Technical Basis for Cementitious Barriers Partnership Models

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July 19, 2012

CBP
Cementitious Barriers Partnership

LeachXS/ORCHESTRA

- LeachXS
  - Database expert/decision support system that includes leaching test results for 600+ materials, scenarios and regulations
  - Platform for assessing short- and long-term release of constituents of potential concern
  - Assists in source term evaluation through reactive transport and damage progression modeling
- ORCHESTRA
  - Numerical reactive transport simulation framework embedded in LeachXS
  - Models geochemical speciation and mass transport
  - Flexible and allows users to add/modify existing equations
  - Automatic usage of multiple processors/parallelization

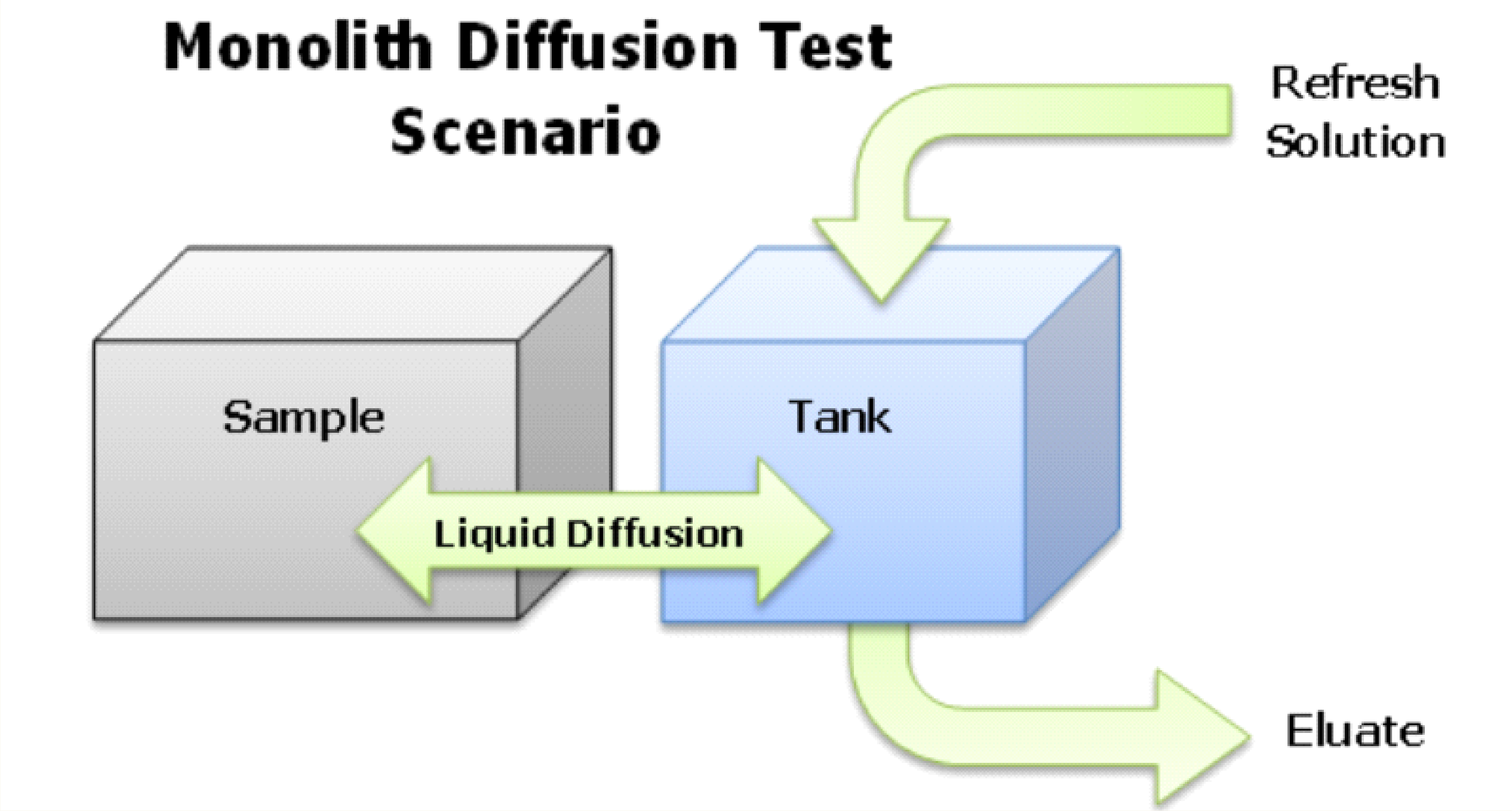
Cementitious Barriers Modeling Scenarios

- Currently available:
  - pH dependent equilibrium
    - Test (M1313) and prediction cases
  - Monolith leaching scenario
    - Test (M1315) and prediction cases
  - Monolith leaching with carbonation and oxidation scenario
    - Prediction cases
  - Leaching with sulfate attack scenario
    - Prediction cases
- In progress:
  - Percolation scenario
    - Test (M1314) and prediction cases (local equilibrium & multiple mixed regime models)

