Energy research Centre of the Netherlands

European standardisation and regulatory developments in relation to release from monolithic materials - stabilised waste and cement-based construction products - to soil and groundwater- an update.

H.A. van der Sloot, J.C.L Meeussen, O. Hjelmar, G. Spanka

ECN, Petten, The Netherlands; DHI, Hørsholm, Denmark; VDZ, Dusseldorf, Germany

2nd Wshop: Mechanisms and modeling of waste/cement interactions, October 12-16, 2008, Le Croisic, France

OUTLINE

- Regulatory needs from the Construction Products Directive (CPD)
- Regulatory needs from waste disposal (EU Landfill Directive)
- Standardisation developments (horizontal standardisation)
- Example results of testing and modelling for different types of cement mortars and stabilised wastes
- Conclusions

CONSTRUCTION PRODUCTS DIRECTIVE (89/106/EEC)

The European Standardization Organisation CEN mandated by DG Enterprise to prepare test methods to assess potential release of dangerous substances to soil and groundwater (Essential Requirement 3 on Health and Environment)

CEN/TC 351 installed to answer the needs in this mandate. This TC is working with a number of task groups to address specific questions (Impact Soil & Groundwater, Impact indoor air, analysis of content, sampling, barriers to trade, WT, WFT and FT).

Substantial progress has been made in providing the necessary horizontal test methods (applicable to different fields or product types) to generate both a sufficiently scientific based approach as well and an economic and practical approach avoiding unnecessary duplication of work.

MONOLITHIC WASTE IN THE LANDFILL DIRECTIVE

EU Landfill Directive - ANNEX II : no provision for stabilised monolithic waste for lack of a proper scenario description (2002)

For the time being Member States asked to deal with this topic at national level – work still ongoing at national level
Key issues:
- Not only transport by diffusion (too simple assumption), but solubility control (particularly for trace constituents)
- Hydrology still insufficiently known (monolith saturated? Infiltration rate?)
- Washout of soluble salts is undesirable as it affects the stability.
- Carbonation is important as it affects the release of substances considerably.

CONCERNS IN RELATION TO LEACHING TEST USE AND INTERPRETATION - WHERE DO WE STAND NOW?

- Far too simple tests used in current regulations
  - regulations are not changed so rapidly, but US-EPA is adopting pH dependence test, percolation test and tank test in SW 846 (EPA bible)
- Too limited focus on the fundamental questions to be answered
  - definite improvements made
- Too many ways of test data representation
  - still a big source of confusion
- Tools applied often too simple to address complicated issues
  - hierarchy in testing is now slowly adopted; Kd approach unsuitable for proper impact assessment on the long term – mechanistic approach needed with all complexity of the real world (e.g. different release controlling phases and hydrological aspects)

CONCERNS IN RELATION TO LEACHING TEST USE AND INTERPRETATION - WHERE DO WE STAND NOW?

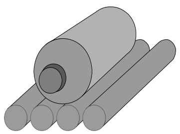
- Too limited relation of test conditions with the actual problem (e.g. L/S)
  - high L/S batch unsuitable to assess pore water, first fraction column test close indicator for granular material and after size reduction also suitable for estimation of pore water in monolithic materials
- Too limited use and relevance of the vast amount of leaching test data generated annually in industry and research (missing parameters)
  - still a big issue, unnecessary protection of data, database needed!!
- Key information relevant to the outcome and possible interpretation of a leaching test often not reported (pH, EC, Eh, DOC)
  - majority still restrict themselves to regulatory required info

SOME IMPROVEMENTS BUT STILL A VERY STRONG NEED FOR HARMONISATION OF LEACHING TEST METHODS, DATA COLLECTION AND DATA EVALUATION!

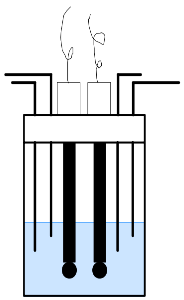
BASIC CHARACTERISATION TESTS

EN 12920

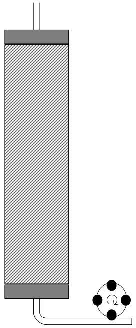
GRANULAR MATERIALS



or



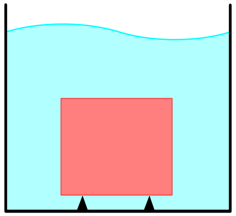
pH DEPENDENCE TEST : BATCH MODE ANC TS 14429 or COMPUTER CONTROLLED TS 14997



PERCOLATION LEACHING TEST (TS 14405) or ISO 21268-3

MONOLITHIC MATERIALS

Same as for granular materials



TANK LEACH TEST (MONOLITH) and COMPACTED GRANULAR LEACH TEST (in progress)

Chemical speciation aspects

Time dependent aspects of release

These basic characterisation tests have a much wider applicability than the field of waste, where they were initially developed!

Scenario Description
Material characterization
Controlling factors
Modelling leaching
Validation verification
Evaluation
Conclusions

CONTROLLING FACTORS

- Mineral precipitation/dissolution
- Hydrated ironoxide sorption
- Organic matter interaction (dissolved and particulate)
- Clay sorption
- Solid solutions

MODELING RELEASE

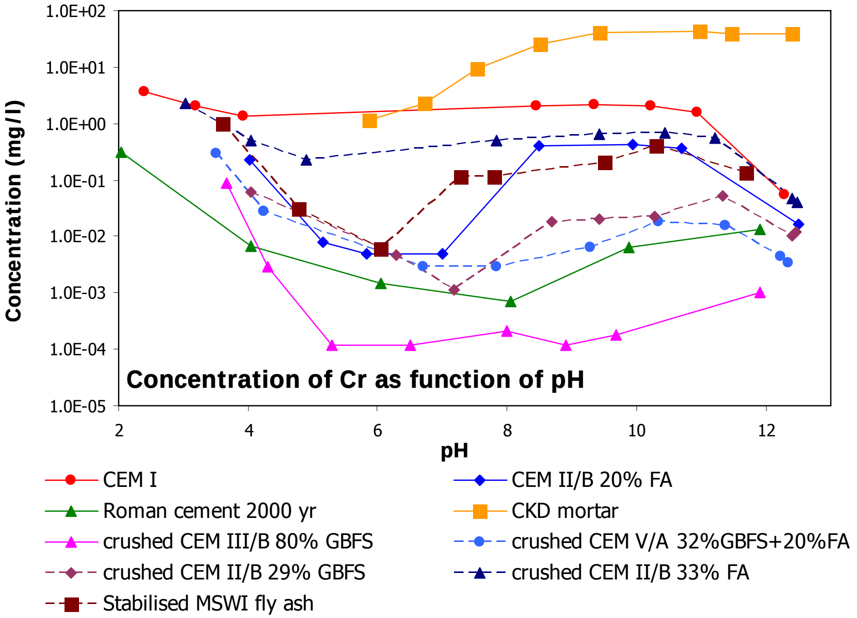
- pH dependence
- Percolation test
- Tank test
- Large scale tests and field measurements

