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# Impact evaluation of coal fly ash in beneficial uses

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## Acknowledgement/Preface

This study was carried out for National Coal Ash Board of Israel.

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## Summary

The coal fly ashes from Israel, which were characterized before have been evaluated against earlier data from other sources and data from test at field sites. By combining the information for the alkaline Israeli ashes with more extended characterisation data from alkaline Dutch fly ash (column test) chemical speciation modelling was applied to understand better the release controlling factors under full operational conditions of ash use in embankment and in road base applications. The modelling using mineral precipitation, sorption on reactive surfaces and incorporation in solid solutions has resulted in a good insight in the chemical forms of relevance in coal fly ash. In addition, the chemical speciation fingerprint obtained in this manner can be used as the starting point for chemical reaction/transport modelling. The results from this part of the work illustrates the potential for Cr (VI) reduction under field conditions to the less leachable Cr(III). The conditions in terms of redox state of the ash at which this switch from the oxidised to the reduced form of Cr occurs has been quantified through modelling. The potential for reaching this lower redox state in an embankment still needs to be proven. The potential for modelling release from coal fly ash in a variety of beneficial uses is demonstrated.



## 1. Introduction

In view of the evaluation of beneficial uses of coal fly ash in Israel, which is mostly focussed on embankments and in roadbase application, better knowledge is needed on the potential long term environmental risks. Since earlier work done in this context (van der Sloot et al, 2001), more data have become available from a variety of sources, which helps to understand the release characteristics under a range of exposure conditions. In addition, data from field work have become available that can be placed in perspective to laboratory leaching test. This allows to clarify the extent to which laboratory data can be used to resolve issues related to actual field exposure scenarios.

The testing approaches as presented before (CEN TS 14429, 2004; CEN TS 14405, 2005; CEN TS 15863, 2009) have been firmed up to the extent that the characterisation leaching tests have now been adopted in CEN as Technical Specifications. In the mean time the same methods have been adopted in US-EPA for inclusion in SW846.

The following topics will be addressed in the report:

- Current status of test development
- Comparability of leaching data from different sources
- Comparability between lab and field data (Israel and other)
- Modelling laboratory test data
- Modelling impact using LeachXS-Orchestra with full chemical speciation
- Modelling impact according to the Dutch Soil Quality Decree
- Evaluation of field conditions on release

The modelling capabilities and benefits of a better understanding of release behaviour for Israel's coal fly ash utilisation program is highlighted.

## 1. Materials and methods

### 1.1 Data

Coal fly ash samples from Israeli installations Orot-Rabin and Ruthenberg were analysed before by ECN (2001). In addition data from the LeachXS database have been used for comparison, as well as a basis for modelling release by percolation. The modelling of release is based on leaching behaviour from Dutch fly ashes by using the chemical composition of the Israeli ashes under the assumption that the release behaviour is very much the same. Results from a study on coal ash leaching back in 1982 running over several years and applying acid addition at the later stages of the column experiment (van der Sloot et al, 1982) are included for comparison as well. Data from field studies carried out in Israel (Yaacov ref) and data from field work in Denmark (Hjelmar, 1990; Hjelmar, 200x ) have been used to illustrate the relationship between laboratory and field.

### 1.2 Leaching tests used

For the characterisation of the coal fly ash samples from Israel only the pH dependence leaching test data were available. For the modelling of release by percolation information from a column test is needed. To complement the information on Israeli ashes, leaching data from a Dutch coal fly ash from the LeachXS database have been used. In Appendix A, a general background on leaching mechanisms and leaching tests is given. Data obtained from the following test have been used:

- *pH dependence leaching test* (CEN/TS 14429, 2004): This test provides information on the pH sensitivity of leaching behaviour of coal fly ash. The test consists of a number of parallel



extractions of a material at an L/S 10 during 48 hours at a series of pre-set pH values based on a prior titration of the acid-base consumption to reach the preset values.. After 48 hours, the suspensions are centrifuged and filtered over a 0.45 µm.

Since pH is one of the main leaching controlling parameters, the information can be used to evaluate the repeatability in testing (resulting from measurement at steep concentration - pH slopes) and to provide information on the sensitivity to pH in specific field scenarios (e.g after carbonation). The acid neutralization capacity (ANC) derived from the test is a useful property in this respect. The method is being standardized in two experimental modes by CEN/TC 292 Working Group 6 (CEN/TS 14429, 2005 and CEN TS 14997, 2006).

- *Column leaching test (CEN/TS14405, 2005 and NEN 7373, 2003)*: The European percolation test is developed in CEN/TC 292 WG6. Seven 7 eluate fractions are collected within the range of L/S = 0.1-10 l/kg. The total test duration is approximately 21 days. The leachant is demineralised water (DMW). The test material is applied as received as coal ash is very fine and meets the specification as stipulated in the test without pre-treatment, ( $\approx 2$  mm Ø) and upflow (14 ml/h) is applied through a column waste height of 20cm and a diameter of 5 cm.

The methods mentioned above are Technical Specifications as the validation has not yet been realised. The validation is in preparation and already a lot of data on repeatability of the methods is available and will be reported within the next months. In the mean time US-EPA has adopted methods very similar to the European standards for inclusion in SW846. The methods are meant as a tool to quantify release from waste and construction materials in case the TCLP provides insufficient information, which is the situation in most cases. Currently, an extensive study on coal combustion by-products is ongoing in the US and will be publicly available soon (pH dependence test : EPA draft method 1313, 2009; percolation test: EPA draft method 1314, 2009; monolith leach test: EPA draft method 1315, 2009 ). This work covers coal combustion residues from installations with different ash and flue gas handling (e.g. Hg removal, SO<sub>2</sub> reduction),

### 1.3 Field data

The field data from Israel were obtained from an earlier study (van der Sloot et al, 2001). The sample specifications are given in Table 1.

Table 1 Field data on coal fly ash from Israel.

No	Sample code	Origin	pH
2	FM2	3 months composite industrial ash	12.05
6	FR2	3 months composite industrial ash	11.85
1	JASR	Road base material Jasr-el-Zarka	9.00
5	D911	Same as JASR one year after placement 2 m	8.38
3	C3-5	Southern Embankment Hadera 1-1.5 m	10.75
4	C41	Southern Embankment Hadera 8 m	9.24

Field data from lysimeter studies carried out at DHI (Denmark) by Hjelmar (1990) have been placed in perspective to the Israeli ash data. Hjelmar et al (1991) have shown that the results from laboratory tests match very well with the field when the results are presented as a function of L/S (liquid to solid ratio (l/kg)).

### 1.4 Required input parameters for modelling

The modelling is used on full chemical speciation taking into account mineral precipitation/dissolution, sorption on hydrated ironhydroxide surfaces, incorporation in solid solutions and interaction with dissolved and particulated organic matter (carbon). This has some consequences for parameter settings in the modelling runs.

#### 1.4.1 Quantification of reactive surfaces

In the chemical speciation modelling independent estimates of the amount of reactive surfaces present in the coal fly ash matrix are required for sorption modelling. Since these data were not available for the Israeli ashes, these parameters have been taken from similar ashes studied in more detail (Dutch coal fly ash). The solid and dissolved organic carbon is usually characterised quantitatively in terms of four fractions, i.e. HA (humic acid), FA (fulvic acid), hydrophilic acids (denoted by HY) by a batch procedure (van Zomeren and Comans, 2007) derived from the method currently recommended by the International Humic Substances Society (IHHS) (Swift, 1996; Thurman and Malcolm, 1981). The amount of amorphous and crystalline iron (hydr)oxides in the coal fly ash matrix is currently estimated by a dithionite extraction described in Kostka and Luther III (1994). The amount of amorphous aluminum (hydr)oxides is estimated by an oxalate extraction according to Blakemore *et al.* (1987). These methods are now being standardized by ISO/TC 190 in cooperation with CEN/TC 292 (under the Vienna agreement).

#### 1.4.2 Chemical composition data

For proper geochemical modelling major, minor and trace elements are needed. The following elements have been analysed before by ICP-AES (Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Se, Si, Sn, Sr, Ti, V, Zn). Dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) were analysed by a Shimadzu TOC 5000a analyser. Chloride and sulphate were analysed by ion-chromatography.

### 1.5 Database/expert system and modelling approach

#### 1.5.1 General description

For the comparison of data from the different test methods applied, a database/ expert system is used that has been developed at ECN ([www.leachXS.com](http://www.leachXS.com)) in cooperation with Vanderbilt University (Nashville, USA) and DHI Water & Environment (Denmark). This database/expert system has been developed and is still further developed for environmental risk assessment in (contaminated) soil, sediment, sludge, waste and construction materials. The first step in setting up the database has been to identify the type of questions to be answered and to ensure that data are implemented in a manner that allow the desired cross comparisons between fields, the mutual comparison between test methods and establishing relationships between lab and field. The database contains results of laboratory experiments (pH-static experiments, column leaching tests, CEN tests, availability tests and diffusion tests) on more than 1200 soil, sludge, waste and construction material samples. It also contains data on lysimeter studies and relevant field data that are linked with laboratory work. This makes the database/expert system a unique tool to study the behaviour of different recycled materials, the comparison of different test on wastes and on construction materials, the comparison of data from laboratory leaching, lysimeter scale studies and field measurements. Furthermore, the system can serve as basis for modelling the chemical behaviour and release of substances in different scenarios. It also allows a direct comparison of obtained leaching data with regulatory criteria. In Figure 1 an outline of the expert system is given comprising software components that provide the aspects shown.

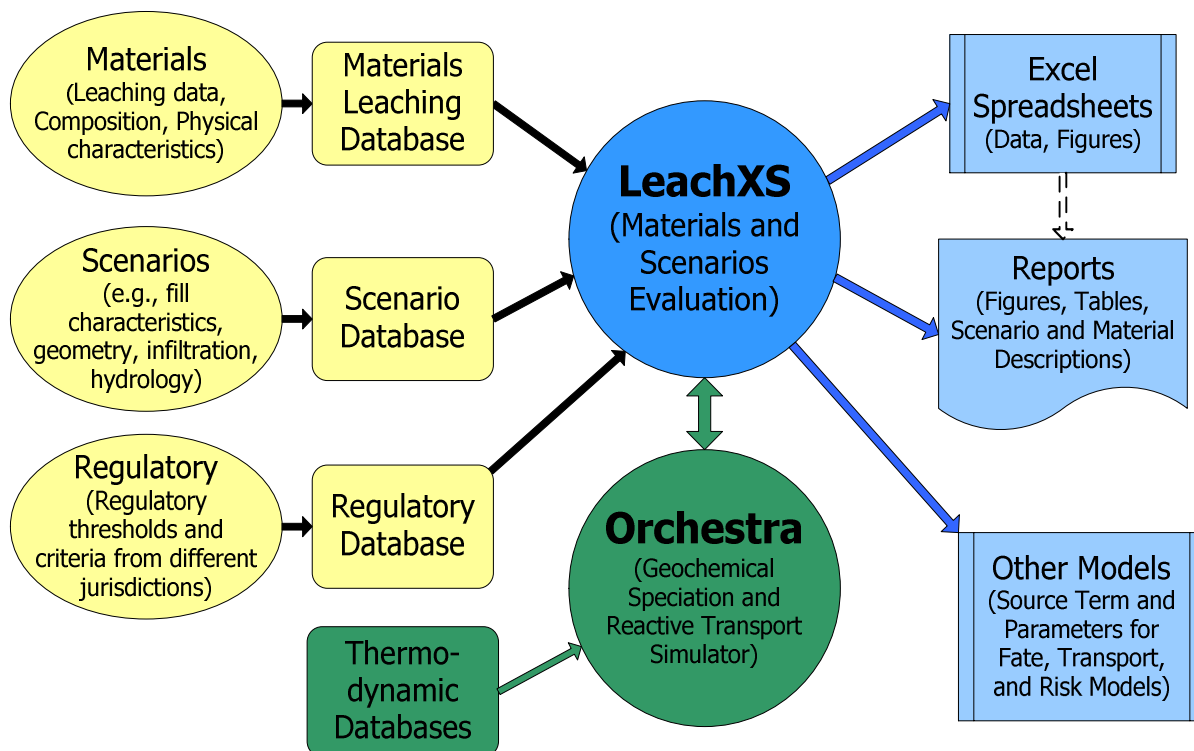


Figure 1: Outline of the database/expert system for environmental impact assessment based on release as derived from leaching tests.

The data obtained from the leaching studies are verified for analytical quality and subsequently transferred electronically to the database manager for check on completeness of data for handling in the database (minimum requirements such as pH, L/S, DOC, Eh, and technical data like moisture content, volumes, weights, etc.). The integrated characterisation of leaching data allows evaluation and decisions on a variety of questions in relation to coal fly ash uses, which will be addressed more specifically in the conclusions.

### 1.5.2 Comparison of release from laboratory tests and from field

Leaching data on Israeli coal fly ashes are compared with available data on coal fly ash leaching for other laboratory studies and field studies to identify the extent to which results obtained with different test can be understood. The basis representation of test data is crucial as presentation of leaching data in tables and in bar graphs is not very meaningful. Leaching data from one test can be presented in different ways to highlight specific aspects of leaching. For granular materials this consists of a presentation of concentration as a function of pH, a presentation of cumulative release as a function of L/S, concentration as a function of L/S and pH as a function of L/S. In Annex A this is explained in more detail. Conclusion on elements controlled by solubility limitations and elements with limited or no retention in the matrix can be identified.

In the comparison between laboratory and field the influence of additional factors or lack thereof can be recognized.

### 1.5.3 Modelling release of substances from coal fly ash (pH dependence)

The pH dependence test data have been modelled to get a better understanding of the release controlling phases in Israeli coal fly ashes. This could now be done along with percolation test data from the LeachXS database, which implies that the modelling run is done at the L/S = 10 of the pH dependence test, but also at a L/S of 0.2 - 0.3, which corresponds with pore water in a coal fly ash column or the first leachate from a coal ash deposit. This model run leads to a

chemical speciation fingerprint (CSF) that can be used as the basis for subsequent modelling of transport.

#### 1.5.4 Modelling release in a laboratory percolation test

In LeachXS a dual porosity model has been developed to describe the simultaneous chemical reaction transport of substances through a layer of granular materials. This approach differs from the common Kd type of transport modelling in that here mutual reactions between substances are possible allowing precipitation and dissolution, while in Kd descriptions this aspect is not covered. In addition, changes in chemical conditions such as pH change and redox change can not be captured. This also implies a challenge as modelling such multitude of reactions is asking a lot from the chemical speciation code. An aspect not as well covered yet is the change in particulate (POM) and dissolved organic matter (DOC). Now the POM is assumed constant and the DOC is assumed to be washed out according to a certain decay function.

#### 1.5.5 Modelling release in an embankment scenario

The modelling of release in an embankment scenario makes use of the chemical speciation fingerprints (CSFs) of the different layers in the scenario. Here it is assumed that there is a soil cover layer, then a certain height of coal fly ash and then at the bottom again soil. This three layer model has been built in LeachXS to be able to generate the graphs and model results readily. This model is a full chemical reaction transport model for the source term and the covering and underlying soil. This in contrast to the Soil Quality Degree model described in the next section, which uses an independent release description for individual substances. Only as soon as the substances enter soil the full chemical interaction is considered.

#### 1.5.6 Modelling impact using SQD model

In The Netherlands, the ministry of Spatial Planning, Housing and the Environment has recently revised the Dutch building materials decree (1995) using a state of the art scenario modelling approach (Soil Quality Decree, 2007). The approach is based on the potential impact of materials on the environment using a specified application scenario. In this scenario, the groundwater at a specified distance from the application is the point of compliance (POC). The result of the assessment is a time dependent concentration profile in the groundwater and comparison of the peak concentration with WQS.

In this study, the leaching behaviour of a coal fly ash from Israel is tested under oxidised and under reduced conditions SQD scenario modelling approach (Verschoor et al., 2006; Verschoor et al., 2008). The application scenario for coal fly ash is given in Figure 2 and was used as input in LeachXS. The model contains three typical soil profiles: sand, peat and clay. Details of the soil profile characteristics can be found elsewhere (van Zomeren et al., 2009; Verschoor et al., 2008). The sand soil profile was used in the modeling assessment. In addition, the model assumes the groundwater level to be at 1m depth (average groundwater depth in the Netherlands). However, groundwater levels in Israel are mostly deeper than 1 m.

Scenario Granular Construction  
Product placed on soil

LeachXS:

Net precipitation

Water percolates through  
granular construction product

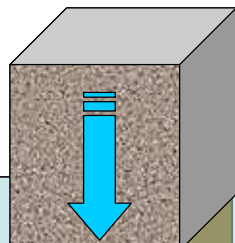
Free percolation in the soil

Unsaturated zone

Groundwater table (-1 m)



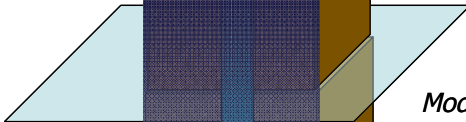
Net precipitation



*Select granular material in  
LeachXS, or user-defined  
(define height, bulk density, L/S  
time relationship)*



*Selection of soil below the  
application (properties of typical  
sand, peat, clay profiles)*



*Model output: dissolved  
concentrations at each depth or  
averaged between 1 and 2 m,  
solid phase concentrations*

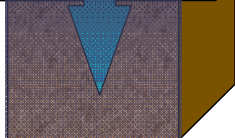


Figure 2 Overview of the “Granular Construction Products” scenario in leachXS. The scenario simulates the leaching of constituents from a granular construction product, and the transport in soil and groundwater. The model calculates concentrations in soil and groundwater as a result of chemical processes in soil such as pH-dependent sorption, inorganic and organic complexation and mineral precipitation.

The scenario involves an application of coal fly ash (oxidised and mildly reducing) with a height of 10 m and a net infiltration of 20 mm/yr (long-term average infiltration in Israel). The source term (concentration profile as a function of time) is given by the results of the upflow percolation leaching test (TS14405). Using information on the application height, density and infiltration rate, the L/S ratio from the laboratory test can be converted to a timescale. The concentration of contaminants entering the underlying soil system is input in the model calculations. To modify the description the pe+pH is modified in the percolation test modelling to derive a new release function under reducing conditions (Figure 3).

The next part of the scenario description is the soil type. Three general soil types are available. Here only the sandy soil was selected for the model scenarios. A summary of the generic soil properties can be found in van Zomeren et al. (2009) and in more detail in Verschoor (2006, in Dutch). The released contaminants are transported through the underlying soil into the groundwater at certain depth. The transport of contaminants is calculated using various reactions and adsorption/complexation models (“multi-surface approach”) using the Orchestra reactive transport approach. The impact of the released contaminants on the groundwater quality is subsequently calculated in the model.

