Energy research Centre of the Netherlands

Modelling release of inorganic substances from cement stabilized waste

Hans Meeussen and Hans van der Sloot

Outline

- Introduction
- Testing - Modelling
- ORCHESTRA model
- Simulation of tank test
- Comparison test methods
- Conclusions

Characteristics of cement stabilized – waste systems

- Solid, Porous
- Alkaline
- Not in equilibrium with environment
- Contain inorganic contaminants
- Possible release of contaminants by diffusion

How fast will contaminants leach from material over time?

Estimation of leaching behaviour of cement-waste materials under environmental conditions

Testing

Ideally: design / use leaching test that provides representative leaching data

However: Leaching is not a material property, depends on conditions!

Modelling

Process knowledge / hypotheses can be used to construct model

- Model helps to design optimal test procedure
- Test can be used to evaluate model
- Model can be used to predict leaching behaviour in application scenario.

Combination of modelling and testing is necessary!

Overview of ORCHESTRA "model"

ORCHESTRA (Object Representation of CHEmical speciation and TRAnsport models)

Is a framework for implementing chemical speciation models with mass transport.

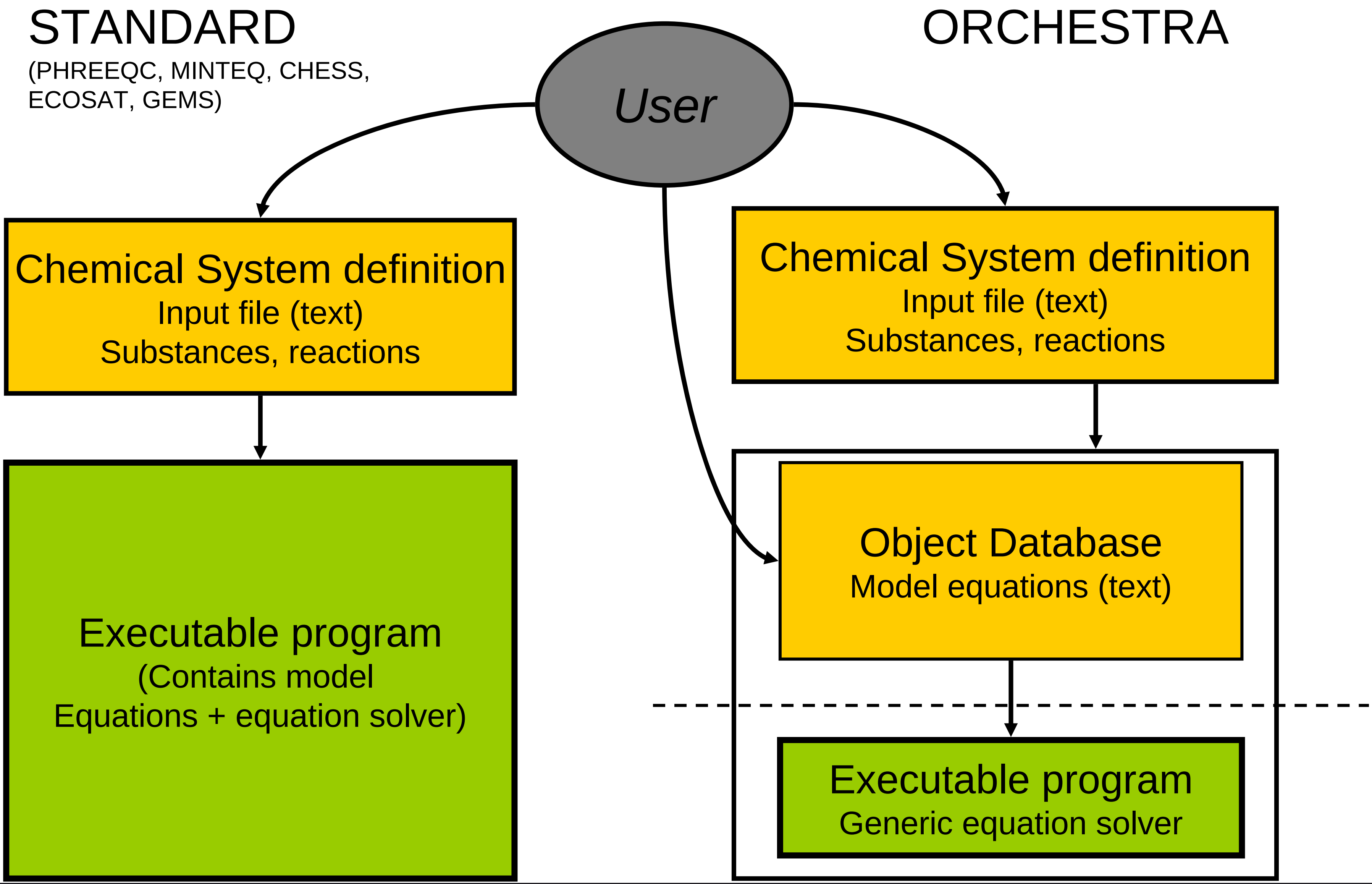
Chemical module:

- **Contains set of "standard" chemical equilibrium models.**
- **Reads standard reaction databases.**
- **Graphical user interface for chemical model definition.**
- **State-of-the-art adsorption models, including Nica-Donnan, CD-MUSIC model.**
- **Open structure, models can be added by users.**

Transport module:

- **Standard, diffusion, convection, dispersion, (unsaturated) waterflow**
- **Flexible system lay-out (1d, 2d, 3d, radial etc.)**
- **User definable transport processes.**