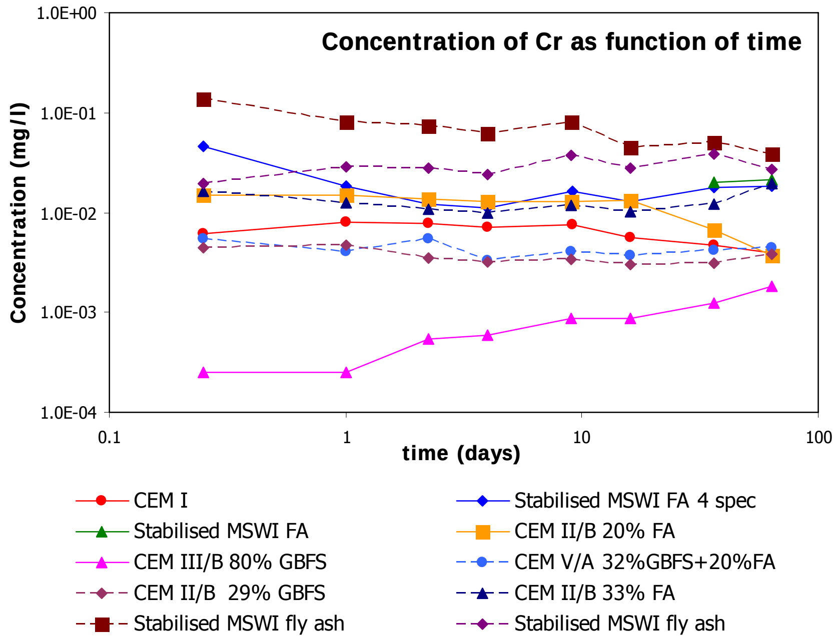
VALIDATION/VERIFICATION

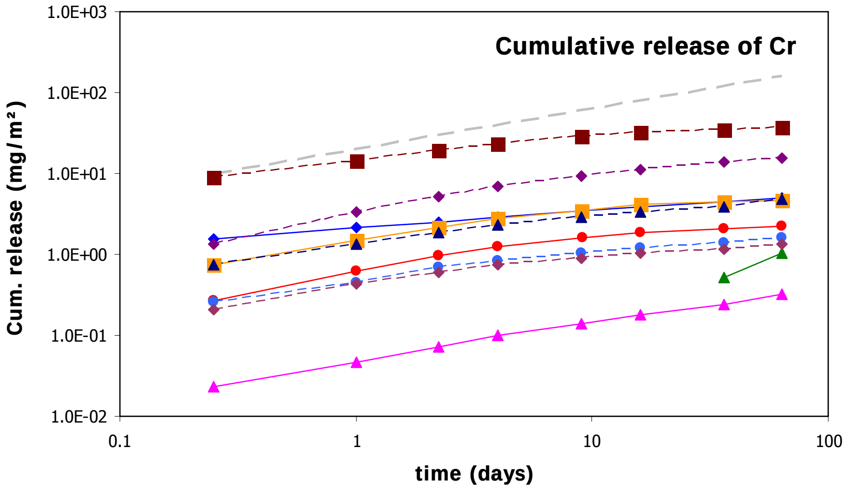
- Lab test data
- Lysimeter scale data
- Field percolate or profile data

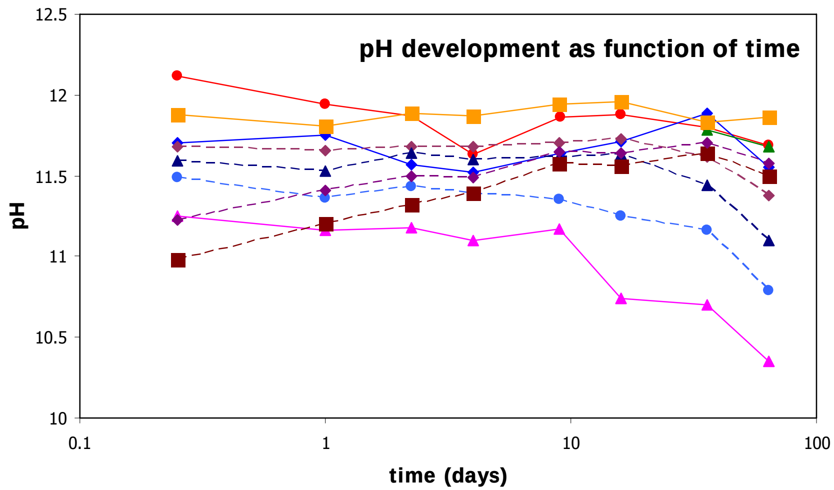
EN 12920

Leaching of cement mortars, CKD, stabilised waste and Roman cement









Besides Cr similar info available for some 70 mortars and >25 elements

STEPS IN CHEMICAL REACTION/TRANSPORT MODELING

- pH dependence leaching test on granular material or size reduced monolithic material for chemical speciation purposes

- measurement of release from granular materials in a percolation test (column) or from monolithic specimen in a diffusion test ("tank test" with leachant renewal)

- speciation modelling using LeachXS, a database-coupled version of the modelling environment ORCHESTRA, to identify relevant mineral phases (SI-indices)

- refined prediction of leaching behaviour in a pH dependence test based on the selected minerals and other relevant phases (Fe, Al, DOC, etc) providing a chemical speciation fingerprint (CSF)

- the resulting CSF is used as input for the chemical reaction/transport modelling to describe the release from a percolation test or from a tank test

- CSF's are also used to model the field scenarios with external factors considered (carbonation, oxidation, biologically mediated reactions) and more realistic estimates of infiltration.

Input data for modeling pH dependence test

Material	Cement stabilised MSWI fly ash - pH dependence test TS14429				
Reactive fraction DOC	0.2		**HFO**	1.000E-05	**kg/kg**
Sum of pH and pe	13.00		**SHA**	5.000E-04	**kg/kg**
L/S	10.0000		**Percolation material**	Cement stabilised MSWI fly ash - TS14405 Percolation test	
Clay	0.000E+00	**kg/kg**	**Avg L/S first perc. fractions**	0.2222	**l/kg**

DOC/DHA data	**pH**	**[DOC] (kg/l)**	**DHA fraction**	**[DHA] (kg/l)**	**Polynomial coeficients**	
	1.00	4.000E-06	0.20	8.000E-07	**C0**	-6.006E+00
	3.60	3.200E-06	0.20	6.400E-07	**C1**	-7.827E-02
	4.78	3.100E-06	0.20	6.200E-07	**C2**	4.355E-03
	6.06	1.900E-06	0.20	3.800E-07	**C3**	5.802E-05
	7.28	2.400E-06	0.20	4.800E-07	**C4**	0.000E+00
	7.80	2.200E-06	0.20	4.400E-07	**C5**	0.000E+00
	9.50	3.100E-06	0.20	6.200E-07		
	10.30	2.300E-06	0.20	4.600E-07		
	11.69	3.000E-06	0.20	6.000E-07		
	14.00	4.000E-06	0.20	8.000E-07		