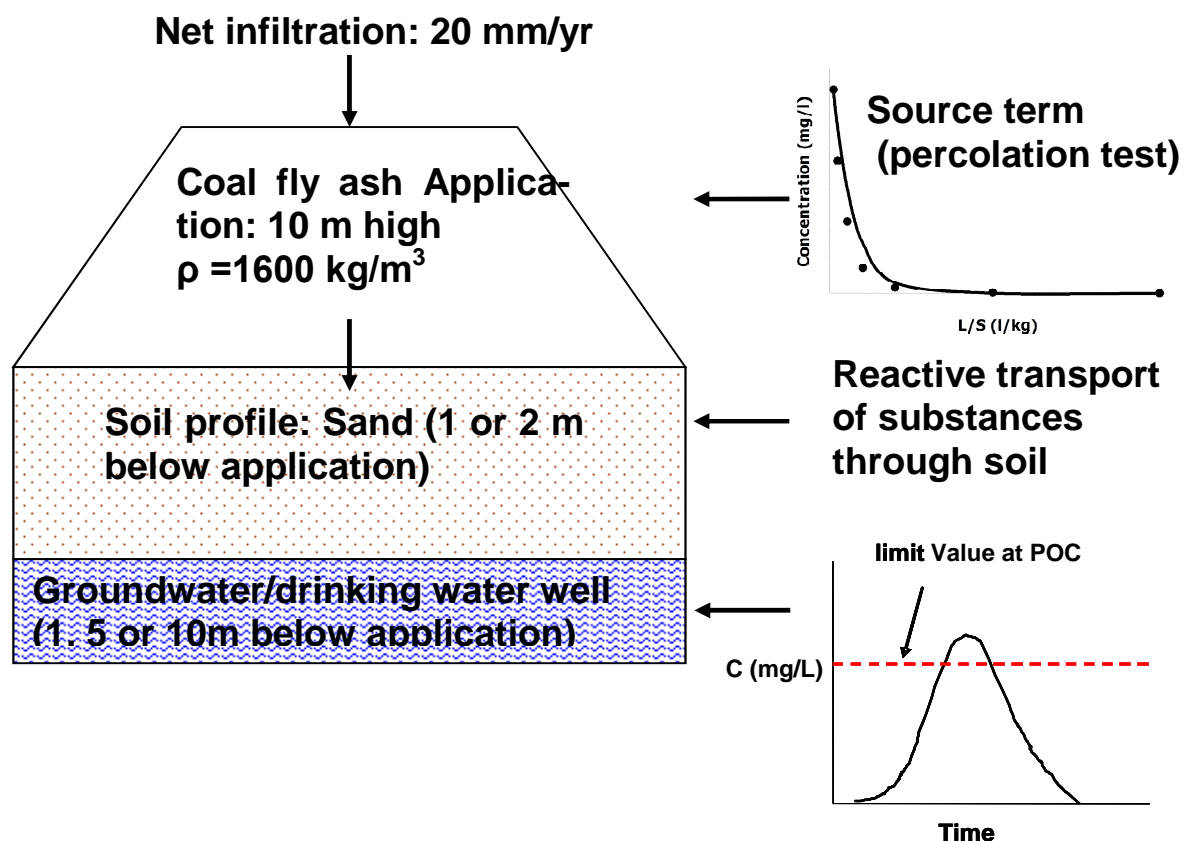


Figure 3 Example of current leach testing and comparison with water quality standards in the Dutch Soil Quality Decree (2008).

## 1.6 Evaluation of impact

From the combination of the laboratory leaching test data, the comparison with field data and the chemical speciation modelling an assessment can be made of the key release controlling factors in the case of coal fly ash application in embankment and road base applications. With the extensive data set in preparation in the US based on the same testing approach as described here a considerable basis for coal fly ash leaching behaviour can be foreseen leading to a benchmark for coal fly ash leaching behaviour from worldwide sources.

## 2. Results and discussion

### 2.1 Comparison of coal fly ash leaching

The leaching data for coal fly ash from laboratory results (pH dependence test data and percolation test) with data from older experiments (van der Sloot et al, 1982) and with field data is given in figures 4 and 5. Per element 3 graphs are presented. Release in mg/l as a function of pH, cumulative release as a function of L/S and concentration as a function of L/S. The elements Al, Cr, Mg, W, Na and Ca are shown. Al is solubility controlled, as the column experiment carried out with acid injection follows the pH dependence curve for Al remarkably well. Similarly, Mg is fully solubility controlled (brucite), as the concentrations in the percolation test with acid injection follow the pH dependence test pattern quite well. This supports the local equilibrium assumption applied in modelling impact by percolation. The Na release is as expected straight wash out (see concentration as a function of L/S. At  $L/S > 1$  the cumulative release curve turns horizontal indicating depletion of leachable Na. In the case of Ca, the laboratory column experiments show a higher leachability, as long as the pH is high (dissolution of  $\text{Ca}(\text{OH})_2$ ). The field experiments show a substantially lower Ca concentration and thus a lower cumulative release. This is due to more extensive carbonation (calcite precipitation). Cr release resembles that of Na, which implies that most of the leachable Cr is present as chromate, since Cr (III) is not leachable at high pH. W release from the column experiment carried out with acid injection follows the pH dependence curve for W quite well. It seems alkaline ashes at high pH are solubility limited, but as soon as pH drops the leachability increases to decrease again as pH drops below 7. This type of data comparison is also available for another 20 elements, which are not shown here, but which allow elements to be classified in exclusively solubility limited substances, non-interacting substances and elements with intermediate behaviour. This classification is very useful for the assessment of long term behaviour. For legend and pH of column tests see Annex C

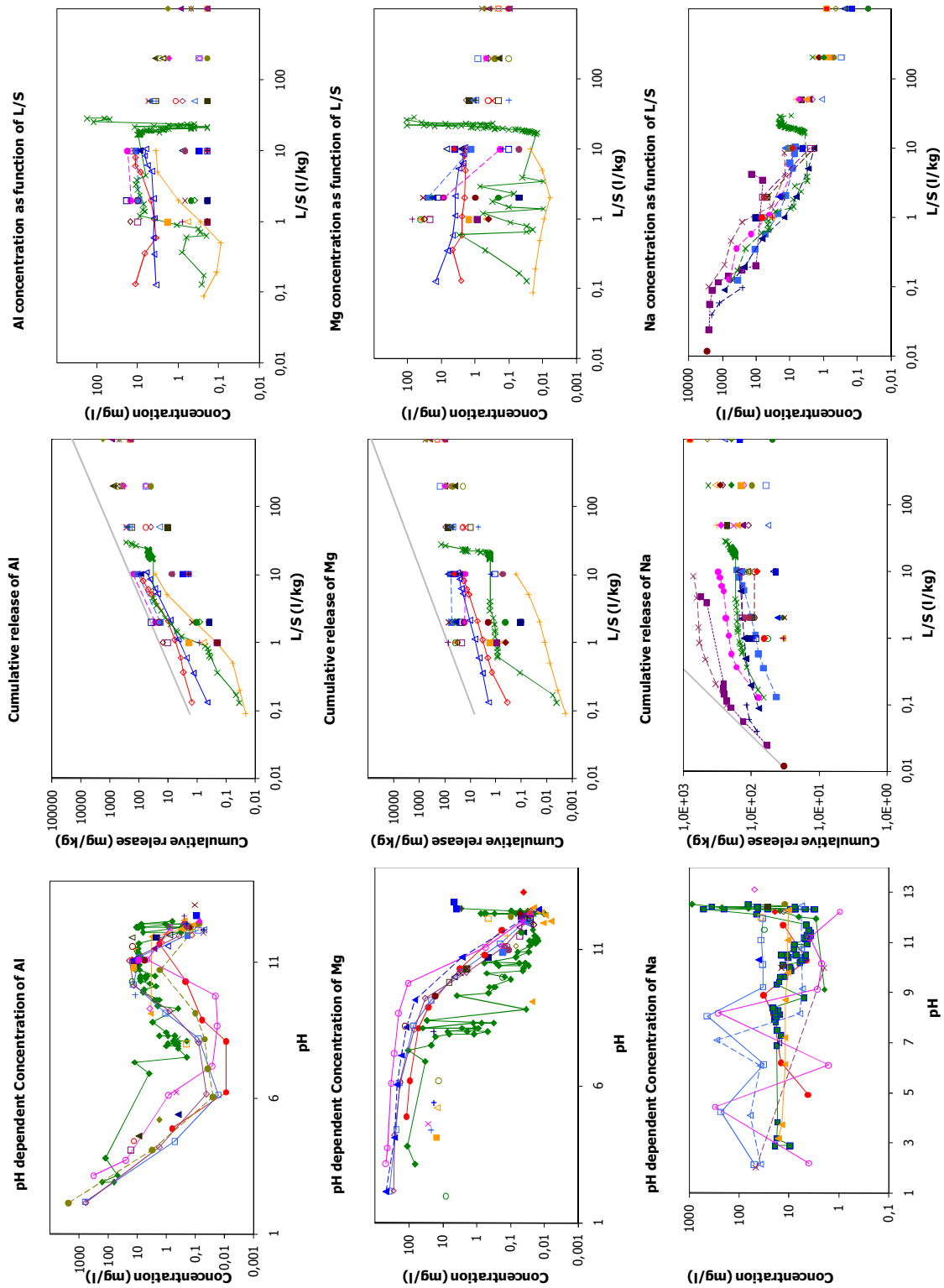




Figure 4 pH dependence test and percolation test data for Israeli coal fly ash in perspective with other coal fly ashes from similar installations, with lysimeter data and with data from a column experiment with acid infiltration.

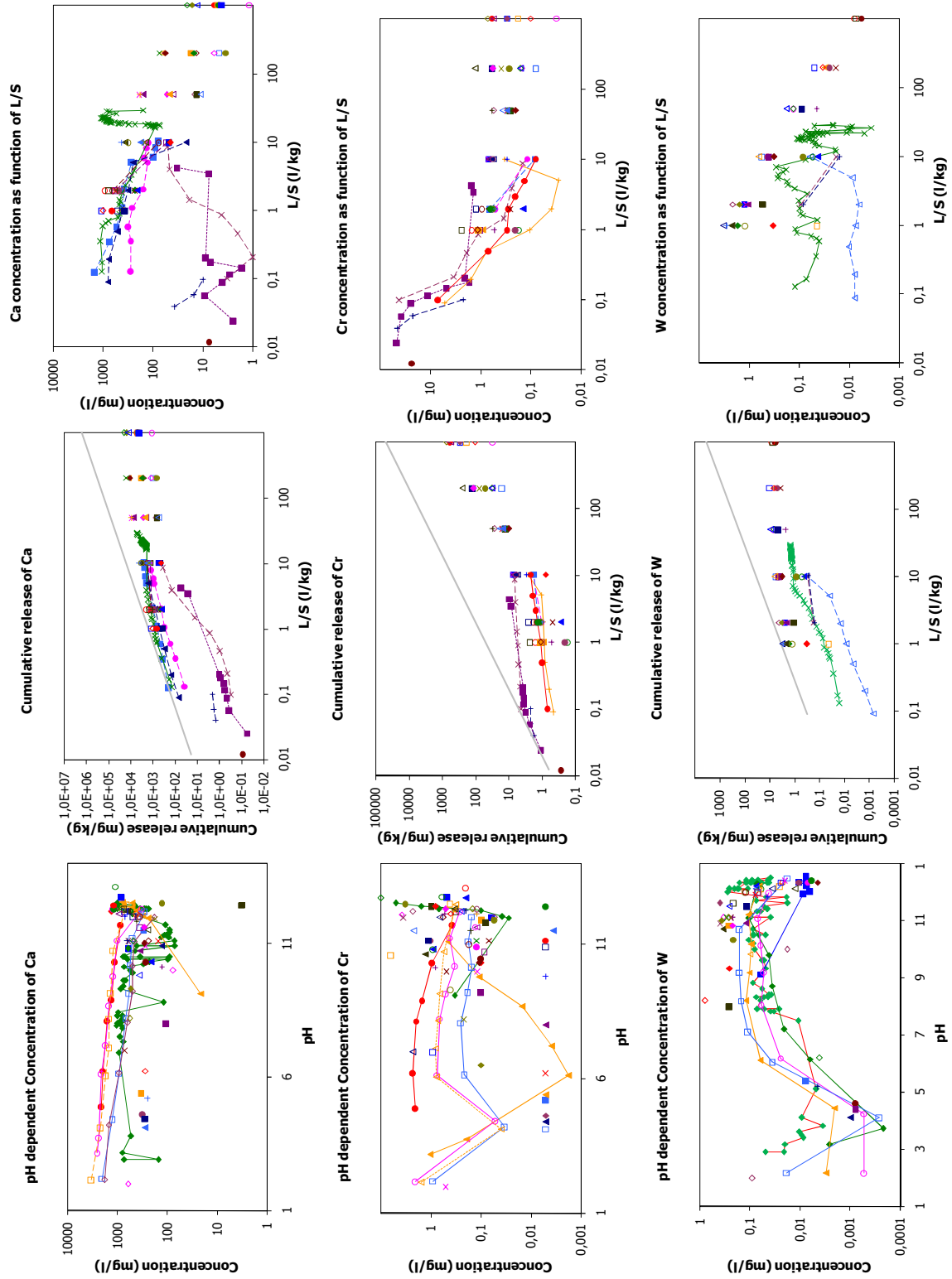


Figure 5 pH dependence test and percolation test data for Israeli coal fly ash in perspective with other coal fly ashes from similar installations, with lysimeter data and with data from a column experiment with acid infiltration.

## 2.2 Chemical speciation modelling of Israeli coal fly ashes

The pH is an important factor that determines the release of many constituents from coal fly ash. The native pH (without addition of acid/base) of coal fly ash (L/S=10 L/kg, 48 h) can vary from almost neutral (low Ca ashes) to alkaline. The two Israeli fly ashes studied in detail both fall in the alkaline range. In Table 2 the input parameters for the chemical speciation modelling are given. In all cases, the percolation test data (Dutch alkaline coal ash) are given for comparison, as the modelling is done both at L/S=10 and at L/S around 0.2 (all other parameters remaining the same) to assess the validity of the mineral and sorption parameter selection for both a wide pH range as well as a wide L/S range.

The starting point for the modelling are the L/S=10 leach test data (TS14429). The optimization of the mineral selection is based on obtaining a prediction that provides the closest fit between model and actual test results. The low L/S modelling (around 0.2) using the first fraction of the percolation test is meant to test, whether the same selection of minerals or a slight modification can simultaneously predict the release behaviour at low L/S under the assumption that local equilibrium prevails. As we have seen before this a very reasonable assumption. The L/S of around 0.2 reflects pore water conditions in the column. Based on the preliminary model run to determine SI values and expert knowledge (relevant mineral phases formed under ambient conditions) a preliminary set of minerals is identified to run the model. Based on a criterion of less than 1‰ of the element present in a given mineral phase, the selection of relevant minerals can be narrowed down.

Although some 25 elements are taken along in the chemical speciation modelling for the coal fly ash not all elements are presented here. The input parameters for the modelling are given in Table 2.

Table 2 Input for modelling pH dependence test data

Prediction case	Coal fly ash Orot_Rabin +col red17 Al Si opt	DOC/DHA data			
Speciation session	Coal fly ash NCAB	pH	[DOC] (kg/l)	DHA fraction	DHA] (kg/l)
Material	Coal_fly_ash_Orot_Rabin (P,1,1)	1,00	1,371E-06	0,10	1,371E-07
		2,17	1,200E-06	0,10	1,200E-07
Solved fraction DOC	0,2	4,42	7,000E-07	0,10	7,000E-08
Sum of pH and pe	17,00	6,10	1,900E-06	0,10	1,900E-07
L/S	10,1920 l/kg	8,19	4,000E-07	0,10	4,000E-08
Clay	1,000E-03 kg/kg	9,15	1,000E-07	0,10	1,000E-08
HFO	3,000E-03 kg/kg	10,17	1,090E-05	0,10	1,090E-06
SHA	1,000E-05 kg/kg	11,19	1,000E-07	0,10	1,000E-08
Percolation material	Coal_fly_ash_Geertruidenberg (C,1,1)	12,20	5,000E-07	0,10	5,000E-08
Avg L/S first perc. fractions	0,3000 l/kg	14,00	9,389E-07	0,10	9,389E-08
Polynomial coefficients					
		C0	-6,960E+00		
		C1	7,944E-02		
		C2	-2,418E-02		
		C3	1,275E-03		
		C4	0,000E+00		
		C5	0,000E+00		
Reactant concentrations					
Reactant	mg/kg				
Ag+	not measured	F-	not measured	NO3-	not measured
Al+3	4,679E+03	Fe+3	1,554E+02	Pb+2	5,653E-01
H3AsO4	4,812E+00	Hg+2	not measured	PO4-3	4,461E+03
H3BO3	1,163E+02	I-	not measured	Sb[OH]6-	2,501E-01
Ba+2	2,142E+01	K+	2,006E+02	SeO4-2	5,236E-01
Br-	not measured	Li+	1,052E+01	H4SiO4	7,468E+03
Ca+2	2,083E+04	Mg+2	4,032E+03	SO4-2	2,859E+03
Cd+2	1,613E-01	Mn+2	7,906E+01	Sr+2	3,949E+02
Cl-	2,208E+02	MoO4-2	3,489E+00	Th+4	not measured
CrO4-2	2,117E+01	Na+	1,500E+02	UO2+	not measured
Cu+2	5,951E+00	NH4+	not measured	VO2+	8,530E+01
H2CO3	2,072E+03	Ni+2	9,287E+00	Zn+2	1,829E+01
Selected Minerals					
AA_2CaO_Al2O3_8H2O[s]	AA_Magnesite	Cr[OH]3[A]	Pb2V2O7		
AA_2CaO_Al2O3_SiO2_8H2O[s]	AA_Portlandite	Cr[OH]3[C]	Pb3[VO4]2		
AA_2CaO_Fe2O3_8H2O[s]	AA_Tobermorite-I	Fe_Vanadate	PbCrO4		
AA_2CaO_Fe2O3_SiO2_8H2O[s]	Akerminite	Fluorite	PbMoO4[c]		
AA_3CaO_Al2O3_6H2O[s]	alpha-TCP	Forsterite	Pyrite		
AA_3CaO_Al2O3_CaCO3_11H2O[s]	BaCaSO4[50%Ba]	Galena	Rhodochrosite		
AA_3CaO_Fe2O3_6H2O[s]	BaSrSO4[50%Ba]	Magnesite	Sb[OH]3[s]		
AA_Al[OH]3[am]	beta-TCP	Manganite	Sepiolite[c]		
AA_Anhydrite	Blaubleil	Millerite	Sphalerite		
AA_Brucite	Blaubleill	MnS[Green]	Strontianite		
AA_Calcite	Ca2Cd[PO4]2	Ni[OH]2[s]	Tenorite		
AA_CaO_Al2O3_10H2O[s]	Ca4Cd[PO4]3OH	Ni2SiO4	Wairakite		
AA_Fe[OH]3[am]	CaZincate	OCP	Willemite		
AA_Gypsum	Cd[OH]2[C]	Otavite	Zincite		
AA_Jennite	Cinnabar	Pb[OH]2[C]	ZnSiO3		

The complete results of the pH dependent leaching tests on the two Israeli coal fly ashes are given in Appendix B. In figure 6, 7 and 8 the results for are shown.

