SECOND INTERNATIONAL
SLAG VALORISATION SYMPOSIUM
THE TRANSITION TO SUSTAINABLE MATERIALS MANAGEMENT

Harmonisation of leaching test methods in support of EU regulations controlling beneficial use of industrial slag in construction

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Outline

- Status of standardisation of leaching tests
- Regulatory context
- Leaching test results for steel slag
- Use of leaching test in assessing impact
- Practicality of testing
- Benchmarking

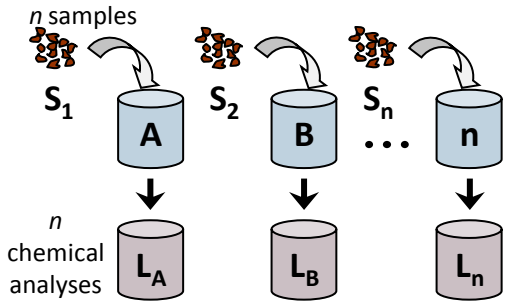
pH Dependence test

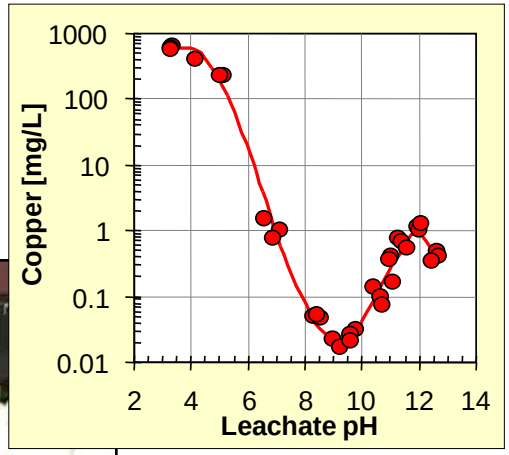
Equilibrium Leaching Test

- Parallel batch as function of pH

Test Specifications

- 8 specified target pH values plus natural conditions
- Size-reduced material
- L/S = 10 mL/g-dry
- Dilute HNO_3 or NaOH
- Contact time
  - 48 hours
- Reported Data
  - Equivalents of acid/base added
  - Eluate pH and conductivity
  - Eluate constituent concentrations





Titration Curve and Liquid-solid Partitioning (LSP) Curve as Function of Eluate pH

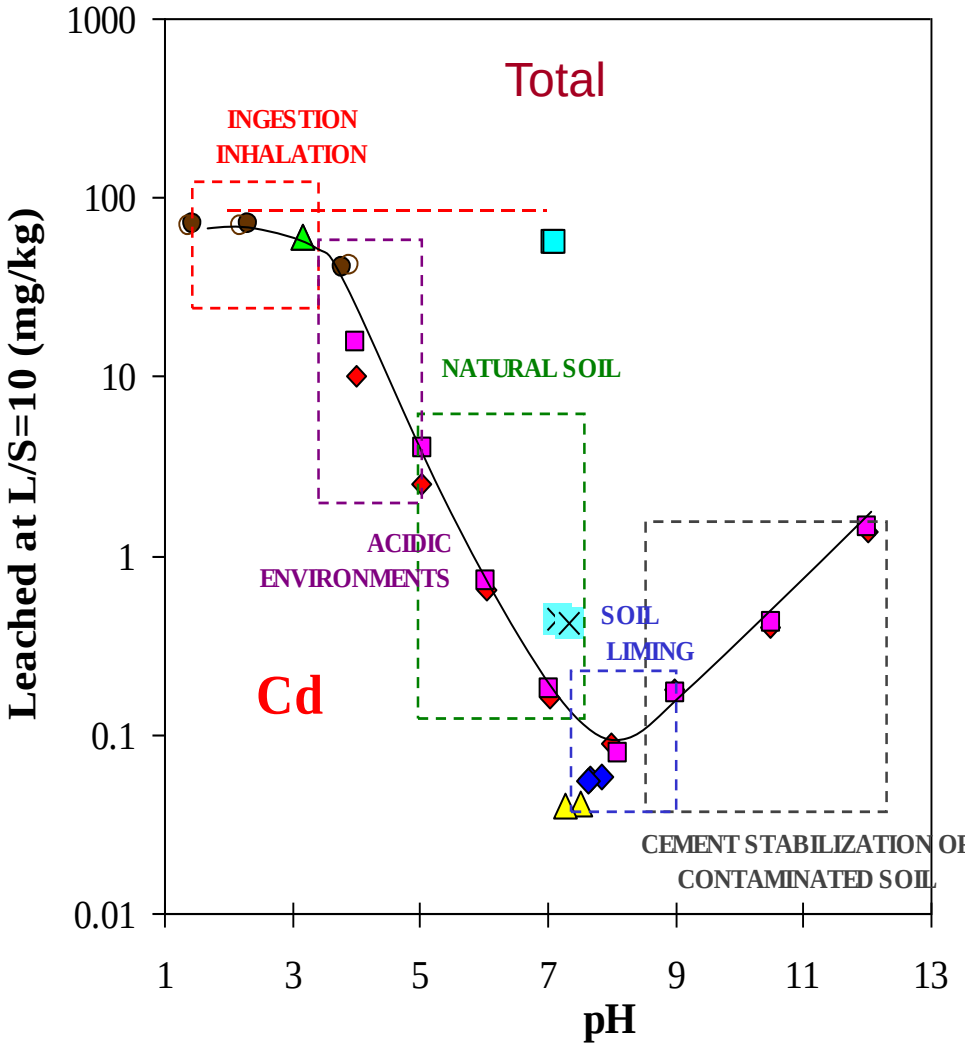
Advantages of pH dependence test

- Identification of sensitivity of leaching to small pH changes
- Provides information on pH conditions imposed by external influences
- Basis for comparison of international leaching tests
- Basis for geochemical speciation modelling
- Provides acid neutralization capacity information
- Mutual comparison of widely different materials to assess similarities in leaching behaviour
- Recognition of factors controlling release
- For non-interacting species possibility to assess sub-sampling error

Applicable to almost any material

Test conditions related to different exposure conditions

Relevant pH domains for assessing different questions in relation to different types of impact



Heavily Sewage Sludge Amended Soil

Percolation Test

Local Equilibrium Leaching Test

- Percolation through loosely-packed material

Test Specifications

- 5-cm or 10 cm diameter x 30-cm high glass column
- Size-reduced material
- DI water or 1 mM $CaCl_2$ (clays, organic materials)

Upward flow to minimize channeling

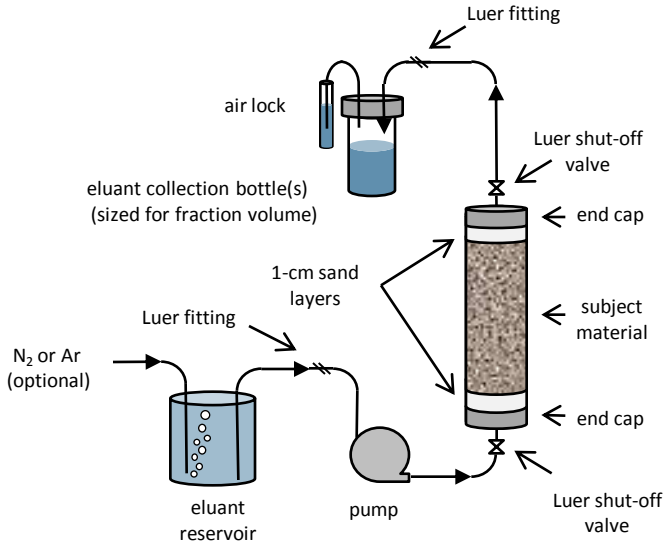
Collect leachate at cumulative L/S

0.1, 0.2, 0.5, 1, 2, 5, 10 mL/g-dry

Reported Data

- Eluate volume collected
- Eluate pH and conductivity
- Eluate constituent concentrations

Liquid-solid Partitioning (LSP) Curve as Function of L/S; Estimate of Pore Water Concentration



Advantages of percolation test

- Identification of solubility control versus wash out
- Indication of pore water concentrations relevant to field leachate from low L/S data (here is where single batch test fail)
- Local equilibrium established quite rapidly
- Basis for geochemical reaction-transport modelling
- Allows comparison with lysimeter and field data provided L/S value can be obtained from such measurements
- Projection towards long term behaviour possible (L/S-time relationship) taking preferential flow into account

Applicable to many materials. Limited or not applicable to clayey soils and sediments (low permeability).

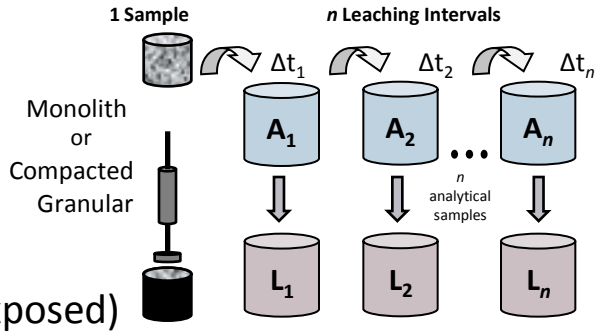
Monolith Leach test

Mass-Transfer Test

- Semi-dynamic tank leach test

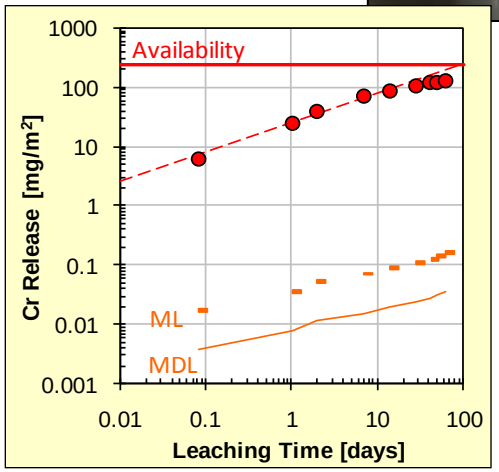
Test Specifications

- Material forms
  - monolithic (all faces exposed)
  - compacted granular (1 circular face exposed)
- DI water so that waste dictates pH
- Liquid-surface area ratio (L/A) of 9±1 mL/cm^2
- Refresh leaching solution at cumulative times
  - 2, 25, 48 hrs, 7, 14, 28, 42, 49, 63 days
- Reported Data
  - Refresh time
  - Eluate pH and conductivity
  - Eluate constituent concentrations



Monolithic

Granular



Flux and Cumulative Release as a Function of Leaching Time

Advantages of tank test or CGLT
(compacted granular leach test)

- Relevant for materials with monolithic character (durable materials) or materials behaving as monolith (low permeability soil and sediments)
- Identification of solubility control versus dynamic leaching possible
- Isolation of surface wash-off effects
- Quantification of intrinsic release parameters
- Basis for reactive/transport modelling
- Projection towards long term behaviour possible

Applicable to stabilised materials, construction products, sediments and clayey soils.