Reactant concentrations

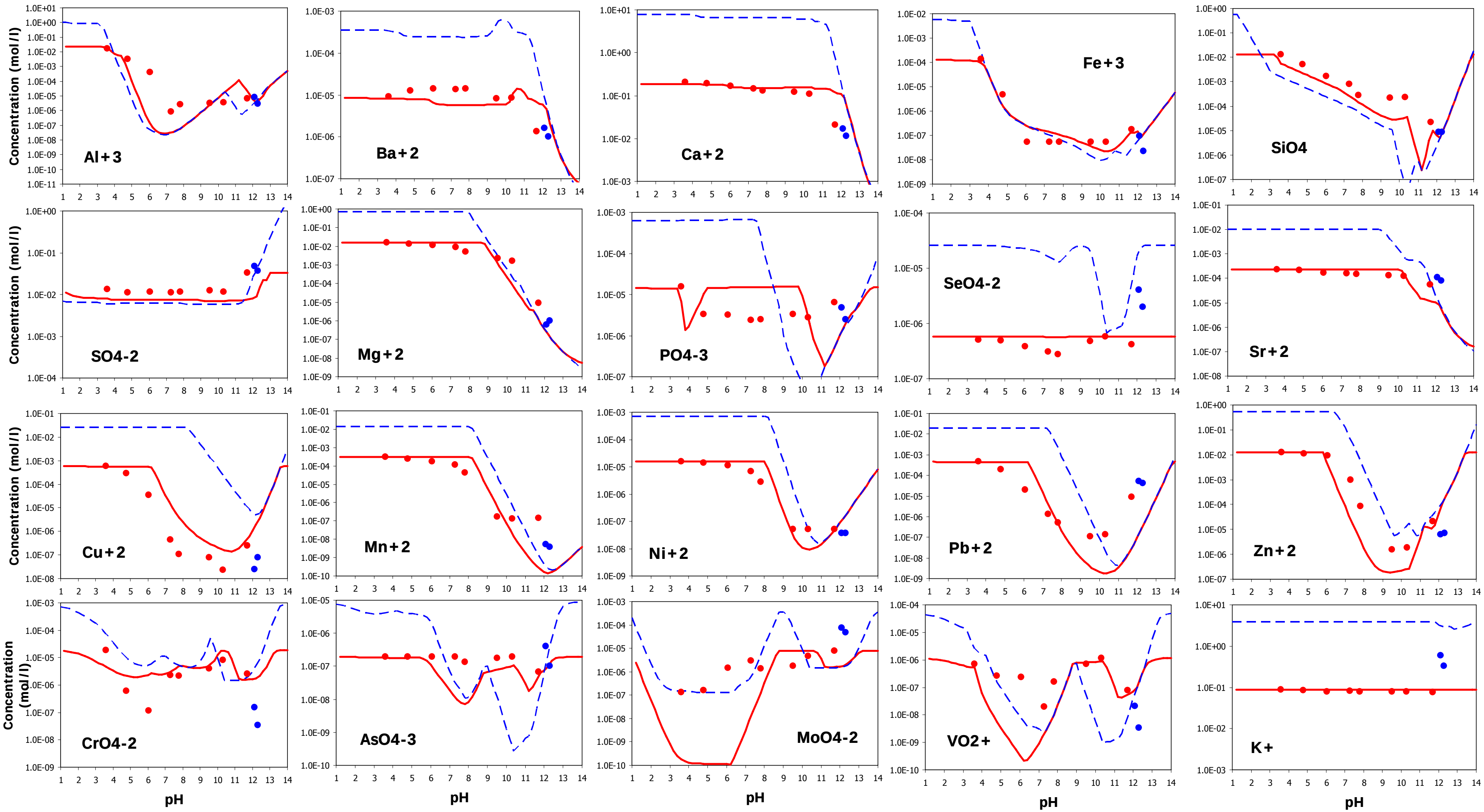
Reactant	**mg/kg**	**Reactant**	**mg/kg**	**Reactant**	**mg/kg**	**Reactant**	**mg/kg**
Al+3	6.056E+03	CrO4-2	9.690E+00	Mn+2	1.750E+02	SeO4-2	4.600E-01
H3AsO4	1.450E-01	Cu+2	3.650E+02	MoO4-2	7.700E+00	H4SiO4	3.556E+03
H3BO3	5.947E+01	F-	1.904E+03	Na+	2.563E+04	Sr+2	2.060E+02
Ba+2	1.933E+01	Fe+3	7.393E+01	Ni+2	9.290E+00	VO2+	5.800E-01
Br-	8.338E+02	H2CO3	1.500E+04	PO4-3	4.740E+00	Zn+2	8.015E+03
Ca+2	8.362E+04	K+	3.381E+04	Pb+2	9.551E+02		
Cd+2	1.782E+02	Li+	2.452E+01	SO4-2	1.066E+04		
Cl-	5.350E+04	Mg+2	3.903E+03	Sb[OH]6-	4.920E+00		

Selected Minerals

AA_2CaO_Al2O3_8H2O[s]	AA_Al[OH]3[am]	**AA_Jennite**	**Corkite**	**Ni[OH]2[s]**	Strontianite
AA_2CaO_Al2O3_SiO2_8H2O[s]	**AA_Brucite**	**AA_Magnesite**	**Cr[OH]3[C]**	**Pb[OH]2[C]**	Wairakite
AA_2CaO_Fe2O3_SiO2_8H2O[s]	**AA_Calcite**	**AA_Portlandite**	**CSH_ECN**	**Pb2V2O7**	**Willemite**
_3CaO_Al2O3[Ca[OH]2]0_5_[CaCO3]0_5_11_5H2O[s]	AA_CaO_Al2O3_10H2O[s]	AA_Syngenite	**Cu[OH]2[s]**	**Pb3[VO4]2**	
AA_3CaO_Al2O3_CaCO3_11H2O[s]	**AA_CO3-hydrotalcite**	AA_Tricarboaluminate	Fe_Vanadate	PbCrO4	
AA_3CaO_Al2O3_CaSO4_12H2O[s]	**AA_Fe[OH]3[microcr]**	**Analbite**	**Fluorite**	**PbMoO4[c]**	
AA_3CaO_Fe2O3_CaCO3_11H2O[s]	**AA_Gibbsite**	**BaSrSO4[50%Ba]**	**Laumontite**	Plgummite[1]	
AA_4CaO_Al2O3_13H2O[s]	**AA_Gypsum**	**Cd[OH]2[A]**	**Manganite**	Rhodochrosite	