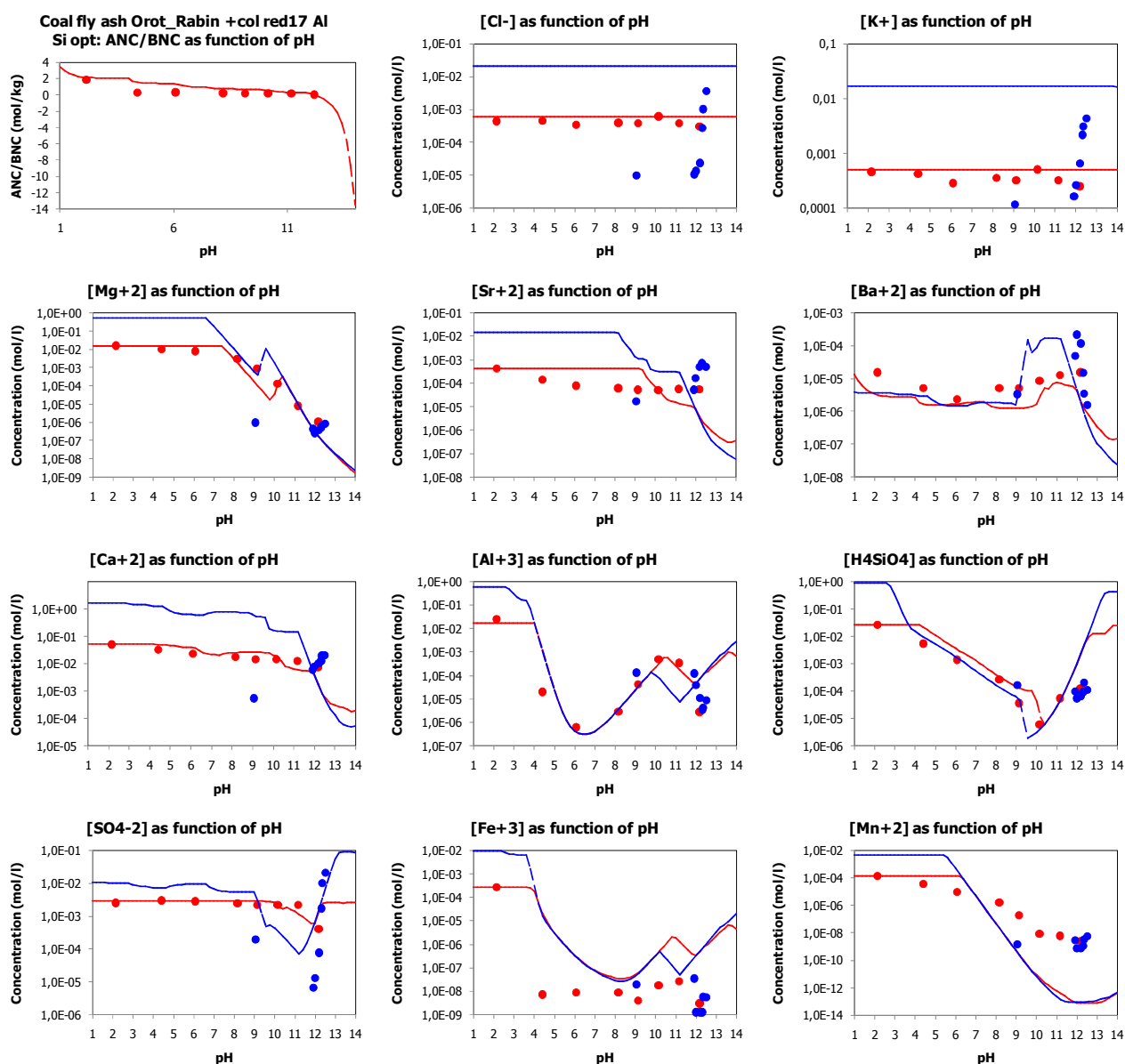


Figure 6 Measured and predicted leaching behaviour of major and minor as a function of pH in the coal fly ash OR. Solid circles: pH dependence test; triangles: percolation test data; line: prediction at L/S=10; dotted line: prediction at L/S=0.2. Although species are given in some cases, the concentrations reflect element concentrations.

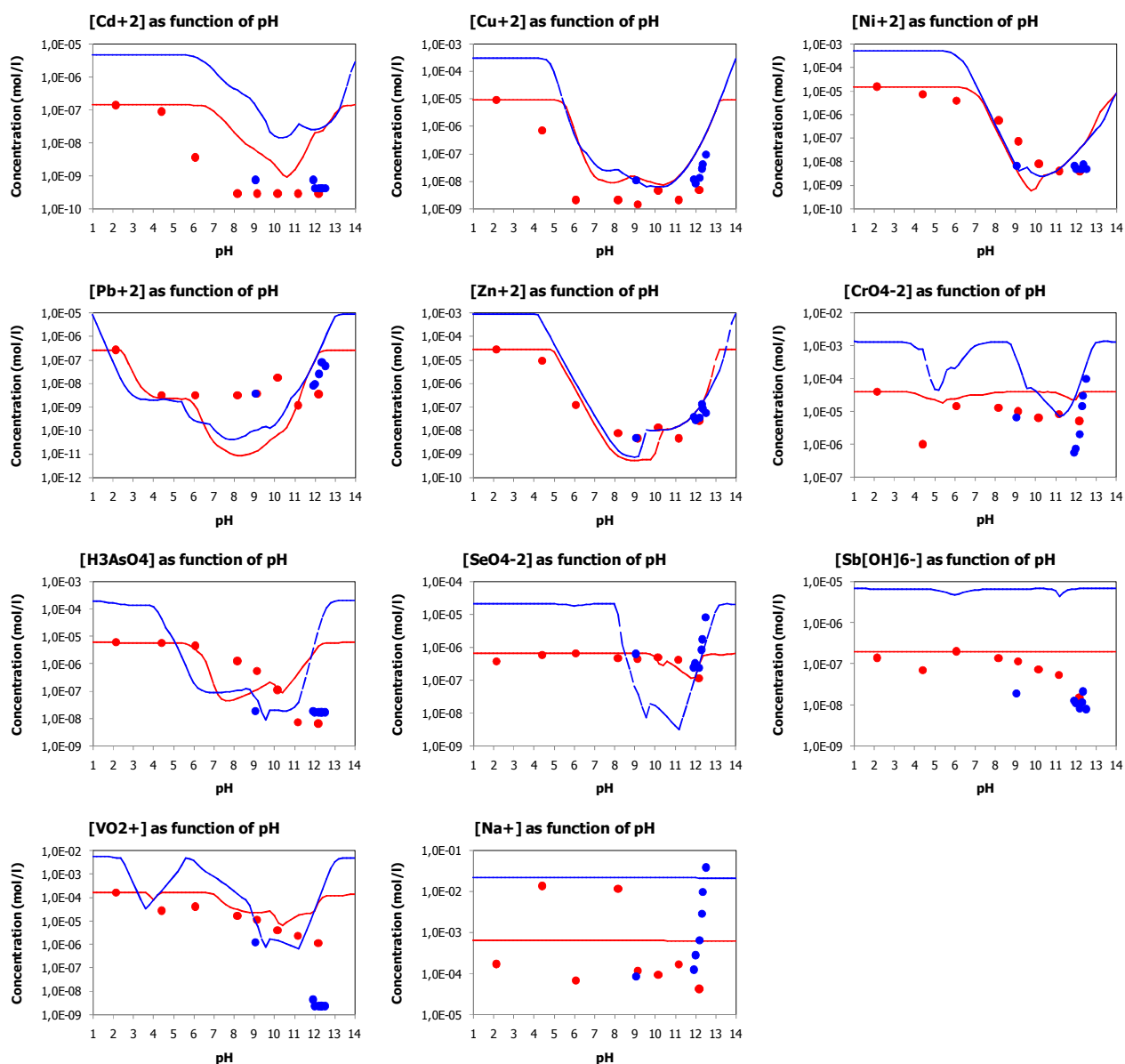


Figure 7 Measured and predicted leaching behaviour of trace elements as a function of pH in the coal fly ash OR. Solid circles: pH dependence test; triangles: percolation test data; line: prediction at L/S=10; dotted line: prediction at L/S=0.2. Although species are given in some cases, the concentrations reflect element concentrations.

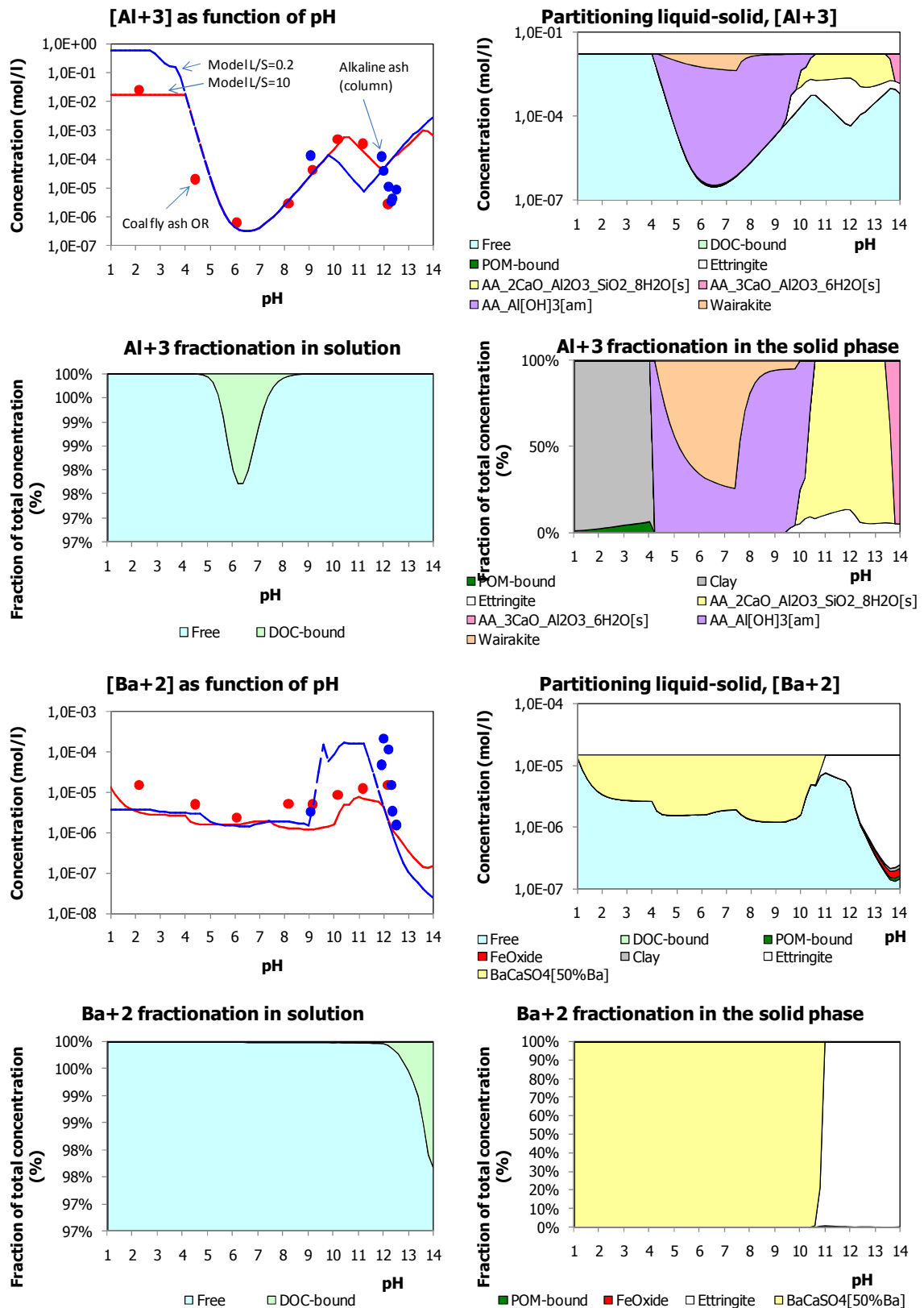


Figure 8 Major (Ca) and minor (Ba) element partitioning from chemical speciation modelling of the coal ash OR using TS 14429 (solid dots) and TS 14405 data (triangles). Line and dotted line: model predictions at L/S=10 and L/S=0.3 respectively. Partitioning in the solution and in the solid is given.

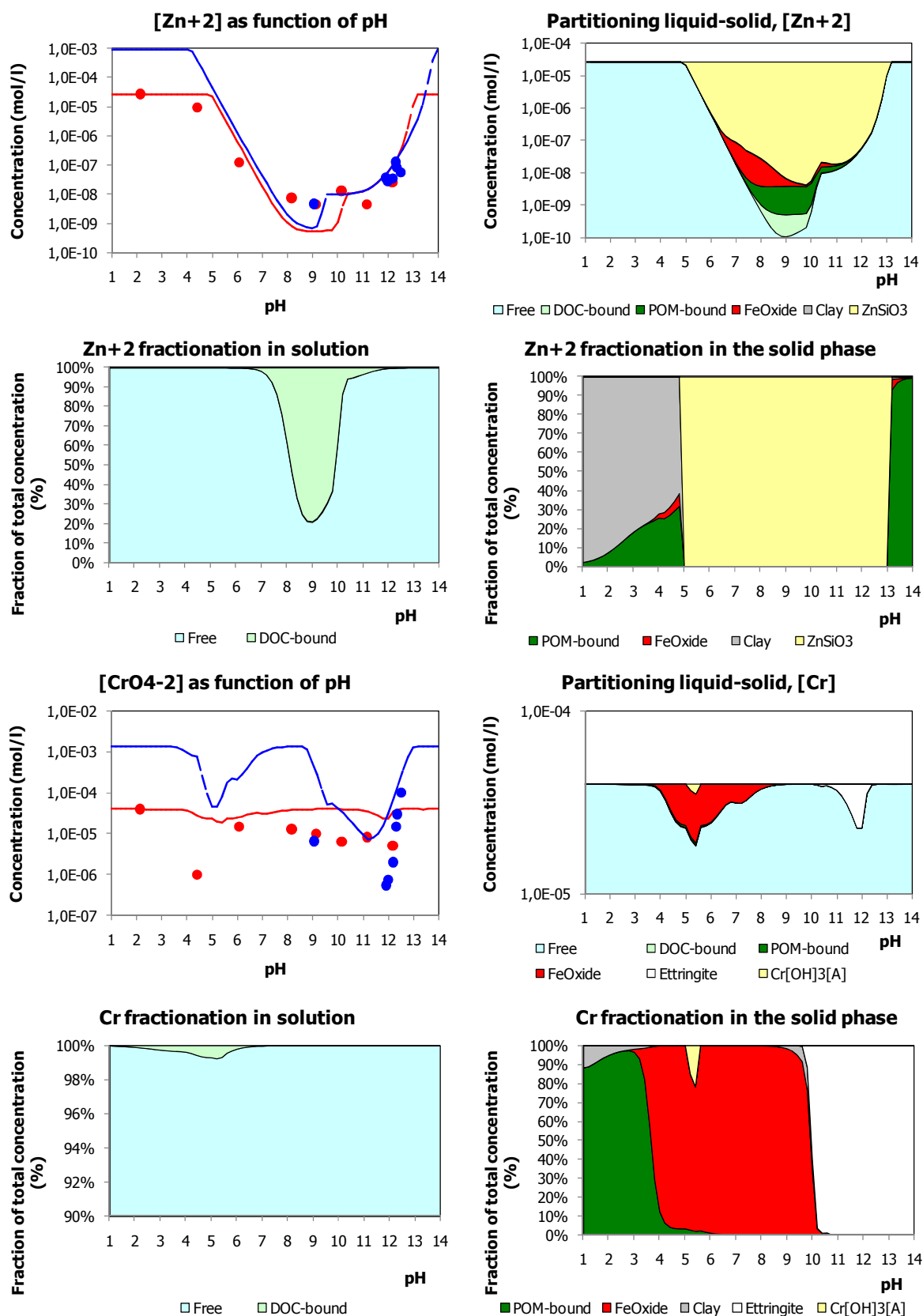


Figure 9 Trace element (Zn, Cr) partitioning from chemical speciation modelling of the coal ash OR using TS 14429 (solid dots) and TS 14405 data (triangles). Line and dotted line: model predictions at L/S=10 and L/S=0.3 respectively. Partitioning in the solution and in the solid is given.



Using the same model description in terms of mineral selection and sorptive parameters to the extent that they were missing from the original data set, coal fly ash R has been modelled for its chemical speciation fingerprint to see to what extent the measurements and the model prediction match for this ash based on the CSF of coal ash OR. In figure 10 the model results are given.

