column experiments are designed to provide missing information of leaching as a function of L/S ratio. This way the "leaching history" is considered. The leaching history can be seen as (i) removal of compounds prior to decrease of pH and/or (ii) a decrement in an "available-fraction" caused by percolation. The available fraction can in turn be defined as a fraction of total content of a given element which would dissolve under drastic leaching conditions (see BOX 3 and references therein for details).

Still, there are several issues to be addressed. Firstly, percolation experiments are, by definition, very sensitive with respect to kinetics. Obviously, the percolation in laboratory experiments is much faster than in a full-scale scenario. Therefore, one should be aware of the results obtained in laboratory experiments when these are used to set-up a full-scale model. The influence of various conditions on the results of column tests is discussed in detail in Chapter 3.2. Secondly, long-term percolation data are scarce. In common laboratory percolation experiments, L/S 10 L kg^{-1} is usually the end-point. Such low-L/S-ratio-data are not suited for long-term leaching predictions because only a small fraction of even major elements leach within L/S 10 L kg^{-1}. Thus, potentially important processes (e.g. depletion of the controlling mineral phase) may be overlooked. In other words, only a minor fraction of the total pollution potential from particularly APC residues is described by current research. This limited knowledge is insufficient for setting up and validating leaching prediction models for evaluating the long-term environmental consequences of utilizing or landfilling APC residues.

3.1.3 Batch tests without pH-control

Batch leaching experiments without continuous pH-control are mostly used as a compliance test. More specifically, batch tests at L/S 2 L kg^{-1} are currently used for material classification prior to landfilling [3;4;18]. The result of L/S 2 L kg^{-1} test is one value (for each element) which presumably reflects the worst-case-scenario cumulative leaching during the initial stage of a full-scale scenario; i.e. at the natural pH of the material. Yet, with respect to long-term leaching it is important to realize the differences between batch and percolation experiments and hence the results of batch experiments should not be used uncritically.

3.1.4 Geochemical modeling in general

Until recently, geochemical modeling has primarily been used to explain various leaching mechanisms outlined in BOX 2 [11;12;20;26;51;61-63]. The geochemical modeling could be done in a sequence of calculation steps similar to those described in BOX 3. Various geochemical models may handle certain specific calculations differently; however, both herein used PHREEQC [64] and particularly ORCHESTRA [65] incorporated in the LeachXS tool [66] were used as described in BOX 3.

At first, the solution speciation is calculated resulting in a list of minerals (also referred to as the "controlling minerals") close to equilibrium with observed solution concentrations. Often, the list is rather comprehensive and therefore comparison with mineralogical studies (see Table 2) is recommendable. Next, solution concentrations of selected elements are calculated assuming equilibrium with the controlling minerals; this way the observed and predicted concentrations can be compared [61]. To further improve the model predictions, both sorption on active surfaces and complexation with DOC should be included. Applying this approach on pH-static leaching data generally results in fair agreements between model-predicted and experimentally-determined concentrations of many elements [12;55;67].

Based on the results from the modeling of pH-static experiments some authors suggest [23;66;68], that a combination of pH-static leaching data and column leaching data for the same material may provide an adequate set of input parameters for forward geochemical modeling of leaching from granular materials. It should be stressed however, that a direct application of the results generated from batch pH-static tests for long-term leaching predictions seems somewhat more problematic. Arguably, the only batch experiment that may provide some description of the real-life leaching is the batch test performed at "natural" pH (i.e. without pH control) of the solid material. In any other batch test (herein done at pH 4; 5.5; 7; 8, 9, 10, and 11) the leaching history is not considered since a fresh portion of untreated material is used for each batch. Hence, conditions which do not exist in full-scale leaching scenarios (e.g. high levels of soluble salts at low pH levels) occur during the pH-static test. Soluble salts are highly unlikely to be present at low pH values as these salts would be dissolved ages before the pH change [15;16;27].

As for the percolation modeling, a short-term leaching quantification (< L/S 2 $L\,kg^{-1}$) can presumably be done using full-scale data. Long-term leaching quantifications (ultimately centuries) on the other hand rely largely on forward geochemical modeling as the full-scale leaching data are obviously unavailable. Currently, the percolation experiments are used to provide both input data and model validation. Considering the above-mentioned differences between lab- and full-scale conditions it appears questionable in particular for column experiments that simple scaling-up could provide adequate description of full-scale scenarios. It is therefore necessary to understand/assess possible impacts on results of leaching experiments caused by different conditions between lab- and full-scale scenarios; this should ideally be done prior to any leaching predictions.

BOX 3. *Overview of calculation steps used in geochemical modeling of pH-dependent leaching from MSWI residues. For further details refer to following studies and references therein [12;19;20;23;27;27;44;55;61].*

1st step: speciation calculations. Calculating solution speciation is the first step in the geochemical modeling. Usually, analytical data from the pH-static experiments is used as it arguably provides the best characterization-like information. Speciation of a given sample is then calculated using the analytically determined concentrations of elements as concentrations in solution while pH is kept at measured value and oxidation conditions are usually assumed. Abundance of different species is then obtained together with saturation indices (SI) of minerals which may form from those species.

2nd step: solubility-controlling minerals. It is assumed that dissolution/precipitation of minerals which are close to the equilibrium with analyzed solutions (i.e. for which $-1 <$ SI $< +1$) controls the solution concentrations of many elements. Hence, those minerals are often referred to as the "solubility-controlling minerals". In the 2nd step the potential controlling minerals are selected from a list of minerals generated during the speciation calculations. Finally, the leachate composition in equilibrium with the selected minerals (i.e. the "solubility curves") is calculated using so-called "semi-empirical" approach [*61*]. This way, model predictions could be compared with the measured data.

3rd step: prediction of pH-dependent leaching. "Available" fractions of all elements are entered in the model [12;23]. There is only one value (in mol kg^{-1}) for each element in the input file. For example, amount of "available" Ca in mol kg^{-1} is distributed between Ca-containing controlling minerals generated in the 2nd step. Such distribution is performed for all considered elements. So far, there is no general approach for the quantification of the "available" fraction. For major ions (e.g. Ca^{2+}, Al^{2+}, SO_4^{2-}, etc.) and metals that do not form oxyanions (e.g. Pb^{2+}, Cd^{2+}, Zn^{2+}, etc), it is implicitly assumed [*23*] that their concentrations observed in leachates at low pH (usually pH ~ 4) reflect their "available" fraction because majority of the solubility controlling minerals will be dissolved and sorption to HFO/AlO can be excluded. Analogically, for elements that form oxyanions (e.g. AsO_4^{3-}, CrO_4^{2-}, MoO_4^{2-}, etc) the values obtained at pH ~ 10 are expected to reflect the "available" fraction [*23*]. In addition, material-specific amounts of DOC and HFO/AlO surfaces are entered as an input parameter as well. Hence, the input data are: the "available" amounts of elements, a list of controlling minerals (i.e. 1st and 2nd step), information about DOC levels, and the amounts of reactive surfaces determined by independent extractions. The model then distributes the "available" amount of a given element between the major controlling processes (i.e. solubility control, DOC complexation, and HFO/AlO sorption) at different pH ($2 <$ pH < 14 by default). All calculations are performed simultaneously to ensure competition.

3.2 Influence of test conditions on results of leaching experiments

3.2.1 Introduction

As outlined in previous chapter it is extremely important to be aware of the factors that may influence outcomes from leaching experiments and address these properly with respect to further full-scale application. For instance, dry materials are usually used for compliance tests (e.g. evaluating of leaching from treated APC residues); however, this does not reflect the full-scale conditions as wet residues are usually landfilled. Such a relatively insignificant difference can have a major impact on the leaching of some elements as discussed in Section 3.2.2. Another example could be the presence of non-equilibrium during pH-static- and/or more importantly column leaching experiments. The dissolution/precipitation kinetics of many minerals is very slow and hence the eluent-solid phase equilibrium may presumably not be reached for some elements during the laboratory experiments. It should be stressed that kinetics-related issues are likely going to be more pronounced in column experiments than in batch leaching test. Batch experiments obviously provide longer equilibration period together with larger contact between solid phase and eluent. In percolation experiments, eluent retention time is shorter; moreover, preferential flows, diffusion resistance of the solid material, and presence of stagnant zones affect the kinetics and thus an impact on observed leaching data may be expected [10;16;23;69].

As mentioned in Section 3.1.2 the purpose of column experiments is to provide an insight to time-dependent leaching preferably as close to full-scale scenarios as possible. Hence, assuming that there is enough time to reach equilibrium for most processes in slowly percolated full-scale scenarios, rather different solution composition may be obtained in much faster laboratory experiments. This would in turn affect sample speciation and hence different solubility controlling minerals would be predicted. Solubility control is important for pH development which is further affecting the sorption/desorption processes.

In this chapter, (i) the influence of sample pretreatment (i.e. drying, washing) and (ii) the influence of kinetics (i.e. equilibration period) on leaching from granular materials are discussed for both batch and column experiments. Furthermore, the impact of different leaching conditions on the results of geochemical modeling is discussed.

3.2.2 Sample drying

An Al(0)-Cr-O$_2$ interaction has been reported to affect the batch-determined leaching of Cr from APC residues [13;14]. Oxygen from the excessive headspace can supposedly oxidize the originally present Al^0 thereby decreasing its potential with respect to reduction of Cr^{VI} to Cr^{III}. In addition, Hu et al [II] conducted a series of batch and column experiments performed on treated APC residues in a dried/non-dried parallel in

order to investigate effect of slow sample drying (i.e. slow oxidation) on leaching of Cd, Cr, Cu, Pb, and Zn (Table 3).