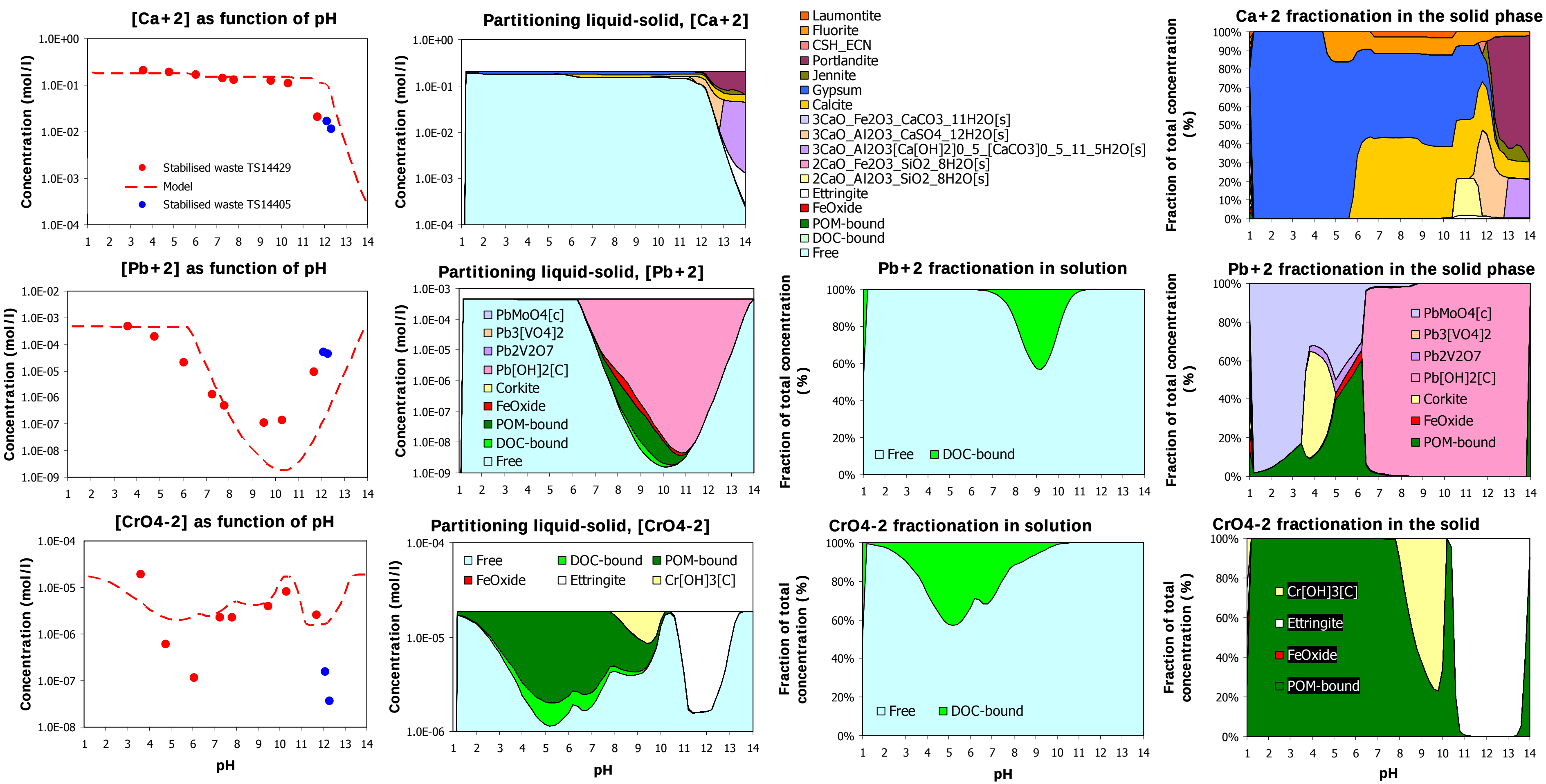
Minerals in bold are ultimately identified in significant proportion

Modeling of pH stat data of cement stabilised MSWI fly ash



Red dots: pH dependence test data; Blue triangle: percolation test data (first fractions); Red line: model result for L/S=10; Blue dotted line: model result for L/S=0.2 (Calculation time : generally ~ 1 minute; graphical display in few seconds)

Partitioning in cement stabilised MSWI fly ash



Partitioning provides insight in release controlling phases, which are of relevance for prediction of long term behaviour

Chemical reaction / transport modeling

- Based on the chemical speciation fingerprint (CSF) of a material (minerals, reactive sorption phases – Fe oxide and Al-oxide surfaces, clay, organic matter – dissolved and particulate) the transport in a percolation experiment is predicted.
- Additional parameters are to be provided:
  - Column dimensions
  - Flow rate
  - Porosity
  - Density
  - Dual porosity parameters (fraction of stagnant phase)
  - Interaction parameter for stagnant and mobile phase
  - Release of reactive fraction of DOC (decay function)
  - Composition of leachant

Input for chemical reaction / transport

Case	Cement stabilised MSWI fly ash 2100 Percolation TS14405				
Solved fraction DOC	0.2		**Density**	2	**kg/l**
Sum of pH and pe	15.00		**Initial pH (solid)**	12.15	
Clay	0.000E+00	**kg/kg**	**Initial pH (liquid)**	7	
HFO	1.000E-04	**kg/kg**	**Column length**	30	**cm**
SHA	2.000E-04	**kg/kg**	**Rel. stagnant volume**	15	**%**
Porosity Fraction	0.35		**Eff. diffusion dist.**	3	**cm**

[DOC/DHA data]

L/S	[DOC] (kg/l)	DHA fraction	[DHA] (kg/l)
0.16	9.580E-05	0.20	1.916E-05
0.28	8.140E-05	0.20	1.628E-05
0.63	5.450E-05	0.20	1.090E-05
1.18	1.240E-05	0.20	2.480E-06
2.18	5.200E-06	0.20	1.040E-06
5.19	2.000E-06	0.20	4.000E-07
10.00	1.300E-06	0.20	2.600E-07

Curve fitting coeficients

Q0	2.064E-05
Q1	1.200E+00
Q2	2.000E-07

Reactant concentrations

Reactant	mg/kg	Reactant	mg/kg	Reactant	mg/kg	Reactant	mg/kg
Al+3	4.456E+03	CrO4-2	9.690E+00	Mn+2	1.750E+02	SeO4-2	4.600E-01
H3AsO4	1.450E-01	Cu+2	3.650E+02	MoO4-2	7.700E+00	H4SiO4	3.556E+03
H3BO3	5.947E+01	F-	1.904E+03	Na+	2.563E+04	Sr+2	2.060E+02
Ba+2	1.933E+01	Fe+3	7.393E+01	Ni+2	9.290E+00	VO2+	5.800E-01
Br-	8.338E+02	H2CO3	1.000E+04	PO4-3	4.740E+00	Zn+2	8.015E+03
Ca+2	8.362E+04	K+	3.381E+04	Pb+2	9.551E+02		
Cd+2	1.782E+02	Li+	2.452E+01	SO4-2	1.066E+04		
Cl-	5.350E+04	Mg+2	3.903E+03	Sb[OH]6-	4.920E+00		