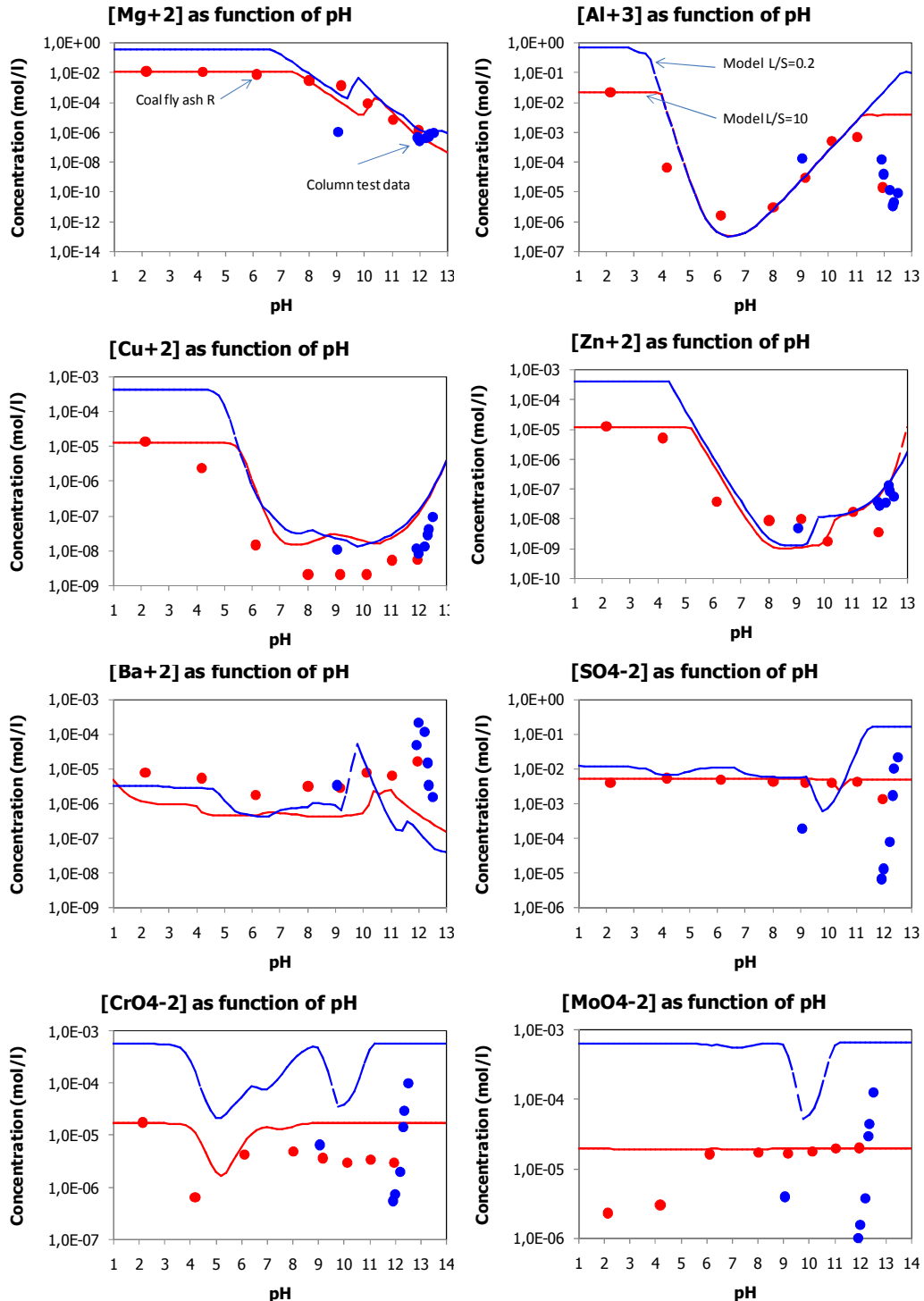


Figure 10 Measured and predicted leaching behaviour of major, minor and trace elements as a function of pH in the coal fly ash R. Solid circles: pH dependence test; triangles: percolation test data; line: prediction at L/S=10; dotted line: prediction at L/S=0.2. Although species are given in some cases, the concentrations reflect element concentrations.

This match is already quite acceptable and indicates that a CSF of another alkaline ash can be used to describe the release from another ash. The extent to which this CSF can be applied to a wider spectrum of coal fly ashes needs to be verified on coal ash from a wider range of sources.

### 2.2.1 Modelling percolation test data

Starting from the chemical speciation fingerprints (CSF) of the Israeli coal fly ash model predictions have been carried out using a dual porosity model coupled to chemical speciation calculations (Dijkstra, 2007; Grathwohl and van der Sloot, 2007) to describe the release from a percolation test carried out with an alkaline coal fly ash, since column data are not available for the same ash. For the column the following parameters are needed: the initial pH, the porosity of the packed column, the density of the material and the height of the packed column. A diffusion distance between stagnant and mobile phase is assumed, which is calibrated on the release of non-interacting elements (usually salts like Na, Cl). Once this parameter is fixed the initial pH is adjusted to be able to predict the pH response as measured. In the model approach local equilibrium dictated by the mineral and sorptive phases as determined in the modelling of pH dependence test (table 2) is assumed. At the start, concentrations throughout the column are assumed to be the same. Normally, the leachant is demineralised water, which has very low concentrations of all substances in the materials. A constant flow is assumed for the duration of the test. For the prediction of pH in the effluent from the column test, it is necessary to assume a certain level of dissolved carbonate in the feed solution or else it is not possible to describe the pH development properly. In Table 3 the model parameters for the coal fly ash column are given.

As a prediction of DOC from the organic matter content of the solid is not (yet) possible, we have used the DOC data as measured in the percolation test. These data have been corrected to obtain the reactive fraction of DOC (DHA) relevant for metal interaction. A power function fit is used based on the equation:  $DHA_{L/S} = q_2 + q_0 \cdot e^{-q_1 \cdot L/S}$ , which gives at present the best possible description for DHA at intermediate L/S values necessary for modelling.

Table 3 Input parameters for chemical reaction transport modelling of coal fly ash.

Case	Coal fly ash Orot_Rabin + col Ox 17 Al Si opt				
Solved fraction DOC	0,2	[DOC/DHA data]			
Sum of pH and pe	17,00	L/S	[DOC] (kg/l)	DHA fraction [DHA] (kg/l)	
Clay	1,000E-03 kg/kg	0,09	1,520E-05	0,20	3,040E-06
HFO	3,000E-03 kg/kg	0,19	7,700E-06	0,20	1,540E-06
SHA	1,000E-05 kg/kg	0,50	3,000E-06	0,20	6,000E-07
Porosity Fraction	0,3	0,99	1,400E-06	0,20	2,800E-07
Density	2 kg/l	1,99	6,000E-07	0,20	1,200E-07
Initial ph (solid)	12,6	5,02	6,000E-07	0,20	1,200E-07
Initial ph (liquid)	5	10,03	1,000E-06	0,20	2,000E-07
Column length	5 cm	Curve fitting coefficients		Q0	9,625E-07
Rel. stagnant volume	15 %			Q1	2,000E+00
Eff. diffucion dist.	3 cm			Q2	1,300E-07
Reactant concentrations					
Reactant	mg/kg	Reactant	mg/kg	Reactant	mg/kg
Ag+	not measured	F-	not measured	NO3-	not measured
Al+3	4,679E+03	Fe+3	1,554E+02	Pb+2	5,653E-01
H3AsO4	4,812E+00	Hg+2	not measured	PO4-3	4,461E+03
H3BO3	1,163E+02	I-	not measured	Sb[OH]6-	2,501E-01
Ba+2	2,142E+01	K+	2,006E+02	SeO4-2	5,236E-01
Br-	not measured	Li+	1,052E+01	H4SiO4	7,468E+03
Ca+2	2,083E+04	Mg+2	4,032E+03	SO4-2	2,859E+03
Cd+2	1,613E-01	Mn+2	7,906E+01	Sr+2	3,949E+02
Cl-	2,208E+02	MoO4-2	3,489E+00	Th+4	not measured
CrO4-2	2,117E+01	Na+	1,500E+02	UO2+	not measured
Cu+2	5,951E+00	NH4+	not measured	VO2+	8,530E+01
H2CO3	2,072E+03	Ni+2	9,287E+00	Zn+2	1,829E+01
Initial water concentrations					
	Reactant	mol/l	Reactant	mol/l	
	All	1,000E-09	H2CO3	3,000E-06	
Selected Minerals					
AA_2CaO_Al2O3_8H2O[s]	AA_Magnesite	Cr[OH]3[A]	Pb2V2O7		
AA_2CaO_Al2O3_SiO2_8H2O[s]	AA_Portlandite	Cr[OH]3[C]	Pb3[VO4]2		
AA_2CaO_Fe2O3_8H2O[s]	AA_Tobermorite-I	Fe_Vanadate	PbCrO4		
AA_2CaO_Fe2O3_SiO2_8H2O[s]	Akermanite	Fluorite	PbMoO4[c]		
AA_3CaO_Al2O3_6H2O[s]	alpha-TCP	Forsterite	Pyrite		
AA_3CaO_Al2O3_CaCO3_11H2O[s]	BaCaSO4[50%Ba]	Galena	Rhodochrosite		
AA_3CaO_Fe2O3_6H2O[s]	BaSrSO4[50%Ba]	Magnesite	Sb[OH]3[s]		
AA_Al[OH]3[am]	beta-TCP	Manganite	Sepiolite[c]		
AA_Anhydrite	Blaubleil	Millerite	Sphalerite		
AA_Brucite	Blaubleill	MnS[Green]	Strontianite		
AA_Calcite	Ca2Cd[PO4]2	Ni[OH]2[s]	Tenorite		
AA_CaO_Al2O3_10H2O[s]	Ca4Cd[PO4]3OH	Ni2SiO4	Wairakite		
AA_Fe[OH]3[am]	CaZincate	OCP	Willemite		
AA_Gypsum	Cd[OH]2[C]	Otavite	Zincite		
AA_Jennite	Cinnabar	Pb[OH]2[C]	ZnSiO3		

SHA = humic acid fraction in the solid phase; DHA = humic acid fraction in dissolved organic matter; mineral selection is the same as in Table 2.

Although as input for the prediction the CSF for coal fly ash OR has been used, it must be realised that the data of release in a column experiment shown belong to an alkaline Dutch coal fly ash. This may lead to some differences. Carrying out a full column experiment on Israeli coal fly ash would eliminate uncertainty in this respect. In spite of that, the results of salt wash out is described well as depicted in figure 11. The data for the samples taken from the Hadeira embankment and extracted at L/S=10 at own pH match rather well. The prediction of pH is quite acceptable, however, at L/S=10 the pH is much lower than predicted. This is related to the long time the eluate stands in contact with the atmosphere in the last time step of the test. This pH reduction does not reflect the behaviour of the ash in the column, This stresses the need to avoid CO<sub>2</sub> uptake in the collection vessel, The release of Mg indicates that this is a side effect of the test, as Mg does not increase in leachability as would be expected based on a significant pH change. This problem can be solved by flushing N<sub>2</sub> in the collection bottle or apply a CO<sub>2</sub> trap in the collection unit (recommended improvements of the test procedure).

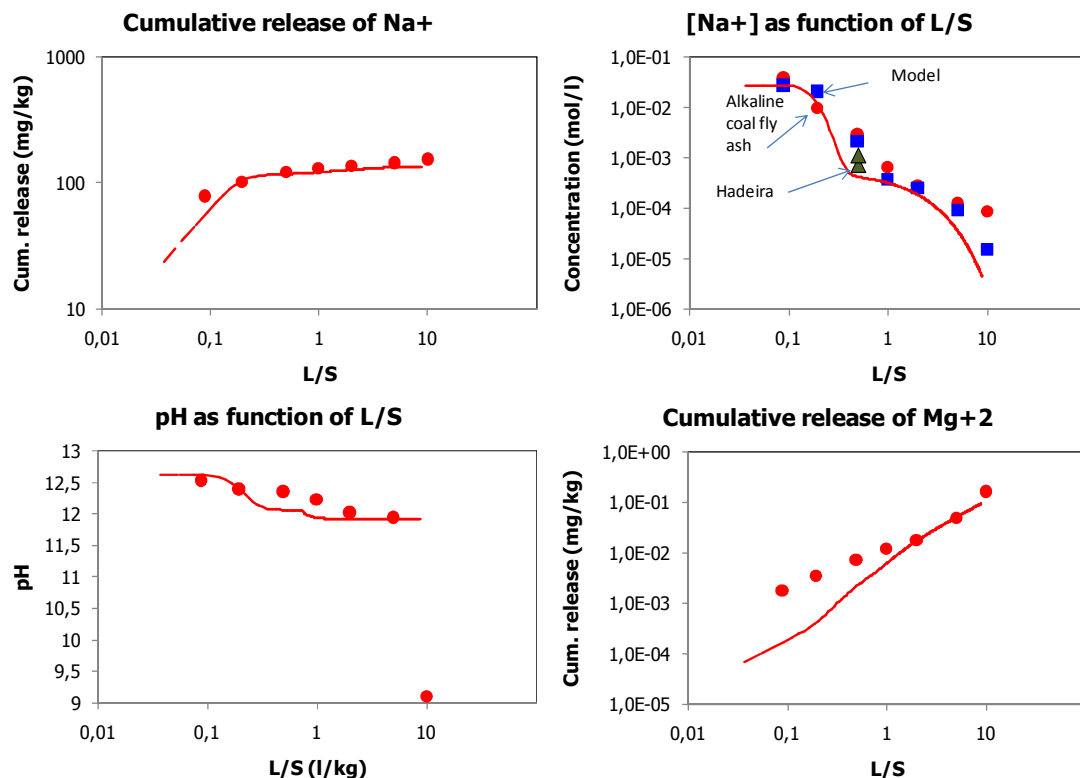


Figure 11 Measured (solid dots) and predicted release (line: continuous concentration change; open circles: calculated concentrations corresponding with the measurement points) in a column test (TS 14405) on the coal fly ash.

The prediction of trace element release from a percolation test is not easily done, when the conditions is that all elements need to be matched simultaneous. In most cases elements are modelled one by one, but this may lead to conflicting descriptions for the same sample. When the pH dependence test data are not fully matched than the prediction of release under the low L/S conditions in the field is a big challenge. Also here the effect of the composition of the ash that was used for modelling (alkaline Dutch coal fly ash) and the actual coal ash modelled (coal fly ash OR) may lead to differences that have nothing to do with the model and everything with the lack of proper data for comparison. As leaching of trace elements is often taking place at minor fractions of the total content, a deviation between modelling and measurement of a factor of 3 to 5 is actually quite good. Important is also the pattern of release as that reflects the release mechanism (wash-out, solubility limitations, etc). In figure 12 results are given for Cr, Mo, SO<sub>4</sub>, Sr, Zn and Cu.

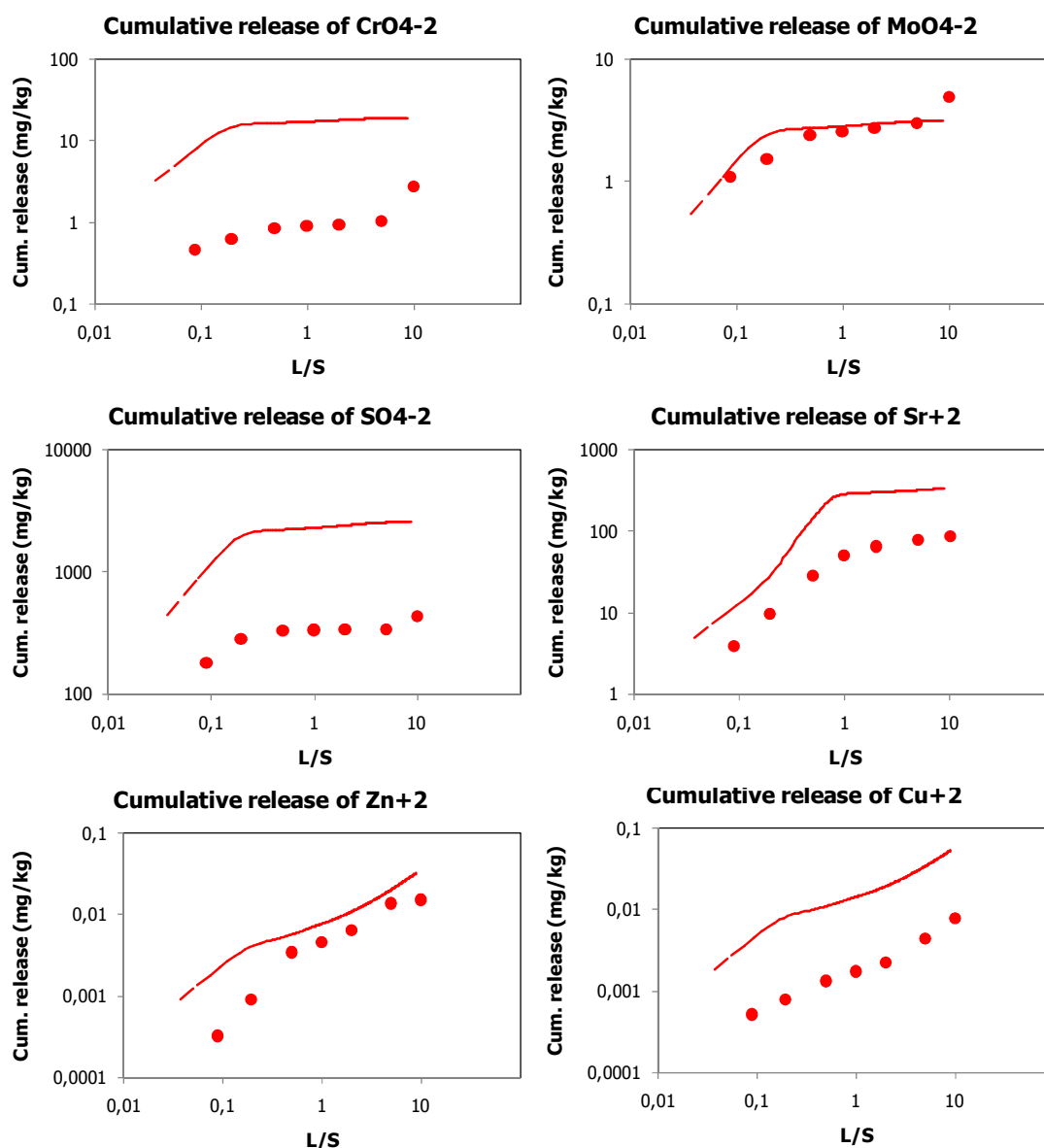


Figure 12 Measured (solid dots) and predicted cumulative release (line: continuous concentration change; open circles: calculated concentrations corresponding with the measurement points) in a column test (TS 14405) on the coal fly ash

In addition to the concentration in the outlet of the column, the modelling also provides insight in the concentration profiles along the column in solid and liquid phase. In figure 13 this type of information is given for Ca. As can be noted from the figure it is important to show data in both linear and logarithmic Y-axis, as the low concentration in solution will not show in a linear graph. On the other hand any partitioning at high concentration is lost in a logarithmic graph. This type of modelling can be very useful in case samples have been taken along the length of the column.