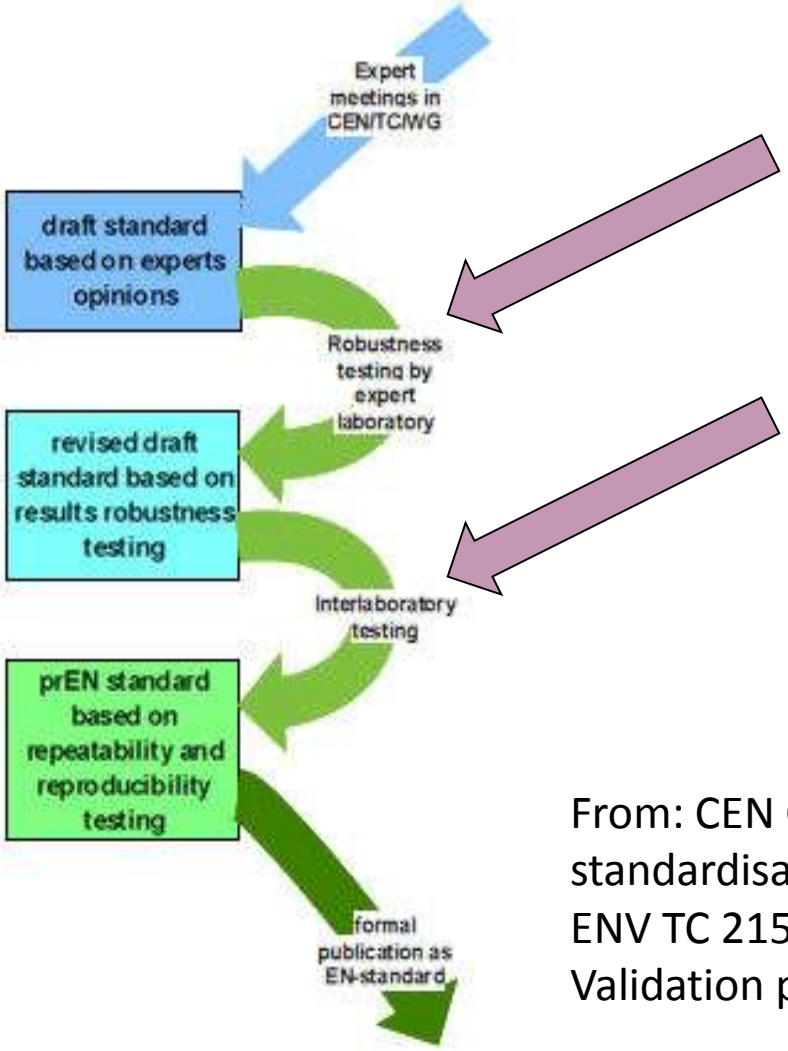
Development of Standards and Materials Covered

Test/Matrix	Soil, sediments, compost and sludge	Waste	Mining waste	Construction products
pH dependence test	ISO/TS21268-4	CEN/TS14429	CEN/TS14429	CEN/TS14429
		CEN/TS14497	CEN/TS14497	
	EPA 1313 *	EPA 1313	EPA 1313	EPA 1313
Percolation test	ISO/TS21268-3	CEN/TS14405	CEN/TS14405	CEN/TC351/TS-3
	EPA 1314 *	EPA 1314	EPA 1314	EPA 1314
Monolith test		CEN/TS15683		CEN/TC351/TS-2
	EPA 1315 *	EPA 1315	EPA 1315	EPA 1315
Compacted granular test		NEN7347		CEN/TC351/TS-2
	EPA 1315	EPA 1315	EPA 1315	EPA 1315
Redox capacity		NEN 7348		NEN 7348
Acid rock drainage			PrEN15875	
Reactive surfaces	ISO/CD12782 parts 1-5	Vienna agreement		

* EPA drafts in preparation for inclusion in SW846

Same basic testing approach in different fields

Steps in validation



This is the status today:

- CEN/TC351 Robustness work granted (TS-2 and TS-3)
- US EPA Intercomparison validation in progress (pH dependence, percolation , monolith, CGLT) Results available end 2011
- CEN/TC292 still seeking funds

From: CEN Guide on validation tasks in the process of standardisation of environmental test methods, April 2008, ENV TC 215rev, supported by SABE Resolution 06/2008 - Validation policy

Steel slag Uses

Use in blended cement

Raw material input in cement production process

Aggregate in concrete

Road base stabilisation

Embankment fill

Coastal protection

Soil improver

With multiple uses of the same material or product multiple testing and judment approaches undesirable.

Single step tests are clearly insufficient to answer questions related to possible environmental impact.

Regulatory context

Construction Products Directive (EU CPD)

Construction Products Regulation (EU CPR).

European Landfill Directive (EU LFD)

End of Waste regulation (EU EoW)

Waste Catalogue (EU WC)

Hazardous Waste Directive (EU HW)

REACH Regulation

Soil Quality Regulation – Fertilizer use

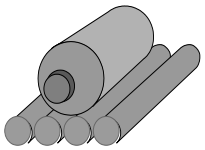
Groundwater Directive

With multiple regulations : preferably not multiple testing and multiple impact judment approaches for the same material or product

Characterisation leaching tests

Standardisation: CEN/TC292, ISO/TC190, CEN/TC345, CEN/TC351, SW846 (US EPA)

GRANULAR MATERIALS



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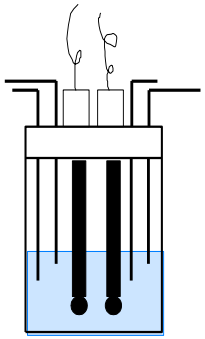
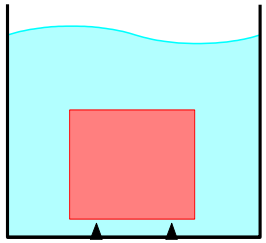


pH DEPENDENCE TEST: BATCH MODE ANC, CEN/TS 14429, or EPA Draft method 1313 or, COMPUTER CONTROLLED CEN/TS 14997

PERCOLATION LEACHING TEST CEN TS 14405 or EPA Draft method 1314

MONOLITHIC MATERIALS

Same as granular **+**



TANK LEACH TEST MONOLITH CEN/TS 15863 and EPA Draft method 1315 and COMPACTED GRANULAR LEACH TEST (NEN 7347 and EPA method 1313).

Chemical speciation aspects

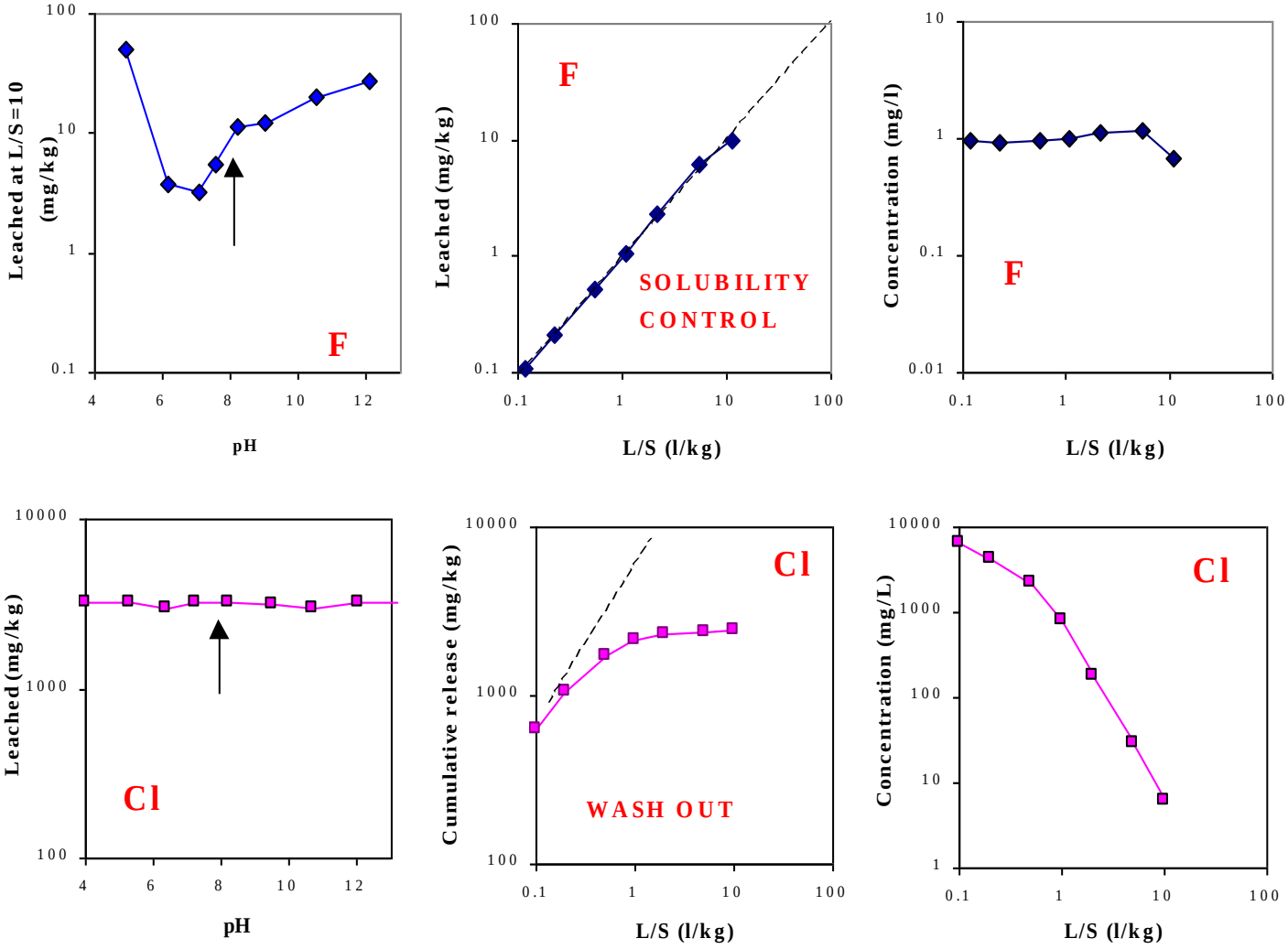
Time dependent aspects of release

Test set covers almost any practical condition for any material

Release from granular materials

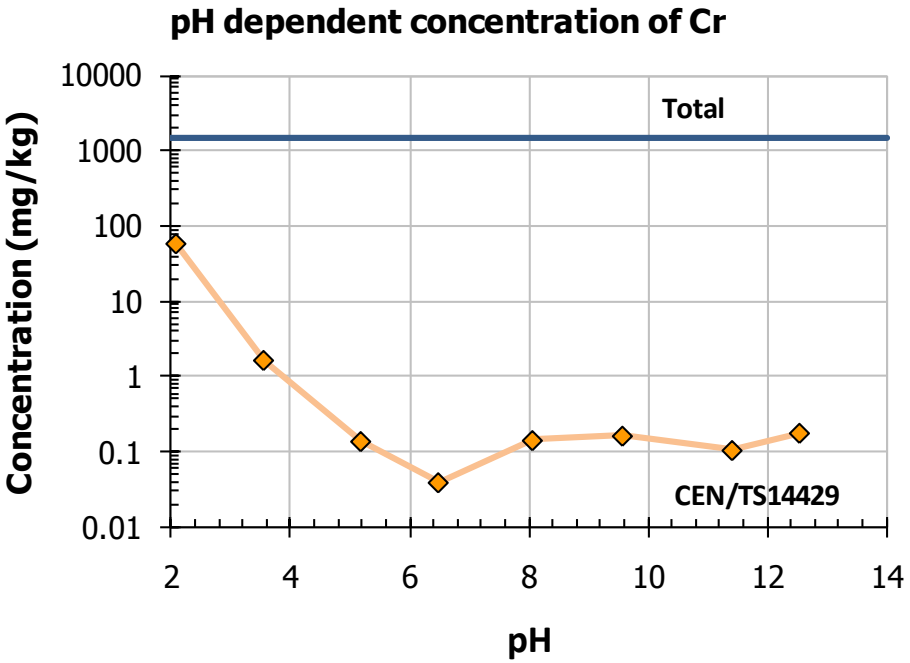
- Leaching of substances from granular materials is assessed by a column leaching test (CEN/TS14405) and pH dependence leaching test CEN TS/14429)
- The column test provides insight in the release behaviour of substances.
- Salts are generally not interacting with the matrix and thus released within a liquid to solid ratio (L/S) of 1
- Many trace contaminants are solubility controlled
- In a column upflow test preferential flow is minimized to ensure repeatability and reproducibility of test data
- Under field conditions a substantial part of the application can be identified as stagnant (dual porosity model)

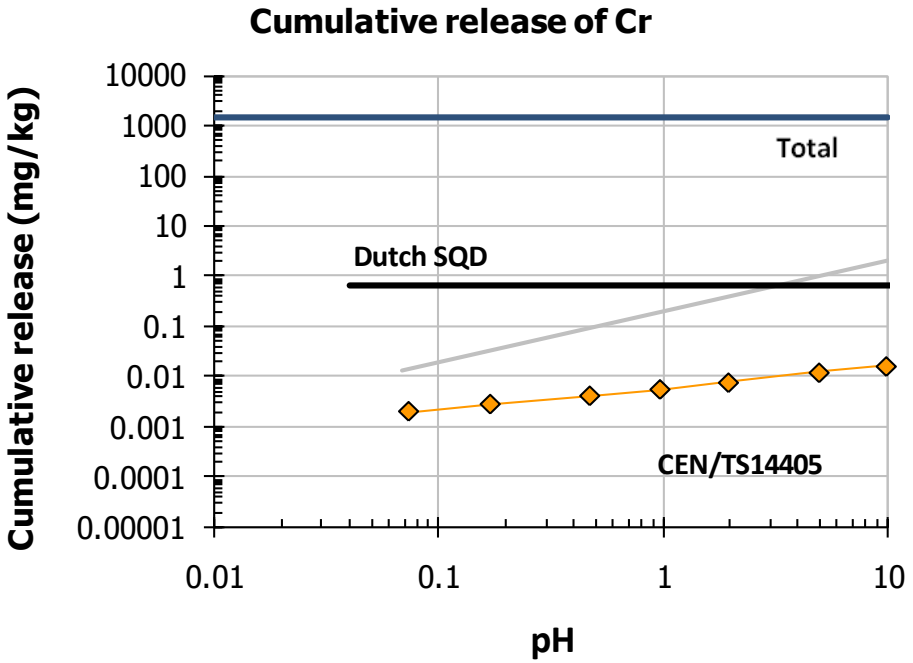
Identification of release processes from testing of granular materials



Judgment of environmental impact on total composition or on leaching?