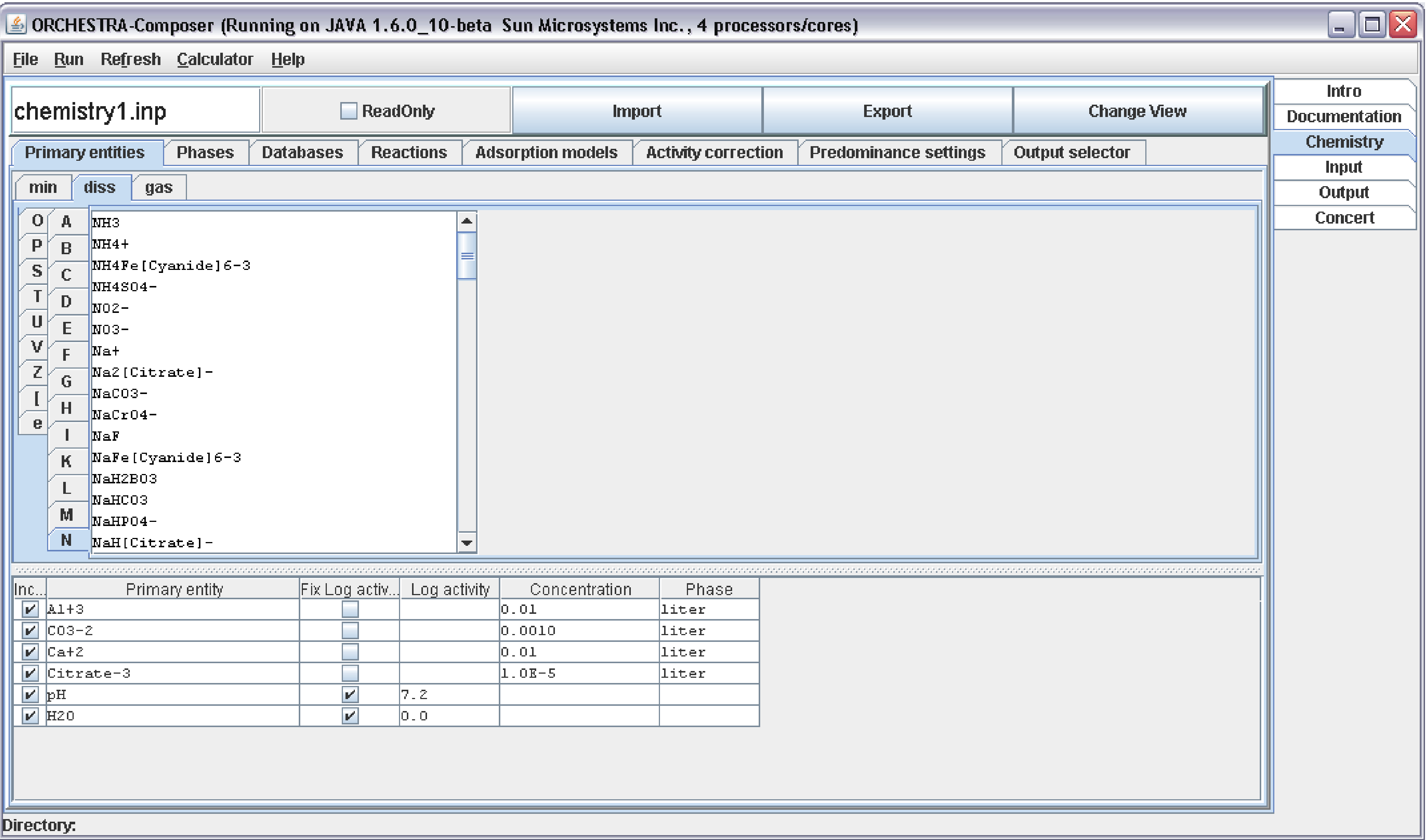
Overview of ORCHESTRA chemical equilibrium module



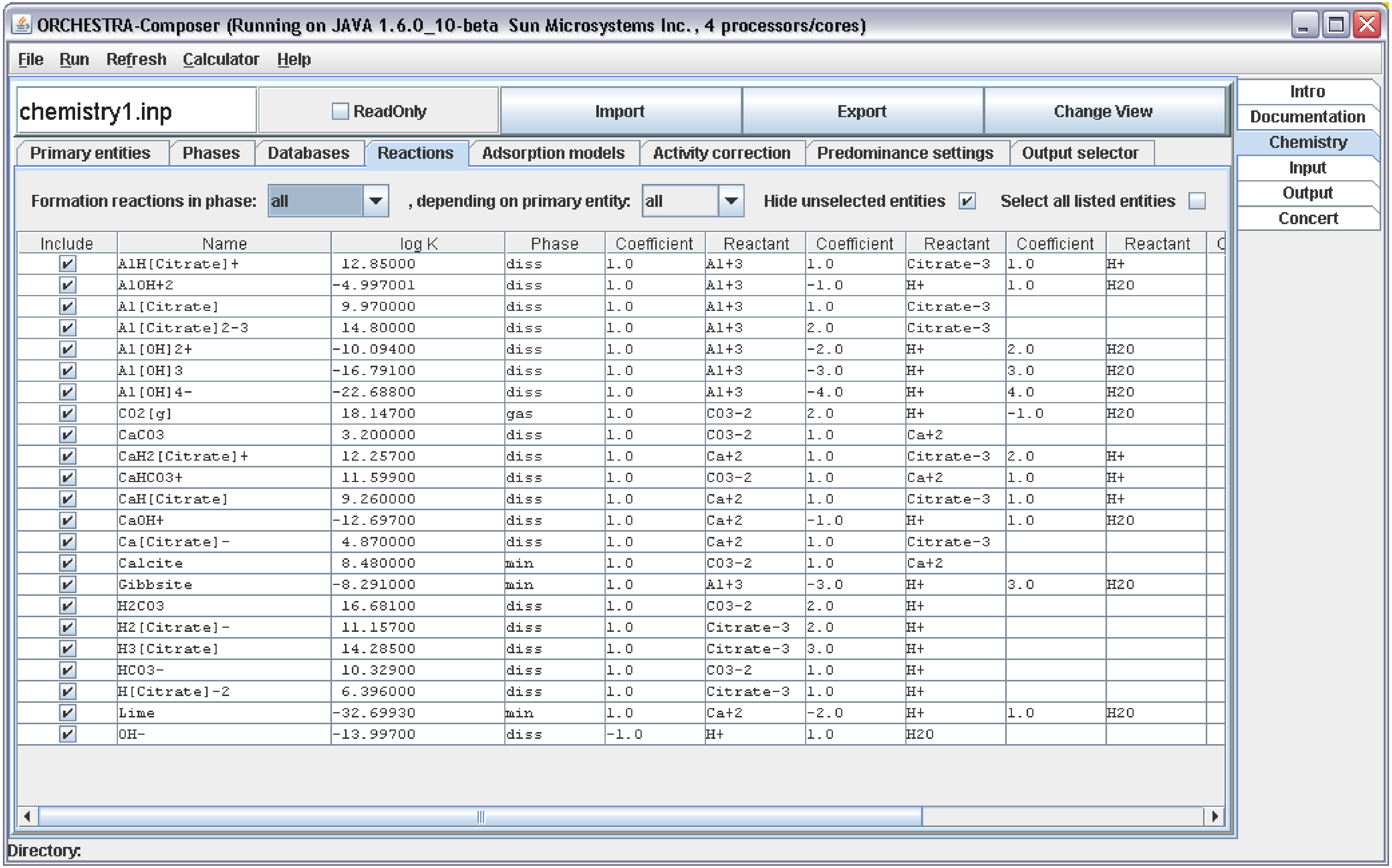
Solid Solution model in ORCHESTRA

```
@Class: solid_solution(name, parent_phase)
{
  @Var:  <name>.un   .1
  @Var:  <name>.eq   0
  @Var:  <name>.est_sum    0

  @entity(<name>, <name>, 0, 0)

  @Calc:(1,"<name>.est_sum = if(<name>.un >= 0,   (<name>.un),   0)  ")
  @Calc:(3,"<name>.eq=if(0><name>.un,(log(<name>.<name>)-<name>.un),1-<name>.<name>)")

  @Uneq2: unknown:(name:, <name>.un, delta:, 1e-6, type:, lin, step: , .1) equation:(name:, <name>.eq, tol: , 1e-3)
}



@solid_solution(ettr_ss, min)

@entity(ettr_ss1, ettr_ss, 1 )
@reaction(ettr_ss1,  1.01859e-57 , 2.0, Al+3, 6.0, Ca+2, -12.0, H+, 3.0, SO4-2, 1.0, ettr_ss)
@entity(ettr_ss10, ettr_ss, 1 )
@reaction(ettr_ss10,  1.01859e-42 , 2.0, Al+3, 6.0, Ba+2, -12.0, H+, 3.0, SO4-2, 1.0, ettr_ss)
@entity(ettr_ss2, ettr_ss, 1 )
@reaction(ettr_ss2,  2.55859e-55 , 2.0, Al+3, 6.0, Ca+2, 3.0, CrO4-2, -12.0, H+, 1.0, ettr_ss)
@entity(ettr_ss3, ettr_ss, 1 )
```