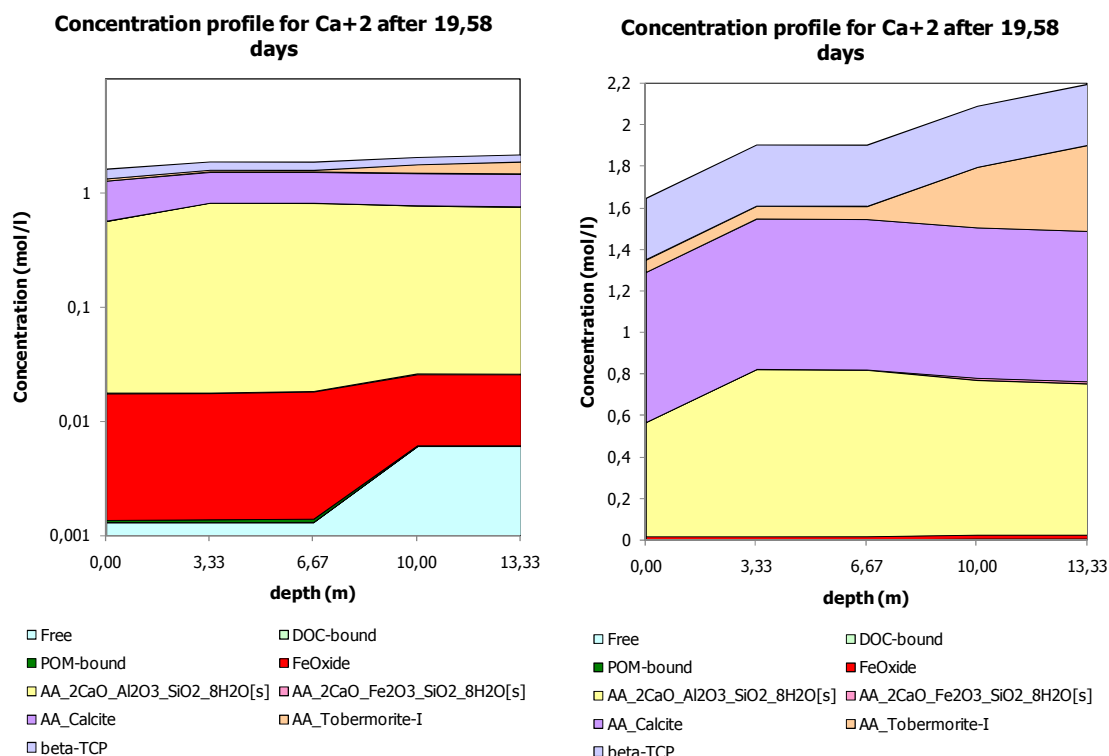


Figure 13 Calcium partitioning from chemical reaction transport modelling of alkaline coal fly ash using TS 14405 as a function of depth at a specified time (19 days) in linear and logarithmic scale. The mineral phases are all expressed as concentrations in Mol/l in a unit volume.

## 2.2.2 Modelling release from an embankment

For assessing the release from an embankment the CSF for coal fly ash OR is used as a starting point. The input parameters are largely the same as those specified in table 2 and 3, where the input for the percolation test model are given. The model has been run with varying conditions of redox status in the embankment (Figure 14). One is assuming fully oxidized conditions in the embankment and then a series of runs were done with other pH + pe conditions. The results shown here relate to the effects on the release of Cr, which under mildly reducing conditions convert from Cr VI to Cr III. The mildly reducing conditions will not affect some of the other oxyanions released from coal fly ash, such as B and Mo, which are not changed in their release behavior under reducing conditions (Figure 15).

In coal fly ash Cr is partly present as Cr (VI). The proportion can be quantified by analysing the amount of Cr leached at pH between 10 and 10.5 (maximum leachability of oxyanions). When in the field reducing conditions develop, Cr (VI) produced in the kiln (similar to Cr VI production in Portland cement production; van der Sloot et al, 2001) can slowly convert to Cr(III). Whether this takes place is currently unknown. Based on the modelling we can see that modelling at pH+pe values ranging from fully oxidised at 17 to 11 (mildly reducing), that at a pH+pe of around 12.5 a reduced Cr concentration is predicted that matches with the observed concentrations in samples taken from the Hadeira embankment. From this it is clear that the reducing does not have to be very strong to facilitate this conversion to the less toxic Cr(III). Independent confirmation of the redox status of the embankment would be necessary to verify whether the release behaviour has been adequately predicted. In case of Cr as Cr (VI) the release is dominated by washout. Only at high pH initially there may be some retention due to ettringite incorporation. Mo is washout out, as it shows the same release behaviour as soluble salts (Na). B partly

washes out, but is in part retained. The chemical form of B is not known and thus the model prediction of the pH dependence test and the percolation test is off.

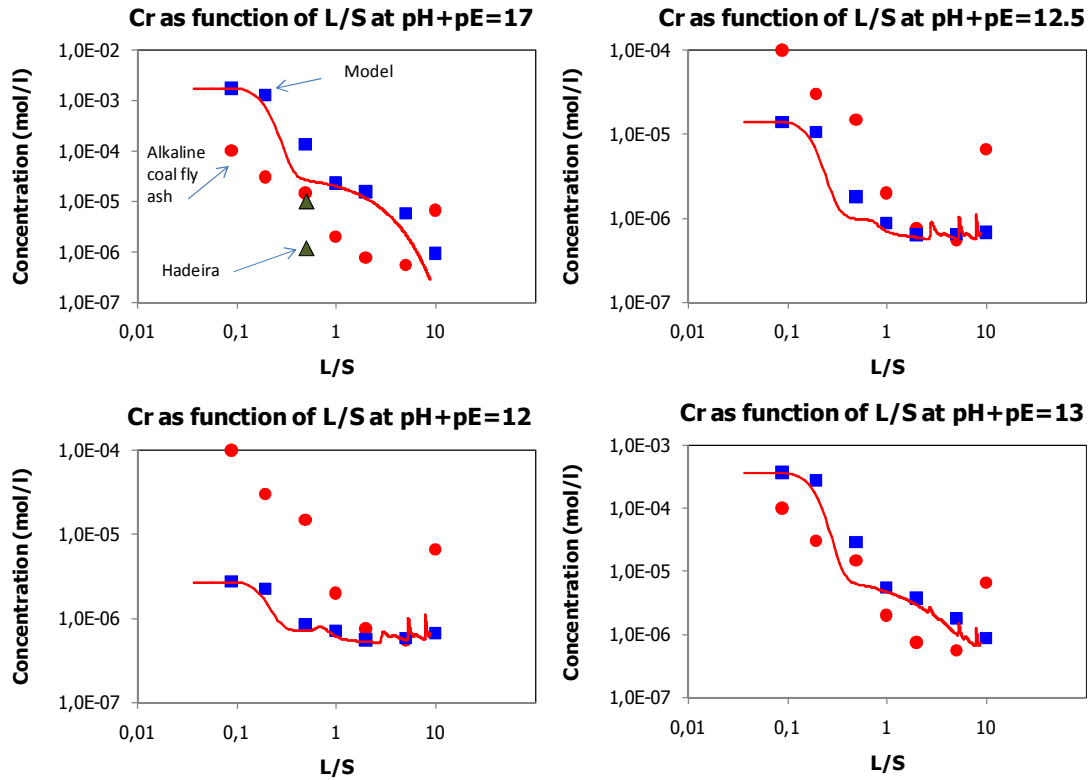


Figure 14 Model predictions of Cr release based on CSF for coal fly ash OR at pH+pe values 17 (oxidised), 13, 12.5 and 12 in comparison with release from alkaline Dutch fly ash and samples extracted at L/S=10 from the Hadeira embankment.

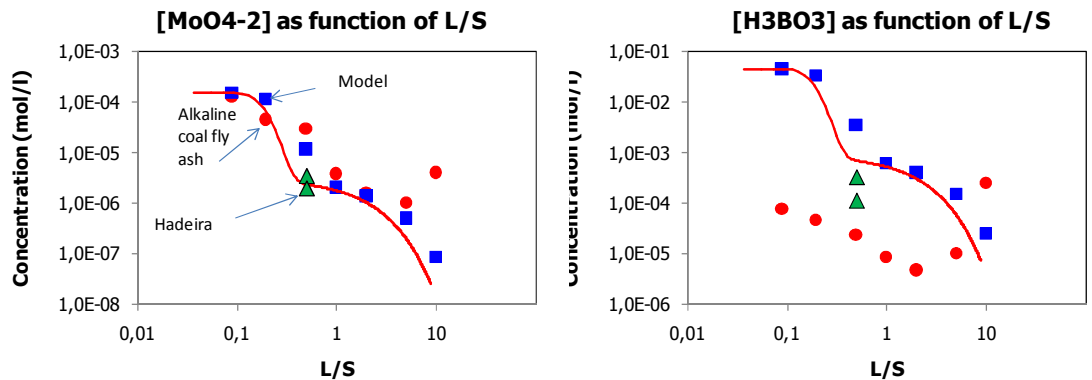


Figure 15 Model predictions of Mo and B release based on CSF for coal fly ash OR at pH+pe value 17 (oxidised and mildly reducing – no difference) in comparison with release from alkaline Dutch fly ash and samples extracted at L/S=10 from the Hadeira embankment.

### 2.2.3 Mechanistic impact model with 3 layers (top cover – material - subsoil)

Based on the CSF's for a top soil, the coal fly ash embankment material and a subsoil, a model run has been carried out. The conditions are specified in table 4.

The run has been done under oxidised conditions (fresh ash) and under mildly reducing conditions ( $\text{pH}+\text{pe}=11$ ). The results are given in figure 16.

Under oxidised conditions at high pH a significant portion of the Cr in fly ash is present as chromate and is very mobile. The chromate front moves out of the ash into the subsoil. Under mildly reducing conditions, the Cr is present largely as Cr III. Only upon entering the oxidised subsoil (assumption in the model) some transformation to Cr VI may occur. As conversion of from Cr III to Cr VI is kinetically slow, it is not very likely to occur in the field. This model study should not be viewed as a final result, as several conditions are not optimised for the local conditions. The flow rate selected is too high to be realistic for field conditions. However, to be able to show effects within a reasonable computation time, this flow rate was selected. The results are mostly to show the current capabilities once the relevant input parameters are available.

Table 4 Input parameters for 3 layer chemical reaction transport model.

Properties	Topsoil	Coal fly ash	Subsoil
pH+pe	15	11	15
pH initial	6.5	12	6.5
porosity	0.3	0.3	0.3
Density (kg/dm <sup>3</sup> )	1.8	1.8	1.8
Height (m)	1	5	1
Stagnant zone (%)	50	70	50
Transfer from stagnant zone (cm)	3	10	3
Hydrated Feoxide (kg/kg)	0.002	0.008	0.0002
Solid Humic Acid (kg/kg)	0.01	0.0002	0.01
Feed solution	pH 6	H <sub>2</sub> CO <sub>3</sub> (mol/l) 3e-4	pH+pe 15
Flow rate (l/m <sup>2</sup> /s)	1e-5		



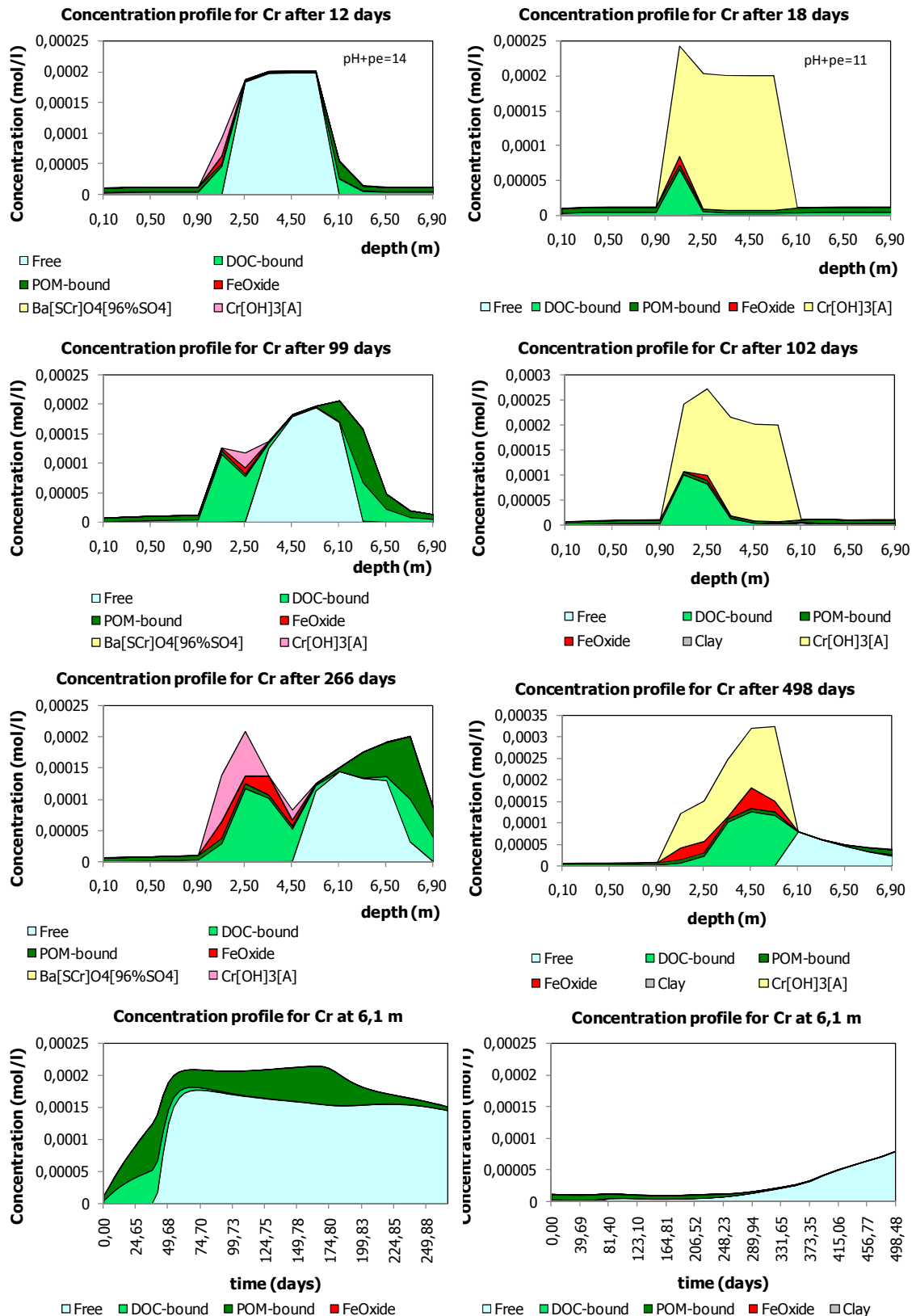


Figure 16. Results of mechanistic modelling of Cr release from coal fly ash under oxidised and mildly reducing conditions showing concentration profiles and partitioning of phases at three exposure times as a function of depth over the 3 layers – topsoil – coal fly ash – subsoil. The two bottom figure show the concentration and partitioning as a function of time at 10 cm underneath the coal fly ash in the subsoil

#### 2.2.4 Release model according to Dutch SQD

Based on the description of the release in a percolation test, the release to soil and groundwater according to the Soil Quality Decree (2008; replacement of the Building Materials Decree, 1995) can be provided. In this case, sand is used as the underlying soil. The sand profile reflects an averaged sandy soil, which does not necessarily match with Israeli soil. Only a small example of the possibilities is given here as the data to base this on are not yet available for Israeli coal fly ashes. In figure 17 a selection of profiles at a specified depth are given for .....

The case for Cr is special as a run has been made with oxidised conditions (fly ash as obtained from a power plant) and with mildly reducing conditions (expected behaviour in an embankment). In figure 18 the comparison between oxidised and mildly reducing conditions are shown. In this case, the mildly acidic conditions (pH 4.9) in the receiving soil results in an equilibrium situation, where Cr is present as Cr (III). The kinetics may be slow in reality and as such release of Cr as chromate to some extent may occur. In the SQD model, the soil pH is not expected to change as a result of input of alkalinity from the fly ash. This is a limitation of the model. The 3 layer model presented before does take these changes into account.