Steel slag BOF





Relevance of total composition for environmental judgment questionable. Leaching by far more relevant for environmental impact assessment and bioavailability

Judgment of environmental impact on total composition or on leaching?

Substances can be judged at different levels:

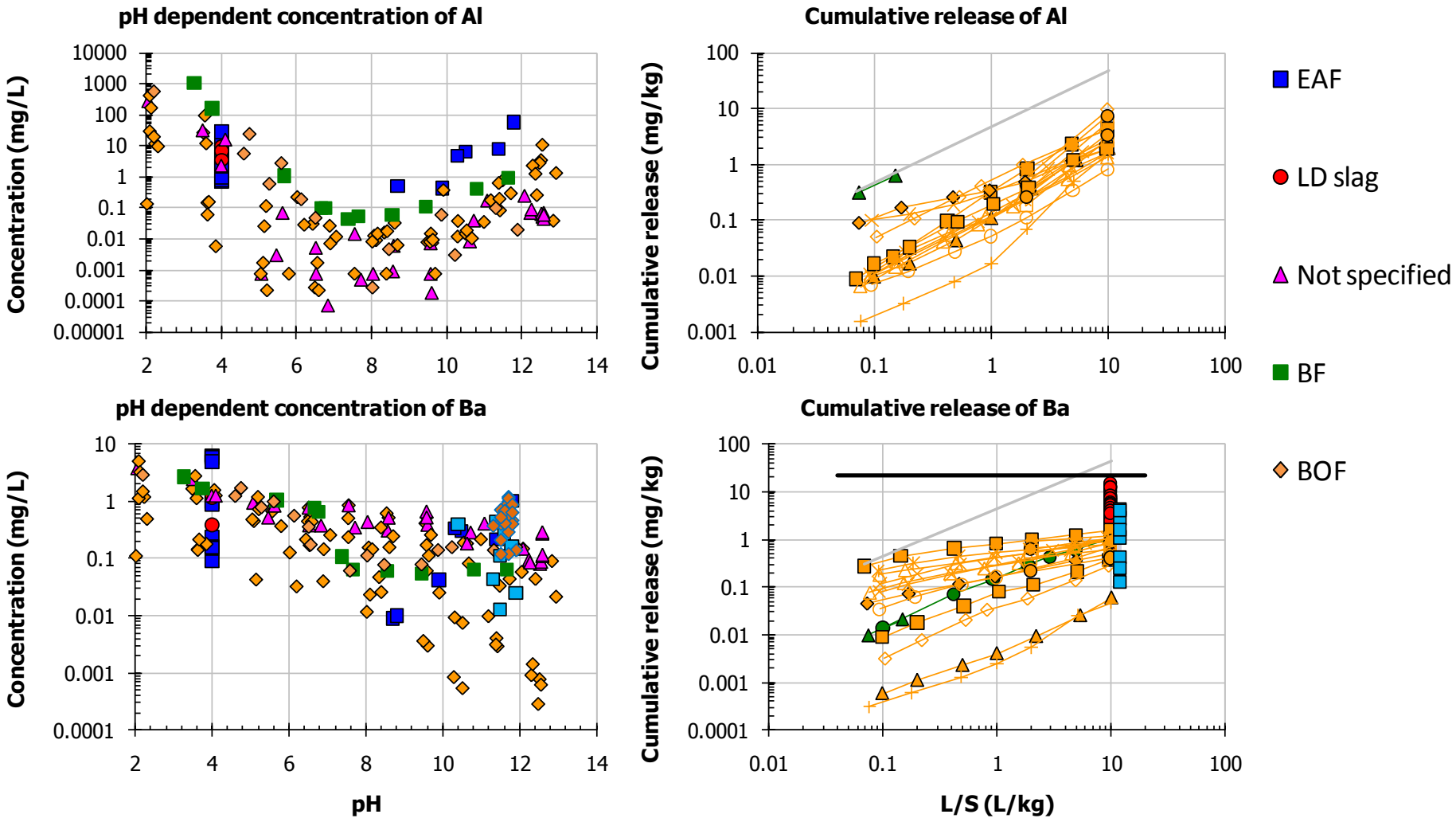
- Total content is generally a poor measure for environmental or health impact as often a small fraction of the total is assessible for uptake or transport
- Potentially leachable (available) is a next level, which can be considered a worst case approach
- Actual leaching in a pH and L/S domain of relevance to the application provides a good measure of possible exposure
- In some case chemical speciation can provide proof that the form in which substances are released is less harmful than assuming the most sensitive form

Understanding of chemical speciation is important for adequate control measures in case of product improvement

Data Management Tools

- Data Templates
  - Excel® Spreadsheets for Each Method
    - Perform basic, required calculations (e.g, moisture content)
    - Record laboratory data
    - Archive analytical data with laboratory information
  - Form the upload file to materials database
- LeachXS (Leaching eXpert System) Lite™
  - Data management, visualization and processing program
  - Compare Leaching Test Data
    - Between materials for a single constituent (e.g., As in two different CCRs)
    - Between constituents in a single material (e.g., Ba and SO_4 in cement)
    - To default or user-defined “indicator lines” (e.g., QA limits, threshold values)
  - Export leaching data to Excel spreadsheets
  - Freely available at http://www.vanderbilt.edu/leaching
- Full LeachXS™ including geochemical tools (subscription fee)

Leaching behaviour of steel slag types



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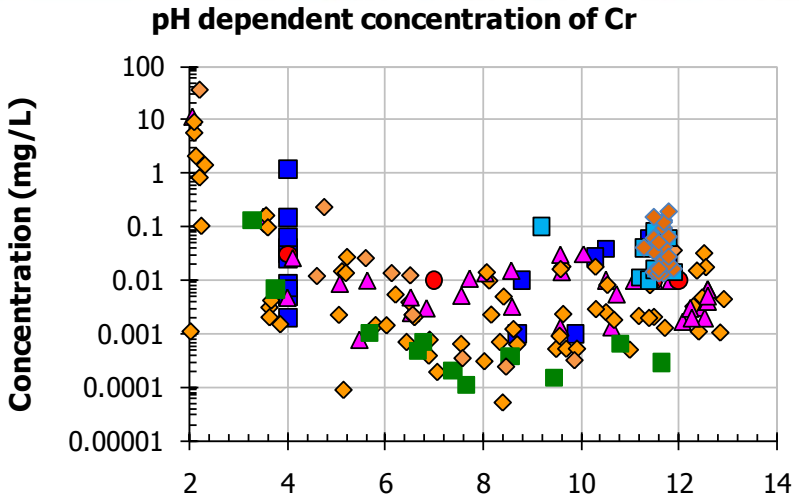
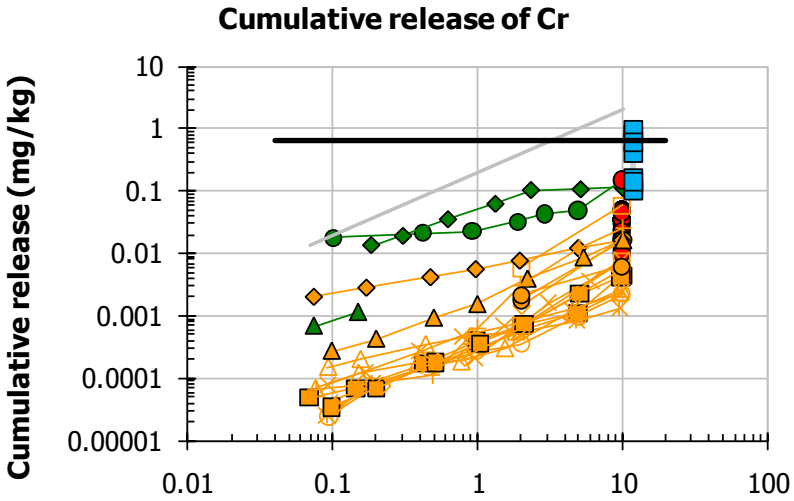
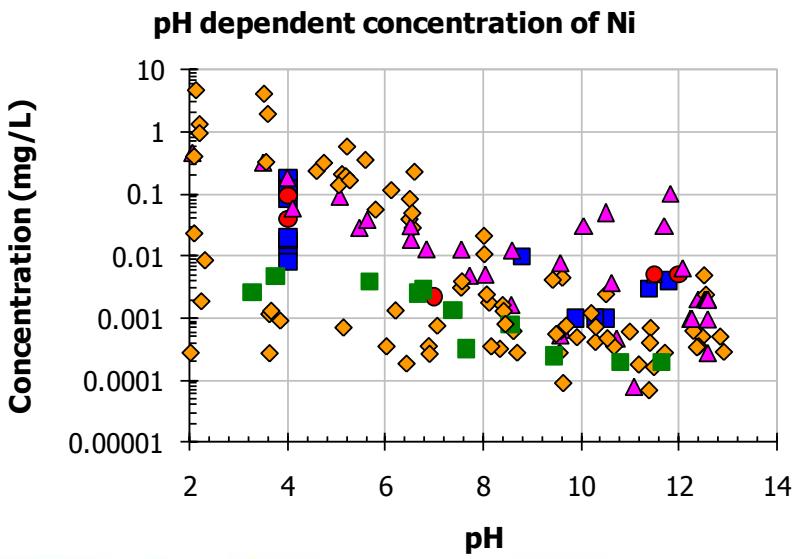
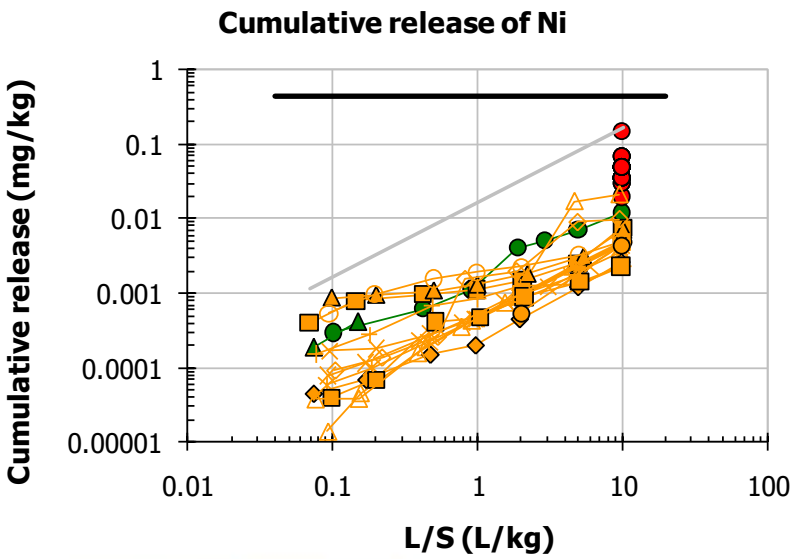