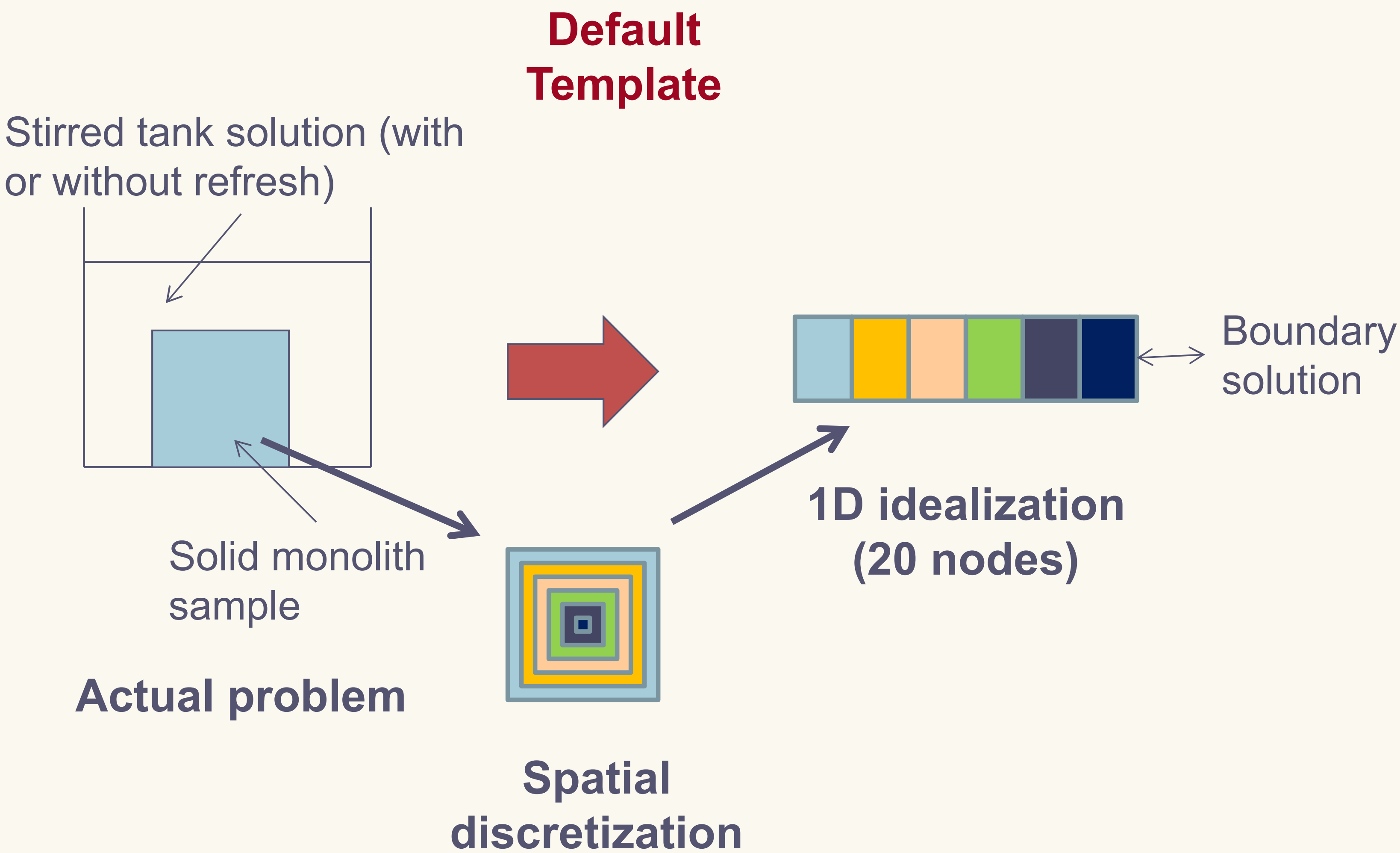
Applications of Cementitious Barriers Models

Models	Applications
pH Dependence	Assessment of waste, waste form, grout and concrete leaching chemistry
Monolith leaching	Waste form leaching; grout and concrete durability
Leaching with oxidation and carbonation	Waste form leaching; grout and concrete durability; HLW tank integrity
Leaching with sulfate attack	Concrete durability and interfacial processes
Column percolation Homogeneous Dual porosity Percolation w/orthogonal diffusion	Leaching from contaminated soils; leaching and pH evolution from tank grouting (cracking scenarios)

Monolith Diffusion Test Scenario



Monolith Diffusion Test Scenario



Monolith Diffusion Test Scenario

Tailoring to specific test scenarios:

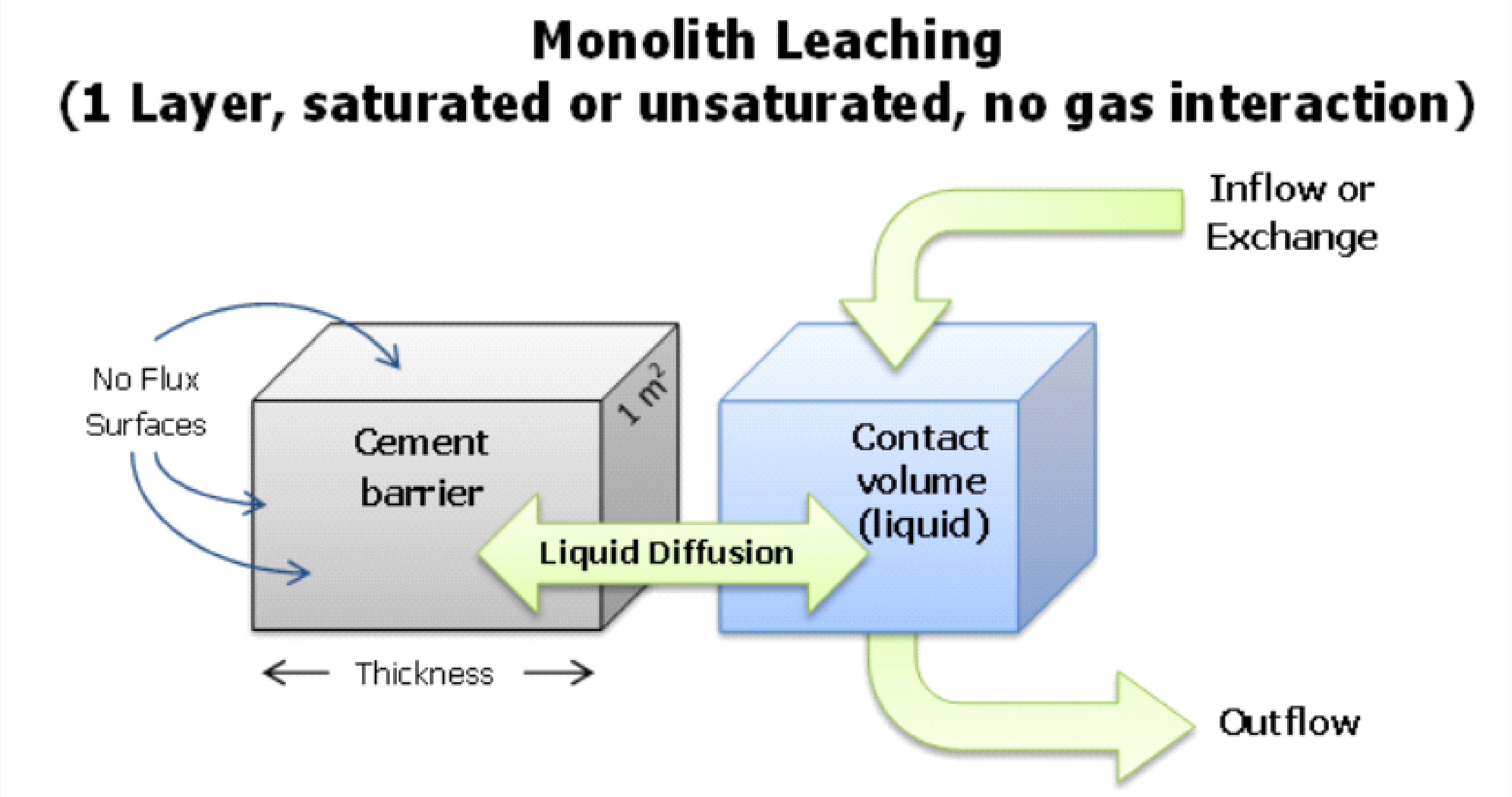
Solution Phase (initial and at refresh intervals)