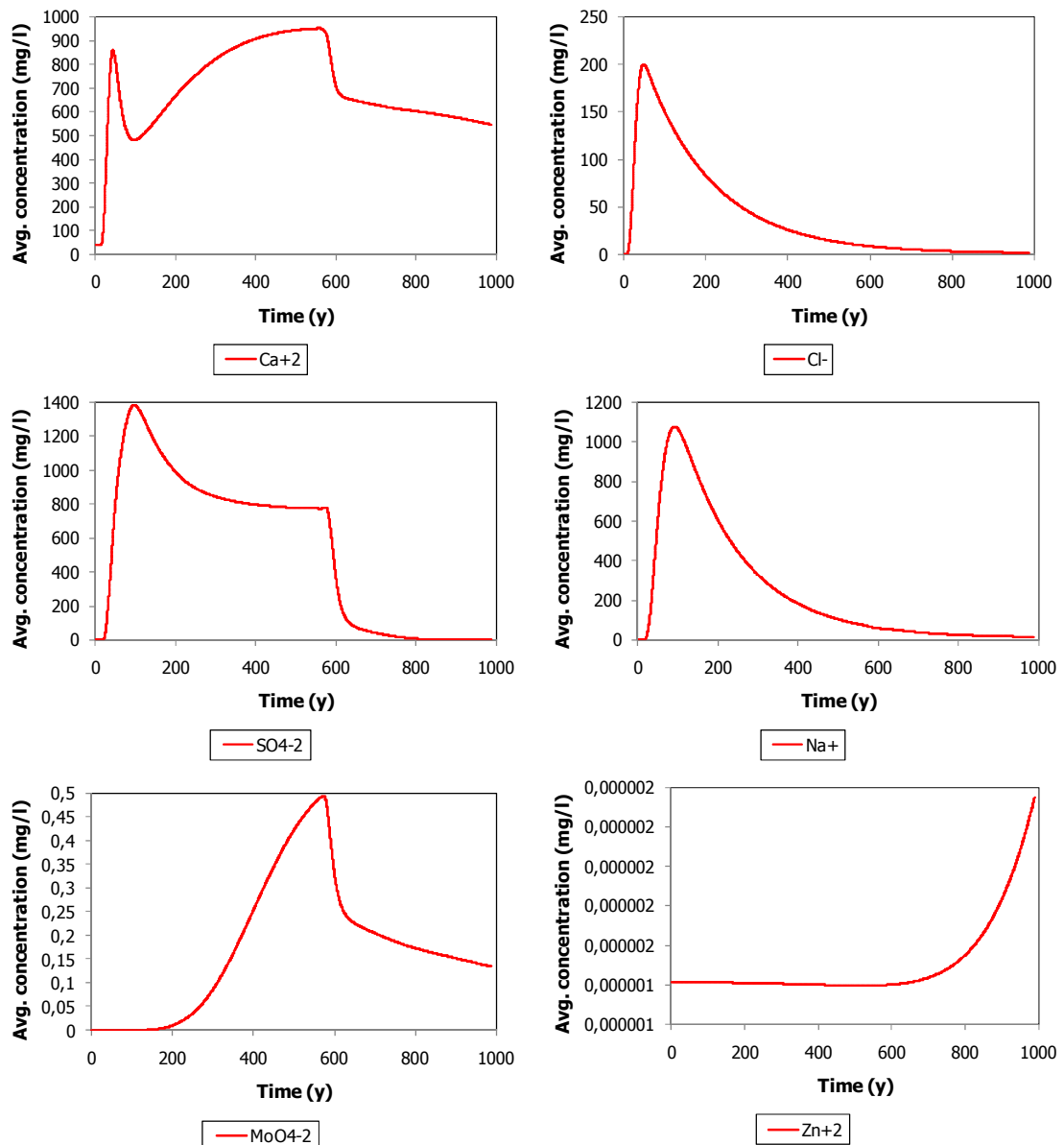
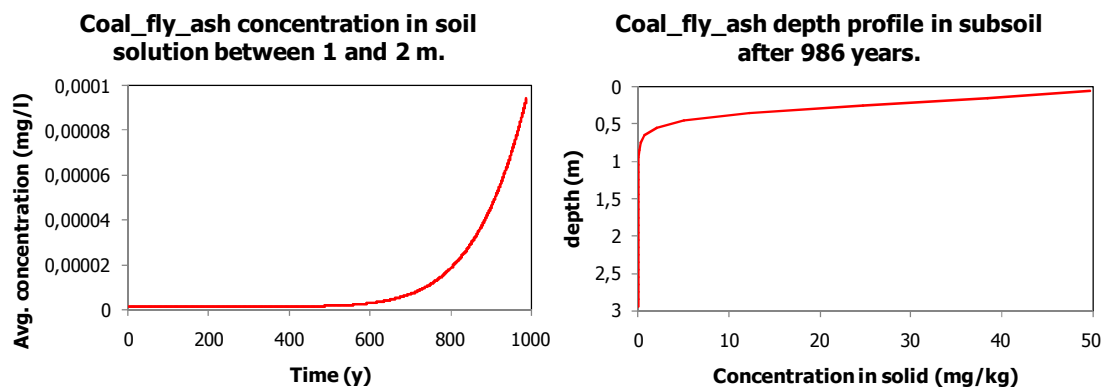


Figure 16 Model results for the SQD model for concentration as a function of time at 1-2 m into the subsoil underneath a coal fly ash layer using column test data as input.



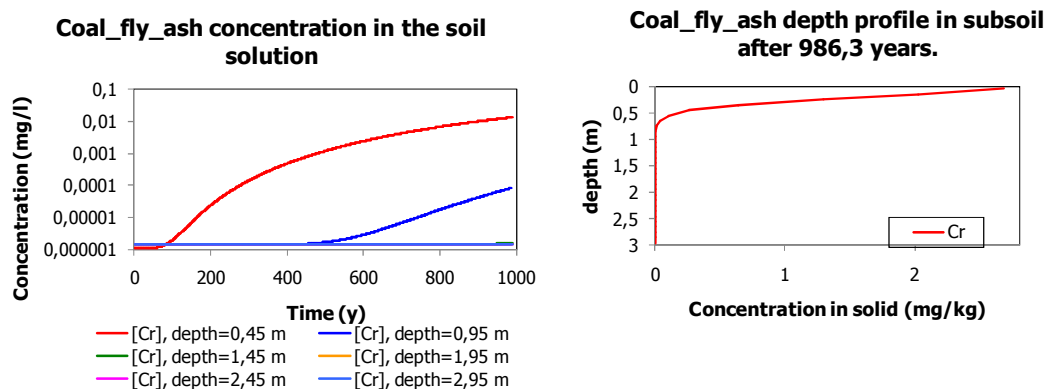


Figure 17 Concentration of Cr in subsoil solution and in soil solid phase under oxidised (bottom) and mildly reducing conditions (top).

## 2.2.5 Evaluation of impact from coal fly ash

Release behaviour from coal fly ash from power plants is more systematic than commonly believed. The release can be described quite well. Although for a limited number of trace elements proper thermodynamic data are scarce or lacking. In spite of that a significant step has been made in multi element modelling of release. Substantial changes in behaviour can be expected when flue gas cleaning processes are implemented for removal of Hg and SO<sub>2</sub>. These will affect the chemistry of the system and consequently the release behaviour. However, for a given type it is expected that release behaviour will be internally consistent.

The redox status of coal fly ash is important for the release of Cr as chromate (produced in the plant). There are ways to reduce Cr beforehand (addition of reducing agent like applied in cement production) or as it seems Cr (VI) is slowly converted in the application to Cr (III). This needs to be confirmed by field measurements.

US EPA is working on a large data set of coal fly ash test data according to pH dependence test and percolation test ( ). This dataset will become publicly available in the course of 2010. This will form a benchmark for coal fly ash and ashes with specific flue gas treatments. Measurements from other locations can be placed in perspective to this data set to identify the extent to which a worldwide reference can be set against which data on single source material can be judged. With the the extent of the dataset statistics can be applied and quality control schemes devised that make efficient use of the existing knowledge to limit testing to key parameters and only occasional verification of full compliance.

Judging the ash from a powerplant against the worldwide set of coal fly ash data will allow several conclusions to be drawn:

- Does the ash produced from the site fit with the worldwide data set?
- How does this fall in the bandwidth?
- Are the same substances of relevance for the site?
- Are the analytical procedures applied adequate to meet the specifications?
- Is the variability in production consistent with that for other facilities?

With the upcoming dataset from US EPA, a full statistical evaluation of the coal fly ash ash data is possible allowing decisions to be made using an objective measure of performance based on the log normal distributed test data. The k-value given here is defined as ( ):

$$k\text{-value} = (\log (\text{regulatory limit}) - Y_{\text{average of log normal data}}) / \text{Stdev}_{\text{log normal data}}$$

This k-value is for a given number of observations linked to a risk of non-compliance. If k corresponding to a defined small risk of non-compliance (to be decided by a notified body or regulator) exceeds such a value, then the parameter can be considered for fall under “without further testing” (WFT).

Based on statistical evaluations of specific test data for a given plant, a test frequency scheme can be developed.

The strength of this combination of characterisation/ITT and compliance/conformity assessment is:

- Avoid unnecessary testing of parameters that are not significant from a regulatory perspective
- Possibility to recognise analytical discrepancies
- Potential to recognise deviations in leaching behaviour on a single data point
- Potential to assess significant changes in release behaviour resulting from modification in process conditions or input variations
- Tools to properly assess impact or provide guidance on treatment for material *improvement*

## 2.3 Additional modelling capabilities of relevance for coal ash utilisation

### **Mixtures with coal fly ash**

Once a chemical speciation fingerprint is available for constituting parts of a mix, the release behaviour of a mixture of materials can be evaluated. This can be the addition of coal fly ash to cement, the addition of coal fly ash to soil as a soil improver (alkalinity), mixtures of fly ash with soil for stabilisation purposes or any other mixture one might consider. The effects of the constituting parts are not additive, since the chemistry of a mixture may change significantly. A mixture with optimized leaching characteristics may be designed based on proper understanding of the release controlling processes.

### **Ecotoxicity testing**

Leaching test are often used for ecotoxicity testing. Presently materials are being subjected to a leaching test without proper regard to the consequences of the changes in the sample preparation for the response of organisms to dissolved substances. Modelling release and knowledge of release controlling processes may help to decide what condition is more likely to be of relevance for testing and what conditions should be considered in data interpretation (Postma et al, 2008).

### **Soil amendment**

Coal fly ash or bottom ash as soil amendment often suffers from an improper judgement, as in many of these case total composition is used. A new judgment has been developed based on leaching of alkaloame (by-product from the Al industry). In this work the amendment of acidic soil was shown to be highly beneficial (Carter et al, 2009).

### 3. Conclusions and recommendations

The characterisation leaching test for assessing long term release behaviour have now been adopted by ISO, CEN and US-EPA as the appropriate tools for quantifying release from soil, and related materials, waste, construction products.

These new tools and the associated modes of data presentation allow comparison of laboratory, lysimeter and field data in a manner that is unprecedented. Data on a special percolation experiment with acid injection now reveals a stunning agreement with pH dependence test data supporting the basic assumption in the development of the percolation that's that local equilibrium is the basis for the method.

Chemical speciation modelling of coal fly ash leaching data has matured significantly in the last decade. The partitioning in different mineral and sorptive phases controlling release have improved considerably to allow a rather good prediction of release in similar ash samples. The chemical speciation fingerprint (CSF) that is obtained in this manner forms the basis for chemical reaction transport modelling.

Already this has helped to understand the possible controlling processes of chromate conversion to Cr (III), thus changing the leachability of Cr substantially. Cr(III) is substantially less mobile than chromate. The minimal redox state that needs to be reached to support this conversion to Cr(III) is  $pH + pe$  of 12.5

A variety of modelling capabilities opens up when the chemical speciation fingerprint is well established for different coal combustion residues.

The comparison of coal ash leaching from the laboratory matches quite well with field observations for a range of substances. This level of understanding of release helps to project forward as to what will likely be happening in the future under changing exposure conditions (e.g. carbonation, oxidation, organic matter infiltration).

The current work by US EPA on coal ash leaching using the methods specified above will significantly expand the available data set on coal ash leaching for comparison purposes.

The modelling of impact based on a mechanistic approach (mineral precipitation, dissolution, sorption on hydrated ironoxides, incorporation in ettringite and interaction with particulate and dissolved organic matter) holds the promise for better prediction in spite of the uncertainties than any single step test can provide. The strong point is that simpler test as possible when placed in proper context with the basic characterisation data.

Independent verification of the redox status in road applications and embankments is important to support the predicted conversion of chromate to the substantially less critical Cr (III).

From the full analysis it is however clear that Cr is not the only aspects of ash leaching. All ox-anions (B, Mo, As, Se, Sb, V and SO<sub>4</sub>) are the potentially critical substances in coal fly ash leaching. Metals are hardly a problem due to the pH range of relevance in road base and embankment applications. Only infiltration of DOC rich water should be avoided to prevent mobilisation of metals as DOC complexes.

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## Appendix A Background on leaching mechanisms and leaching tests

### A.1 Chemical processes controlling release of contaminants from waste materials and alternative materials for construction

In several European member states and through EU funded projects, knowledge on leaching issues for a wide range of materials has increased significantly in the last decade. This relates to different fields - soil, sludge, sediments, waste, recycled materials and construction products - as environmental impact is relevant in all of these areas. In the framework of a European project on Harmonisation of leaching/extraction test (van der Sloot et al., 1997), it was found that there are more common aspects than there are fundamental differences in mechanisms and test methods that have been developed for different materials. This is an expected outcome because a common set of physical and chemical phenomena controls the release of contaminants from solid materials to water under a wide range of environmental conditions.

The current vertically oriented (material specific) approach in the existing CEN Construction Product TC's is for the issue of "dangerous" substances changing into a more *horizontal* approach (i.e., covering a wider range of materials to be characterized by the same release methods). This development coincides with a change to an approach in which the *mechanism* of release is the primary focus for the adoption/development of methods to quantify release, facilitating the relationship between laboratory data and a range of field conditions.

In this chapter, an overview of chemical processes controlling the release of contaminants from waste materials is given (van der Sloot and Dijkstra, 2004). This "horizontal" approach of test method use and data interpretation has already been extensively described for construction products in the development of the construction product directive (CPD).

#### *Total composition of the waste material versus leaching*

Somewhat contra-intuitive, the total composition (in the sense of mg of an element / kg of material) has only a limited influence on the maximum leaching of most elements. Exceptions are non-reactive soluble salts, of which the maximum leached amount over time is often similar to the total amount present in the material. The release of other elements is primarily caused by geochemical mechanisms and physical factors, and leached amounts therefore seldomly correlate with its total content.

#### *Basic chemical mechanisms*

Three different chemical mechanisms control the release of contaminants; by the dissolution of a mineral (**solubility control**), by adsorption processes (**sorption control**) or by its **availability** (or total content) in the waste material. Some contaminants show affinity for adsorption to reactive surfaces. Positively charged heavy metal cations (e.g.,  $\text{Cu}^{+2}$ ) that are not controlled by the dissolution of a mineral, are often controlled by adsorption to (negatively charged) surfaces present in the material such as organic material or oxide surfaces (*sorption control*).

A number of inorganic constituents are not very reactive and show neither solubility control nor sorption control. Examples are the very soluble salts such as NaCl. Upon contact with water they will dissolve instantaneously and quantitatively. Those elements are availability controlled, as the total available concentration can be released from the material.

## pH

The pH of the material and the pH of its environment are crucial in determining the release of many constituents. This is valid for all sorts of materials (monolith, granular, cements, soil, waste, sediment etc.). The pH value of the surrounding fluid determines the maximum water phase concentration at that pH value, and each material has its own pH-dependent release curve (see Figure A1). Release curves are similar and systematic for different groups of elements, only the absolute level may differ between different materials. This implies that the solubility controlling phases are the same; only the relative importance of the influencing factors may differ from one material to another (Fe oxides, Mn oxides, Al oxides, clay, organic matter).

The strong influence of pH on release is because the dissolution of most minerals, as well as sorption processes, are pH dependent. That means that the release of virtually all contaminants that are solubility controlled or sorption controlled, show pH dependent release. The general shape of the release curves is shown in Figure A1.

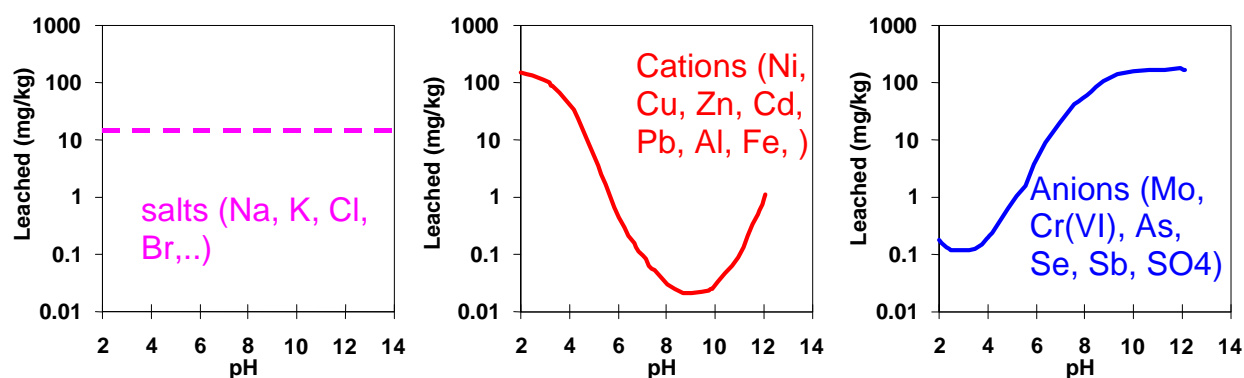


Figure A1. General leaching behaviour of three groups of constituents as a function of pH. Cations, anions and soluble salts have a distinct leach pattern, caused by their chemical speciation, and vary orders of magnitude as a function of pH.

The pH values of materials vary greatly. Cement-based materials superimpose a pH of around 12 (or higher) to its environment, whereas predominantly inorganic waste has a pH of around neutral (pH 6-8). The actual pH at which leaching takes place, depends on the pH of the material itself, the pH of the surrounding environment and the buffering capacity of the material. This is illustrated in Figur A2. The total amount of a contaminant does not change as a function of the pH. It is clear that the potentially leachable amount is also significantly lower than the total amount. The potentially leachable amount is used as an input parameter in geochemical model calculations to predict the leaching behaviour of waste materials. The red line shows the actual leaching behaviour of metals (in this example Cd) as a function of pH. In a landfill, the pH of the leachate is around 6-8, indicated by the pink dashed box. The actual leaching behaviour of a metal can change when the composition of the waste changes (i.e. more ironoxides for sorption processes, more DOC causes increased leaching at neutral to high pH, reducing environment generally causes a lower metal solubility). More information on specific chemical properties are given in the paragraphs below.

When the chemical processes that lead to release of contaminants are understood, a basis is formed for long-term prediction of the emissions from waste materials. The basic characterisation and geochemical modelling approach is therefore an important part of the total environmen-

tal risk assessment of landfills. This approach was also followed in the first Dutch sustainable landfill project (Mathlener et al., 2006; van Zomeren et al., 2006; van Zomeren and van der Sloot, 2006a; van Zomeren and van der Sloot, 2006b). The standardised leaching tests that are developed for this approach are described in Chapter A.2.

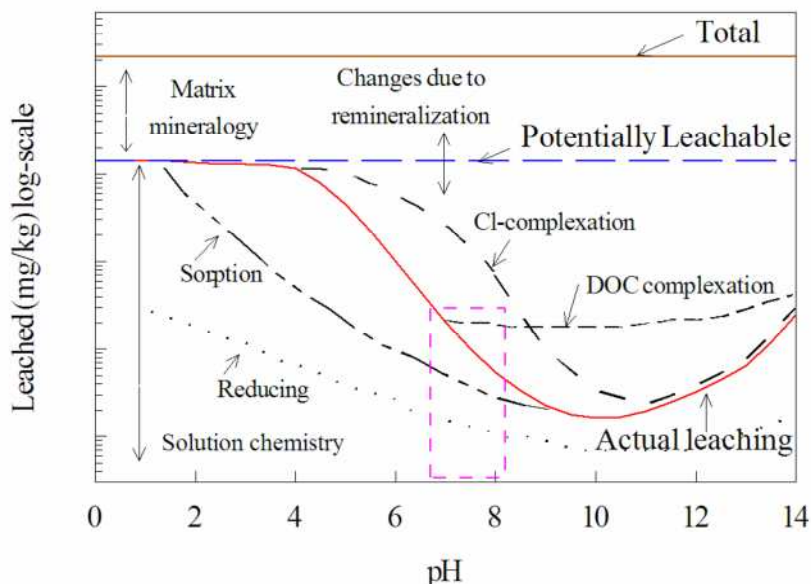


Figure A2. Leaching behaviour as a function of pH versus total composition. In the figure, also the difference between the total composition in the material is shown versus "potentially leachable" and "actually leachable" (the red curve) is shown. Note the log scale on the y-axis.