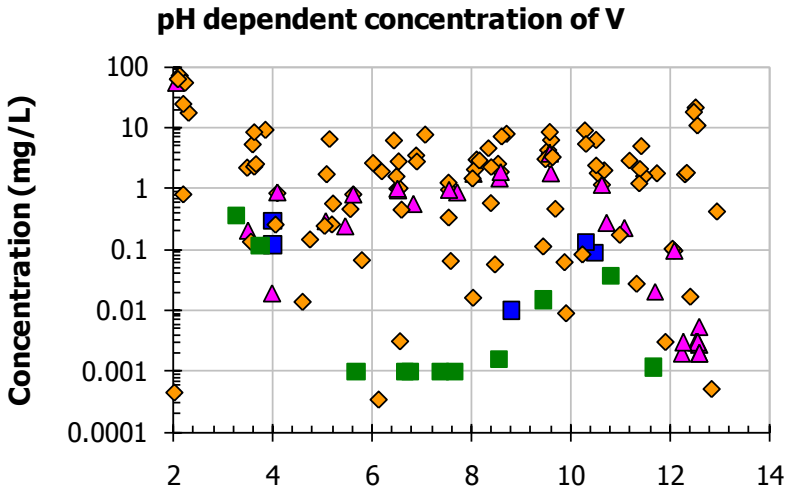


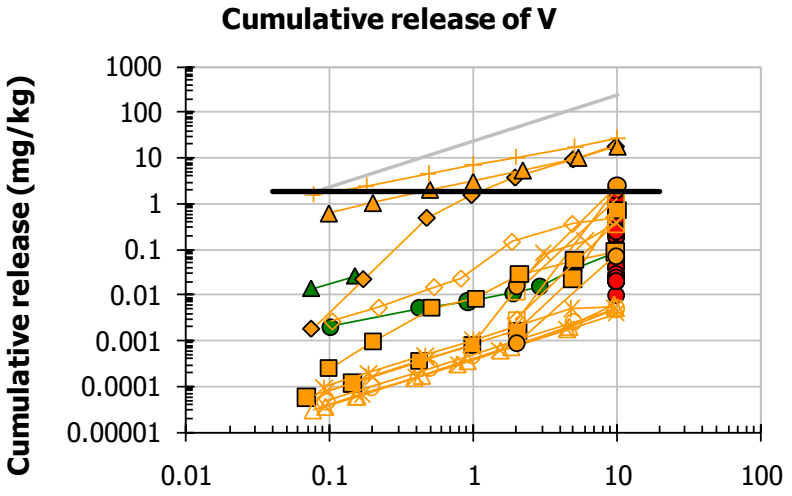


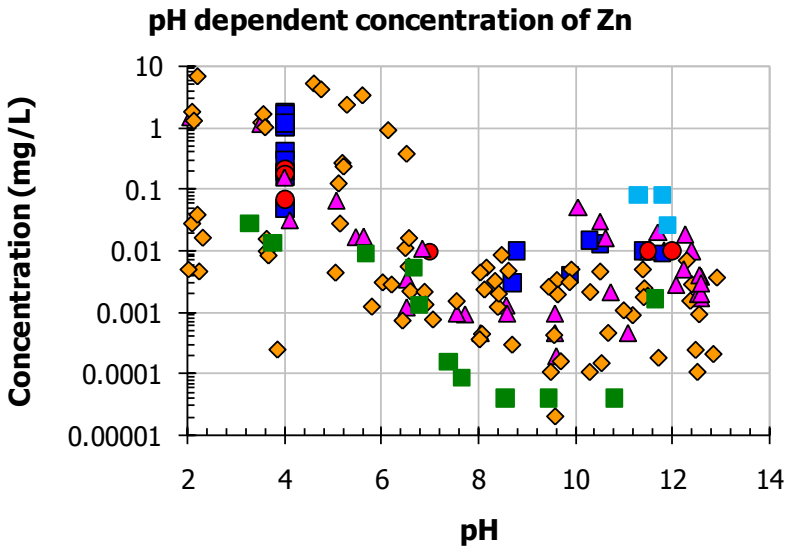


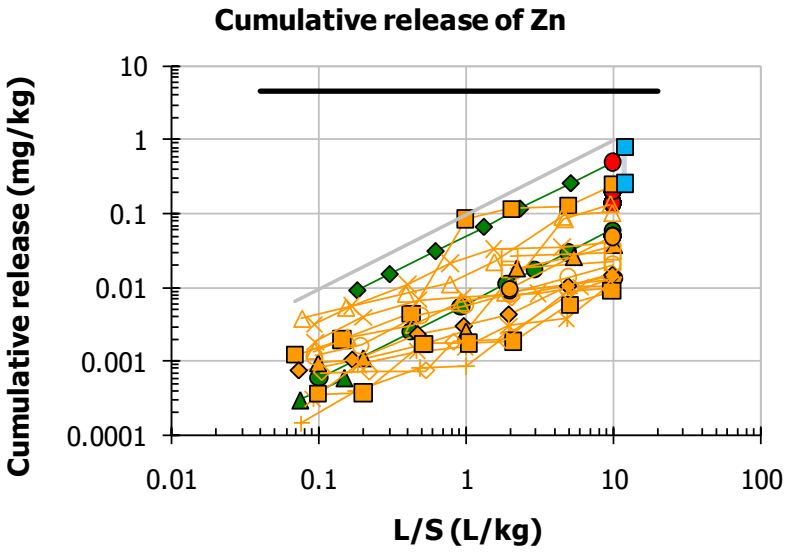
EAF
LD slag
Not specified
BF
BOF

Leaching behaviour of steel slag types









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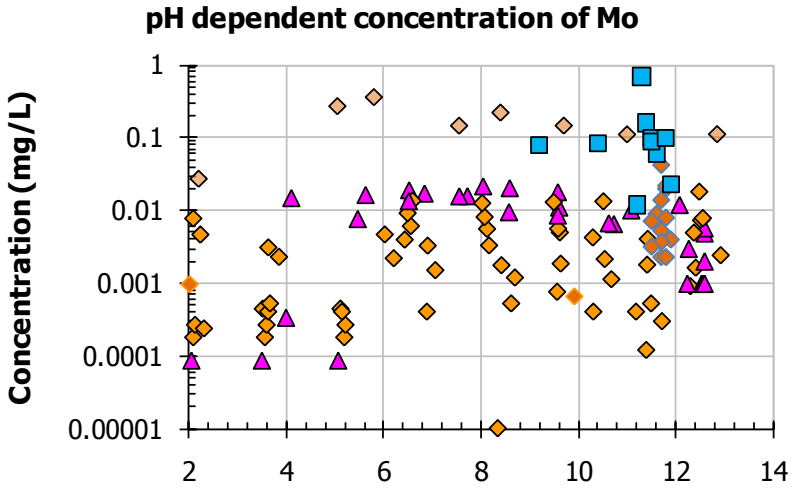
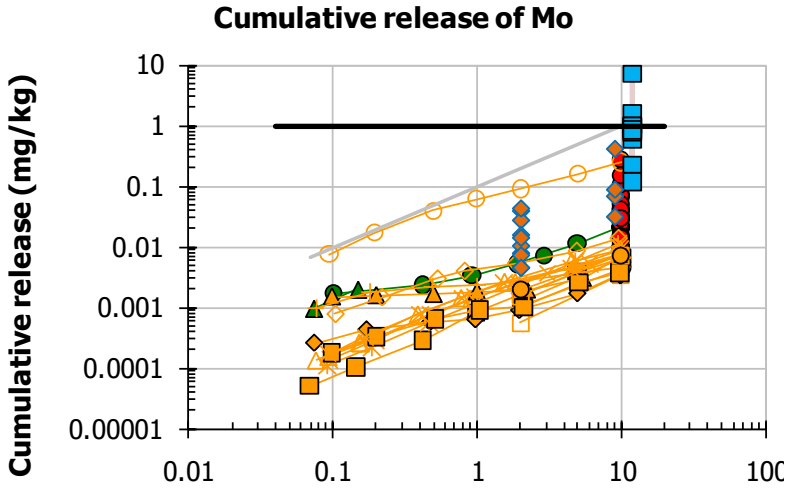
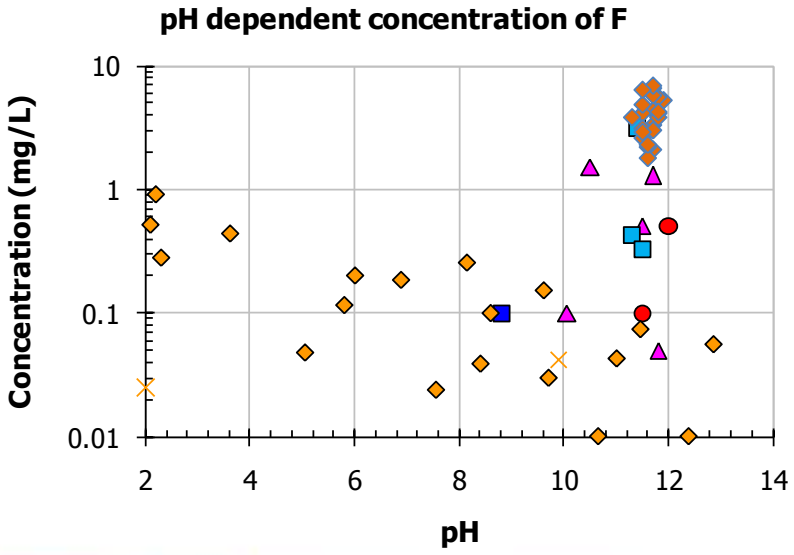
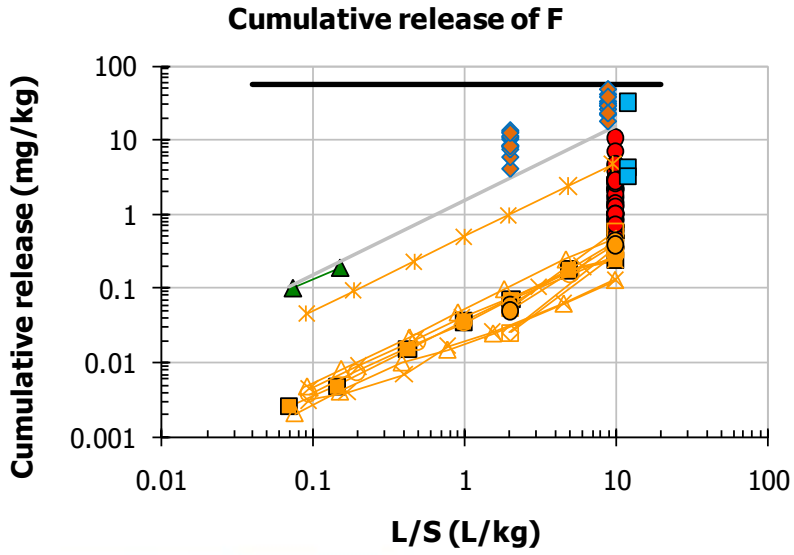