- Liquid to surface area ratio
- Refresh scheme
  - Intermittent wetting
  - Continuous flow
  - Refresh at predefined rate
- Solution chemistry (preset or user defined)

Solid Phase (homogeneous or layers by node)

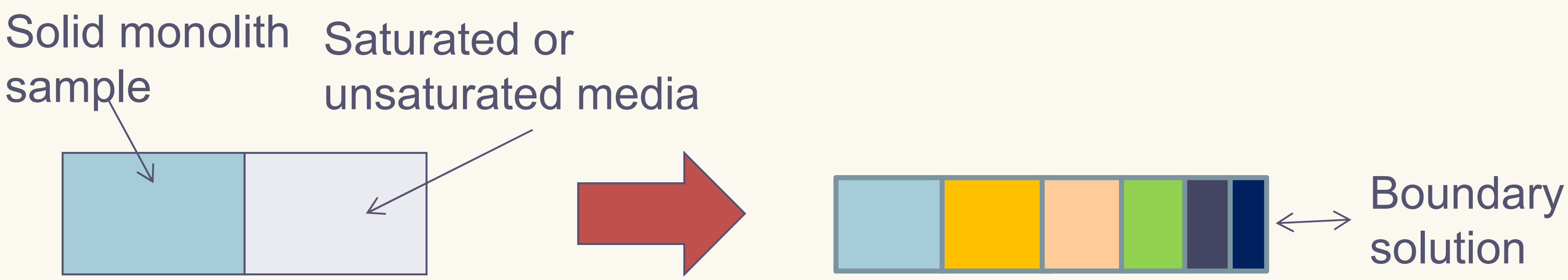
- Sample dimensions
- Number of nodes
- Saturation
- Chemical composition
- Mineralogical composition
- Physical properties (porosity, tortuosity)

Prediction Scenario – Monolith Leaching



Prediction Scenario – Monolith Leaching

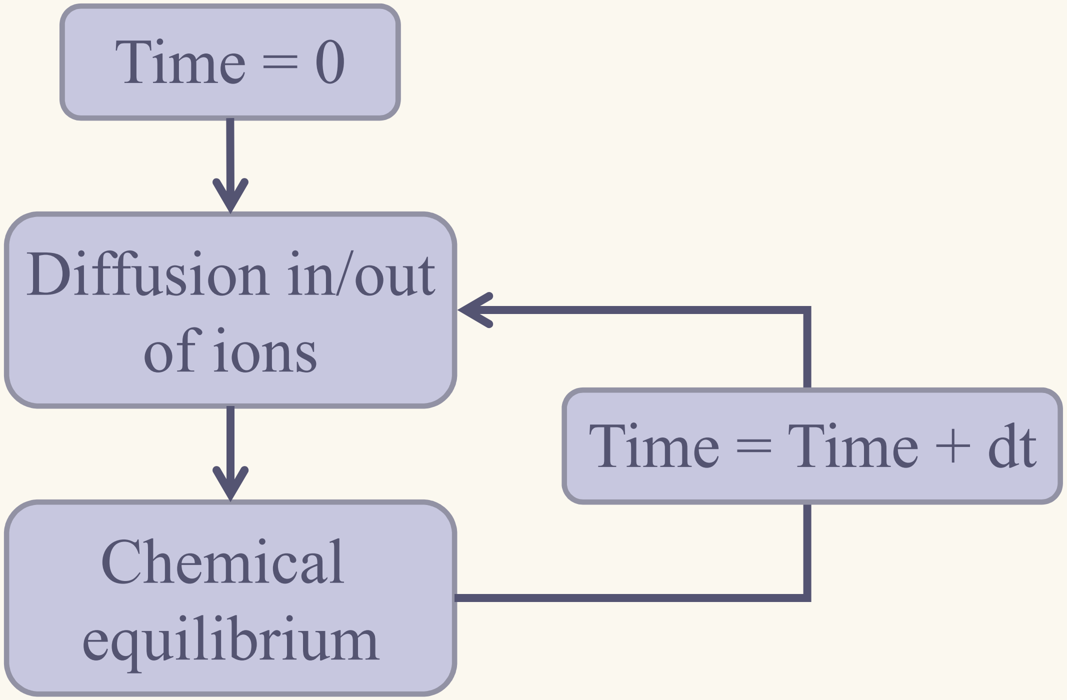
Default Template



Actual problem

1D idealization (1 m divided into 140 nodes using polynomial meshing scheme)

Monolith Diffusion Tank Model Framework



Diffusion of Ions

- Governing Equation for Diffusion

(saturated porous material under isothermal condition)

$$\frac{\partial(\varphi c)}{\partial t} = \frac{\partial}{\partial x}\left(\frac{D_0 \varphi}{\tau}\left(\underbrace{\frac{\partial c}{\partial x}}_{\text{concentration gradient}} + \underbrace{c\frac{\partial \ln \gamma}{\partial x}}_{\text{chemical activity gradient}}\right)\right)$$

Being implemented currently

$c-$ concentrations of species (moles/L)

$\phi-$ porosity (for saturated materials) (L/L)

D_0- free solution diffusivity (m^2/s)

$\tau-$ tortuosity (m/m)

$\gamma-$ chemical activity coefficient (-)

$x-$ spatial dimensions (m)

$t-$ time (s)

Solved using a finite difference scheme.