ECN

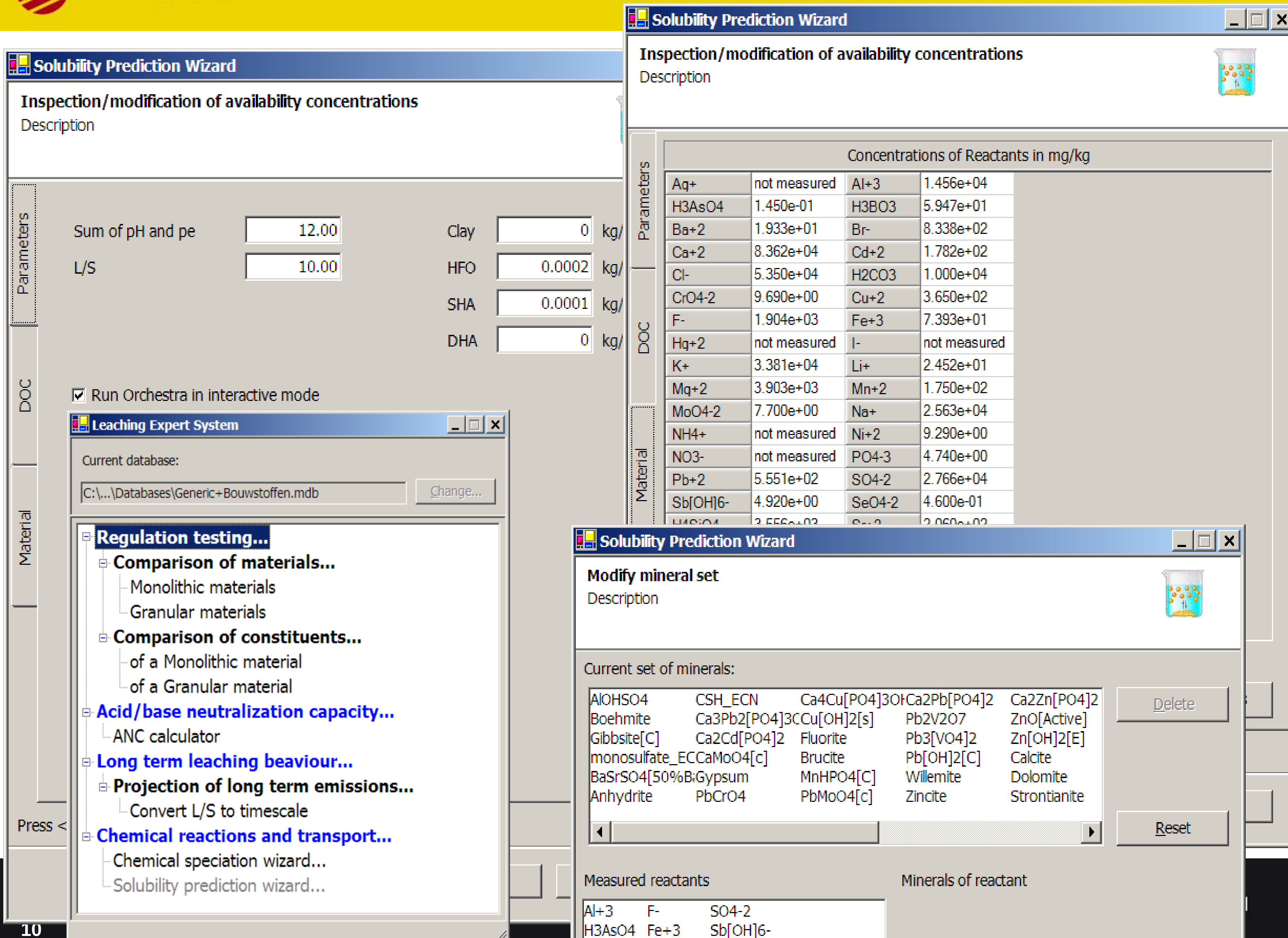

ORCHESTRA-Composer (Running on JAVA 1.6.0_10-beta Sun Microsystems Inc., 4 processors/cores)
File Run Refresh Calculator Help
chemistry1.inp
ReadOnly
Import
Export
Change View
Intro
Documentation
Chemistry
Input
Output
Concert
Primary entities
Phases
Databases
Reactions
Adsorption models
Activity correction
Predominance settings
Output selector
min
diss
gas
O P S T U V Z [e
A B C D E F G H I K L M N
NH3
NH4+
NH4Fe[Cyanide]6-3
NH4SO4-
NO2-
NO3-
Na+
Na2[Citrate]-
NaCO3-
NaCrO4-
NaF
NaFe[Cyanide]6-3
NaH2BO3
NaHCO3
NaHPO4-
NaH[Citrate]-
Inc... | Primary entity | Fix Log activ... | Log activity | Concentration | Phase
Al+3 | 0.01 | liter
CO3-2 | 0.0010 | liter
Ca+2 | 0.01 | liter
Citrate-3 | 1.0E-5 | liter
pH | 7.2
H2O | 0.0
Directory:

ECN

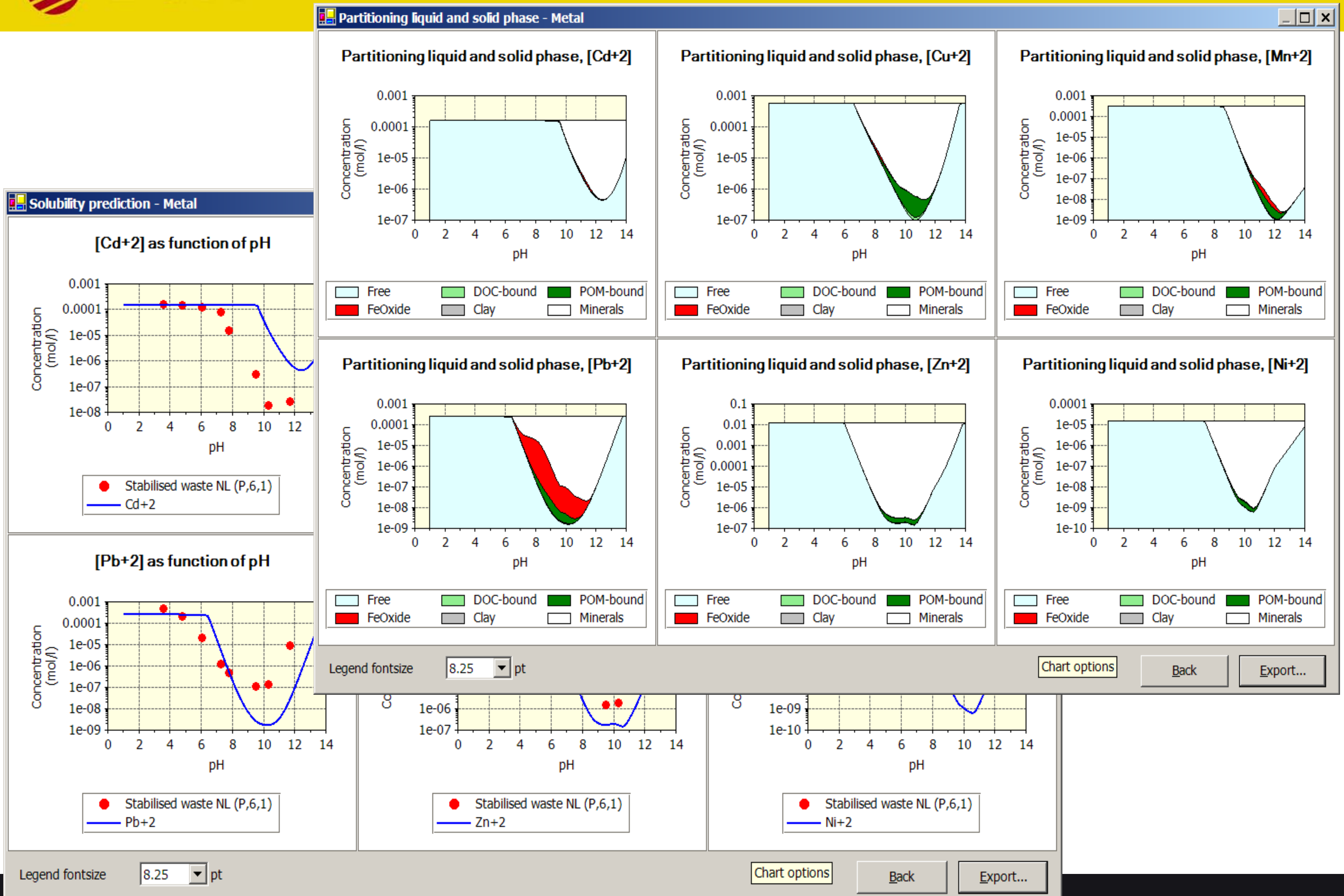


Include	Name	log K	Phase	Coefficient	Reactant	Coefficient	Reactant	Coefficient	Reactant	C
✔	AlH[Citrate]+	12.85000	diss	1.0	Al+3	1.0	Citrate-3	1.0	H+	
✔	AlOH+2	-4.997001	diss	1.0	Al+3	-1.0	H+	1.0	H2O	
✔	Al[Citrate]	9.970000	diss	1.0	Al+3	1.0	Citrate-3			
✔	Al[Citrate]2-3	14.80000	diss	1.0	Al+3	2.0	Citrate-3			
✔	Al[OH]2+	-10.09400	diss	1.0	Al+3	-2.0	H+	2.0	H2O	
✔	Al[OH]3	-16.79100	diss	1.0	Al+3	-3.0	H+	3.0	H2O	
✔	Al[OH]4-	-22.68800	diss	1.0	Al+3	-4.0	H+	4.0	H2O	
✔	CO2[g]	18.14700	gas	1.0	CO3-2	2.0	H+	-1.0	H2O	
✔	CaCO3	3.200000	diss	1.0	CO3-2	1.0	Ca+2			
✔	CaH2[Citrate]+	12.25700	diss	1.0	Ca+2	1.0	Citrate-3	2.0	H+	
✔	CaHCO3+	11.59900	diss	1.0	CO3-2	1.0	Ca+2	1.0	H+	
✔	CaH[Citrate]	9.260000	diss	1.0	Ca+2	1.0	Citrate-3	1.0	H+	
✔	CaOH+	-12.69700	diss	1.0	Ca+2	-1.0	H+	1.0	H2O	
✔	Ca[Citrate]-	4.870000	diss	1.0	Ca+2	1.0	Citrate-3			
✔	Calcite	8.480000	min	1.0	CO3-2	1.0	Ca+2			
✔	Gibbsite	-8.291000	min	1.0	Al+3	-3.0	H+	3.0	H2O	
✔	H2CO3	16.68100	diss	1.0	CO3-2	2.0	H+			
✔	H2[Citrate]-	11.15700	diss	1.0	Citrate-3	2.0	H+			
✔	H3[Citrate]	14.28500	diss	1.0	Citrate-3	3.0	H+			
✔	HCO3-	10.32900	diss	1.0	CO3-2	1.0	H+			
✔	H[Citrate]-2	6.396000	diss	1.0	Citrate-3	1.0	H+			
✔	Lime	-32.69930	min	1.0	Ca+2	-2.0	H+	1.0	H2O	
✔	OH-	-13.99700	diss	-1.0	H+	1.0	H2O			

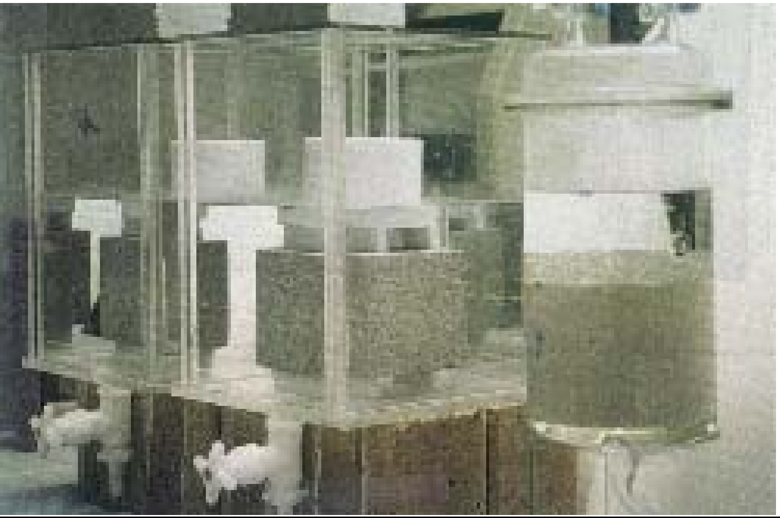
LEACHXS - ORCHESTRA



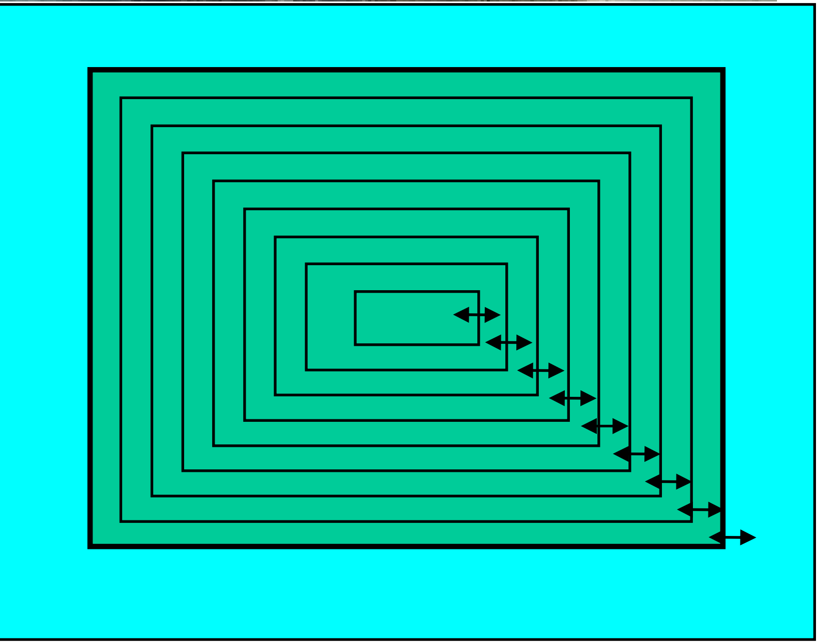
LEACHXS - ORCHESTRA



Diffusion of ions from cement stabilized waste



- Cube of cement stabilized fly ash
- CEM I + MSWI Fly ash > 80%
- Porosity 32 %
- Tank test, periodical renewal of solution
- 64 days
- Measurement of concentrations in water