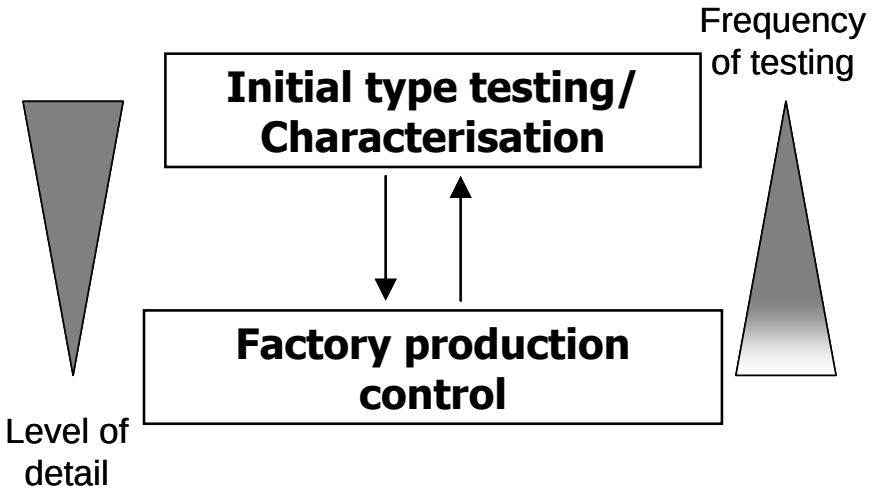




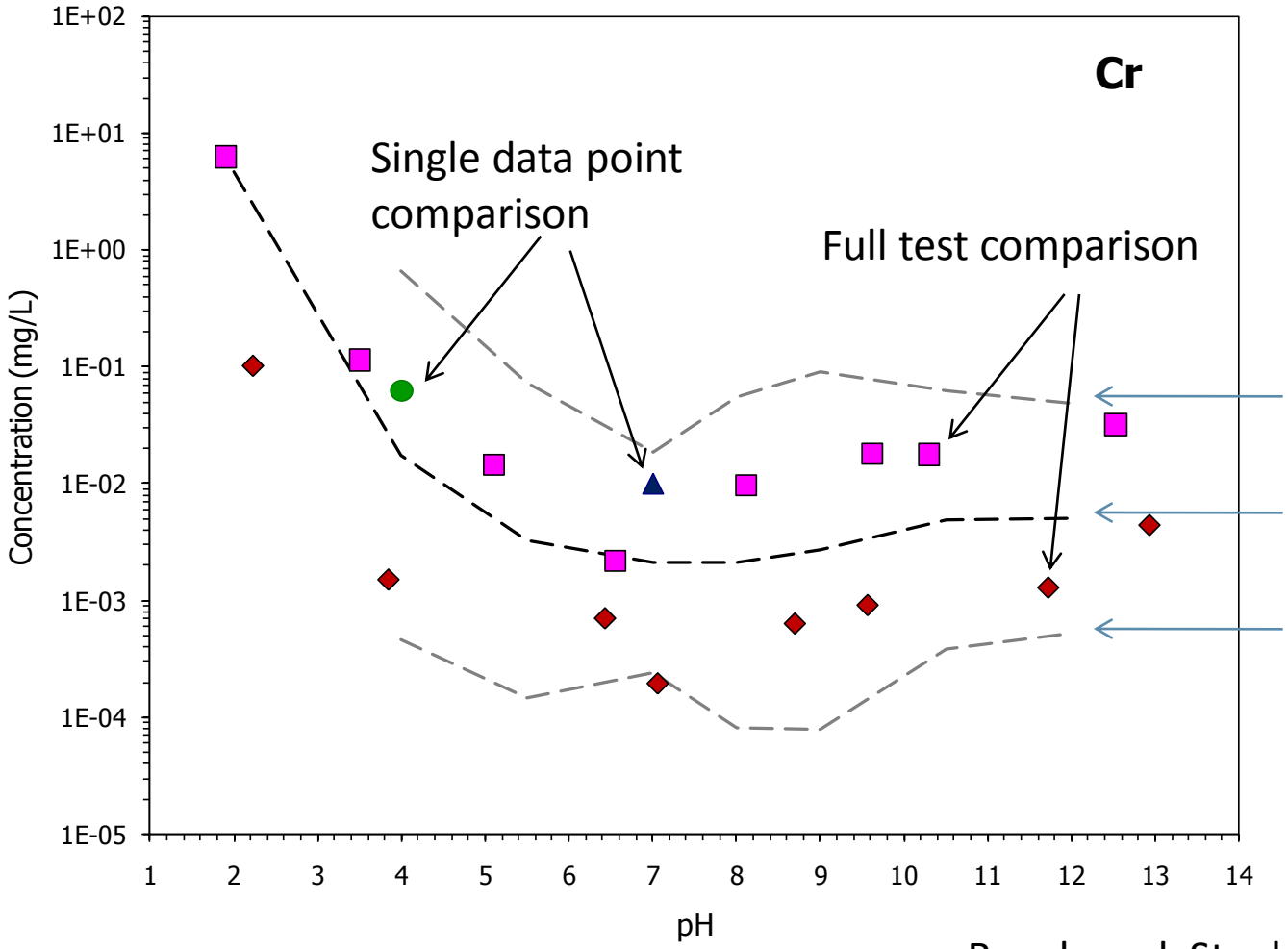
Tiered approach in testing

- Different users of the release information have different needs. Both regulators and industry need information with sufficient detail to allow proper judgment of the materials in their intended use scenario.

- Once the release characteristics of a product type or class are established much simpler conformity testing will suffice for potentially critical parameters only at a frequency consistent with the risk of approaching/ exceeding set limit values by notified regulations.



Statistics applied to consistent data sets for quality control purposes



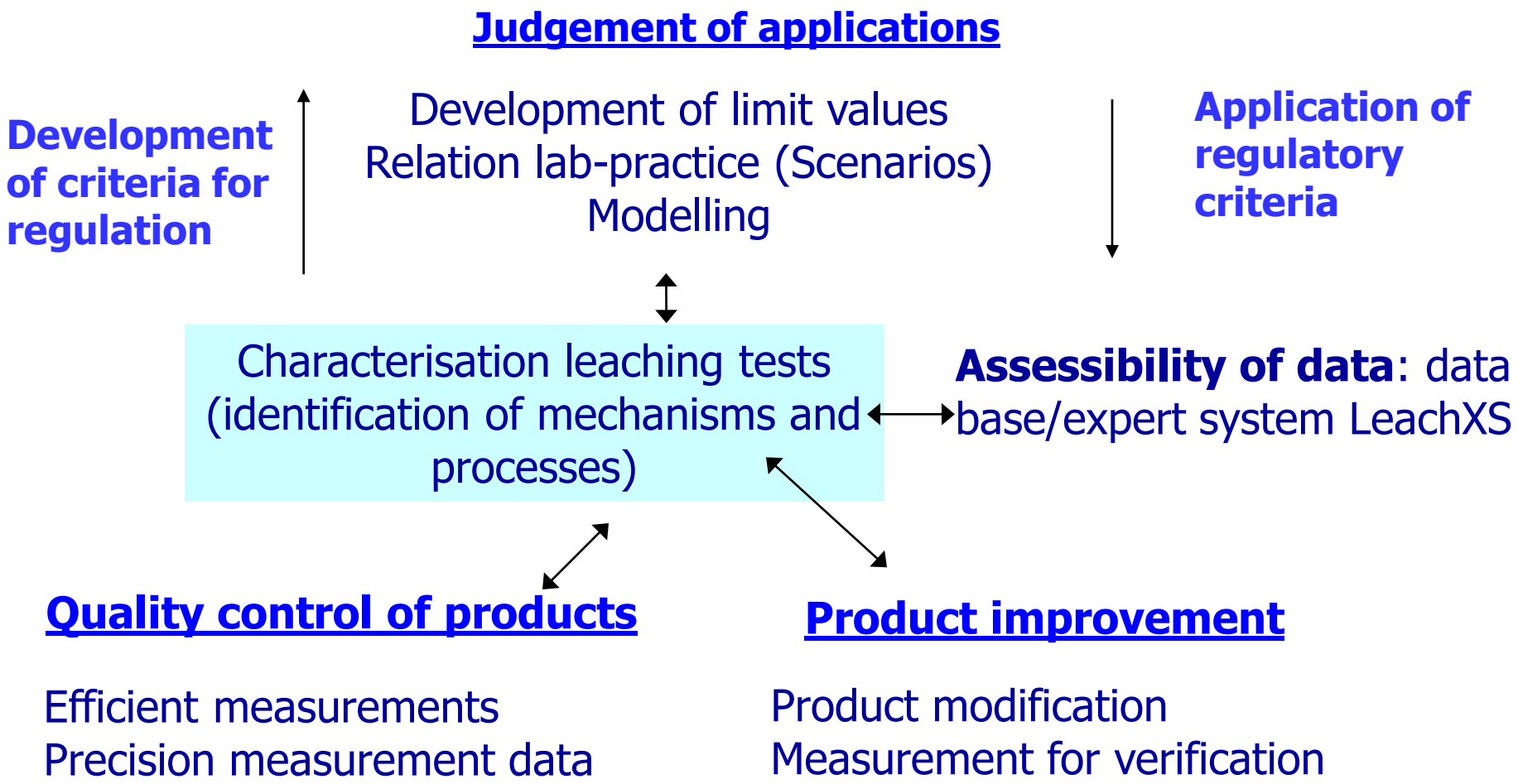
Upper 90 % confidence interval

Mean value for product type

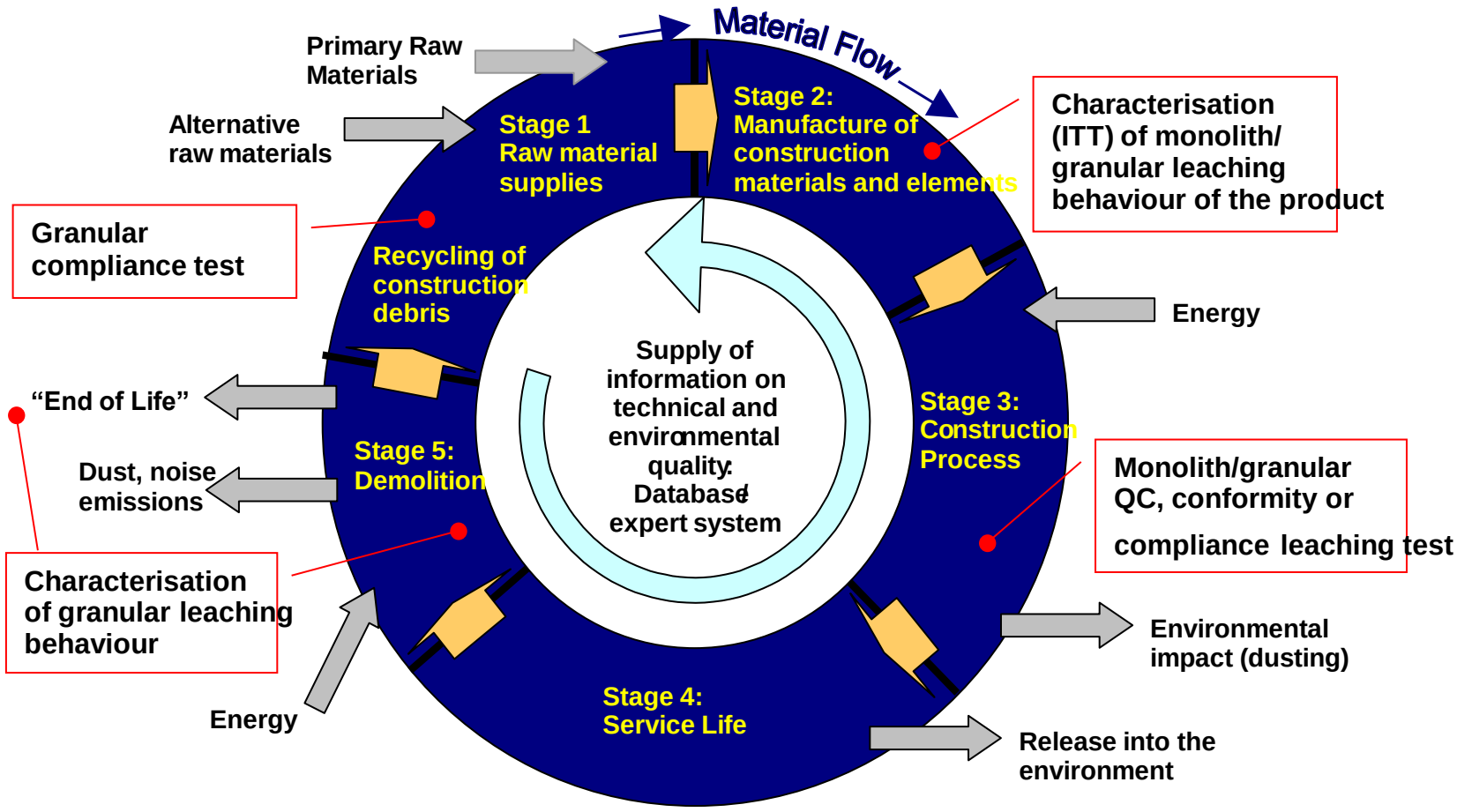
Lower 90 % confidence interval

Benchmark Steel slag - pH dependence

Role of Characterisation Leaching Tests in Environmental Judgement of Materials



Tiered approach linked to the building cycle



CPD -> CPR

Steps in chemical speciation modelling

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

2. measurement of release from granular materials in a percolation test or from monolithic specimen according to a type of tank test

3. speciation modelling to identify relevant mineral phases (SI-indices)

4. refined description of multi element 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)

5. the resulting chemical speciation fingerprint (CSF) is used as input for the chemical reaction/transport modelling to describe the release from a percolation test or from a monolithic specimen (tank test simulation).