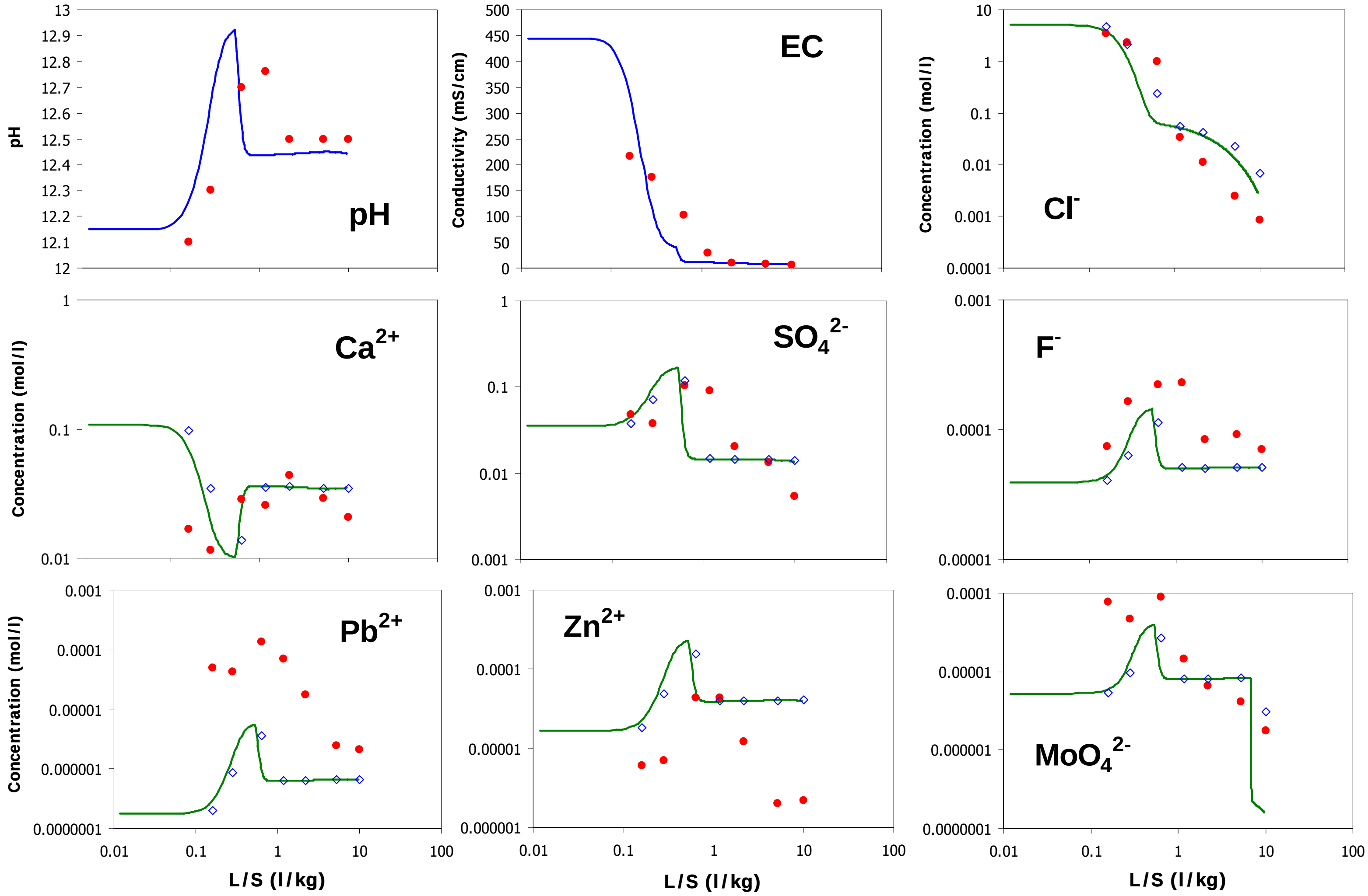
Initial water concentrations

Reactant all	1.000E-09	**mol/l**

Selected Minerals

2CaO_Al2O3_8H2O[s]	3CaO_Fe2O3_CaCO3_11H2O[s]	Fe[OH]3[microcr]	Tricarboaluminate	Ferrihydrite	PbMoO4[c]
2CaO_Al2O3_SiO2_8H2O[s]	3CaO_Fe2O3_CaSO4_12H2O[s]	Gibbsite	alpha-TCP	Fluorite	Rhodochrosite
2CaO_Fe2O3_8H2O[s]	4CaO_Al2O3_13H2O[s]	Gypsum	Ba[SCr]O4[77%SO4]	Magnesite	Strontianite
2CaO_Fe2O3_SiO2_8H2O[s]	4CaO_Fe2O3_13H2O[s]	Jennite	BaSrSO4[50%Ba]	Manganite	Tenorite
3CaO_Al2O3[Ca[OH]2]0_5_[CaCO3]0_5_11_5H2O[s]	Al[OH]3[am]	Magnesite	Ca3[AsO4]2:6H2O	Ni[OH]2[s]	Willemite
3CaO_Al2O3_6H2O[s]	Anhydrite	Portlandite	CaMoO4[c]	Ni2SiO4	Zincite
3CaO_Al2O3_CaCO3_11H2O[s]	Brucite	Silica[am]	Cd[OH]2[C]	Pb[OH]2[C]	
3CaO_Al2O3_CaSO4_12H2O[s]	Calcite	Syngenite	Cr[OH]3[A]	Pb2V2O7	
3CaO_Fe2O3[Ca[OH]2]0_5[CaCO3]0_5_11_5H2O[s]	CaO_Al2O3_10H2O[s]	Tobermorite-I	Cu[OH]2[s]	Pb3[VO4]2	
3CaO_Fe2O3_6H2O[s]	CO3-hydrotalcite	Tobermorite-II	Fe_Vanadate	PbCrO4	

Multi-element prediction of percolation data for size-reduced cement stabilised waste



Low Liquid to Solid ratio data of relevance for estimating pore water composition

Chemical reaction / transport modeling of monolith

- Based on the chemical speciation fingerprint (CSF) of a material (minerals, reactive sorption phases – Fe oxide and Al-oxide surfaces, clay, organic matter – dissolved and particulate) the transport in a tank leach test is predicted.
- Additional parameters are to be provided:
  - Specimen dimensions
  - Liquid to area ratio
  - Porosity
  - Density
  - Tortuosity (derived from soluble salt release)
  - Cell thickness for modeling
  - Reactive fraction of DOC (pH dependence)
  - Composition of leachant

Input for chemical reaction / transport

Case	Cement stabilised MSWI fly ash DMLT-PLR				
Solved fraction DOC	0.2		**SHA**	1.000E-04	**kg/kg**
Sum of pH and pe	13.00		**Porosity Fraction**	0.4	
Clay	0.000E+00	**kg/kg**	**Density**	2.403333333	**kg/l**
HFO	1.000E-04	**kg/kg**	**Tortuosity**	1.7	

Refresh data	**Included**	**Fraction**	**Time (h)**	**Volume (l)**	**Flowspeed (l/sec)**
	TRUE	1	6.00000	4.000E+00	0.000E+00
	TRUE	2	24.00000	4.000E+00	0.000E+00
	TRUE	3	54.00000	4.000E+00	0.000E+00
	TRUE	4	96.00000	4.000E+00	0.000E+00
	TRUE	5	216.00000	4.000E+00	0.000E+00
	TRUE	6	384.00000	4.000E+00	0.000E+00
	TRUE	7	864.00000	4.000E+00	0.000E+00
	TRUE	8	1536.00000	4.000E+00	0.000E+00

[DOC/DHA data]	**pH**	**[DOC] (kg/l)**	**DHA fraction**	**[DHA] (kg/l)**	**Polynomial coeficients**	
	1.00	3.549E-06	0.35	1.242E-06	**C0**	1.496E-06
	3.60	3.200E-06	0.25	8.000E-07	**C1**	-2.586E-07
	4.78	3.100E-06	0.20	6.200E-07	**C2**	1.400E-08
	6.06	1.900E-06	0.20	3.800E-07	**C3**	2.255E-10
	7.28	2.400E-06	0.20	4.800E-07	**C4**	0.000E+00
	7.80	2.200E-06	0.20	4.400E-07	**C5**	0.000E+00
	9.50	3.100E-06	0.20	6.200E-07		
	10.30	2.300E-06	0.20	4.600E-07		
	11.69	3.000E-06	0.25	7.500E-07		
	14.00	3.549E-06	0.35	1.242E-06		