A comprehensive overview of different experimental set-ups is given elsewhere [**II**]. It could be seen that drying was found particularly important with respect to leaching of Cr; drying (i.e. slow oxidation) apparently reduced the reduction capacity present in APC residues (most likely Al^0). Consequently, 10-100 times higher Cr concentrations were observed in leachates from both batches and columns. Moreover, the leaching of Cd was likely affected by inorganic complexation as there was a significantly higher release of chloride caused by drying. Finally, drying was also shown to influence the pH of the residues and this could have had an impact on leaching.

*Table 3. pH and heavy metal release determined by batch leaching test (L/S 10 L kg^{-1}). Source: [**II**].*

	pH	Cd (µg kg^{-1})	Cr (µg kg^{-1})	Cu (µg kg^{-1})	Pb (µg kg^{-1})	Zn (mg kg^{-1})
Untreated ash	12.47	15	1185	695	354000	6
AE-D [a]	9.29	9	1235	13	< 50	0.20
AE-ND	11.44	< 1	< 20	< 10	< 50	< 0.20
ANAE-D	9.13	6	1355	22	< 50	0.21
ANAE-ND	11.47	1	< 20	< 10	< 50	< 0.20
AN-D	9.69	21	1140	36	< 50	0.26
AN-ND	10.96	2	< 20	< 10	96	< 0.20

[a] *Reader should be notified that the "–D" suffix in Table 3 refers to dried residues. Analogically, "-ND" refers to non-dried residues.*

3.2.3   Sample pre-washing

A common method to determine the influence of pH on the release of constituents from a solid waste material is a batch pH-static leaching test. However, the test conditions may not necessarily provide an adequate description of full-scale scenarios as the residues are subjected to these tests without consideration of whether the test conditions mimic real-life conditions appropriately. Specifically, the removal of readily soluble salts by percolating water prior to any significant pH change [*15*] may induce a substantial difference between test and full-scale conditions. Hence, the effect of sample washing on the results of pH-static experiments and the subsequent predictions of solubility controlling minerals was investigated [**I**]; experiments were done on semi-dry APC residue (SD residue). It was shown that pre-washing of residues and the associated removal of soluble salts (Figure 2; right) has only a minor impact on model predictions of solubility controlling minerals. However, it was also shown that up to 57 % of the

originally present Pb was removed by water-washing at natural pH of the APC residues. Moreover, similar amounts of Pb were shown to be removed at all other pH levels. Inorganic complexation with OH⁻ and Cl⁻ could be significant at high and low pH, respectively. In addition, high mobility of Pb could occur due to organic complexation; a large fraction of DOC was removed by the washing procedure (Figure 2; left).

Still, from a long-term point of view, solution concentrations of Pb as observed in pH-static test were likely overestimated with respect to the real-life scenarios simply because they included the "mobile fraction" of Pb. This fraction would have been dissolved at the initial stage of leaching and at natural pH of the material. In turn, including this fraction in our long-term leaching predictions would result in an overestimation of the late release of Pb. The only exception, of course, is the batch test performed at natural pH.
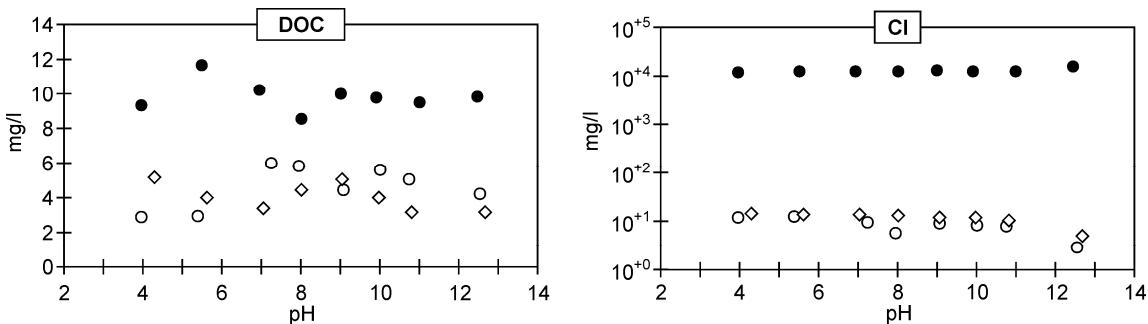

Figure 2. *Concentrations of dissolved organic matter (DOC) and Cl as a function of pH. Solid spheres represent untreated residues (SD residue), while both open spheres and open diamonds represent data for washed residue samples. Source: [I].*

3.2.4   Kinetics during batch experiments on APC residues

Batch experiments as described in Box 1 are usually considered to provide an adequate leaching description since 24-48 hours equilibration period has been shown sufficiently long for most elements [*12*]. And yet, dissolution/precipitation of some solubility controlling minerals is known to be extremely slow (e.g., formation of Ba-Sr-SO$_4$ solid solution) [*70*]. Accordingly, it was shown [**I**] that longer equilibration time (i.e. 172 hours) during a pH-static leaching test had a positive impact on model predictions of solubility control minerals particularly in the case of Ba and Sr (Figure 3). It should nevertheless be realized that the benefits from using an equilibration period longer than 48 hours are small when compared with the saved time and resources.

Overall, the kinetics-related issues were shown to be of minor importance in batch experiments although longer leaching period was shown to provide more accurate fit between modeled and observed concentrations.
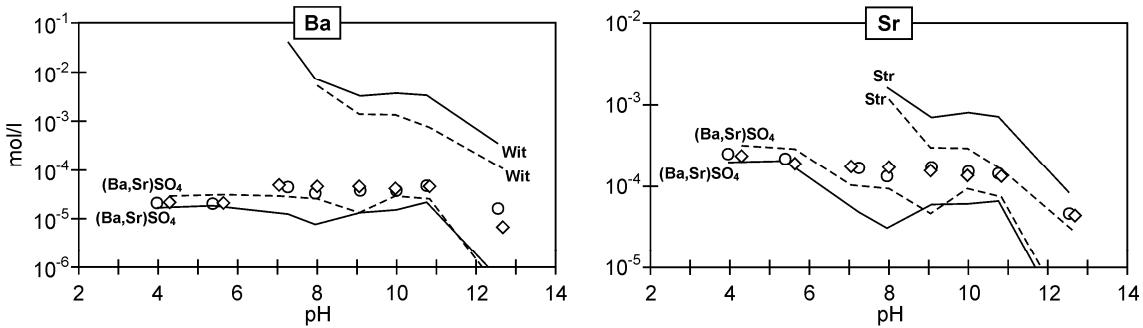
Figure 3. Concentrations of Ba and Sr (mol L^{-1}) as a function of pH. Open spheres and diamonds represent experimental data from 48-h and 172-h leaching experiments, respectively. Solid lines are model predictions for 48-h experiments while dashed lines refer to 172-h experiments. Abbreviations are: (Ba,Sr)SO$_4$: Ba$_{0.5}$Sr$_{0.5}$SO$_4$ solid solution, Wit: witherite (BaCO$_3$), Str: strontianite (SrCO$_3$). Source: [I].

3.2.5 Kinetics during column percolation experiments on bottom ash

Not surprisingly, kinetics-related issues were found much more pronounced in column experiments. In [**III**] impacts of non-equilibrium on the results of the percolation experiments were evaluated. Three-parallel column experiments were performed on MSWI bottom ash. Two columns (C1 and C2) were operated according to the CEN standard [*47*]. In addition, two sets of so-called dynamic flow interruptions [69;71] were performed in the third column (C3) in order to assess possible non-equilibrium. Flow interruptions were employed at L/S 2 and L/S 12 L kg^{-1}, respectively. These L/S ratios were chosen deliberately as L/S 2 L kg^{-1} is usually assumed to be reached in a conventional landfill after 100 years [*48*]; 100 years is also often considered as an end-point in the life-cycle-impact-analyses [*5*]. L/S 12 L kg^{-1} is beyond the scope of the standardized column test (i.e. L/S 10 L kg^{-1}). However, such L/S ratio may be reached in many thin-layer scenarios (e.g. road constructions).

Generally, during the flow interruption the eluent flow in column was stopped and the whole system was kept undisturbed allowing equilibrium between the solid and liquid phase to be established. After 7 days, eluent inflow was slowly initiated while a sample of eluate was taken from the column outlet. Special attention was paid to remove only about ¼ of the total pore volume. Then the flow was stopped again and the whole procedure was repeated. In total, four samples were taken during one month of continuous flow interruption. Assuming initial non-equilibrium, solution concentrations of most elements were expected to change as the initially misbalanced system was approaching "near" equilibrium. Moreover, concentration trends were observed and hence the possible equilibrium could be confirmed.