6. model the field scenario using the CSFs for the different layers of material involved using external factors (carbonation, oxidation, biologically mediated reactions) and realistic estimates of infiltration (e.g. preferential flow)

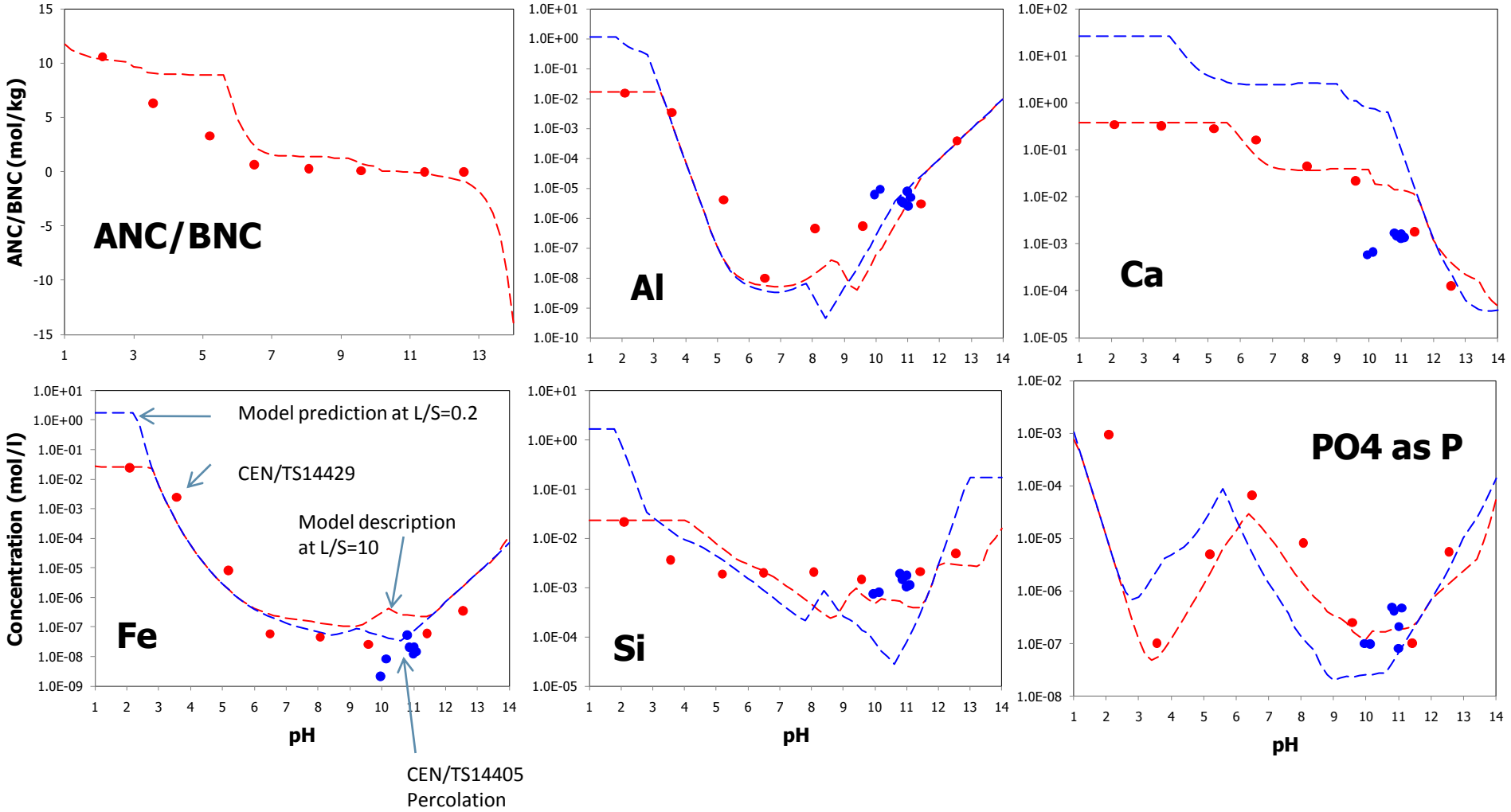
Input (Chemical Speciation Fingerprint)

- Element availabilities (major minor and trace elements from pH dependence test)
- Liquid to Solid ratio (L/S=10)
- Redox status of material/product pH+pe = 15 (oxidised)
- Clay content (kg/kg)
- Reactive Hydrated Ironoxide surface (HFO in kg/kg)
- Reactive Solid Humic Acid (SHA in kg/kg)
- Dissolved Organic Carbon (DOC in kg/l from pH dependence test)
- Selection of potentially relevant minerals controlling solubility (Partly taken from a model run to determine saturation indices (SI) for all available minerals in the thermodynamic database)

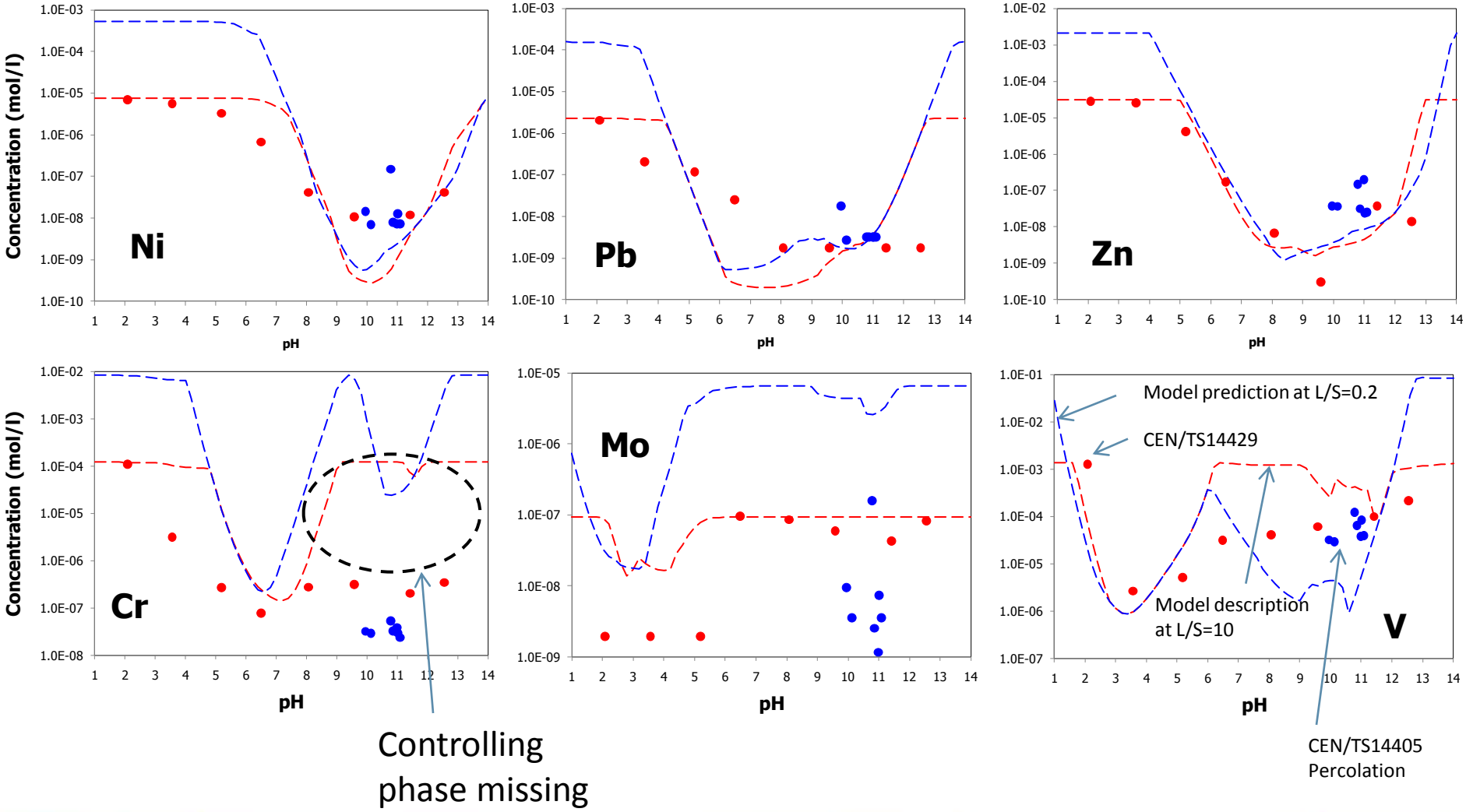
Example Input (Chemical Speciation Fingerprint)

Input specification								
Prediction case	Steelslag Carb + columnAA EA		**DOC/DHA data**					
Speciation session	Steelslag Carb + columnAA EA		**pH**	**[DOC] (kg/l)**	**DHA fraction**	**[DHA] (kg/l)**	**nomial coeficients**	
Material	Steel_slag_carbonated_30% (P,1,1)		1.00	2.000E-05	0.20	4.000E-06	**C0**	-5.775E+00
			2.09	1.000E-05	0.20	2.000E-06	**C1**	6.397E-01
Solved fraction DO	0.2		3.56	4.000E-06	0.20	8.000E-07	**C2**	-3.793E-01
Sum of pH and pe	15.00		5.19	4.250E-06	0.20	8.500E-07	**C3**	6.435E-02
L/S	10.4258	**l/kg**	6.49	1.000E-06	0.20	2.000E-07	**C4**	-4.332E-03
Clay	0.000E+00	**kg/kg**	8.07	1.000E-06	0.20	2.000E-07	**C5**	1.017E-04
HFO	3.000E-03	**kg/kg**	9.58	6.300E-06	0.20	1.260E-06		
SHA	2.000E-04	**kg/kg**	11.42	7.100E-06	0.20	1.420E-06		
Percolation materi	steelslag_Corus_K1RCS_treated_1 (C,1,1		12.55	2.400E-06	0.20	4.800E-07		
Avg L/S first perc. f	0.1495	**l/kg**	14.00	3.000E-06	0.20	6.000E-07		
Reactant concentrations								
Reactant	**mg/kg**							
Ag+	not measured	Fe+3	1.573E+04	Mn+2	7.044E+03	SO4-2	1.011E+03	
Al+3	4.689E+03	H2CO3	4.200E+04	MoO4-2	9.358E-02	Sr+2	8.935E+01	
Ba+2	5.684E+01	H3AsO4	8.351E-01	Na+	8.996E+01	VO2+	7.311E+02	
Ca+2	1.588E+05	H3BO3	3.080E+01	Ni+2	4.627E+00	Zn+2	2.103E+01	
Cd+2	1.300E-01	H4SiO4	6.864E+03	Pb+2	4.871E+00			
CrO4-2	6.560E+01	K+	1.580E+02	PO4-3	1.016E+03			
Cu+2	5.644E+00	Li+	4.572E-01	Sb[OH]6-	3.464E-01			
F-	not measured	Mg+2	1.211E+04	SeO4-2	2.407E+00			
Selected Minerals								
AA_2CaO_Al2O3_SiO2_8H2O[s]			AA_Fe[OH]3[am]	Barite	Ca3[VO4]2	Fe2[MoO4]3[1]	Ni[OH]2[s]	Rhodochrosite
AA_2CaO_Fe2O3_SiO2_8H2O[s]			AA_Gibbsite	BaSrSO4[50%Ba]	Ca4Cd[PO4]3OH	Ferrihydrite	Ni2SiO4	Sphalerite
AA_3CaO_Al2O3[Ca[OH]2]0_5_[CaCO3]0_5_11_5H2O[s]			AA_Gypsum	beta-TCP	Calcite	Fluorite	OCP	Strengite
AA_3CaO_Al2O3_6H2O[s]			AA_Portlandite	Boehmite	CaMoO4[c]	Huntite	Otavite	Strontianite
AA_3CaO_Al2O3_CaCO3_11H2O[s]			AA_Tobermorite-I	Brucite	Cd[OH]2[C]	Laumontite	Pb[OH]2[C]	Tenorite
AA_3CaO_Fe2O3_CaCO3_11H2O[s]			AA_Tricarboaluminate	Ca_Vanadate	Cr[OH]3[A]	Magnesite	Pb2V2O7	Wairakite
AA_Calcite			Ba[SCr]O4[96%SO4]	Ca2Cd[PO4]2	Diaspore	Manganite	Pb3[VO4]2	Willemite
AA_CO3-hydrotalcite			BaCaSO4[75%Ba]	Ca2V2O7	Fe_Vanadate	Morenosite	PbMoO4[c]	ZnSiO3