- 20 Concentric cells,
- Chemical equilibrium in each cell
- Molecular diffusion between cells
- Outer solution with given initial pH

Chemical model description (set of chemical reactions used)

Components master species

H, Ca, Al, K, Na, Cl, SO4, Si, Mg

Measured total available concentrations

Aqueous reactions from Minteq Database

Selected minerals

Gibbsite, Gypsum, Brucite, CSH, Calcite, Portlandite, SiO2[am], Ettringite

Physical model

Molecular diffusion of aqueous ion fractions

Numerically solved with finite differences method

Different spatial discretizations, outer cell thickness:

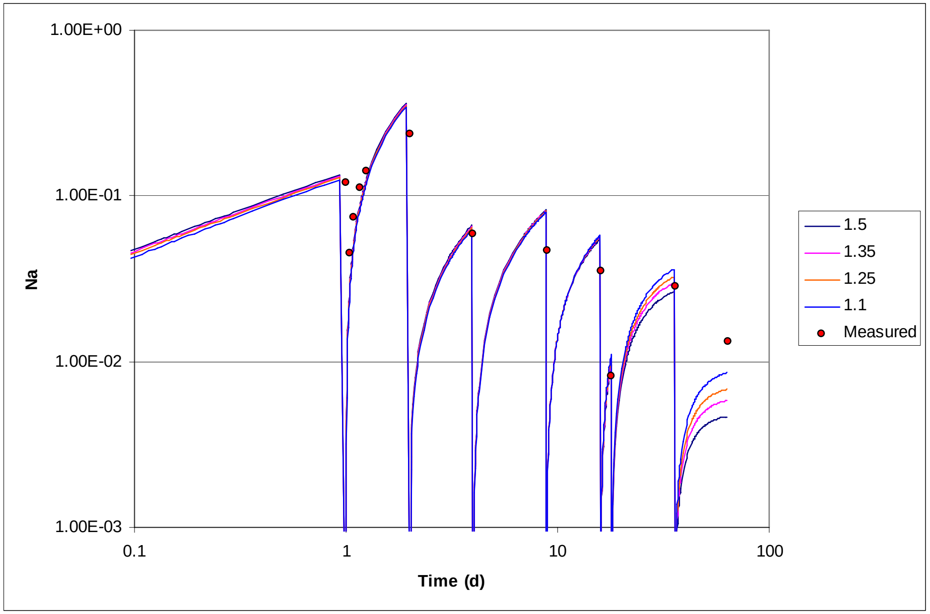
1.1 5e-4 m

1.25 1e-4 m

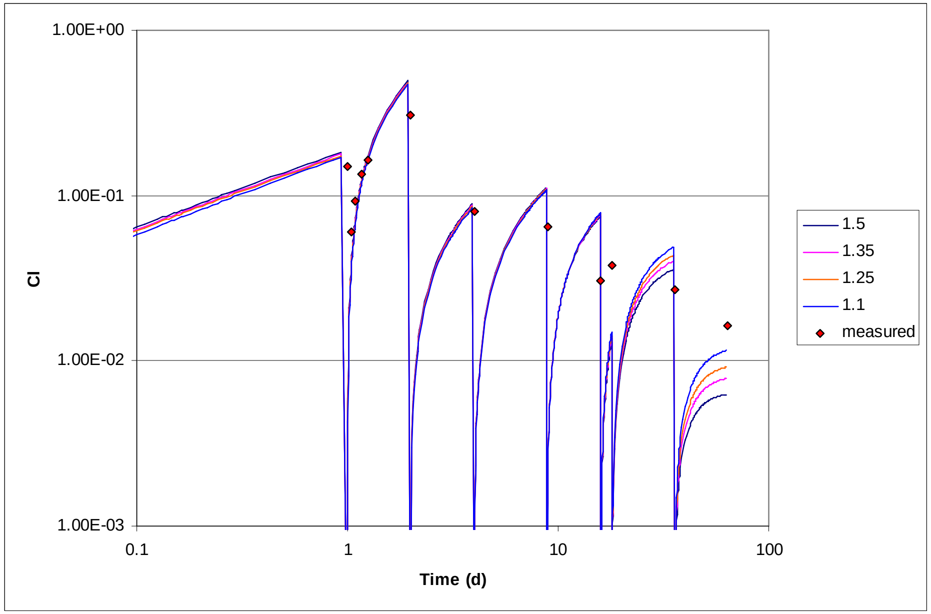
1.35 2e-5

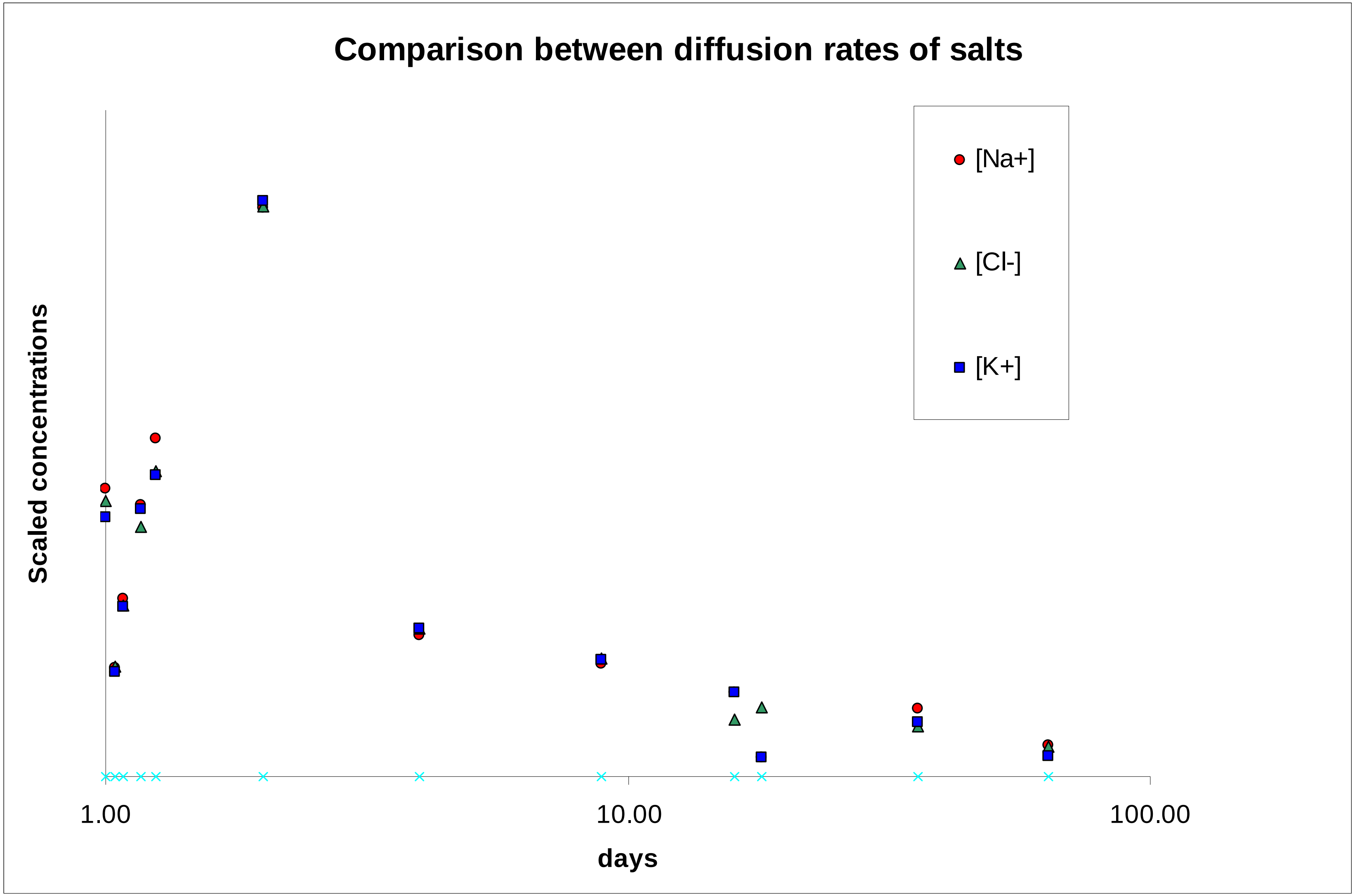