Predefined Orchestra-LeachXS Solid-Aqueous (Gas) models

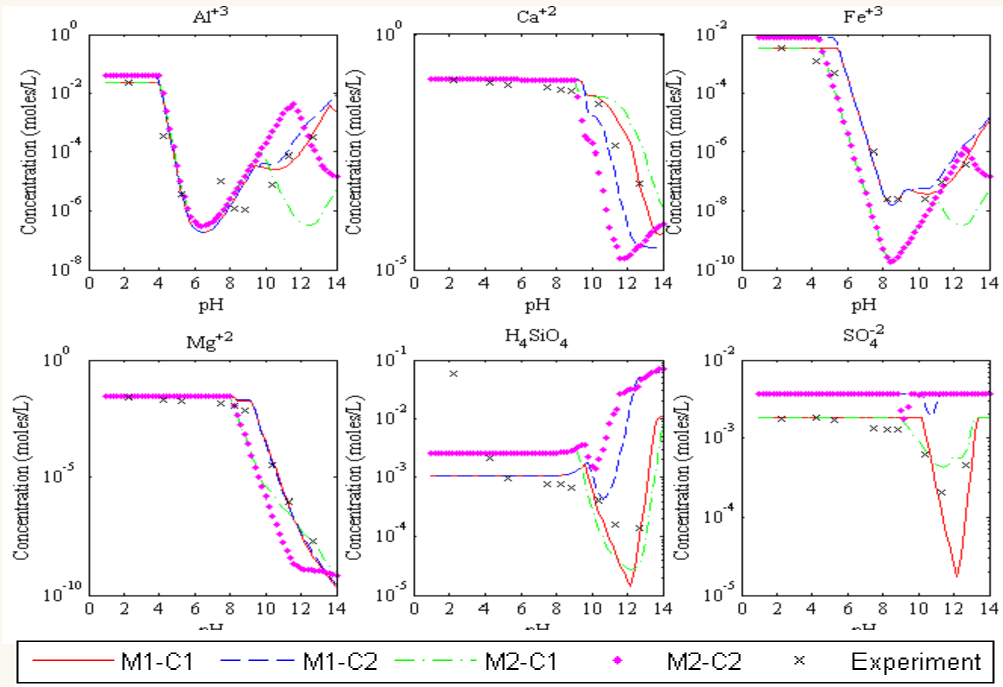
Using multi-component chemical interaction model

Including:

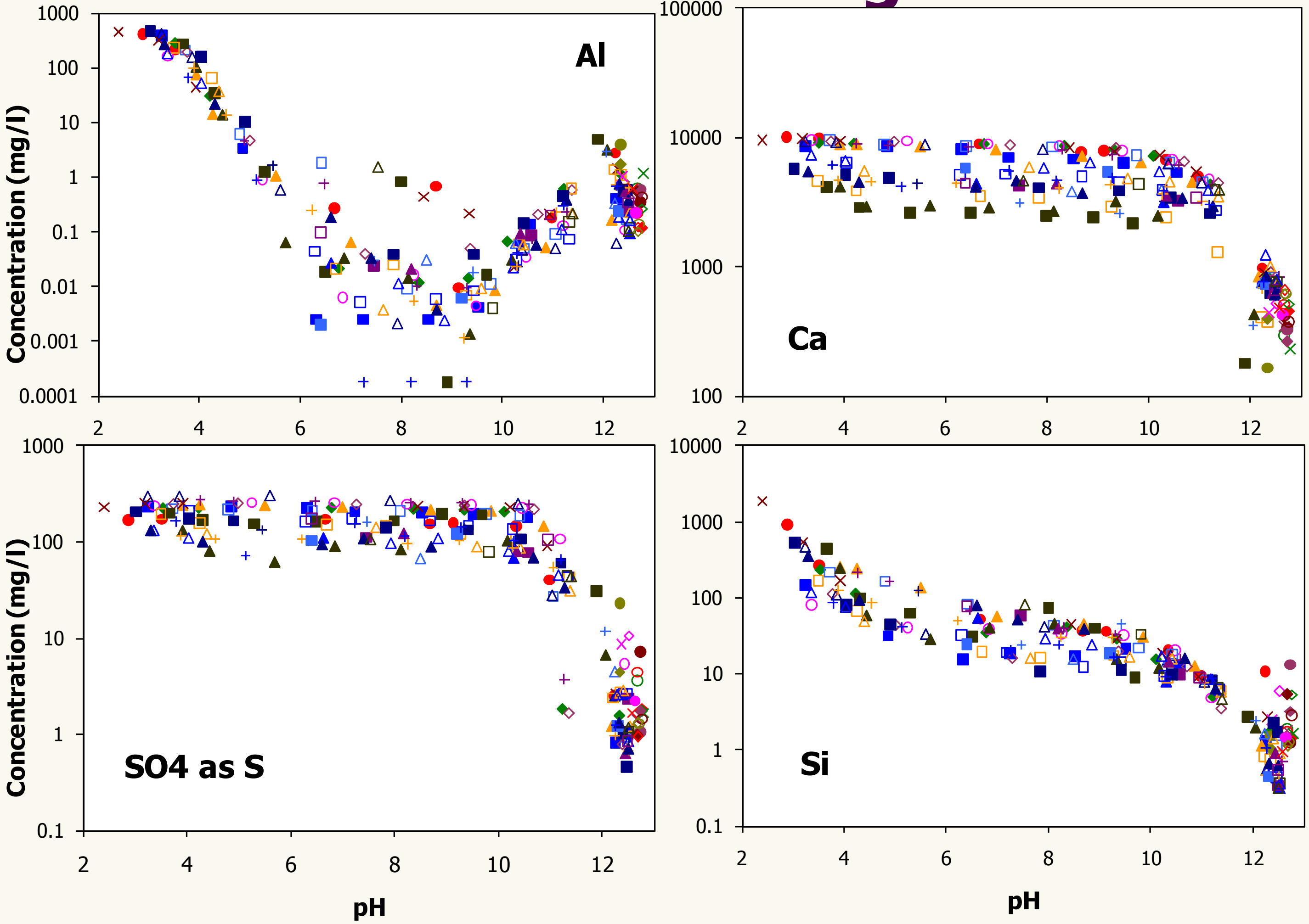
- 45 Elements / Master species including radionuclides
- Literature aqueous chemical complexation reactions (NIST/MINTEQV4)
- Literature adsorption models (Fe Al oxides: Dzombak & Morel 1990; Organic Matter Nica–Donnan: Kinniburgh et al 1996, Clay Ion exchange)
- Solid solution (ideal) for Ettringite + oxyanions, C-S-H
- Activity models: Davies, modified Davies, Pitzer (Samson *et al.*, 1999)