Reactant concentrations

Reactant	**mg/kg**	**Reactant**	**mg/kg**	**Reactant**	**mg/kg**	**Reactant**	**mg/kg**
Al+3	4.600E+03	CrO4-2	9.690E+00	Mn+2	1.750E+02	SeO4-2	4.600E-01
H3AsO4	1.450E-01	Cu+2	3.650E+02	MoO4-2	7.700E+00	H4SiO4	3.556E+03
H3BO3	5.947E+01	F-	1.904E+03	Na+	2.563E+04	Sr+2	2.060E+02
Ba+2	1.933E+01	Fe+3	7.393E+01	Ni+2	9.290E+00	VO2+	5.800E-01
Br-	8.338E+02	H2CO3	1.000E+04	PO4-3	4.740E+00	Zn+2	8.015E+03
Ca+2	8.362E+04	K+	3.381E+04	Pb+2	9.551E+02		
Cd+2	1.782E+02	Li+	2.452E+01	SO4-2	1.066E+04		
Cl-	5.350E+04	Mg+2	3.903E+03	Sb[OH]6-	4.920E+00		

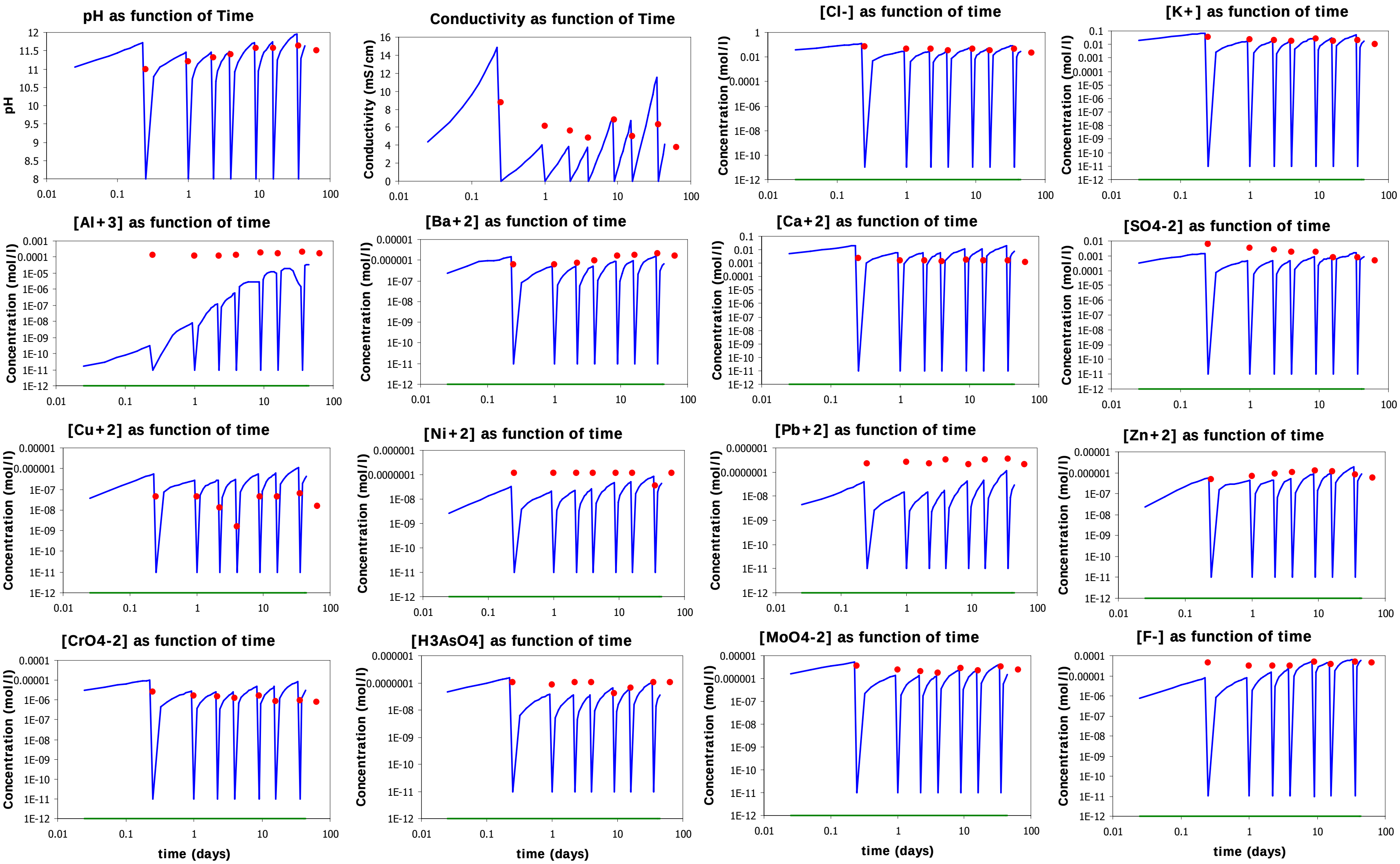
Initial water concentrations

Reactant	all	1.000E-11	**mol/l**

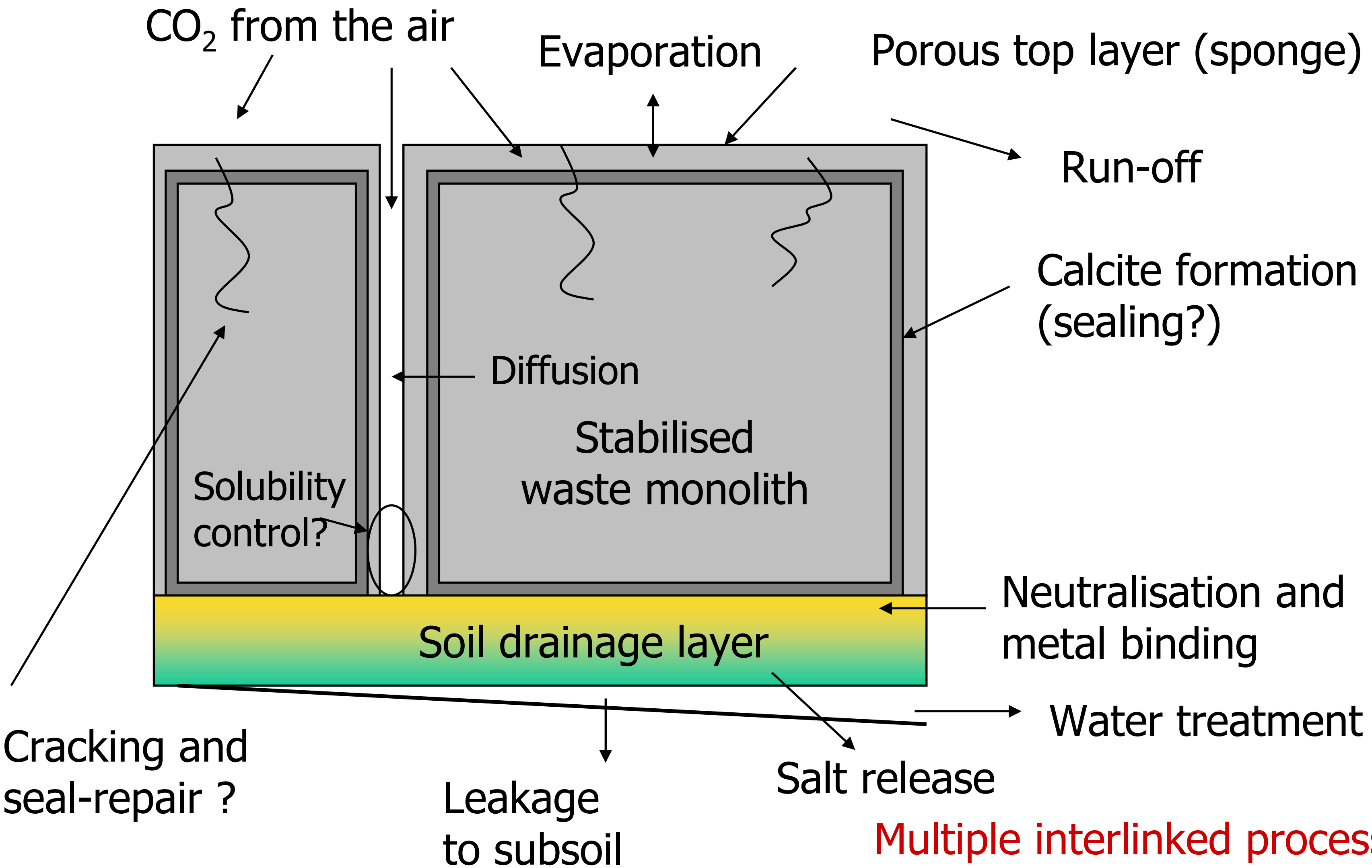
Selected Minerals

AA_2CaO_Al2O3_8H2O[s]	AA_Calcite	Analbite	Pb[OH]2[C]
AA_2CaO_Al2O3_SiO2_8H2O[s]	AA_CaO_Al2O3_10H2O[s]	BaSrSO4[50%Ba]	Pb2V2O7
AA_2CaO_Fe2O3_SiO2_8H2O[s]	AA_CO3-hydrotalcite	Cd[OH]2[A]	Pb3[VO4]2
AA_3CaO_Al2O3[Ca[OH]2]0_5_[CaCO3]0_5_11_5H2O[s]	AA_Fe[OH]3[microcr]	Cr[OH]3[C]	PbCrO4
AA_3CaO_Al2O3_CaCO3_11H2O[s]	AA_Gibbsite	Cu[OH]2[s]	PbMoO4[c]
AA_3CaO_Al2O3_CaSO4_12H2O[s]	AA_Gypsum	Fe_Vanadate	Rhodochrosite