Using flow interruptions (FI) allowed us to identify a clear physical non-equilibrium during the standardized column percolation experiments. It can be seen (Figure 4; left)

that in the case of C3 solution concentrations of chloride (Cl) increased significantly while the flow was stopped; i.e. at both L/S 2 and L/S 12 L kg^{-1}. Leaching of Cl was monitored deliberately since Cl is considered a "conservative" element [72], and may therefore be used to map transport conditions in the columns. Further, Cl behaves as an availability-controlled element, i.e. its leaching is not limited by solubility constraints as its solution concentrations in bottom ash leachates are usually well below saturation with common Cl-containing minerals (e.g. NaCl). A simplest explanation of Cl behavior during the FI was the fact that the advection during column experiments was too fast to allow equilibrium to be reached in the system.
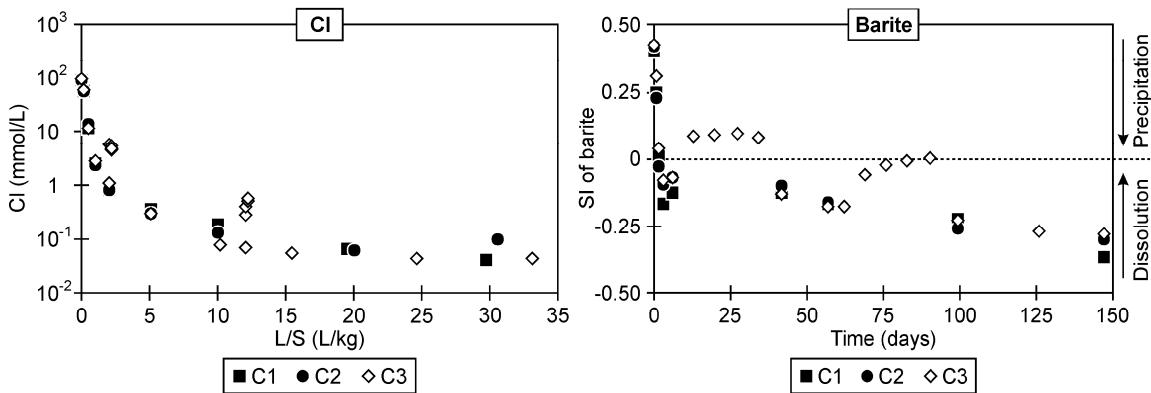

Figure 4. Column percolation experiments on bottom ash. Left: solution concentrations of chloride (Cl) as a function of L/S ratio. Solid squares and circles represent leaching from columns without the flow interruption while open diamonds represent leaching from column with flow interruption at L/S 2 and 12 L kg^{-1}, respectively. Right: saturation index of barite as a function of time. Again, solid squares and circles represent leaching from columns without the flow interruption while open diamonds represent leaching from column with flow interruption at L/S 2 and 12 L kg^{-1}, respectively. Source: [III].

3.2.6   Influence of non-equilibrium on leaching from bottom ash columns

Presence of physical non-equilibrium in the bottom ash columns did not affect leaching of all elements in the same way. In order to provide a systematic overview three groups of elements (i.e. Group I – III) were identified based on their predominant behavior during the flow interruptions. For details refer to [III]; in addition, the most important findings are summarized in Table 4.

Generally, "satisfactory" level of information about the leaching of the availability-controlled elements (Group I) was obtained as it is assumed that the non-equilibrium causes an overestimation (on concentration basis) in the leaching of soluble salts after L/S 2 L kg^{-1} in the columns when compared with full-scale scenarios; this is however

suitable from worst-case-scenario point of view. In other words, advection during column experiments was likely too fast to obtain equilibrium. Thus, if the same material with the same fraction of dual-porosity was assumed both in a slow full-scale system and a fast column system, the contribution of the diffusion-controlled mass from the stagnant zones to the total leached mass would be larger in the slower scenario, because there are no solubility limitations and the reaction period is longer. This is in agreement with generally observed "total" depletion of salts within L/S 2 L kg^{-1} in full-scale scenarios [1;27;38;73]. Therefore, different shapes of leaching curves (i.e. different solution concentrations) may be expected in columns and full-scale scenarios, even though the total released mass may be similar in either case (i.e. the available fraction). Further, assuming that the same mass is released, solution concentrations should likely be higher during the initial leaching in full-scale scenarios. In other words, because advection is faster in the columns, the concentrations in the stagnant zone remained higher during the column experiments and the diffusion from the stagnant zones became the overall controlling process. Thus, after L/S 2 L kg^{-1}, the diffusion from the stagnant zone would still be of importance and leaching of Na, K, and Cl from the columns would be higher than in full-scale scenarios. Consequently, both "tailing" and an increase in the solution concentrations during the flow interruptions would be observed.

Table 4. Element groups according to their leaching behavior during the column test. Source: [III].

Group	I	II	III
Elements	Na, Cl, K,	Ca, S, Ba, Si, Al, Zn	Ni, Cu, Mo, Pb
Leaching curve description – no FI[a]	Large concentration drop in initial period, often several orders of magnitude; tailing due to slow diffusion from stagnant zones (dual porosity)	Relatively steady leaching over long L/S periods	Large concentration drop in initial period, often several orders of magnitude
Leaching curve description – effect of FI in C3[b]	An increase in solution concentrations by up to one order of magnitude	A slight changes in solution concentrations	An increase in solution concentrations by up to one order of magnitude, (except Pb)
Overall suggested leaching control	Fast dissolution of readily soluble compounds followed by depletion in the mobile zone; then diffusion from stagnant zone becomes the controlling process	Dissolution/precipitation of "common" minerals (could be affected by chemical non-equilibrium and /or changes in pH due to diffusion of OH^-)	Cu, Ni: complexation with DOC; Mo: apparently controlled by availability of MoO_4^{2-} in the mobile zone; Pb: solubility control
Effect of non-equilibrium on model prediction of solubility control minerals	Minimal, solubility control is usually not observed	Minimal, but FI could still be used to confirm some controlling phases	Minimal
Implications for leaching predictions	The test provides adequate information as it overestimates the concentrations; it could be used for direct assessment	Adequate information for solubility-based predictions is obtained; non-equilibrium could slightly alter the observed concentrations	Should not be used for direct assessment of Cu, Ni, and Mo. Transport of DOC in considered scenario must be described beforehand (Cu, Ni). Alternatively, dual-porosity models may be included in order to account for the physical non-equilibrium

[a] Leaching experiments at "standard" flow velocity in C1 and C2; without the FI.

[b] Leaching experiments at "standard" flow velocity in C3; FI at L/S 2 and L/S 12 L kg^{-1}, respectively.

For the solubility-controlled elements grouped in Group II (i.e. Ca, S, Ba, Si, Al, and Zn) it was shown that regardless the non-equilibrium which in some cases caused up to 5 times higher observed solution concentrations associated with changes in SI (see Figure 4; right), the same controlling minerals were predicted (Figure 5) by geochemical modeling. Hence, a factor of 5 may arguably be the "sensitivity" of the SI-based input and leaching predictions of Ca, Si, S, Al, Ba, and Zn based on dissolution/precipitation of minerals may not be expected more accurate.
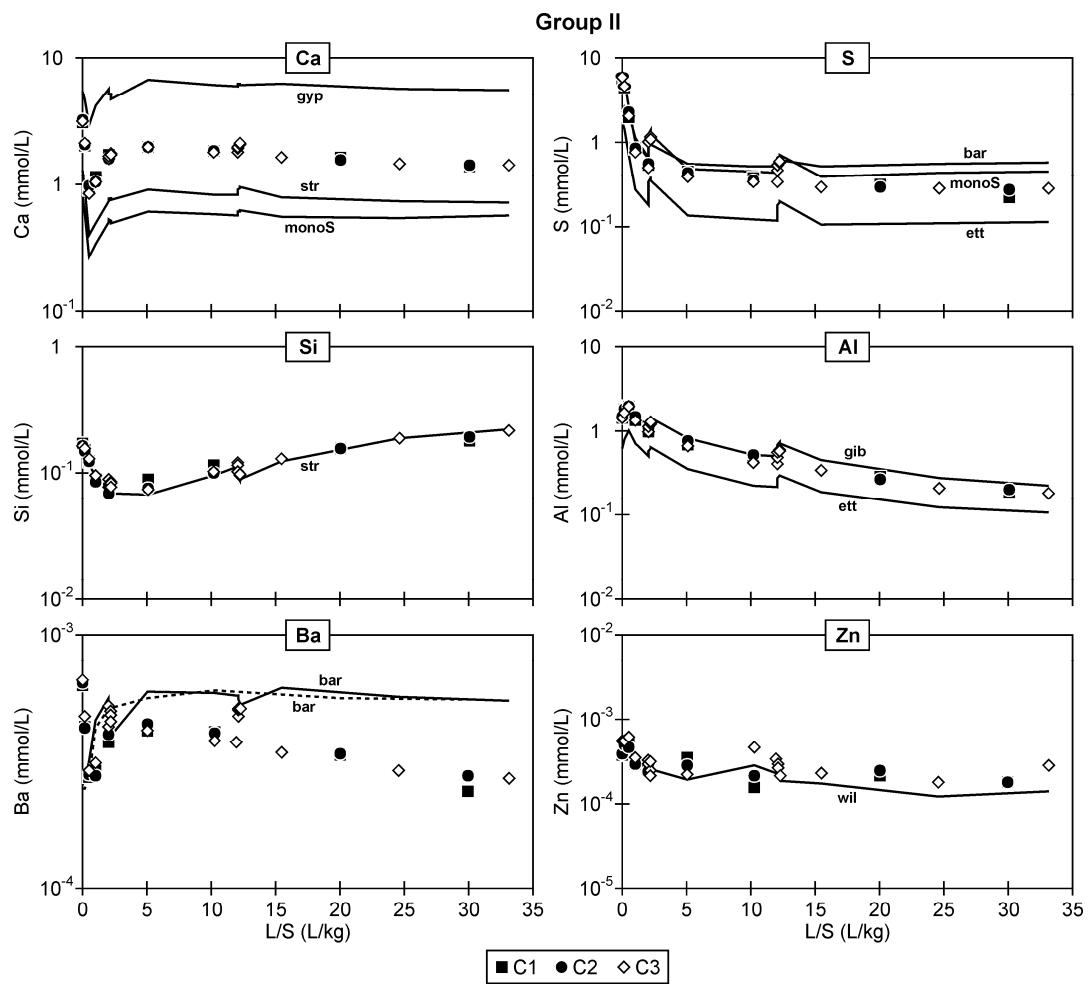
Figure 5. *Concentrations of Ca, S, Si, Al, Ba, and Zn as a function of L/S. Points represent experimental data while solid lines represent model predicted equilibrium concentrations of relevant minerals calculated for C3 (interrupted). Dashed line in case of Ba represents model predicted equilibrium concentrations of relevant minerals calculated for C1 (non-interrupted). Abbreviations are: gyp, gypsum; str, strätlingite; monoS, monosulphate; bar, barite; ett, ettringite; gib, gibbsite; wil, willemite. Source: [III].*

The leaching of Cu and Ni (i.e. metals with high affinity for DOC complexation [20;22;51;74]) was shown to be correlated with the presumably diffusion-controlled release of DOC. Release of DOC was more pronounced during the flow interruptions and has caused a significant increase in solution concentrations of these metals (Figure 6). Accordingly, I assume that the release of Cu and Ni as obtained from column experiments does not reflect concentrations that would have been observed for the same material in a full-scale scenario. In fact, these solution concentrations are most likely underestimated up to one order of magnitude (see Figure 6). Consequently, it appears that using lab-scale data to predict full-scale long-term release of these metals in terms of solution concentrations (e.g. mg L^{-1}) at any given L/S ratio is not possible without a detailed knowledge of (non)equilibrium conditions in the tested system.