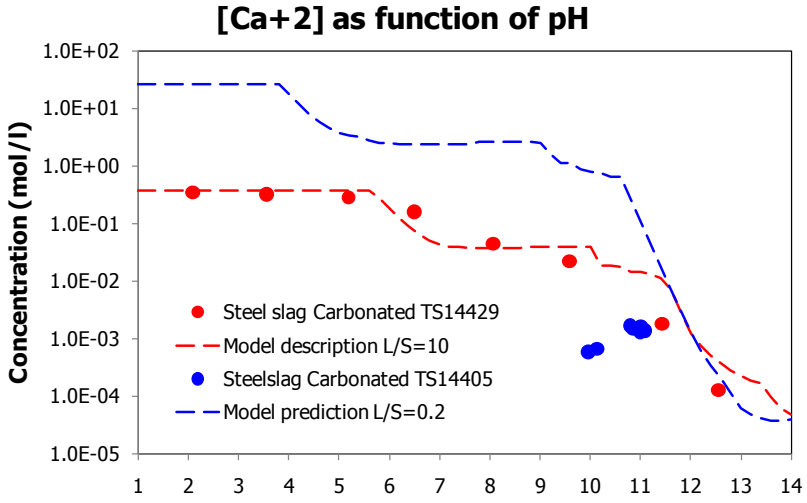
Chemical speciation modelling of carbonated steel slag

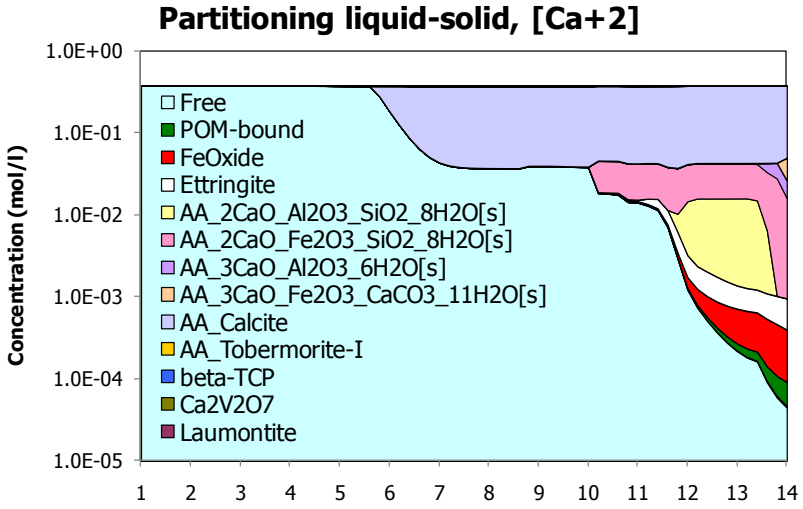


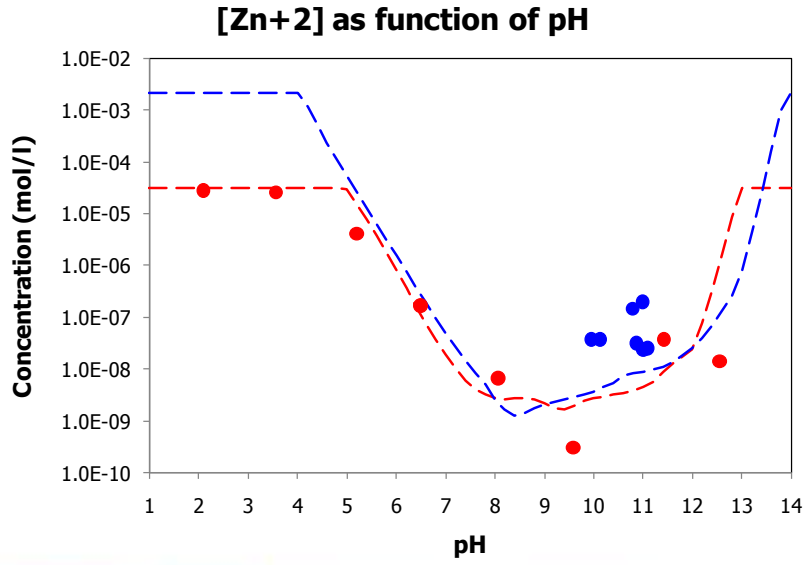
Chemical speciation modelling of carbonated steel slag

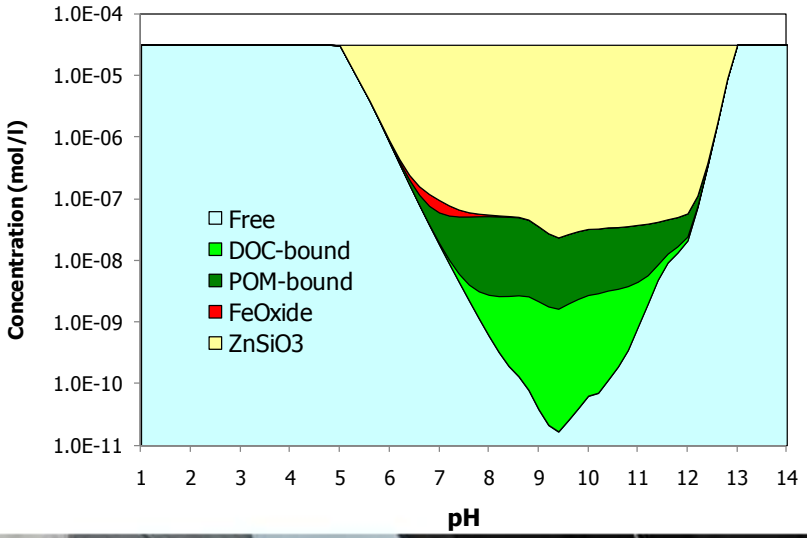


Ca and Zn leaching description and partitioning

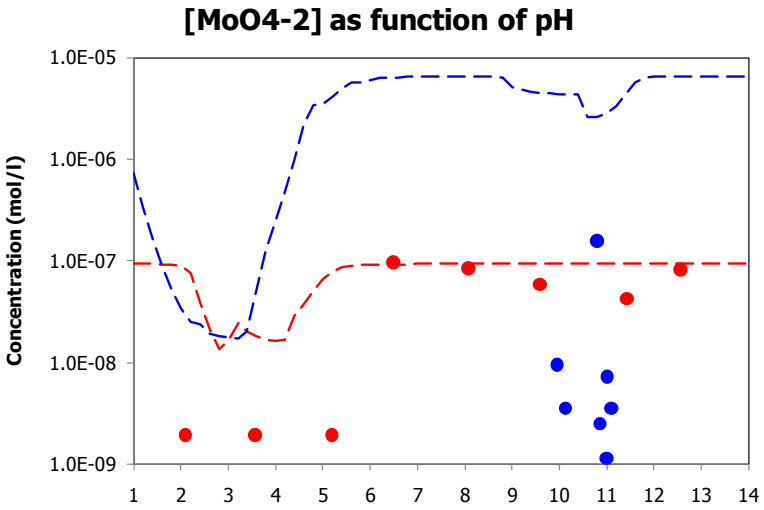


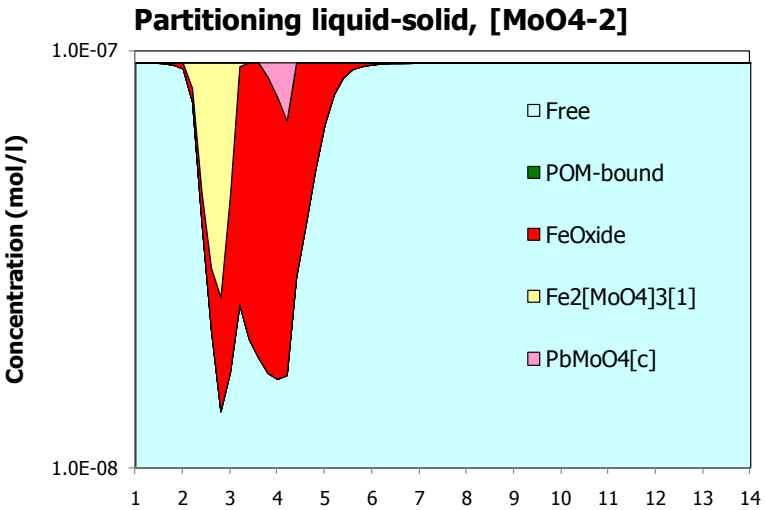




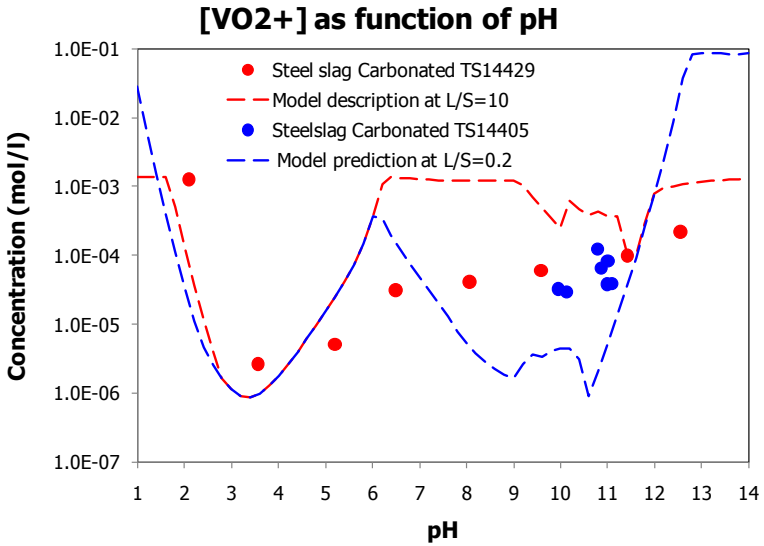


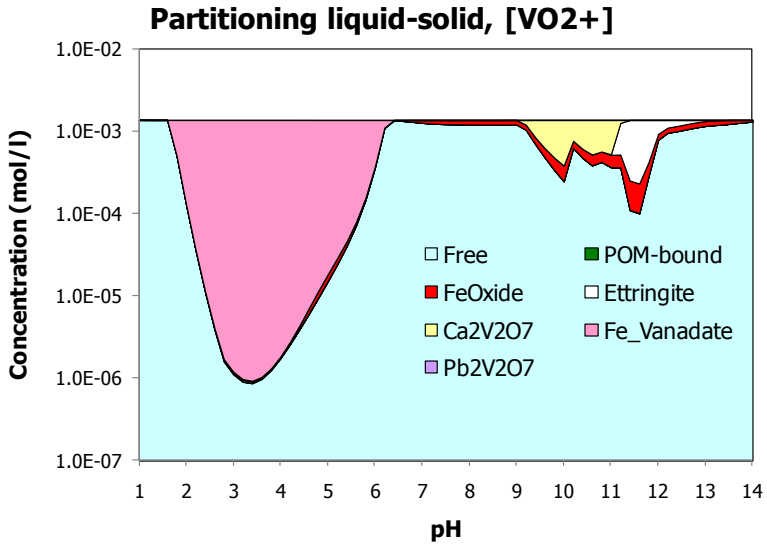
Mo and V leaching description and partitioning