AA_3CaO_Fe2O3_CaCO3_11H2O[s]	AA_Magnesite	Fluorite	Strontianite
AA_4CaO_Al2O3_13H2O[s]	AA_Portlandite	Laumontite	Wairakite
AA_Al[OH]3[am]	AA_Syngenite	Manganite	Willemite
AA_Brucite	AA_Tricarboaluminate	Ni[OH]2[s]	

Multi-element prediction of tank test data for cement stabilised MSWI fly ash

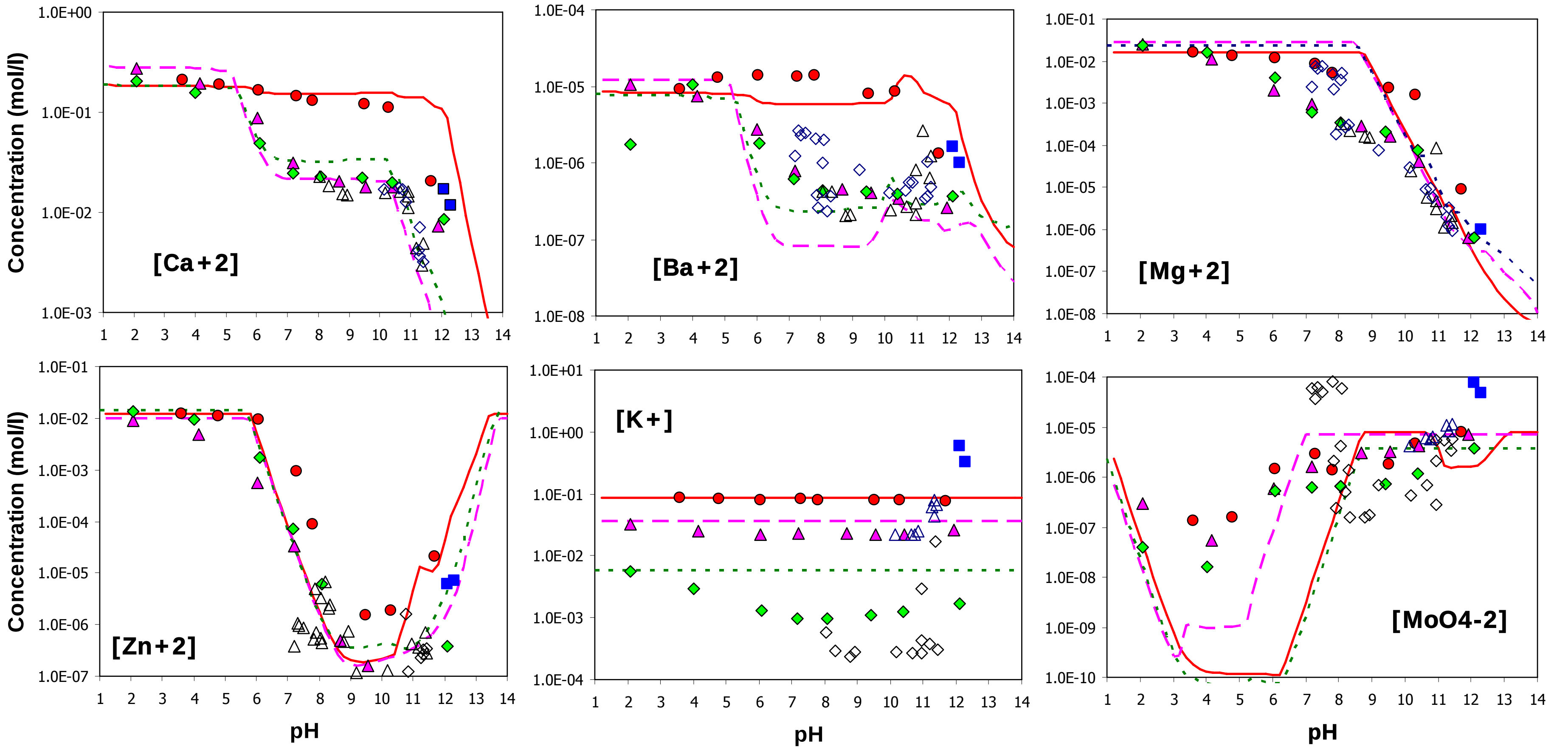


SCENARIO DESCRIPTION: IDENTIFICATION OF PROCESSES IN STABILISED WASTE DISPOSAL



Multiple interlinked processes

Integration of test results from lab, lysimeter, core sample leaching, field percolate and modelling



Red dots: pH dependence test TS14429 fresh
Blue square : percolation test TS14405 fresh
Purple triangle: Aged core material exposed TS14429
Green diamond: Aged core material sealed TS 14429
Open triangle: Core samples EN 12457-2
Open diamond: Core samples EN 12457-2

Red line: model prediction fresh

Purple broken line: model exposed cell

Green dotted line: modeling sealed cell

CONCLUSIONS

The questions to be answered for cement stabilised waste disposal, radioactive waste disposal and issues related to the use of “alternative” materials in construction are basically very similar.