Chemical Reactions

- Available databases: MINTEQ, CEMDATA (Lothenbach *et al.*, 2007 and 2008), NEA patch
- Identify primary ions, complex ions automatically selected
- Potential solid phases: Identified by comparing results of pH-dependent leaching tests (M1313) and simulations with different solid phase mineral sets



pH Dependent Release from Cement Mortars from Worldwide Origin



Leaching behavior of substances from cementitious products
(Hans van der Sloot, David S. Kosson, Rob Comans and Ole Hjelmar)

Uncertainty Quantification of Chemical Equilibrium Model

Inputs
- Total concentrations
- pH

Chemical Equilibrium Model
- K_{sp} (Equilibrium constants)

Outputs
- Dissolved concentrations = f(pH)

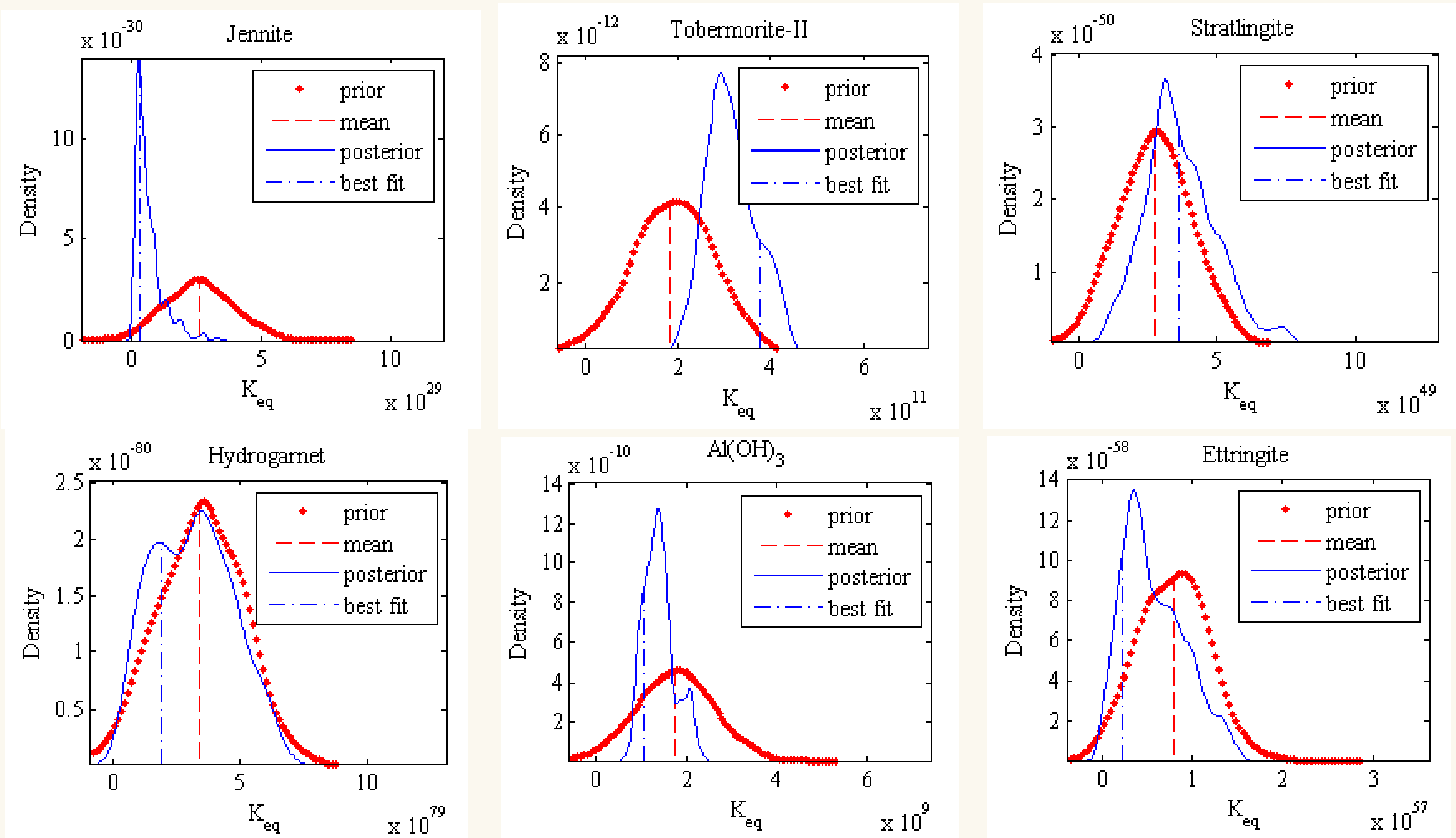
Experimental Observations
- Dissolved concentrations = f(pH)
- Experimental errors

Uncertainty Quantification of K_{sp}s using Bayesian Calibration

Problem Description (for the purpose of illustration)

- Experimental observations: pH dependence test data of 6 major species (Al, Ca, Fe, Mg, Si, S) for a concrete sample
- Calibration parameters: Equilibrium constants of 17 mineral phases
- Stochastic parameters: total leachable concentrations, measurement errors (pH, leahced concentrations