1.5 6e-6m

Na


1.00E+00
1.00E-01
1.00E-02
1.00E-03
Na
0.1
1
10
100
Time (d)
1.5
1.35
1.25
1.1
Measured

Cl


1.00E+00
1.00E-01
1.00E-02
1.00E-03
Cl
0.1
1
10
100
Time (d)
1.5
1.35
1.25
1.1
measured

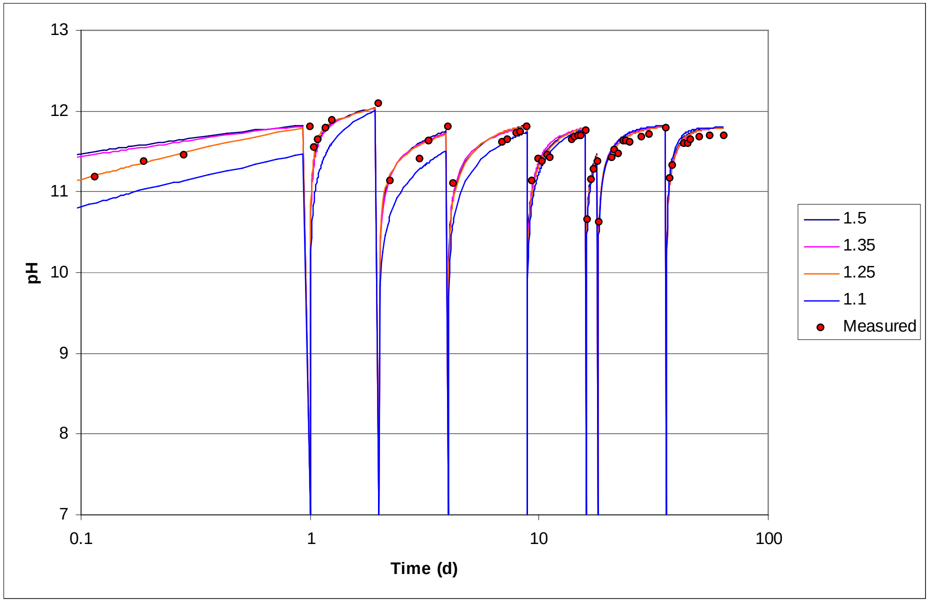


Comparison between diffusion rates of salts
[Na+]
[Cl-]
[K+]
Scaled concentrations
1.00
10.00
100.00
days

Results modelling “non-reactive” elements

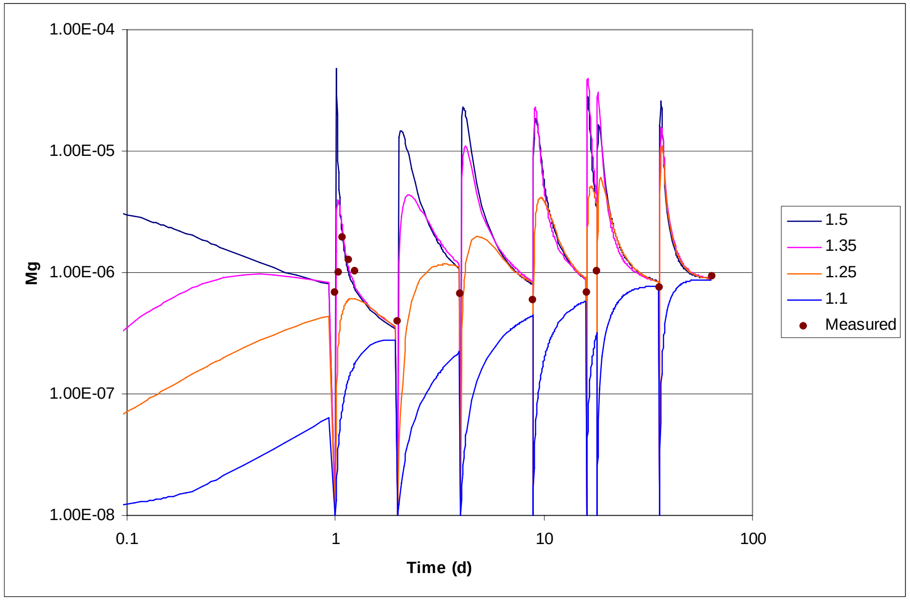
- Behaviour of Na, Cl and K very similar
- Behaviour of salts can be predicted from behaviour of Na
- Similar effective diffusion coefficients
- No indication for significant interaction with solid phase
- Constant effective diffusion coefficient during experiment (64 days)
- Not very sensitive for spatial discretization