*Chemical form of the constituent in the waste material (redox form, minerals, sorbed phases, etc)*

Aside from these basic chemical mechanisms, the chemical *form* of a contaminant determines its characteristic leaching behaviour (e.g., the pH dependence shown in the above figures). Contaminants may be in the oxidised or reduced form (e.g., Chromium may be present as  $\text{CrO}_4^{2-}$  or  $\text{Cr}^{+3}$ ) which is important for their leaching behaviour.

Heavy metals tend to complex strongly with natural humic substances present in natural waters, soils and waste materials. Complexed forms of heavy metals are generally highly soluble and therefore, are released more rapidly than uncomplexed forms of heavy metals (see also 'organic matter').

#### *Redox*

Oxidation /reduction state of the material or its environment ("redox") influences the chemical form of a contaminant. For heavy metals, the oxidation of an initially reduced material usually enhances leached amounts while reduction will have the opposite effect. This relates to the chemical form of the elements of interest. An example of the effect of the redox state of materials is given in Figure A2 and A3.

#### *Acid-base buffering*

The acid- base buffering capacity of a material determines how the pH develops over time under influence of external factors. Examples are the neutralization of cementitious products due to the uptake of atmospheric carbon dioxide. In such cases, the alkaline buffering capacity of the alkaline material determines the time needed until the pH drops from strongly alkaline (pH > 12) towards a neutral pH value (pH ~ 8).

#### *Organic matter and DOC*

Solid and dissolved organic matter or humic substances (often expressed as "DOC", dissolved organic carbon) consists of complex molecules that have a high affinity to bind heavy metals. The presence of DOC can enhance leaching by several orders of magnitude (see Figure ). As a result, a new partitioning between DOC-bound metal and free metal will be established. Organic matter is usually present in relatively large amounts in organic environments (soils, sediments, sludges). An example of the effect of organic matter and DOC in waste materials is given in Figure and Figure .

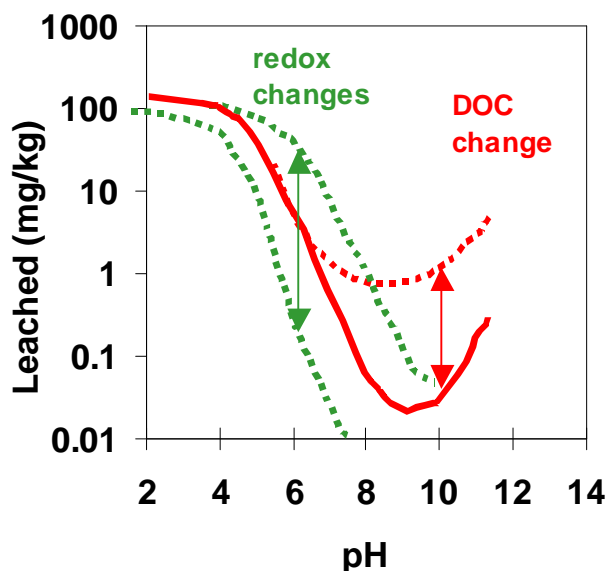


Figure A3. Absolute levels of leached amounts are different for each material due to influence of redox, DOC (dissolved organic carbon) and other factors. The leaching patterns of different groups of elements for all sorts of materials are very systematic, but differ in absolute levels (leading to a "chemical fingerprint" of a material).

#### *Composition of the water phase and ionic strength*

The ionic strength influences the solubility of other components (generally, a higher salt strength increases the leaching of contaminants). Other components present in the solution may cause enhanced leaching due to complexation, such as metal complexes with chloride or carbonates.

#### *Temperature*

Temperature increase generally leads to a higher solubility of contaminants. In addition, an increase in temperature has an increasing effect on chemical reaction rates, and thus also an increasing effect on transport by diffusion.

## Time

Time is an important factor for the amount released when

- In general, the *time scale* applies to the disposal scenario of the landfill;
- The *rate* at which processes proceed, which may be limiting for the release in case of slow reaction kinetics (slow dissolution of minerals) or diffusion. It may not be feasible to allow such reactions to run to completion, as the time to reach that stage may be far too long. In that case, one has to estimate the possible consequences of such slow processes on the overall release.
- The change of material properties or environmental conditions over time. Examples are the degradation of organic matter, changes in permeability of the landfill, carbonation of alkaline waste materials (altering its release properties) or the increased surface area of a monolithic waste material due to erosion.

Test methods that include several steps provide insight in the short and long term effects of leaching. Such tests may give information for interpolation or extrapolation towards shorter or longer leaching periods. A summary of factors influencing release is given in Table A1 (obviously, not all factors are equally relevant and depend on the scenario taken into account).

Table A1. Summary of the main factors influencing release.

Chemical processes	Physical factors	External factors
<ul style="list-style-type: none"> <li>- Dissolution</li> <li>- pH</li> <li>- Chemical form</li> <li>- Total composition/ availability</li> <li>- Redox.</li> <li>- Acid-base buffering</li> <li>- DOC</li> <li>- Composition water</li> <li>- phase/ionic strength</li> <li>- Temperature</li> <li>- Time</li> </ul>	<ul style="list-style-type: none"> <li>- Percolation</li> <li>- Diffusion</li> <li>- Surface wash off</li> <li>- Granular/monolithic</li> <li>- Size (particles or monoliths)</li> <li>- Porosity</li> <li>- Permeability</li> <li>- Tortuosity</li> <li>- Erosion</li> </ul>	<ul style="list-style-type: none"> <li>- Amount of water,</li> <li>- Contact time</li> <li>- pH of environment</li> <li>- Temperature</li> <li>- Redox of environment</li> <li>- DOC / Adsorption</li> </ul>

### Example of geochemical modelling results based on a pH dependence leach test

The results of the pH dependence test and the results of organic matter fractionation and reactive Fe/Al-oxide extractions are used for geochemical modelling. With geochemical modelling, the underlying chemical processes leading to release of contaminants can be estimated. A general overview of chemical processes that can be identified in both the solid and the liquid phase is given in Table A2.

Table A2: General speciation of contaminants in the solid phase and in the leachate of waste materials. The major phases and species are specified in both the solid phase as well as in the leachate.

Solid phase	Dissolved (leachate)
Mineral phases (e.g. CuO, Pb(OH) <sub>2</sub> )	Free ion (e.g. Cu <sup>2+</sup> , Pb <sup>2+</sup> )
Bound to solid organic matter	Inorganic complexes (e.g. [Pb(OH) <sub>4</sub> ] <sup>2-</sup> )
Adsorbed to Fe/Al-(hydr-)oxides	Complexed to DOC

An example of the measured and predicted leaching behaviour is given in Figure A4. The leaching data from a laboratory pH-static leaching test is represented as a function of pH by the red datapoints. The black solid line represents the predicted total concentration of the considered

element in solution, which should ideally meet the data points for good understanding of the chemical processes that determine the leaching behaviour. Moreover, Figure A5 shows the calculated chemical speciation of the element in both the solid matrix and the sample solution. The predicted leaching behaviour is therefore the intersection between the calculated speciation in the solid matrix (minerals, sorption to Fe-Oxides and binding to solid organic matter) and in the solution (free+inorganic and complexed by dissolved organic carbon). This type of data presentation integrates the predicted total leached concentration as well as the different species that determine the leached concentrations.

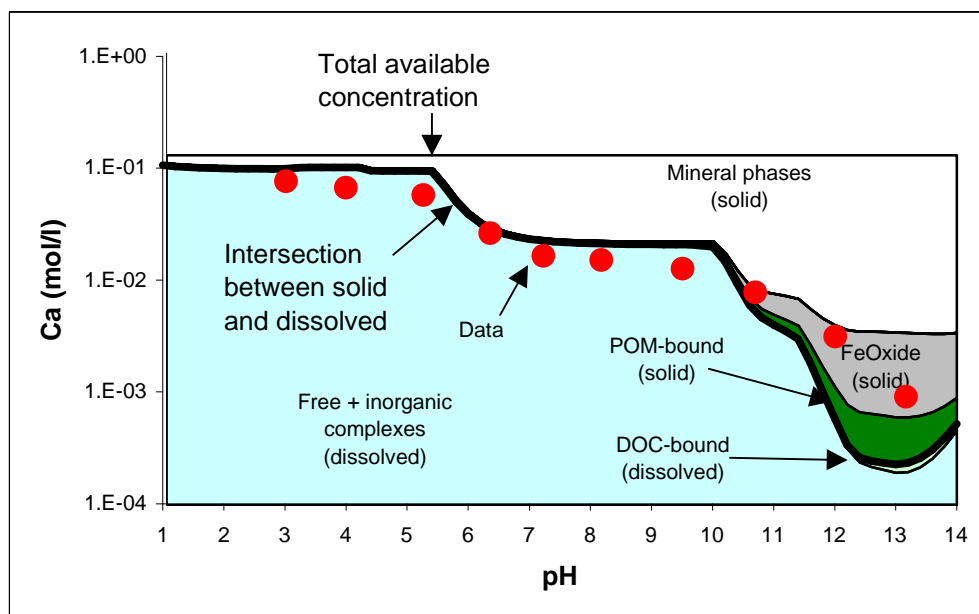


Figure A5 Example of integrated data presentation for pH-static leaching test results and geochemical speciation modelling. Red data points represent leaching data, black solid line is the predicted leached concentration. Areas represent the element speciation: White=minerals, Gray=FeOxide sorption, Dark green=complexation to solid organic carbon, Light green=complexation to dissolved organic carbon and Light blue=free+inorganically complexed form (van Zomeren et al., 2006).

The upper line in Figure A5 gives the total available concentration (input in model). The white area shows the amount of the element bound as minerals in the solid phase. Sorption to Fe-Oxides is represented by the gray area while complexation to solid organic matter is dark green. These areas represent the total amount in the solid matrix as a function of pH. In the leachate solution, the light blue area is the total amount of the free ion and the inorganically complexed form. The light green area represents the amount of the element that is organically complexed.

## A.2 Application of an existing leaching test framework on waste materials

### A.2.1 How are the release mechanisms reflected in the test protocols?

Test protocols should provide the information from which in principle a mechanistic interpretation can be made. CEN TC 292 already developed such a testing framework, which will be discussed in this chapter. The basic characterization step in the test hierarchy (as specified in ENV 12920) should include the measurement of an extensive set of elements (preferably all elements with ICP-AES, Cl, Br, SO<sub>4</sub>, F, DOC). Currently, the main *characterization tests*, the first step in the CEN TC 292 test hierarchy, are or will be:

- **Percolation test**, PrEN 14405 (up-flow percolation test to determine the leaching behaviour of **granular** waste materials under specified conditions). The test is performed in using columns (20 x 5 cm) and the leaching is performed with demineralised water of natural pH (the material tested will superimpose its 'own' pH to the solution). Concentrations are measured in usually 7 different fractions up to a cumulative liquid to solid ratio of 10 L/kg (about 50 pore volumes). The choice of 10 L/kg is often representative for a long-term situation in practice. At the same time, results at L/S 10 make comparison with results of the pH dependence test possible (also performed at L/S 10). The test is designed such that local chemical and physical equilibrium is attained.
- **Tank test ('diffusion test')**: under development in CEN TC 292 with similarities to NEN 7345 (Determination of the Leaching of Inorganic Components from **Monolithic** Building and Waste Materials with the Diffusion Test) and other national standards (France, Austria and Nordic countries). A monolithic material is placed in a tank and is surrounded by water of natural pH. At specified times, concentrations in the leachant are measured and the leachant is refreshed.
- **pH dependence test**, PrEN 14429 (Influence of pH on leaching with initial acid/base addition). The test is carried out on (crushed/grained) samples at a liquid/solid ratio of 10 L/kg, and various amounts of acid and base are added to obtain a final pH. After equilibration period of 48 hours, concentrations of elements are measured in the eluates. The test also gives an indication of the buffer capacity of the material. The test is designed to represent chemical and physical equilibrium conditions. A standard for the automated pH dependence test is also under development (prCEN TS 14997).

## A.2.2 Basic data presentation and interpretation

For the *pH dependence test* and the *percolation test*, the results are preferably expressed in mg of substance leached per kg of dry solid matter (release units). The results can also be expressed as a concentration (mg/l) when necessary for specific aspects (e.g., evaluation of solubility control). The reason for this way of data presentation is that it enables comparison of results for different L/S ratios (the amount of water in contact with the material, expressed in L/kg) for groups of constituents showing similar release behaviour (salts as well as solubility controlled release). Also, it makes a direct comparison possible between results from the percolation test and a pH dependence test. It must be realised that, the concentrations in the eluate of a leaching can generally not be related directly to the impact of soil, groundwater or surface water. The eluate from a leaching test reflects the release under the conditions imposed in the test. In an actual landfill situation, e.g. the first pore volumes (L/S=0,1-0,5) may have much higher concentrations, than the release after a longer period. Furthermore one should realise that many leached substances may be adsorbed first by the soil particles and may later be transported to the ground water. So the concentrations of substances in an eluate directly from a test will often be strongly different from the concentrations of substances in the landfill leachate that enters groundwater.

The leaching pattern obtained with the *pH dependence test* is the result of a combination of the material-specific chemical factors that control release, such as the presence of organic matter and salts in the material, redox properties, buffering capacity (implicitly measured in the pH dependence test), ionic strength and chemical speciation. The test result also allows extrapolating the result to relevant field conditions - such as what happens with the release when the material is exposed to different environmental conditions (see Figure A6). The result of a pH dependence test gives the amounts expected to be released under different exposure conditions. In addition, the test results form the basis for geochemical modelling of the dominant chemical processes leading to release of contaminants in the environment. These chemical processes can subsequently be used in long-term predictions of the mobility of contaminants.

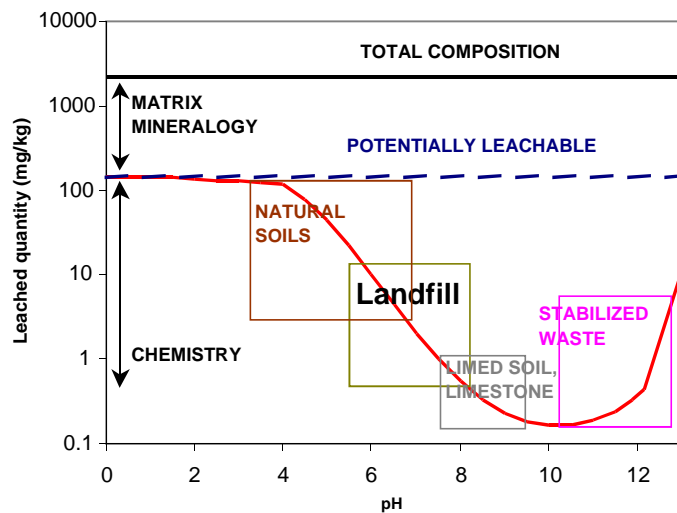


Figure A6. Standard presentation and interpretation of results from a pH dependence test (PrEN14429, expressed as release in mg/kg at L/S 10). The curved line illustrates an hypothetical release curve of a metal cation. The different pH values found in specific environments are indicated with boxes. Note that there may be a considerable difference between the total content of a material and the amount that is available for release ('available' = potentially leachable).

Results from a *percolation* test for granular materials can either be expressed as concentration (mg/L) versus percolated amount of water (L/S ratio) or as cumulatively leached concentration (mg/kg). The latter is often preferred, because cumulatively leached concentrations (mg/kg) enables comparison with legislative values (Annex II of the Landfill Directive) and to compare emissions between samples. In addition, the released amount at L/S 10 can be directly compared to leached concentrations in the pH dependence test at L/S 10. Materials leach at their *own* (native) pH value in the percolation test.

From the cumulative release curve, the underlying release mechanism can be identified for the entire range of L/S values, when the conditions during the test do not differ too much (e.g., pH) or for part of the range, when changes in major controlling factors occur during the test. The most important mechanisms include solubility control (dissolution of a mineral, e.g.,  $\text{Pb}(\text{OH})_2$ ), and wash-out (relevant for non-reactive soluble salts such as Na and Cl). This is illustrated in Figure A7.