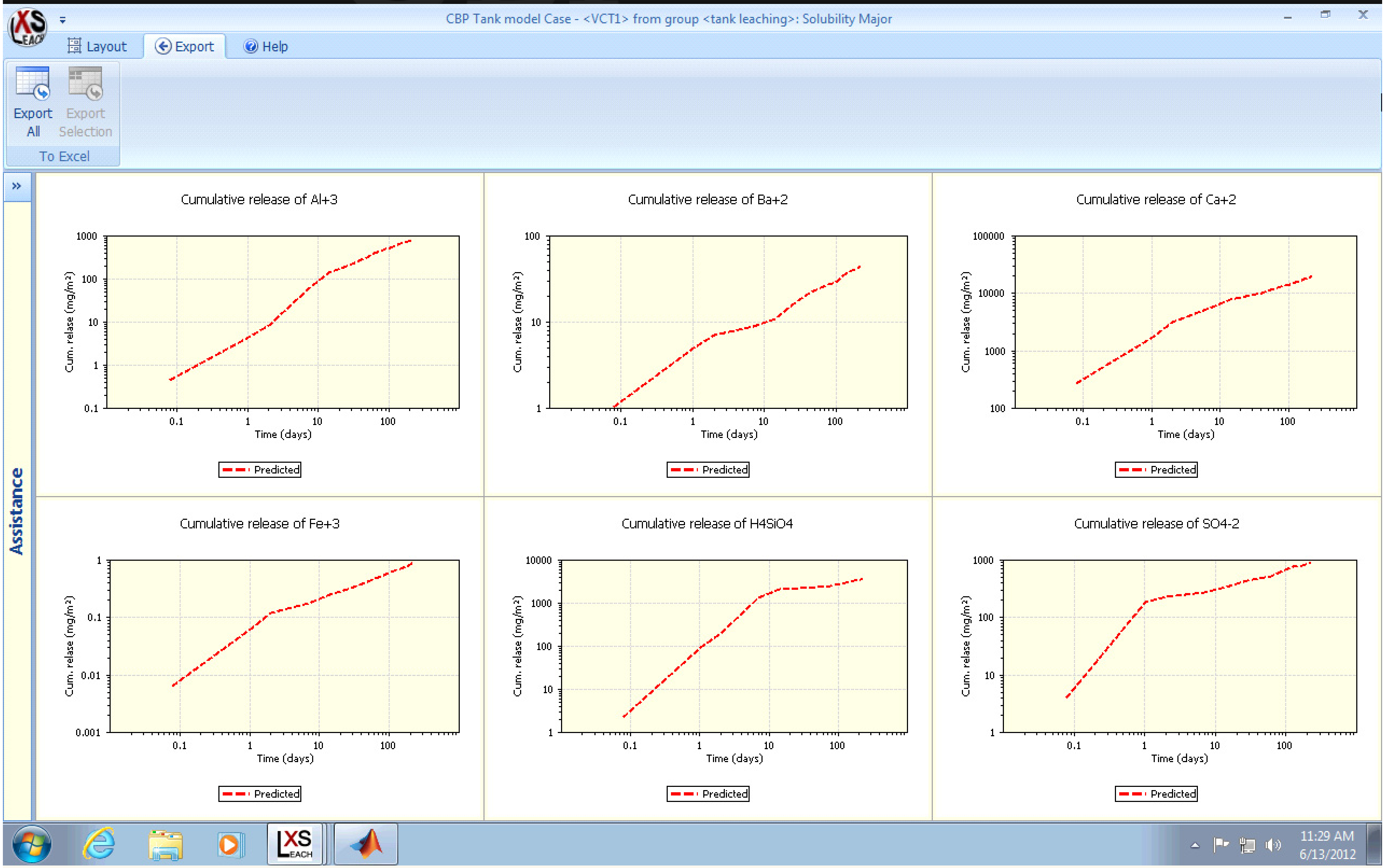
Uncertainty in Chemical Equilibrium Constants



Sarkar *et* al., Bayesian calibration of thermodynamic parameters for geochemical speciation modeling of cementitious materials, Cement and Concrete Research, 42(7), 889-902, 2012

Available Outputs

- As a **function of time** at a certain depth in solid or external solution
- As a **function of depth** at a certain time
    - Distribution and percentage profiles
        - All phases
        - Solid phases
        - Dissolved phases
    - Concentrations
        - Total
    - Other variables
        - pH, pe, dissolved humic acid etc.


CBP Tank model Case - <VCT1> from group <tank leaching>: Solubility Major
Layout
Export
Help
Export All
Export Selection
To Excel
Assistance
Cumulative release of Al+3
Cumulative release of Ba+2
Cumulative release of Ca+2
Cumulative release of Fe+3
Cumulative release of H4SiO4
Cumulative release of SO4-2
Cum. relase (mg/m2)
Time (days)
Predicted
11:29 AM
6/13/2012