pH



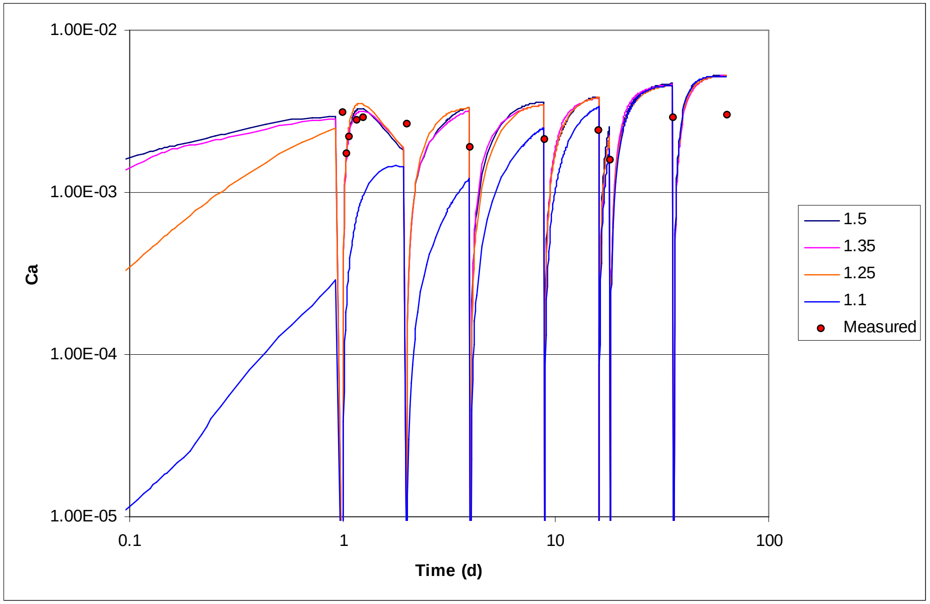
13
12
11
10
9
8
7
pH
0.1
1
10
100
Time (d)
1.5
1.35
1.25
1.1
Measured

Mg



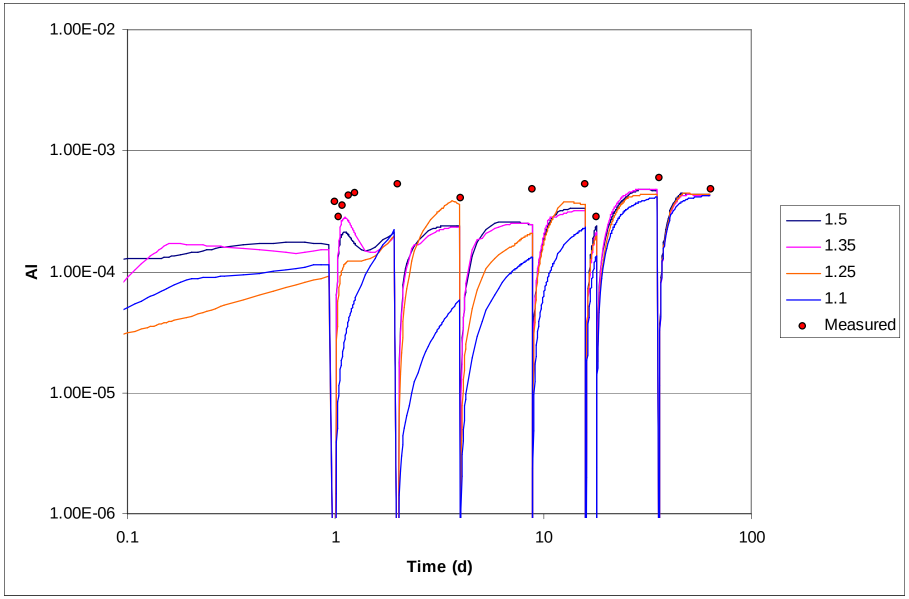
1.00E-04
1.00E-05
1.00E-06
1.00E-07
1.00E-08
Mg
0.1
1
10
100
Time (d)
1.5
1.35
1.25
1.1
Measured

Ca



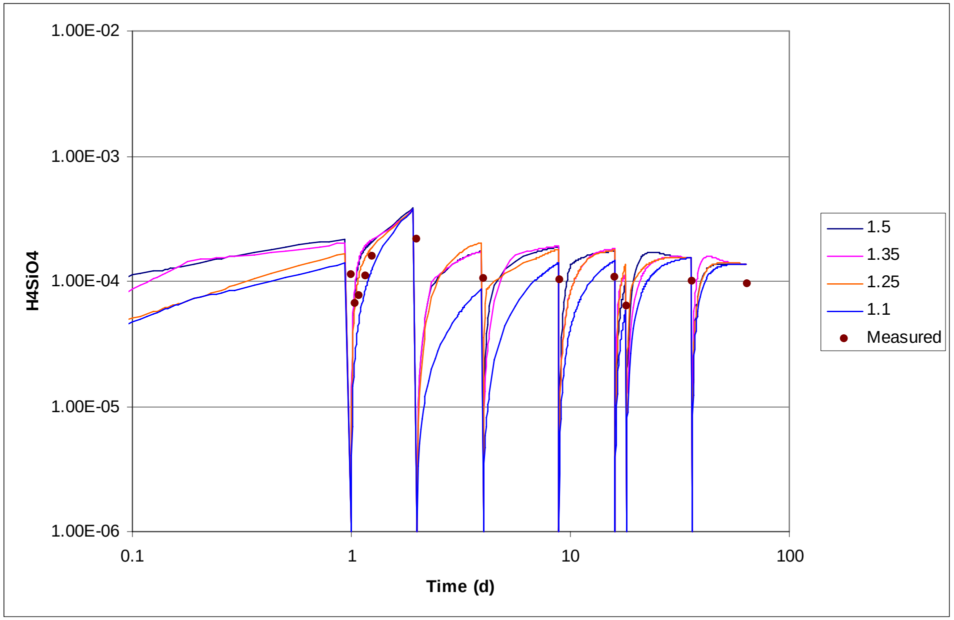
1.00E-02
1.00E-03
1.00E-04
1.00E-05
Ca
0.1
1
10
100
Time (d)
1.5
1.35
1.25
1.1
Measured

Al

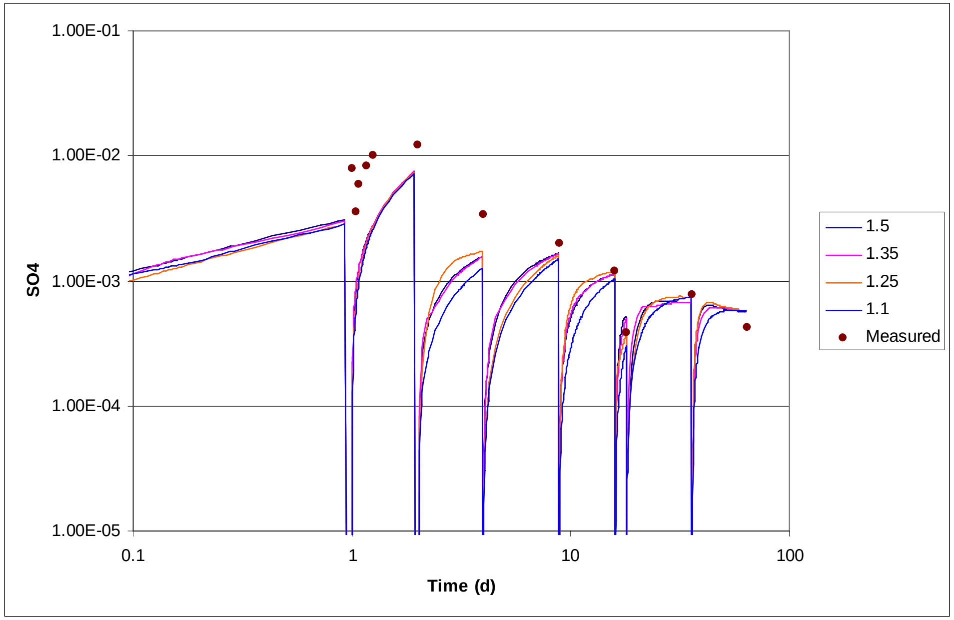


1.00E-02
1.00E-03
1.00E-04
1.00E-05
1.00E-06
Al
0.1
1
10
100
Time (d)
1.5
1.35
1.25
1.1
Measured