Similarly to Cu and Ni, the leaching of Mo was also found identical to that of Group I, i.e. an increase of solution concentrations was observed during both FI. However, the controlling mechanism is likely different as no evidence of Mo-DOC complexation was found in literature. Adsorption could also be excluded as Mo is present as MoO_4^{2-} at high pH [12;21;75]. Further, no Mo-containing minerals were found to explain observed solution concentrations of Mo in either standard or interrupted columns; eluates were found undersaturated towards powellite ($CaMoO_4$) by two orders of magnitude in standard columns and by one order of magnitude during both FI in C3. Apparently, release of MoO_4^{2-} was not limited by organic complexation, sorption or dissolution/precipitation but simply by its availability in mobile zones (compare release curve of Mo and Cl$^-$ during FI), i.e. by diffusion of MoO_4^{2-} from stagnant zones during both FI.

In order to avoid large underestimations when using lab-scale data for the full-scale leaching assessment of Cu, Mo, and Ni it is imperative either to describe the time-dependent transport of DOC (in any tested system) or to minimize the physical non-equilibrium during column experiments by changing the set-up (e.g. bigger column, slower flow).

The leaching of Pb (not shown graphically) was somewhat elevated during the initial leaching period; i.e., 15 µg L^{-1}. Both organic and inorganic complexation of Pb can be expected under high pH conditions [22]. After L/S 2 L kg^{-1} the leaching of Pb was not affected by the FI, despite the increase in DOC concentration. On the contrary, the measured Pb solution concentrations were rather stable at 6 x 10^{-3} mg L^{-1} while no common mineral has been found appropriate to explain the observed values. This would, indirectly, point to other controlling process, e.g. sorption on hydrous ferrous oxides (HFO) [11;76]. Sorption of HFO is very likely at pH > 10.5 determined in the columns [21]. Hence, the inorganic complexation before L/S 2 L/kg and a sorption on HFO after L/S 2 L/kg may be the controlling processes.

Note that the leaching of Cd from the columns was generally found below the ICP-AES detection limit of 5 x 10^{-5} mg L^{-1}. Low leaching of Cd at high pH is notoriously

observed for both bottom ashes and APC residues (see Figure 7). Usually, a surface complexation is suggested to be the major controlling process [11;12;77].
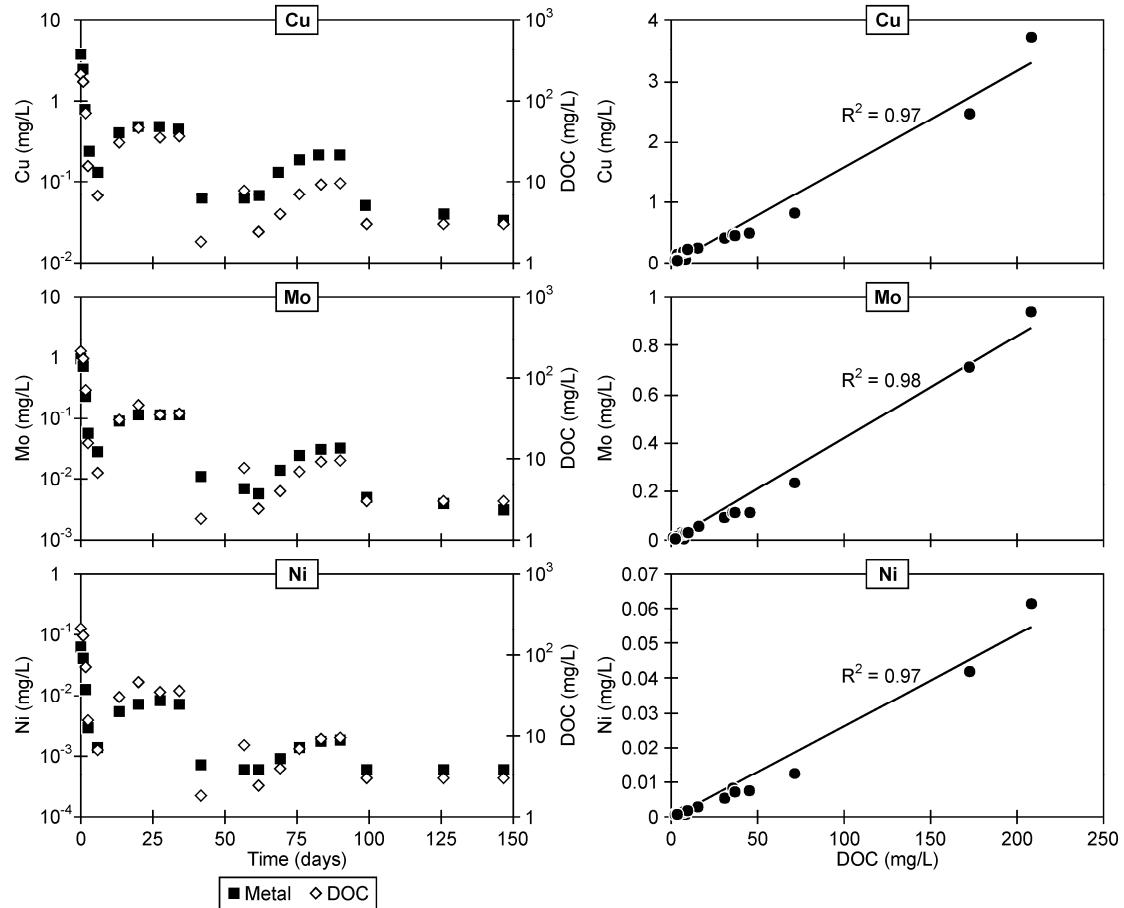

Figure 6. *Left: concentrations of Cu, Mo, Ni, and DOC as a function of time in C3 (interrupted). Solid squares represent metal concentrations while open diamonds represent dissolved organic matter (DOC). Right: concentrations of Cu, Mo, and Ni as a function of DOC in C3 (interrupted). Data correlation is represented by a solid line. Source: [**III**].*

3.3 Leaching from MSWI residues

3.3.1 Characterization of leaching from the pH-static experiments

The first step in understanding leaching behavior of any element is obviously the characterization of its leaching control preferably using pH-dependent leaching data (i.e. pH-static batch test). Such characterization is relatively simple and widely used [19;51;53;61].

For further details refer to [**I**] and/or BOX 3; in general, the solution speciation of each batch is calculated and possible solubility controlling minerals are selected based on their saturation index ($-2 < SI < 2$) and the probability of appearance under the experimental conditions (Table 2). Next, the leachate composition in equilibrium with the selected minerals is calculated [*61*] so that the predicted and the measured data could be compared.

In [**I**], the CEN/TS pH-static test was used to obtain leaching data for Al, Ca, Mg, Si, S, Ba, Sr, Mo, Zn, Cd, Pb, Cu, Cl, and DOC from two APC residues (composition shown in Table 1). Subsequently, leaching data was modeled in ORCHESTRA code [*65*] incorporated in LeachXS user interface [*66*] in order to (i) specify possible solubility controlling minerals for those elements that are actually controlled by dissolution/precipitation and (ii) identify other possible controlling processes (i.e. complexation with DOC). Complexation with DOC was accounted for during the speciation calculations using generic Nica-Donnan parameters [78]. A summary of the results for both APC residues is given in Table 5.

The results shown in Table 5 were in good agreement with the outcomes of other studies which were performed on both bottom ashes and APC residues [12;19;20;51;55;61;62;67;79;80]. The release of many elements was apparently controlled by the solubility of the same minerals. Consequently, it was assumed that using a "generic" set of minerals may provide an adequate description of the pH-dependant leaching for any given residue. This would naturally reduce the necessity of performing expensive and time consuming material-specific pH-static leaching experiments.

Table 5. *Overview of solubility controlling mineral phases and other leaching controlling processes. Source: [**I**].*

Element	Solubility controlling minerals and other leaching controlling processes
Al	gibbsite (Al[OH]$_3$), wairakite (CaAl$_2$Si$_4$O$_{12}$·2H$_2$O), monosulphate (Ca$_4$Al$_2$O$_6$[SO$_4$]·6H$_2$O)
Ca	gypsum (CaSO$_4$·2H$_2$O)
Mg	dolomite (CaMg[CO$_3$]$_2$), forsterite (Mg$_2$SiO$_4$), magnesite (MgCO$_3$)
Si	akermanite (Ca$_2$MgSi$_2$O$_7$), SiO$_2$, wairakite
S	gypsum
Ba	(Ba,Sr)SO$_4$, witherite (BaCO$_3$)
Sr	(Ba,Sr)SO$_4$, strontianite (SrCO$_3$)
Mo	powellite (CaMoO$_4$), wulfenite (PbMoO$_4$)
Zn	zincite (ZnO)
Cd	Cd(OH)$_2$, otavite (CdCO$_3$)
Pb	anglesite (PbSO$_4$), Pb$_3$(VO$_4$)$_2$, Pb$_2$(OH)$_3$Cl, DOC
Cu	atacamite (Cu$_2$[OH]$_3$NO$_3$), DOC, Cu(OH)$_2$

3.3.2   Modeling of pH-dependent leaching from APC residues

In order to validate the above assumption (i.e. a "generic" set of minerals may be used to provide a reasonable description of the pH-dependent leaching), a modeling exercise using the pH-static leaching data obtained for the SD residue (see Table 1 or [**I**]) was used for leaching description of Ba, Sr, Pb, Zn, Cr, Mo, Cu and Cd.