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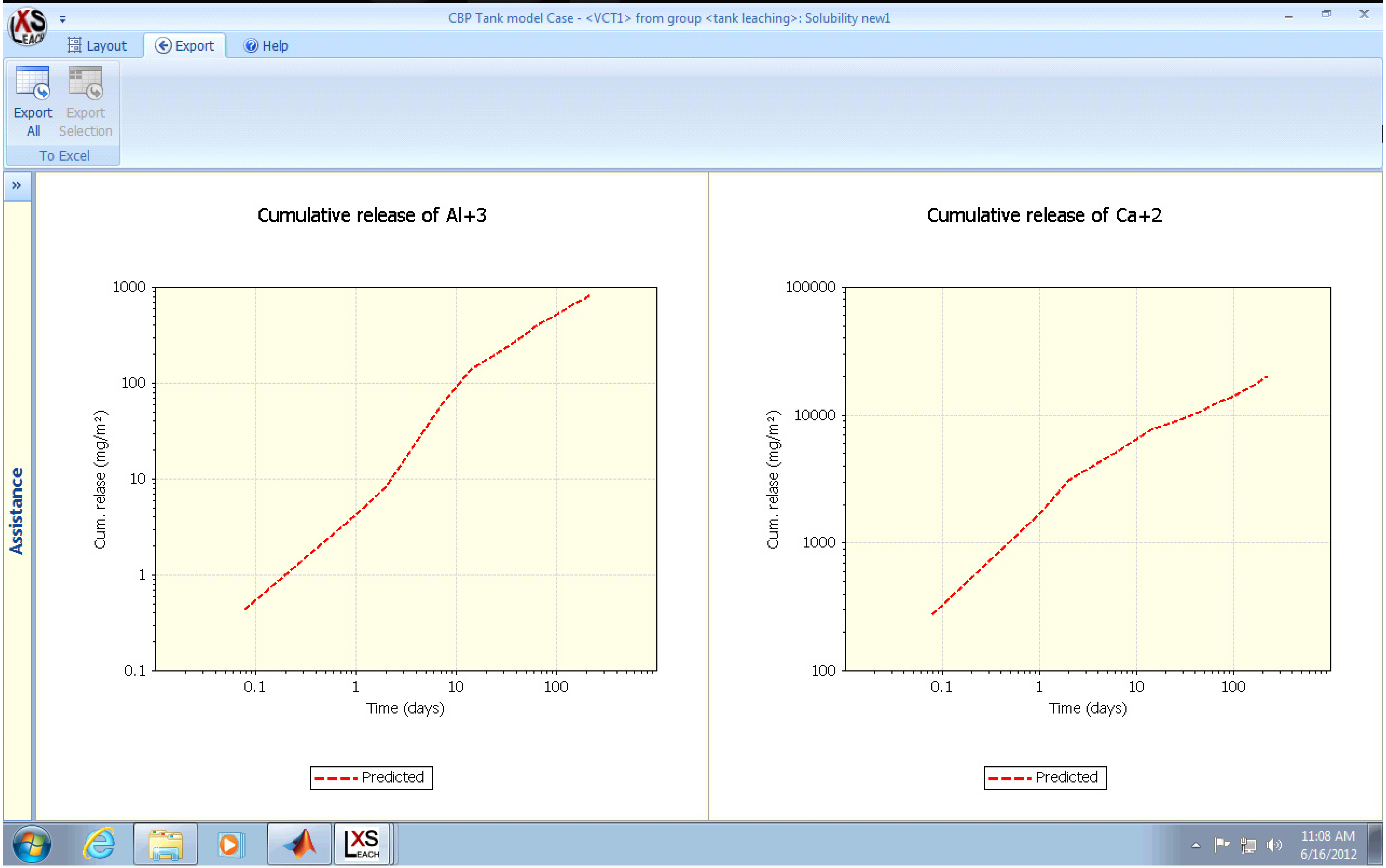
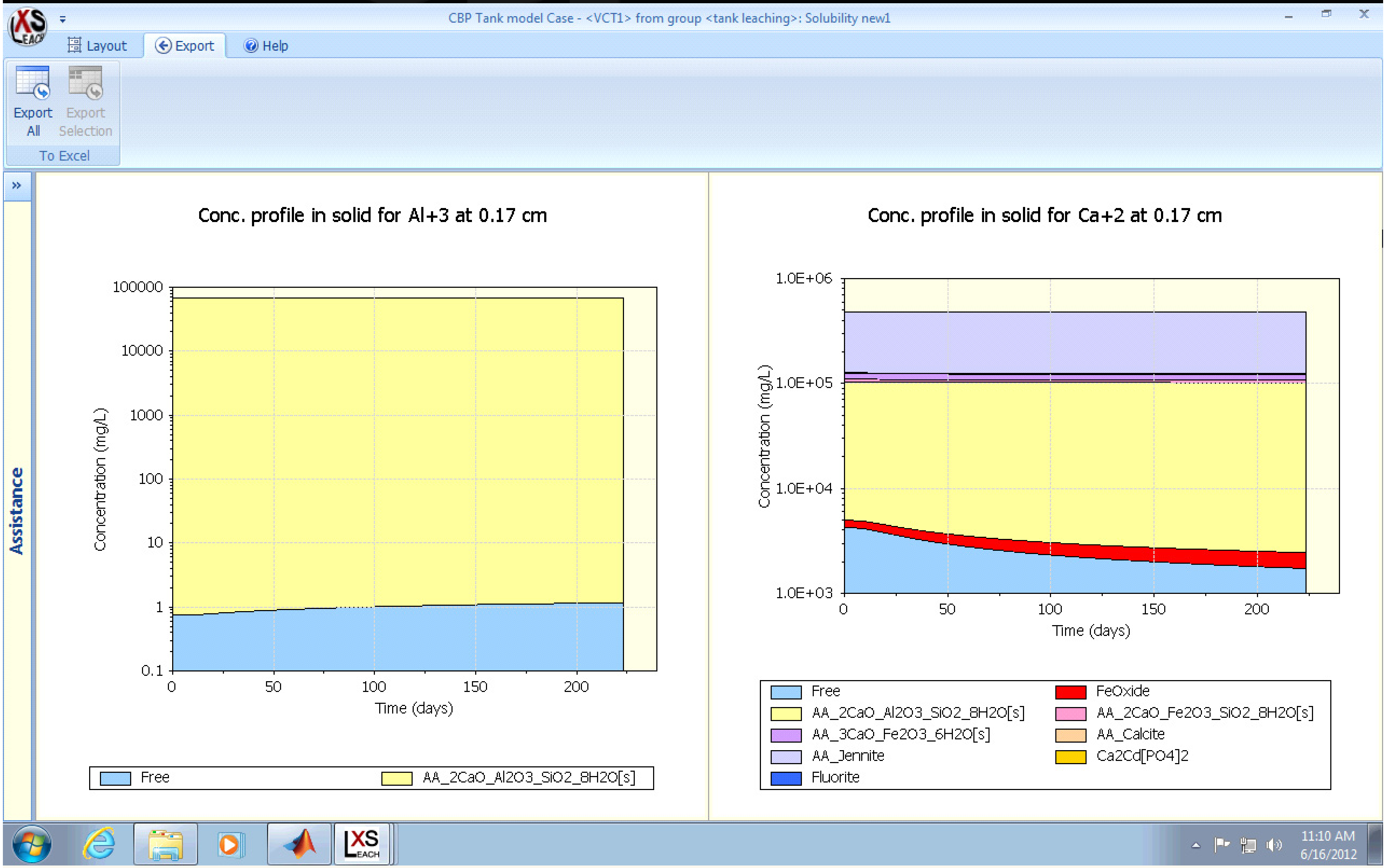
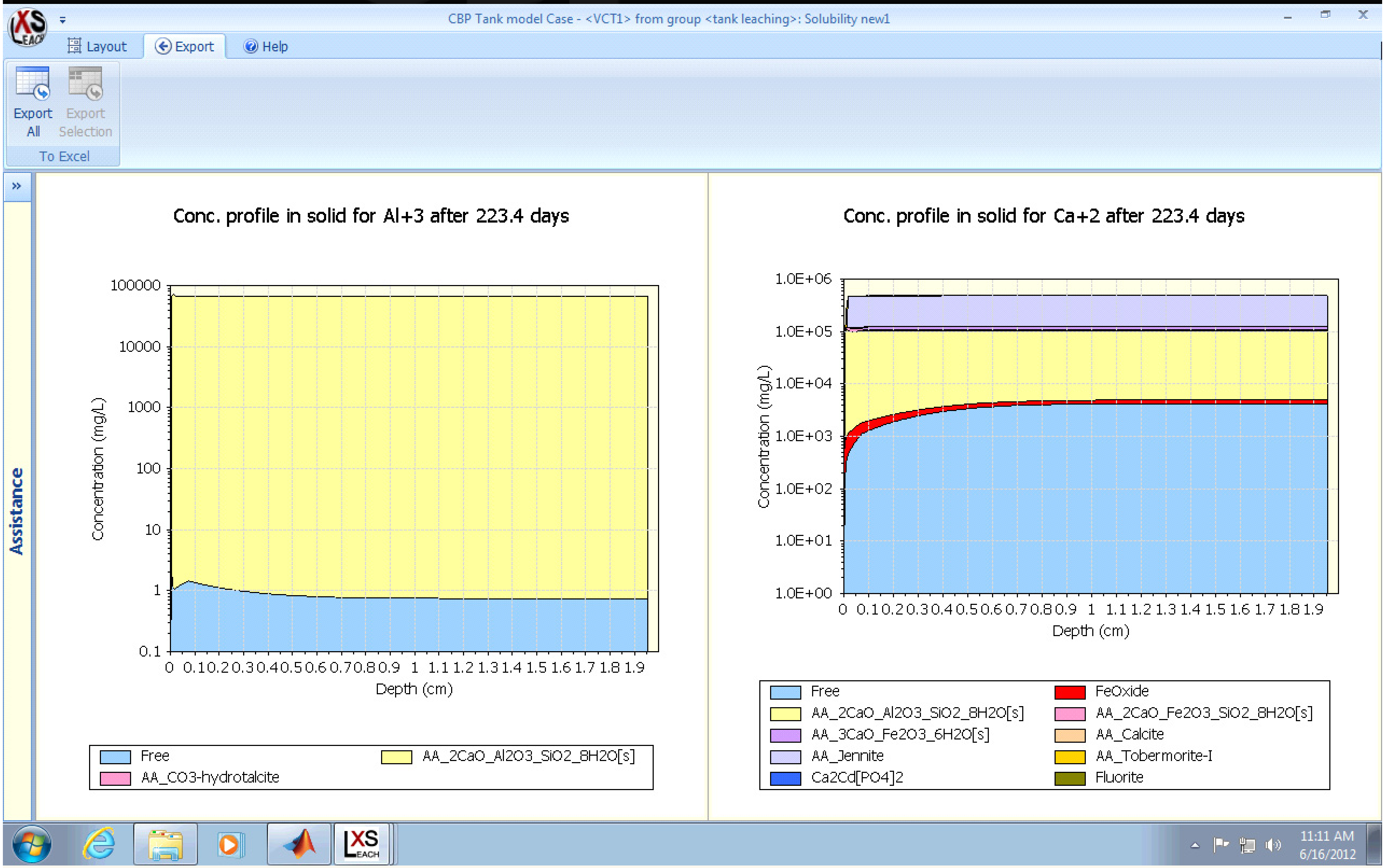