Mo largely mobile at pH 10-11 – wash out



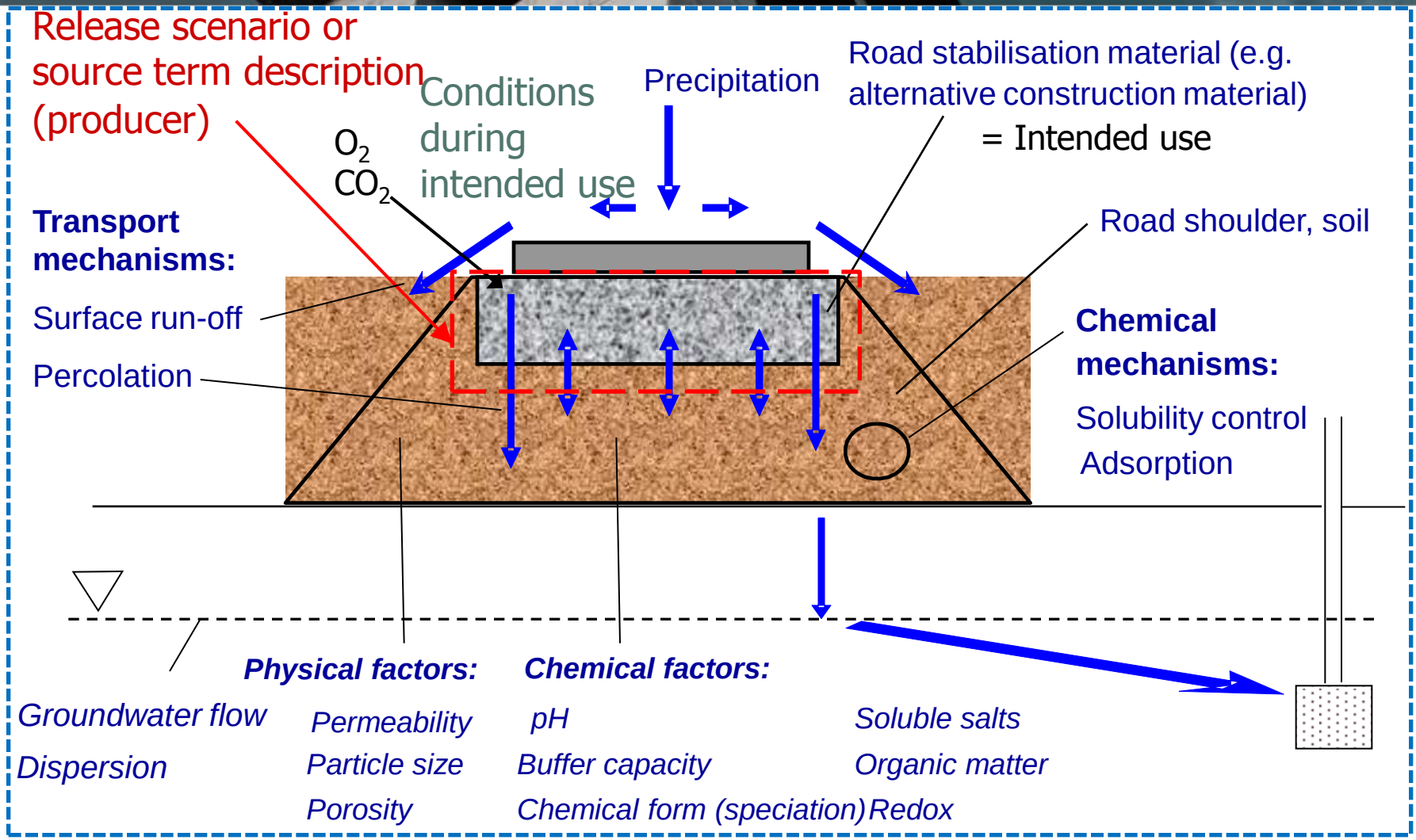


Solubility control for V at pH10 -11 and L/S 0.2 - 10

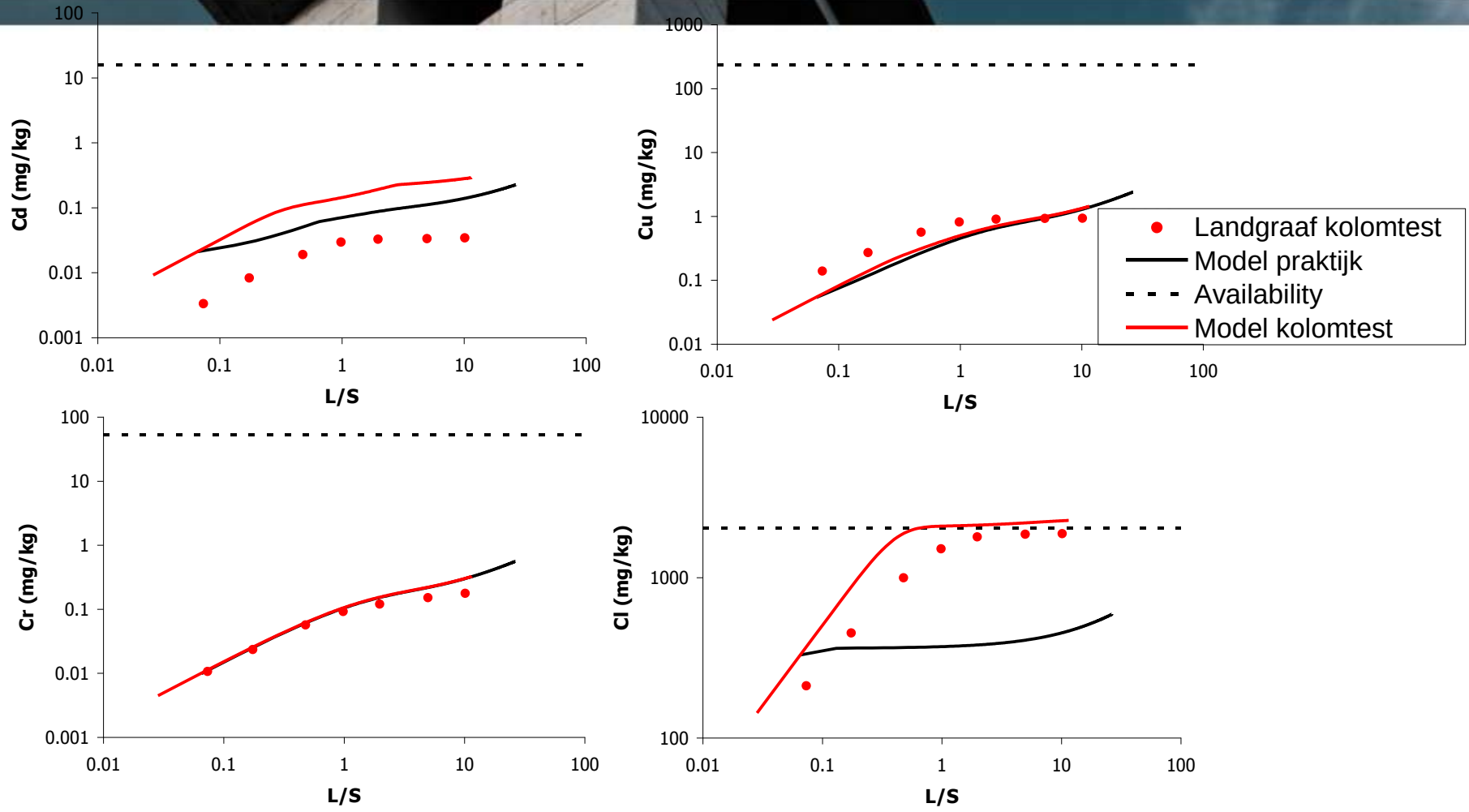
Why is speciation and partitioning important?

- The chemical form of elements dictates their potential environmental risk
- Whether Cr is present as chromate, Cr III or Cr-DOC complex has significant consequences for the actual impact
- Chromate (Cr VI) generally present in coal fly ash at pH > 8 is more toxic than Cr III
- Cr III – DOC complex is almost as mobile as chromate and may travel relatively fast through soil. The two forms should not be confused.
- DOC complexation of metals is important for their ecotoxicity as many organisms are insensitive to DOC complexed metals
- Understanding speciation allows focussed material management

Processes in a Road Base Application - definitions



Prediction leachate quality taking preferential flow into account (80% stagnant- dual porosity model)

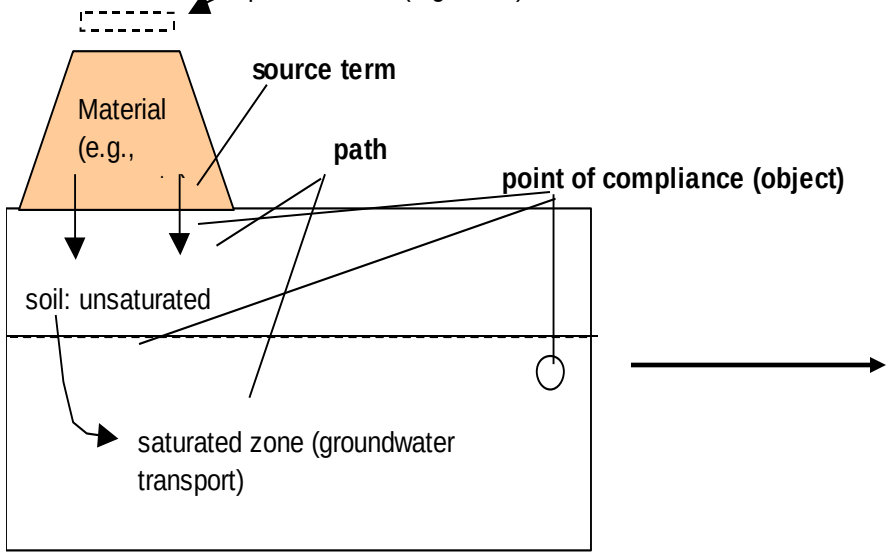


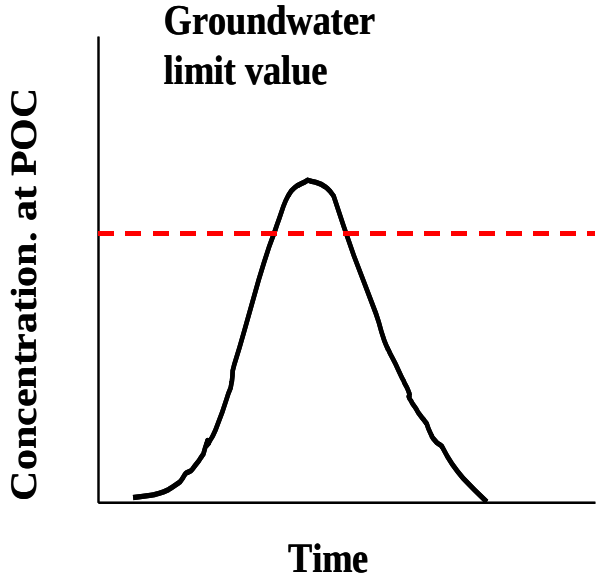
Cd affected by substantially reduced Cl release, other metals not influenced (solubility controlled). Cl substantially reduced by preferential flow

Impact Evaluation and Criteria Development

Depending on the modeled groundwater quality at the POC (which might be chosen anywhere), limits to the release of the construction products might be adjusted such that the product eventually complies with the groundwater limit value at the POC.

Approach with POC in groundwater applied for EU LFD, Dutch BMD and Dutch SQD





POC = point of compliance

Conclusions

- A limited set of proper characterisation tests suffices to describe release behaviour from materials and products in a variety of applications
- Harmonisation and horizontal standardisation is possible
- Significant progress in understanding release controlling processes has been made
- Test results can not be compared directly with water quality criteria, as mimicking the field in the lab is generally not possible.
- Many substances are solubility controlled, thus providing a good understanding of effects at longer term.
- Highly soluble substances are generally most sensitive from an impact assessment perspective (initial peak concentrations).
- The multi-element multi-phase chemical reaction transport modelling is a challenge, but a highly rewarding one, when the behaviour of steel slag in laboratory tests can be described.

Recommendations

- Emphasize release based judgment as opposed to content based judgment for environmental impact purposes
- Bring together more data on steel slag leaching to be able to define the bandwidth of release behaviour
- Generate information where gaps are identified
- Steel slag release behaviour is process related and thus sharing test data at global scale makes a lot of sense
- Develop benchmark characterisation data for steel slag and where needed subdivided for specific steel slag types - LeachXS Lite (free) can provided such service

Thank you for your attention

Questions?