First, the solution speciation was calculated and possible solubility controlling minerals were selected based on their saturation index and probability of appearance under experimental conditions; this step is the same as described in Section 3.3.1. Accordingly, the minerals considered to be the controlling phases were: (Ba,Sr)SO$_4$ (50% Ba) solid solution strontianite (SrCO$_3$), laurionite (PbClOH), zincite (ZnO), PbCrO$_4$, powellite (CaMoO$_4$), wulfenite (PbMoO$_4$), atacamite (Cu$_2$Cl[OH]$_3$), otavite (CdCO$_3$), and Cd(OH)$_2$(s).

Next, the "available" fractions of all elements were entered in the model as described in BOX 3. In addition, material-specific amounts of DOC (i.e. the highest value from pH-static test) and HFO/AlO surfaces were included in the input. Amounts of HFO were obtained during an ascorbate extraction according to Kostka and Luther [81] while amounts of AlO were obtained during an oxalate extraction in dark as described by Blakemore[82]. Similarly to Dijkstra et al [77] I considered HFO and AlO to be equal in the model. Accordingly, the extracted amounts were added up assuming that 1 mol of Fe ~ 1 mol of Al [53;77] and recalculated to kg of HFO/kg of solid phase; a gram formula weight of 89 g HFO/mol Fe was used [*21*]. In the end the input

consisted of: the "available" amounts of elements, a list of controlling minerals, information about DOC levels, and amounts of reactive surfaces. During the calculation ORCHESTRA uses the "available" amount of a given element and calculates its concentration in solutions at different pH (2 < pH < 14 by default) while simultaneously accounting for all three major controlling processes (i.e. solubility control, DOC complexation, and HFO/AlO sorption); this way a competition is ensured.

The result of this modeling exercise are summarized in Hyks et al [83]. It can be seen (Figure 7) that one set of minerals provided rather adequate description of the leaching from two different materials (i.e. the SD- and the FA-residue), especially in the case of Ba, Sr, Zn, and Cd, despite the differences in solid composition (see Table 1). Hence, the pH-dependant leaching of Ba, Sr, Pb, Zn, Cr, Mo, Cu, and Cd from two different MSWI residues was adequately predicted using a combination of a "generic" set of minerals derived for one of the MSWI residues and material-specific amounts of HFO and DOC.

3.3.3 Possible application of generic set of minerals

Using the "generic" set of minerals could, to some extent, enable us to omit resources-consuming leaching experiments (i.e., at least 8 batch experiments) which are usually done for every material. Apparently, "a dataset containing the generic minerals, results of three batch tests (pH 4, pH 7-8, and pH 10) and amounts of HFO/AlO could provide the same quality of input information as 8-batch experimental set-up" [84].

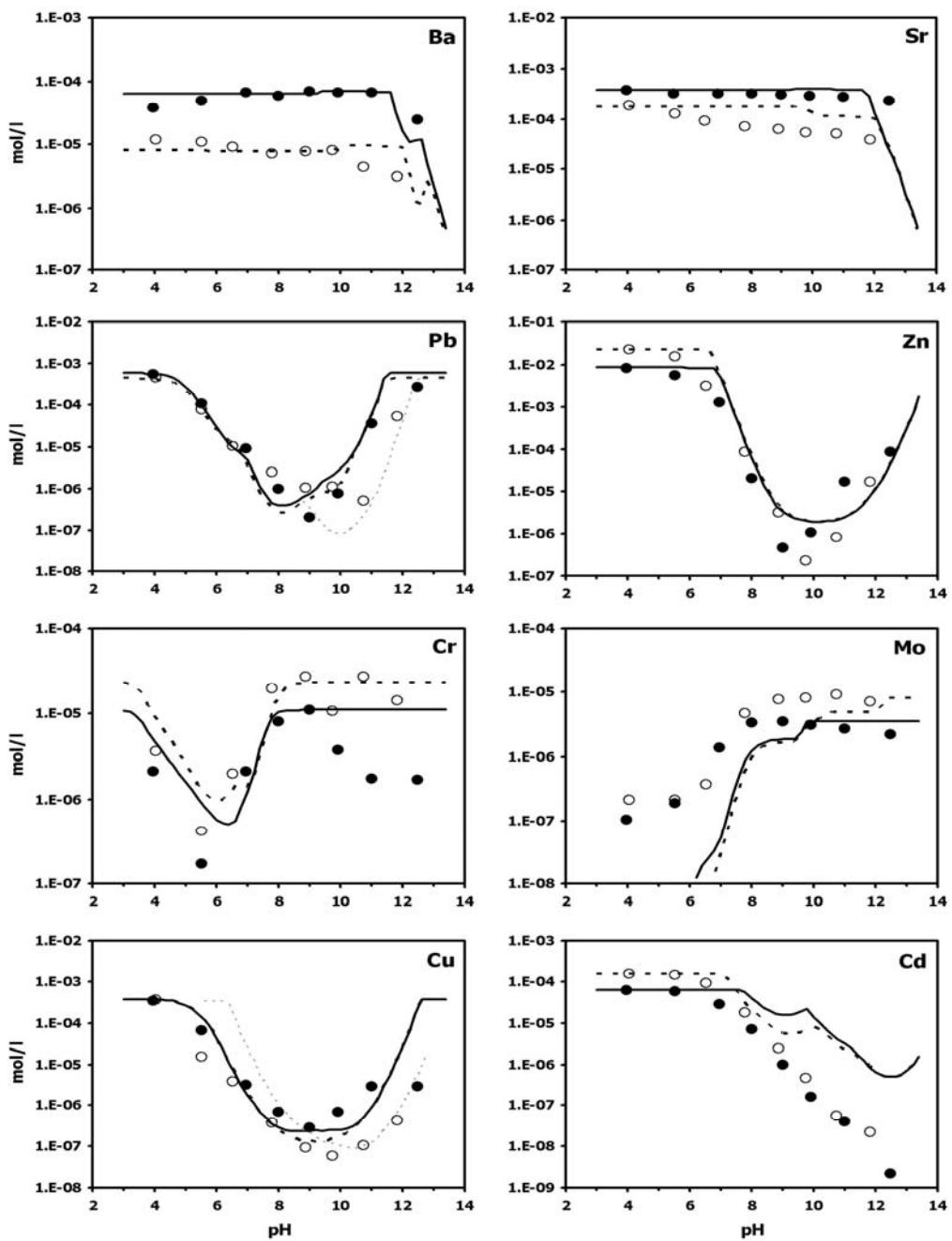*Figure 7. Leaching of Ba, Sr, Pb, Zn, Cr, Mo, Cu and Cd as a function of pH. Experimental data are represented by solid and open points for SD- and FA-residue, respectively. Solid lines represent model predictions for the SD- while dashed lines represent model predictions for the FA-residue. Grey dashed lines for Pb and Cu represent model runs using $Pb(OH)_3Cl$ and $Cu(OH)_2(s)$ respectively. Source: Hyks et al [83].*

3.3.4 Long-term percolation experiments on APC residues

As the next step of leaching characterization a series of extended column percolation experiments was performed on both APC residues [**IV**]. Leaching of Ca, Fe, Mg, K, Na, S, Al, As, Ba, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Zn, Mo, Sb, Si, Sn, Sr, Ti, V, P, Cl, and DOC was studied during 24 months of column percolation experiments; L/S 200-250 L/kg was reached. This L/S would correspond to more than 10,000 years in a conventional landfill [*48*]. Geochemical modeling in PHREEQC [*64*] was used (i) to predict the solubility controlling minerals, and (ii) to evaluate their role on both pH development and leaching of alkalinity, Ca, S, Al, Si, Ba, and Zn in a water-percolated system. A comprehensive discussion of the results is given in [**IV**].

Interestingly, the leaching of Cd, Fe, Mg, Hg, Mn, Ni, Co, Sn, Ti, and P from both materials was generally found below the associated detection limits (in mg/L): Cd (5×10^{-5}), Fe (2×10^{-2}), Mg (1.4), Hg (2×10^{-5}), Mn (9×10^{-4}), Ni (6×10^{-4}), Co (2×10^{-4}), Sn (5×10^{-4}), Ti (2×10^{-2}), and P (1×10^{-2}) respectively. Accordingly, their leached mass was negligible. For elements with measurable leachate concentrations the total released mass was calculated in MATLAB [85] using cumulative Simpson's integration with uneven spacing [86] and is shown in Table 6.

A typical availability-controlled leaching behavior was observed for Na, K, and Cl in both columns as the leaching of these elements was most likely controlled by the dissolution of readily soluble compounds such as halite (NaCl) and sylvite (KCl). Consequently, significant amounts of Na and K were removed during the course of the experiments. Chloride was removed to a lesser extent than expected (~ 50 %) possibly due to precipitation of Friedel's salt ($3CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot 10H_2O$) which is known to form in cementious systems [87-89].

It can be seen in Table 6 that only a minor fraction of the total content of many elements leached during 24 months of percolation experiments. Despite the rather high initial concentrations and the late release in the leaching of some metals, about 97-99 % of the total content As, Cu, Cd, Pb, Zn, Cr, and Sb remained in the solid material after 2 years of column leaching.