Si


1.00E-02
1.00E-03
1.00E-04
1.00E-05
1.00E-06
H4SiO4
0.1
1
10
100
Time (d)
1.5
1.35
1.25
1.1
Measured

SO4


1.00E-01
1.00E-02
1.00E-03
1.00E-04
1.00E-05
SO4
0.1
1
10
100
Time (d)
1.5
1.35
1.25
1.1
Measured

Results modelling “reactive” elements: H, Ca, Al, Si, S, Mg

- Concentration levels can be reasonably well predicted
- Behaviour different from salts
- Significant interaction with solid phase
- Spatial discretization important!
- Good description of macro elements essential for prediction of trace elements

Comparison batch renewal vs flow through test

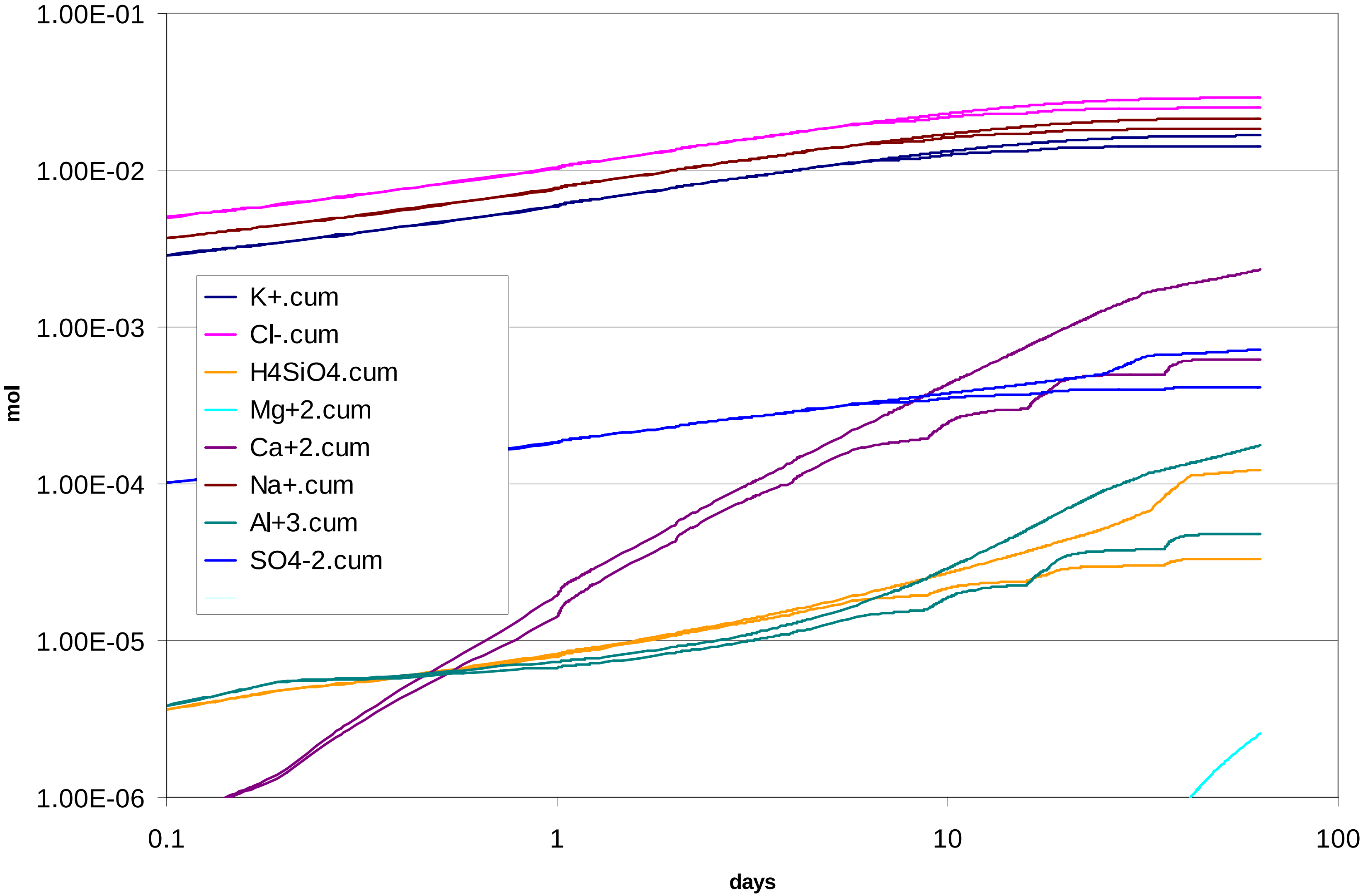
Commonly used methods of performing diffusion test

1) Batch renewal set up with periodical renewal of solution
   - Variable external concentrations and pH

2) Flow through system set up
   - Constant (assumed zero) concentrations and pH CO_2 concentration.

Will there be effects on measured diffusion constants for trace elements?
Will there be effects on measured leaching rates of reactive elements?
Will changing concentrations in method 1 be significant

Cumulative leached amounts in flow through and batch system



Comparison batch renewal- flow through test

Non-reactive elements

- Diffusion of salts will not be affected by test method
- Both methods will give equal estimations of (effective) diffusion constants.
- In batch procedure diffusion can be monitored over longer period, less emphasis on initial diffusion rates, therefore more accurate.

Reactive elements

- Difference in external pH will affect leaching of reactive elements.
- Leaching behaviour is not a material property but depends on test conditions.
- Both methods can be used to test model descriptions.
- In batch test pH is sensitive indicator for model description.

Overall conclusions

Leaching behaviour of Cement Stabilized wastes

- Tests AND models are necessary to evaluate environmental impacts
- Understanding of processes necessary to compose models
- Testing necessary to obtain model parameters + evaluate model predictions
- Models are not (and never will be) perfect, but already able to describe leaching processes
- Evaluation of models on more materials is required

ORCHESTRA

- Software tool to set up chemical equilibrium and reactive transport models
- Similar to PHREEQC, CHESS, GWB, but users can add new models
- Database with large set of state-of-the-art adsorption models

LeachXS

- Expert system for combining test data with predefined ORCHESTRA models
- Comparison of test data with legislation standards
- Application scenarios

Thank you for your attention!