The release controlling processes are not very different between the three fields and exchange of knowledge between the fields can be mutually beneficial.

It needs to be recognised by industry and by regulators in the waste and construction sector that major and minor elements control release processes and as such testing only for the target contaminants will not lead to acceptable long term solutions. On the other hand focusing only on major elements is not solving the problem either.

CONCLUSIONS

The approach presented here aims at proper testing to assess as far as possible intrinsic properties of the products to be tested, mechanistic multi-element modelling taking into account multiple release controlling phases and ensuring adequate verification of modelling output to validate as good as possible the predictions

This means simulation of the field in a lab test is not a way to go, as results can not be used in the next case

Standardisation of adequate test protocols is highly beneficial as it improves comparability and transparency of data. A multiplicity of test to address the same question is not very useful.

The multi-element approach shows quickly, where main gaps in the knowledge are (incomplete prediction, lack of thermodynamic data).

CONCLUSIONS

The proposed set of test methods (pH dependence CEN/TS14429, the percolation test on crushed material CEN/TS14405, and the tank leach test – DMLT-PLR) provide the necessary information for modelling release and are more and more widely accepted.

Additional parameters are reactive iron-oxide surfaces, reactive organic matter (dissolved and particulate), clay and, when relevant reducing capacity.

The characteristic leaching behaviour of cement-based products forms a sound basis for subsequent chemical reaction transport modeling.

Cement mortars worldwide prove to behave very systematic with relatively narrow bandwidth for most elements. Cr being the main exception

CONCLUSIONS

The proposed testing regime for characterisation of stabilised waste has been shown to be useful in addressing various question related to the disposal and even the potential use as a construction material.

This type of characterisation will provide the basis for answering the question by regulators if a certain material use will pose unacceptable risk or not.

To address the complex issue of environmental impact evaluation of long term behaviour too simple approaches lead to poor management decisions

Good progress has been made in understanding the processes in monolithic materials (Meeussen presentation)

Development of LeachXS as an expert system comprised of methodology guidance, databases of laboratory and field data, geochemical speciation modeling tools, and multiple scenario simulations, will provide a very useful tool for various end-users.

ECN

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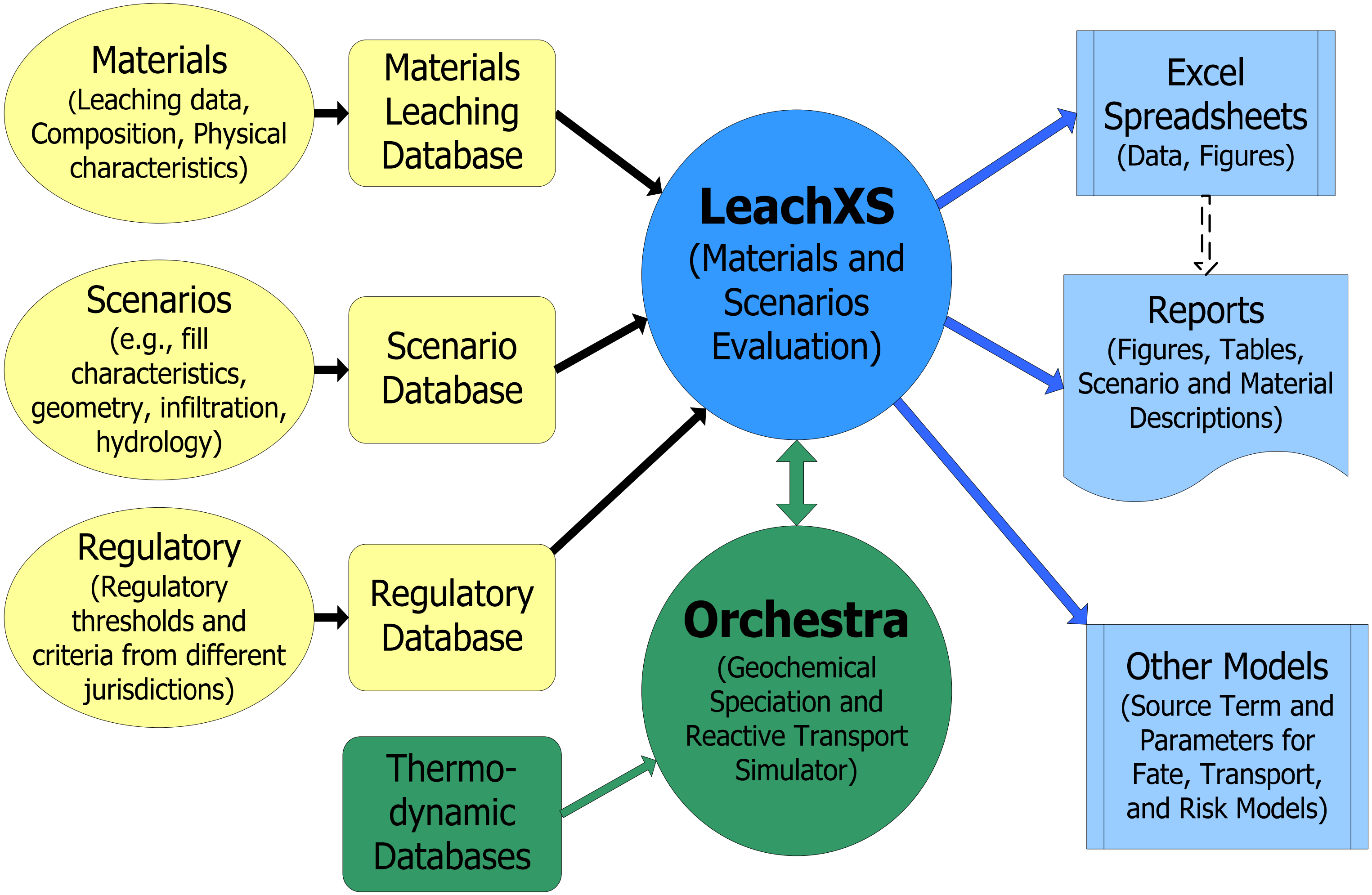
LeachXS Structure



Main goal: easy access to large datasets and advanced data processing for decisionmaking and presentation

DEVELOPMENT OF STANDARDS

European:

Granular waste compliance leaching test – EN 12457 1- 4 validated CEN TC 292 WG2

Monolith compliance leaching test – Tank leach test 3 days (in development) CEN TC 292 WG2

pH dependence leaching test – 2005 TS 14429 CEN TC 292 WG6

Percolation test – 2005 TS 14405 CEN TC 292 WG6

NWIP Dynamic leach test (similar to NEN 7345; in preparation) CEN TC 292 WG6

International:

Batch tests and percolation test for soil materials (based on CEN TC 292 procedures; 2005 F-DIS) ISO TC 190 SC7 WG6

These basic characterisation tests have a much wider applicability than the field of waste, where they were initially developed!