Table 6. *Element fractions (% of initial mass) leached during 24 months of the column experiments (i.e. L/S 245 L/kg for the SD-residue and L/S 207 L/kg the FA-residue) as calculated in MATLAB by cumulative Simpson's integration with uneven spacing. Source: [**IV**].*

Element	FA	SD	Element	FA	SD
Na	~ 65	~ 103	Sr	~ 41	~ 71
K	~ 82	~ 115	Cr	< 1	< 1
Cl	~ 53	~ 64	Mo	~ 34	~ 38
Ca	~ 39	~ 68	Sb	~ 1	< 1
S	~ 104	~ 59	Cu	< 1	< 1
Si	< 1	< 1	Cd	< 1	< 1
Al	< 1	< 1	Pb	~ 1.6	~ 1.1
As	< 1	< 1	Zn	< 1	~ 3
Ba	~ 3.5	~ 24	V	~ 4.4	~ 3.7

Speciation calculations in PHREEQC suggested that the leaching of major elements (i.e. Ca, S, Al, and Si) was presumably controlled by the dissolution/precipitation of portlandite, gypsum, ettringite, diaspore, akermanite, and strätlingite, respectively. In addition, dissolution/precipitation in a portlandite-gypsum-ettringite system was shown to be the most important process with respect to development in both pH and alkalinity (discussed in next chapter).

Further, the removal of Ca and S due to the dissolution of portlandite and gypsum could cause increased dissolution of ettringite and strätlingite; this corresponded with the observed increase in Al and Si solution concentrations in late stage of the experiments. Dissolution of ettringite could, in turn, cause an increase in concentrations (Figure 8) of some metals especially those forming oxyanions (e.g. Sb, As, V, and Cr) which are suspected to substitute sulfate in the ettringite structure [56-58].
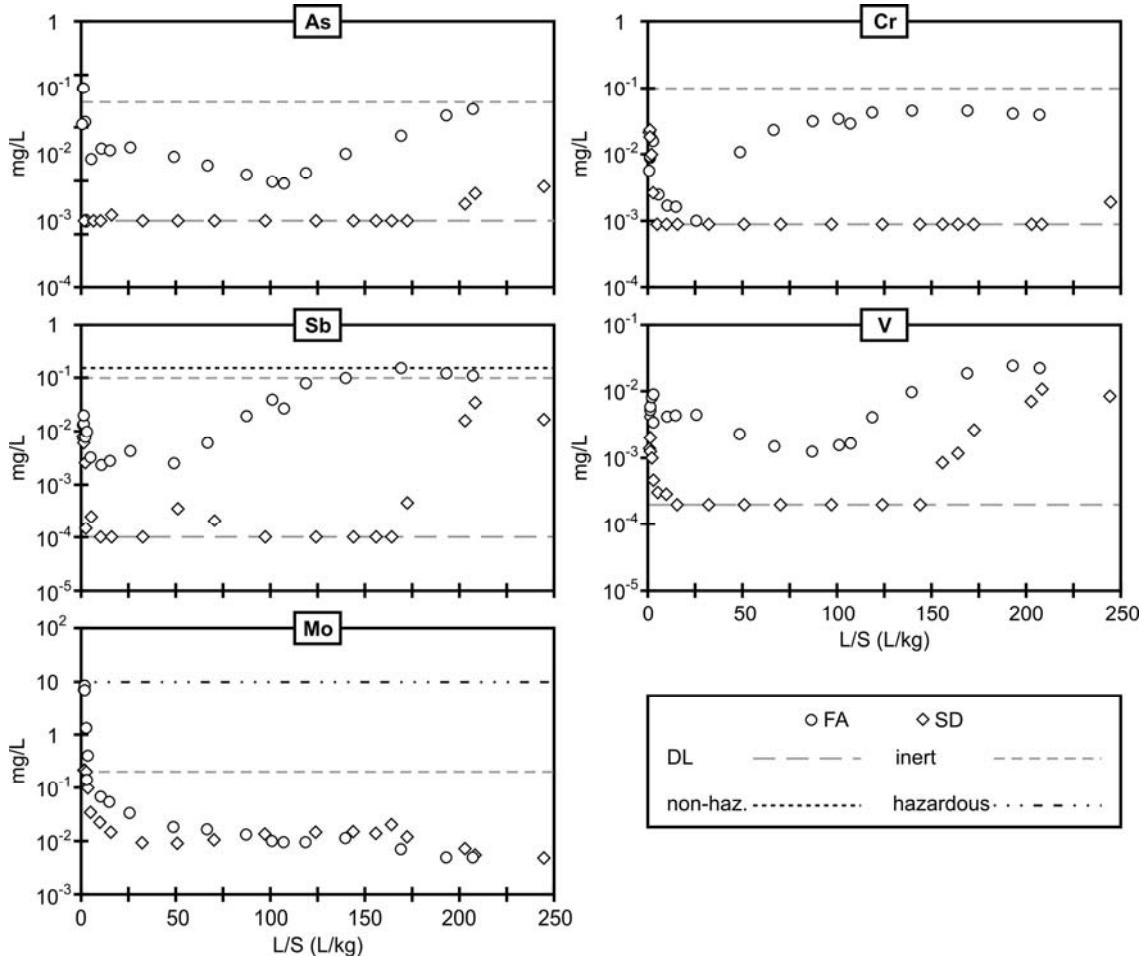
Figure 8. *Solution concentrations of As, Cr, Sb, V, and Mo as function of L/S ratio. Leaching data for FA and SD are represented by open spheres and diamonds, respectively. Detection limits (DL) are indicated by wide grey dashed lines where appropriate. Leaching criteria for waste acceptable at landfills for inert, non-hazardous, and hazardous waste[4] are indicated by grey dashed-, black dashed- (non-haz.), and combined black dashed lines, respectively. Source: [**IV**].*

The leaching of Ba and Sr (Figure 9) was suggested to be controlled by the dissolution/precipitation of barite, $Ba(Ca)SO_4$ solid solution, $Ba(S,Cr)O_4$ solid solution, and $Ba(Sr)SO_4$ solid solution [70;90;91]. An interaction between barite and gypsum was also used to explain the observed leaching behavior of Ba in forward geochemical modeling; an adequate fit between modeled and experimental data was obtained. It can be mentioned that initial leaching of both elements from the SD-residue was significantly higher than from the FA-residue. In both cases these high values are comparable with the leaching of Ba and Sr in batch pH-static experiments [**I**]. Apparently, significant fraction of particularly Sr is "available" at natural pH of both residues; i.e. at pH > 11.

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The leaching of Cu (Figure 9) resembled the wash-out of DOC which is commonly suggested to be the major process controlling Cu via complexation [52;55;67]. Similarly for both materials, leaching of Cu decreased rapidly during the initial leaching period and stayed around 1-6 μg/L for the rest of the experiments. This concentration level could also be explained by solubility of $Cu(OH)_2(s)$ which was suggested to control the leaching of Cu from APC residues at pH > 10 [**I**].
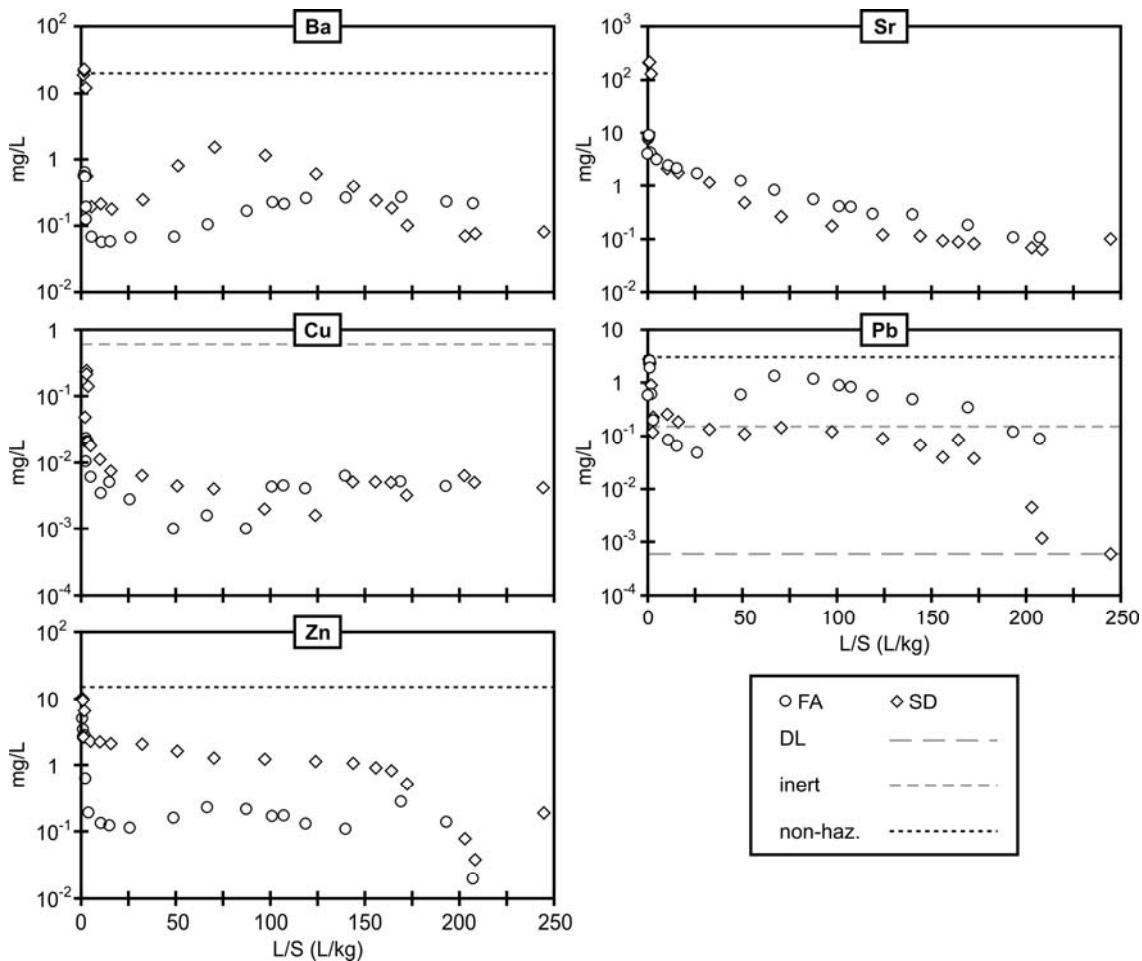
Figure 9. *Solution concentrations of Ba, Sr, Cu, Pb, and Zn as function of L/S ratio. Leaching data for FA and SD are represented by open spheres and diamonds, respectively. Detection limits (DL) are indicated by wide grey dashed lines where appropriate. Leaching criteria for waste acceptable at landfills for inert and non-hazardous waste are indicated by short grey dashed lines and black dashed lines (non-haz.), respectively. Source: [**IV**].*

The high initial release of Pb (~ 3 mg/L) was almost level with the limits for hazardous waste [4]. Still, this is not uncommon in solutions with high levels of soluble salts as inorganic complexation might be of importance [35]. Overall, sorption to HFO/AlO [21;23] and/or substitution in ettringite structure [56] could explain the observed leaching behavior of Pb; for details refer to [**IV**]. The final leached amounts corresponded to only 1.6 % (FA) and 1.1 % (SD) of the total mass of Pb in the solid phase.