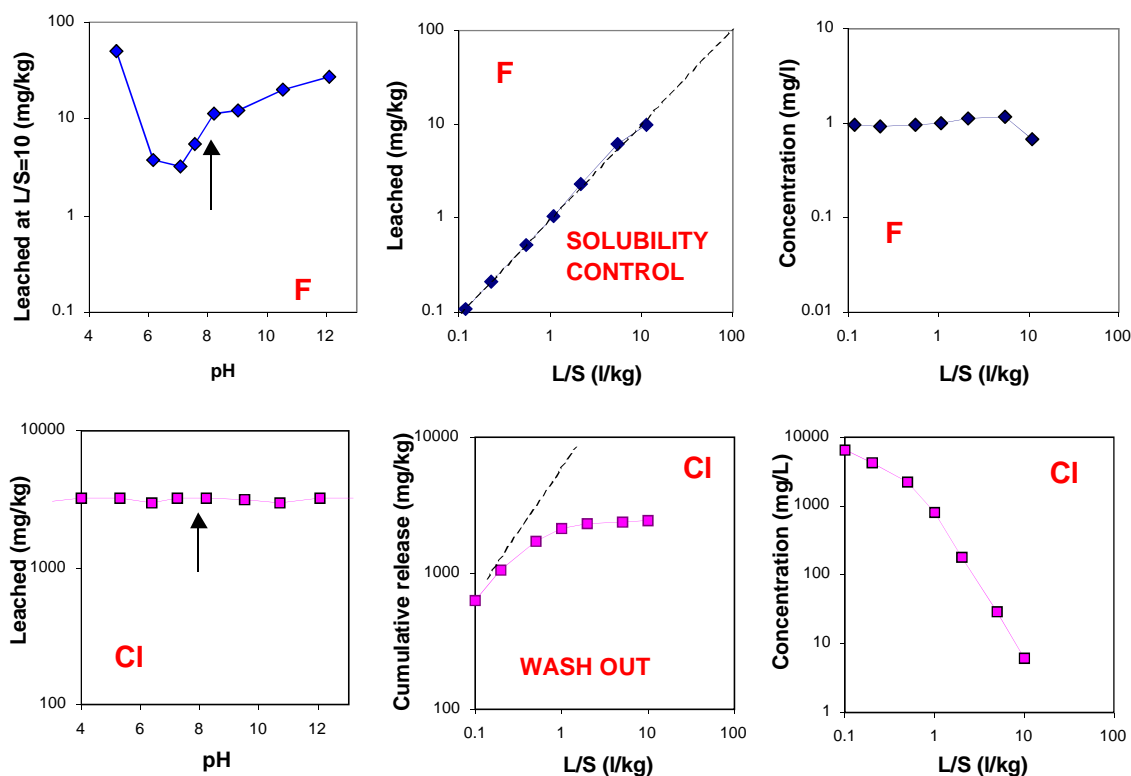
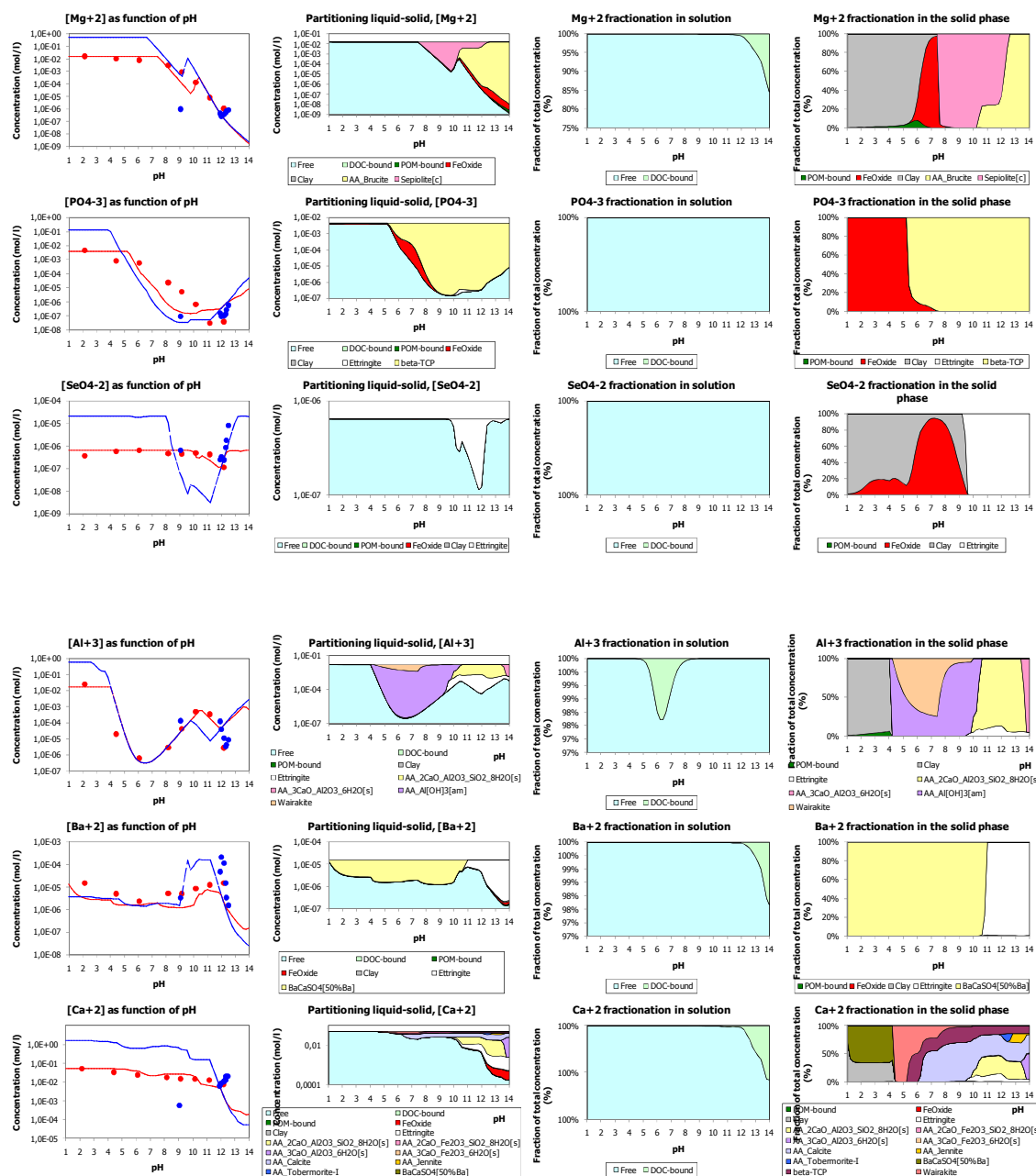
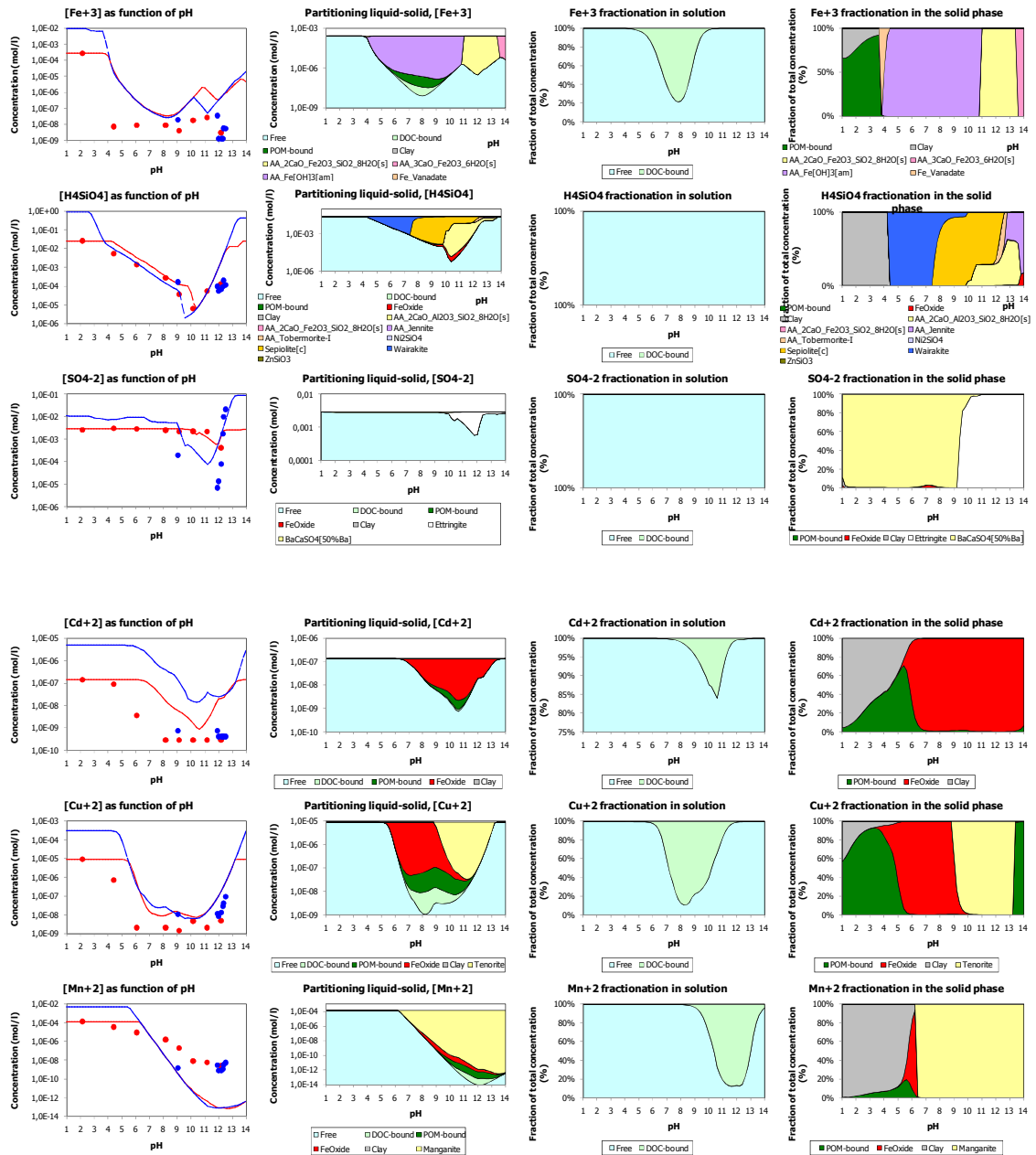
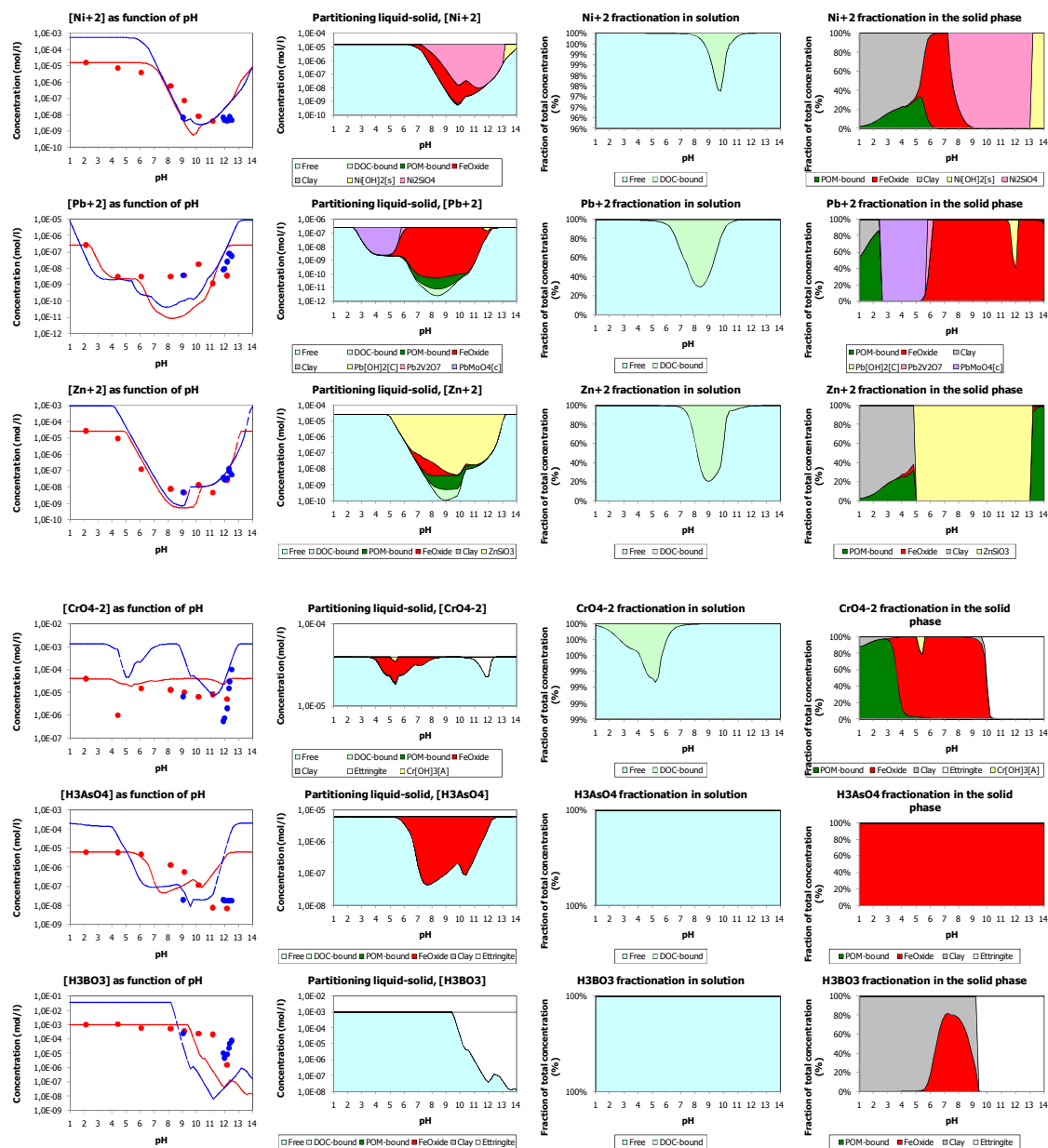


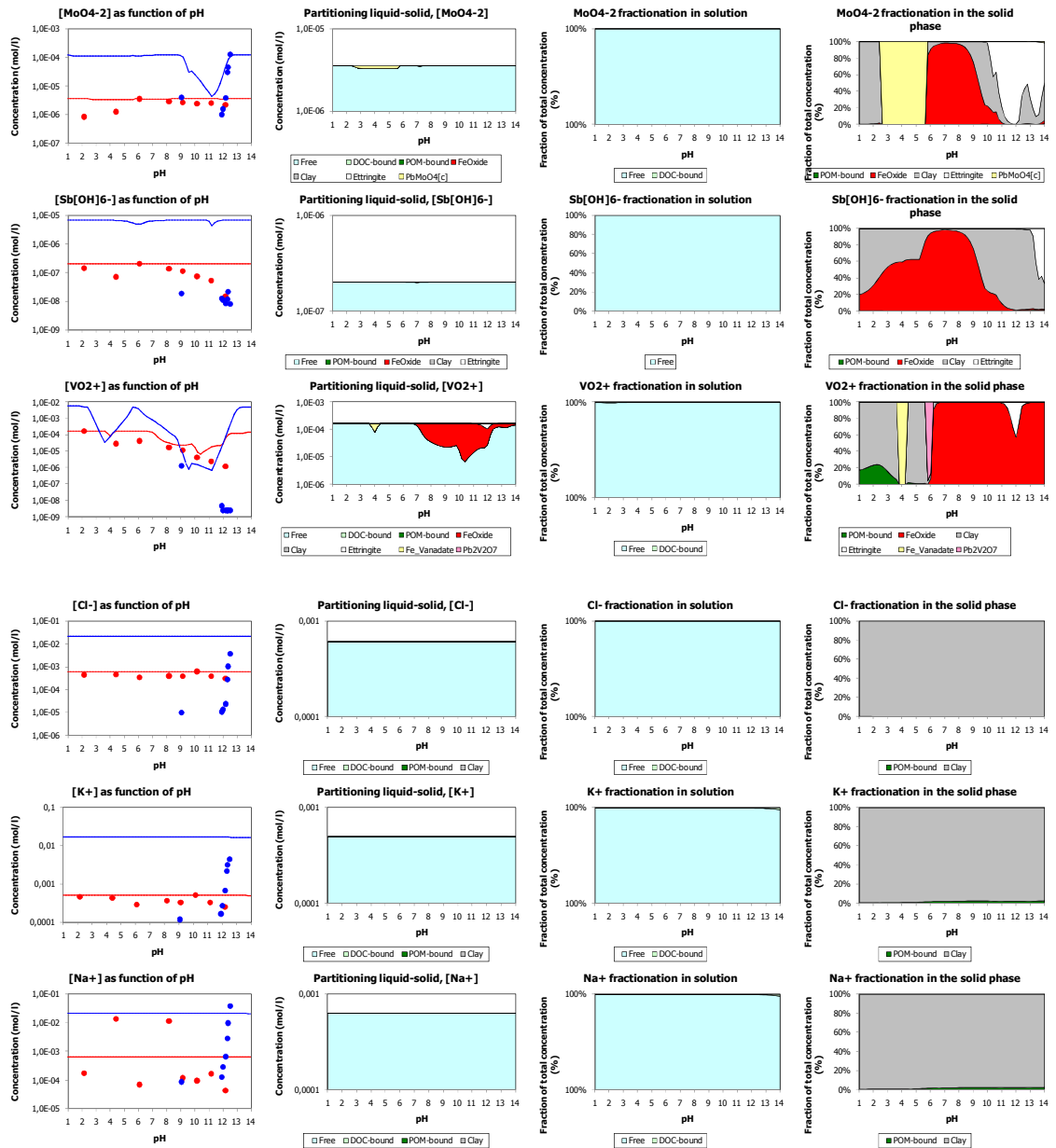
Figure A7. Data from a column leaching test on MSWI bottom ash. When a constant concentration is measured in each time interval (mg/L), this leads to a 1:1 slope in a cumulative leaching curve (case of fluoride). For soluble salts (e.g Cl), that readily wash out, concentrations decrease rapidly as a function of L/S which leads to a cumulative slope lower than 1:1. The L/S scale (Liter water percolated/kg material) can be used for extrapolation of test results to field situations, relevant for impact assessment.

## Appendix B Chemical speciation modelling of Israeli coal fly ash.





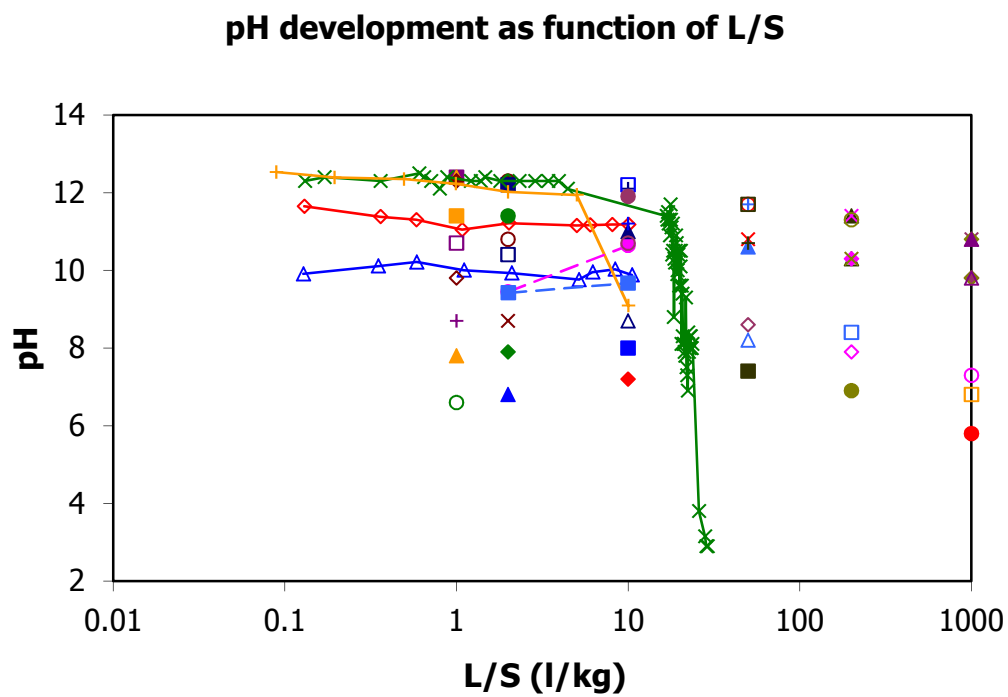




Coal fly ash Orot Rabin pH dependence test (red dots) percolation test Dutch alkaline fly ash (blue dots) Red line multielement geochemical model at L/S=10 and blue line same at L/S=0.3.

## APPENDIX C Detail of pH and coal ash samples included in comparison

pH variation as a function of L/S in percolation and lysimeter experiments shown in figure..



## pH dependent Concentration of Al