The leaching of Zn was similar for both residues and most likely controlled by dissolution/precipitation of zincite. This was further confirmed by forward geochemical modeling. The decrease in Zn concentrations at the late stage of percolation experiments could be caused by a simple change in the solubility of zincite as a function of pH.

3.3.5   Forward modeling of column leaching from APC residues

In addition to predictions of the solubility controlling minerals, a forward geochemical modeling for prediction of the long-term behavior of pH, alkalinity and major elements (Ca, S, Al, Si, Ba and Zn) in a water-percolated SD-column was applied [**IV**]. Again, all calculations were performed in PHREEQC.

Following the approach of Astrup et al [92], 1 kilogram of a hypothetical mineral assemblage which was composed of few controlling minerals for the above elements was created. The mineral assemblage would then be flushed with water to simulate column leaching. In total, 250 flushes (mass of water pushed in each flush equaled 1 L) would be performed corresponding to L/S 250 L/kg. However, there is no general approach to specify the exact amount of a particular mineral (e.g. portlandite) from the total mass of a specific element determined by sample digestion (e.g. Ca). Analytical techniques such as X-Ray diffraction may be used in this respect, but these techniques generally have a relatively high detection limit and quantitative data are often associated with significant uncertainties. A different approach had to be used for the determination of the amounts of the individual minerals in the modeling.

It was assumed that portlandite will likely determine the pH of the system and thus leaching of other elements. Therefore, in the first step, the amount of portlandite in the SD-column was derived to match the decrease in both Ca and alkalinity (for details refer to [**IV**]); 3 moles/kg were found appropriate. Similarly, the amount of gypsum was adapted to match the decrease in S; this time, about 0.2 moles kg^{-1} were found appropriate. These amounts of Ca and S did not account for the entire solid mass (see Table 1); the residual mass was thus distributed between other possible solubility controlling minerals. Of course, the amounts of other constituents in the selected minerals had to be considered as well and the whole procedure was therefore an iteration process. In the end, 3 moles of portlandite, 0.2 moles of gypsum, 2.6 moles of calcite, 0.35 moles of ettringite, 0.022 moles of akermanite, 0.005 moles of barite, and 0.14 moles of zincite formed the mineral assemblage. All these minerals are commonly

identified in APC residues (see Table 2). Compared with the total mass of Ca, S, Al, Si, Ba, and Zn in the SD-residue this accounted for 96 % of Ca, 116 % of S, 103 % of Al, 2 % of Si, 110 % of Ba, and 101 % of Zn respectively. The mineralogy of APC residues is unquestionably much more complicated. However, for a first approximation this assemblage was found to be sufficient.

During the percolation, portlandite was allowed to equilibrate with the solution whereas, in agreement with the speciation calculations performed for the early eluates, gypsum, calcite and ettringite were kept slightly oversaturated. Furthermore, monosulphate and diaspore which were not considered in the initial assemblage were allowed to precipitate if needed. Both phases were suggested by the speciation calculations at later L/S ratios; in addition, monosulphate has been reported to form from ettringite at low sulfate concentrations [56].

It can be seen (Figure 10) that adequate fit between modeled and measured data was obtained for pH and alkalinity; decrease in either was predicted well. Further, excellent model predictions were obtained for Ca, S, Ba and Zn while the leaching of Al and Si was predicted within one order of a magnitude.
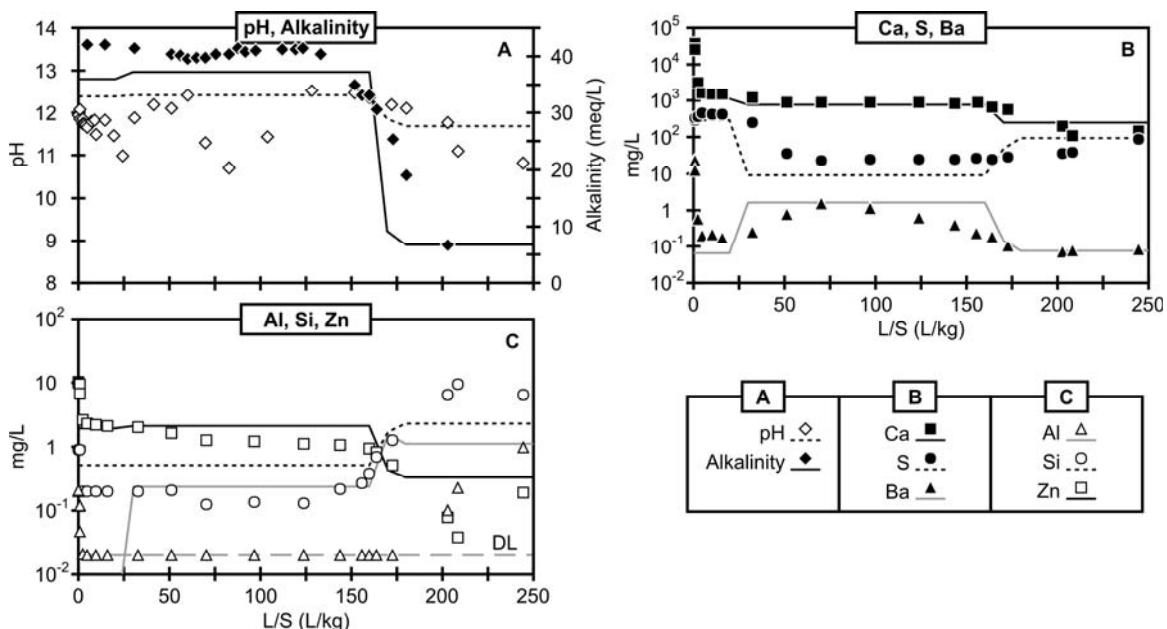

Figure 10. *Long-term development in pH, alkalinity (Figure A) Ca, S, Ba (Figure B), Al, Si, and Zn (Figure C) as a function of L/S ratio. As outlined in legend points refer to laboratory experiments (SD residue) while associated lines represent model predictions. Source: [IV].*

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It should be emphasized that these predictions were accomplished using a rather "simple" set of minerals suggested for controlling the release and that the modeled L/S ratio would correspond to over 10,000 years in a typical landfill. The modeling exercise, results of which are shown in Figure 5, was therefore an extreme simplification of the leaching system. Moreover, with limited information of the physical properties of the columns (i.e. dual-porosity fraction, preferential flows, etc.) the percolation was set-up using default parameters in PHREEQC (i.e. assuming equilibrium) and no parameter fitting was used. Notably, about 20-40 % of mass initially present in the columns was removed within L/S 2 L/kg (primarily easily soluble elements like Na, K, Cl, Ca, and S). Such a removal of solids will indeed influence flow conditions in the column (increase in porosity, dynamic changes in dual-porosity, structure collapse) thereby likely affecting leaching of many elements. None of these issues were considered in our modeling exercise.

Nevertheless, in spite of being a simplified system, the modeling provided useful insight. Most importantly, the interaction between portlandite, gypsum and ettringite was shown crucial as these minerals influenced both pH and the leaching of major elements (i.e. Ca and S), which in turn had an impact on the leaching of the remaining elements (e.g. oxyanions). Unaccounted late release of oxyanions may present a significant environmental threat.

Calcite played a limited role at pH > 10.5 in the portlandite-gypsum-ettringite governed system. Similarly, the initial pH of the eluent (i.e. pH of distilled water before entering the columns) had only a negligible effect due to the huge acid-neutralization-capacity of the residues [92;93].

4 Conclusions

Finally, an overview of the major conclusions drawn from this work is given in comparison with goals stated in Introduction:

i) *Investigate the influence of sample handling on results of laboratory leaching experiments*

- Drying of materials prior to batch leaching experiments can induce changes in material properties (e.g. its reduction capacity) thereby significantly affecting the leaching of some elements, Cr in particular. This could cause a significant overestimation of Cr leaching when the results of such test are used for compliance purposes.
- Removal of soluble salts prior to pH-static batch leaching experiments does not improve the model predictions with respect to the identification of solubility controlling minerals; however, it can indicate "easily removable" fractions of other elements (e.g. Sr and Pb).

ii) *Evaluate the effects of non-equilibrium conditions on the results of percolation experiments*

- Significant differences regarding leaching behavior of different elements with respect to (non)equilibrium conditions in the column percolation experiments were observed. As a result, three groups of elements were proposed based on their predominant leaching control and the influence of (non)equilibrium on the results of laboratory column experiments:

  I.   Predominantly availability-controlled elements (e.g. Na, K, Cl)
  II. Solubility-controlled elements (e.g. Ca, S, Si, Al, Ba, and Zn)
  III. Complexation-controlled elements (e.g. Cu and Ni)

- With respect to the above groups it was suggested that results from laboratory column experiments can, with consideration, be used to estimate full-scale leaching of elements from Group I and II.
- Because of the impact of physical non-equilibrium on the release of DOC, the leaching of Cu and Ni (Group III) in column experiments does not reflect leaching which is likely to occur for the same material in a full-scale scenario. In fact, their solution concentrations are most likely underestimated by up to one order of magnitude (Figure 6). Consequently, it appears that using the lab-scale data to predict full-scale long-term release of these metals in terms of solution

concentrations (e.g. $mg\,L^{-1}$) is not possible without a detailed knowledge of the (non)equilibrium conditions in the tested system. Thus, in order to avoid large underestimation in assessment of leaching from Group III it is imperative to describe the time-dependent transport of dissolved organic carbon (DOC) in any tested system or to minimize the physical non-equilibrium during laboratory experiments by changing the set-up (e.g. bigger column, slower flow).

iii) Describe the long-term leaching behavior of various MSWI residues by means of laboratory experiments and geochemical modeling.

- Only a minor fraction of many potential pollutants (e.g. heavy metals) present in MSWI residues have been shown leachable even during long-term percolation experiments (L/S 250 $L\,kg^{-1} \approx$ 10,000 years in typical landfill); less than 1% of initially present As, Cr, Sb, Cu, Cd, and Pb has leached.
- The leaching of Ca, S, Al, Si, Ba, and Zn in the semi-dry APC residue was likely controlled by the dissolution/precipitation of portlandite, gypsum, ettringite, diaspore, akermanite, monosulphate, strätlingite, barite and zincite. This was both suggested by speciation calculations and confirmed by forward geochemical modeling over L/S ratio of 250 L/kg.
- The removal of Ca and S due to the dissolution of portlandite and gypsum could cause increased dissolution of ettringite and strätlingite. Dissolution of ettringite could, in turn, cause a late increase in the concentrations of elements which are suspected to substitute sulfate in the ettringite structure; e.g. Sb, As, V, and Cr.

In addition to the above conclusions it should be explicitly noted that the leaching of Cd monitored in the columns (both with bottom ashes and APC residues) was generally found below the IPC-AES detection limit; i.e. 5×10^{-5} $mg\,L^{-1}$. Consequently, a very little fraction (< 1%) of the initially present Cd has leached even during fairly long leaching experiments. Note that low leaching of Cd at high pH is notoriously observed for both bottom ashes and APC residues (see Figure 7). Usually, a surface complexation is suggested to be the major controlling process.

Finally, it was shown in Chapter 3.3.2 that using a dataset that contains the generic minerals, the results of three batch tests (pH 4, pH 7-8, and pH 10) and the amounts of HFO/AlO could provide the same quality of input information for the geochemical modeling of the pH-dependent leaching as the 8-batch experimental set-up. Hence, a few of the resources-consuming pH-static experiments can be omitted.

5 Future work

Based on the level of knowledge that has been obtained from this research I would take the liberty of pointing out several objectives for future work:

Most importantly, the long-term environmental impacts from leaching of pollutants from MSWI residues should definitely be related to the "leaching-available" fraction of those pollutants rather then to the total pollutant content in solids. It was shown that leaching of many potential pollutants was almost negligible and that up to 99% of the initially present mass of some pollutants remained in the solids even after fairly long leaching experiments.

The "leaching-available" fraction is without doubt the most crucial yet often missing input parameter for today's geochemical models that are basically build in order to distribute this "available" amount over studied leaching period (e.g. percolation scenario) while simultaneously accounting for various controlling processes. So far, there is no general approach to classify the "leaching-available" fraction of various contaminants in different types of residues and hence further research should be pointed towards solving this issue.

With respect to the abovementioned issue, I truly believe that it is possible to suggest a simplified approach for assessing the long-term leaching availability from any MWSI residue based on the L/S 2 L kg^{-1} batch experiments and the long-term column experiments performed in this study. Of course, it should not be expected that this will provide detailed information about solution concentrations. However, information about released mass (in mg kg^{-1}) over some pre-defined leaching periods could be obtained (i.e. leaching available mass). This would indeed be sufficient as an input for forward geochemical modeling as well as for direct LC(I)A of MSWI residues.

Secondly, unlike other researchers I am rather skeptical towards using the results from laboratory column experiments for the long-term leaching predictions of DOC-dependent metals without actually having a time-dependent leaching description for DOC release in various materials/scenarios. Such a model for DOC behavior implemented into current geochemical models would indeed provide better a description of long-term leaching of for ex. Cu, Ni, and Mo.

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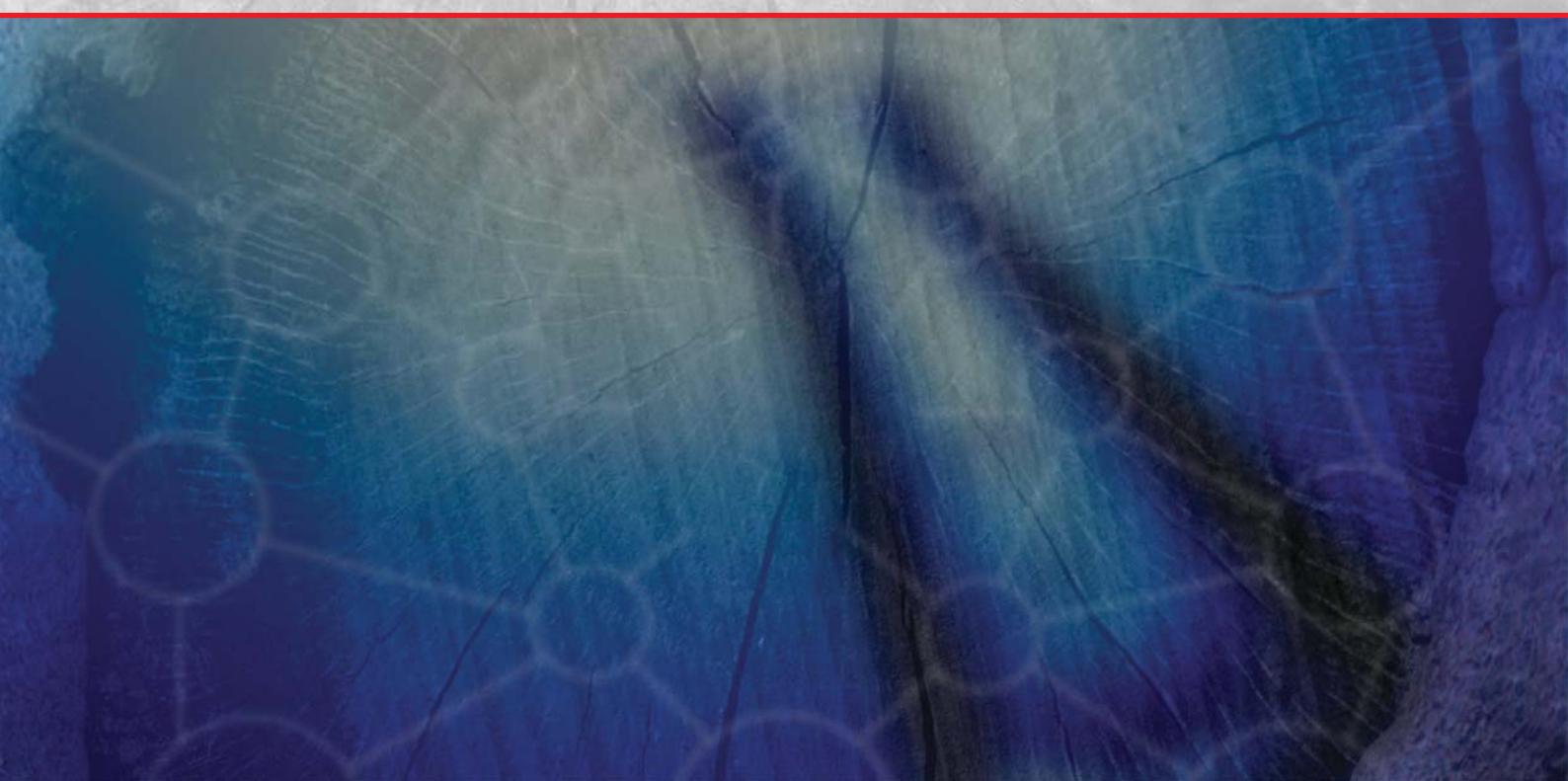
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7 Appendixes

I.   **Hyks, J.**; Astrup, T. & Christensen, T.H. Influence of test conditions on solubility controlled leaching predictions from air-pollution-control residues. *Waste Management & Research 2007, 25 (5), p. 457-466.*

II.   Hu, Y.; **Hyks, J.**; Astrup, T. & Christensen, T.H. Effect of drying on leaching testing of treated municipal solid waste incineration APC-residues. *Accepted in Waste Management & Research 2008.*

III.   **Hyks, J.**; Astrup, T. & Christensen, T.H. Leaching from MSWI bottom ash: Effects of non-equilibrium during column experiments. *Submitted to Waste Management.*

IV.   **Hyks, J.**; Astrup, T. & Christensen, T.H. Long-term leaching from MSWI air-pollution-control residues. *Submitted to Journal of Hazardous Materials.*

The appendixes are not included in this www-version but may be obtained from the Library at the Department of Environmental Engineering, Bygningstorvet, Building 115, Technical University of Denmark, DK-2800 Kgs. Lyngby (library@env.dtu.dk)