CBP Tank model Case - <VCT1> from group <tank leaching>: Solubility Major
Layout
Export
Help
Export All
Export Selection
To Excel
Assistance
Conc. profile in solid for Al+3 at 0.17 cm
Concentration (mg/L)
Time (days)
Free
AA_2CaO_Al2O3_SiO2_8H2O[s]
Conc. profile in solid for Ba+2 at 0.17 cm
Concentration (mg/L)
Time (days)
Free
FeOxide
Conc. profile in solid for Ca+2 at 0.17 cm
Concentration (mg/L)
Time (days)
Free
FeOxide
AA_2CaO_Al2O3_SiO2_8H2O[s]
AA_2CaO_Fe2O3_SiO2_8H2O[s]
AA_3CaO_Fe2O3_6H2O[s]
AA_Calcite
AA_Jennite
Ca2Cd[PO4]2
Fluorite
Conc. profile in solid for Fe+3 at 0.17 cm
Concentration (mg/L)
Time (days)
Free
AA_2CaO_Fe2O3_SiO2_8H2O[s]
AA_3CaO_Fe2O3_6H2O[s]
Conc. profile in solid for H4SiO4 at 0.17 cm
Concentration (mg/L)
Time (days)
Free
FeOxide
AA_2CaO_Al2O3_SiO2_8H2O[s]
AA_2CaO_Fe2O3_SiO2_8H2O[s]
AA_Jennite
Willemite
Conc. profile in solid for SO4-2 at 0.17 cm
Concentration (mg/L)
Time (days)
Free
FeOxide
11:30 AM
6/13/2012

CBP
Cementitious Barriers Partnership



CBP
Cementitious Barriers Partnership


CBP Tank model Case - <VCT1> from group <tank leaching>: Solubility new1
Layout
Export
Help
Export All
Export Selection
To Excel
Assistance
Conc. profile in solid for Al+3 after 223.4 days
Concentration (mg/L)
100000
10000
1000
100
10
1
0.1
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1 1.1 1.2 1.3 1.4 1.5 1.6 1.7 1.8 1.9
Depth (cm)
Free
AA_2CaO_Al2O3_SiO2_8H2O[s]
AA_CO3-hydrotalcite
Conc. profile in solid for Ca+2 after 223.4 days
Concentration (mg/L)
1.0E+06
1.0E+05
1.0E+04
1.0E+03
1.0E+02
1.0E+01
1.0E+00
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1 1.1 1.2 1.3 1.4 1.5 1.6 1.7 1.8 1.9
Depth (cm)
Free
FeOxide
AA_2CaO_Al2O3_SiO2_8H2O[s]
AA_2CaO_Fe2O3_SiO2_8H2O[s]
AA_3CaO_Fe2O3_6H2O[s]
AA_Calcite
AA_Jennite
AA_Tobermorite-I
Ca2Cd[PO4]2
Fluorite
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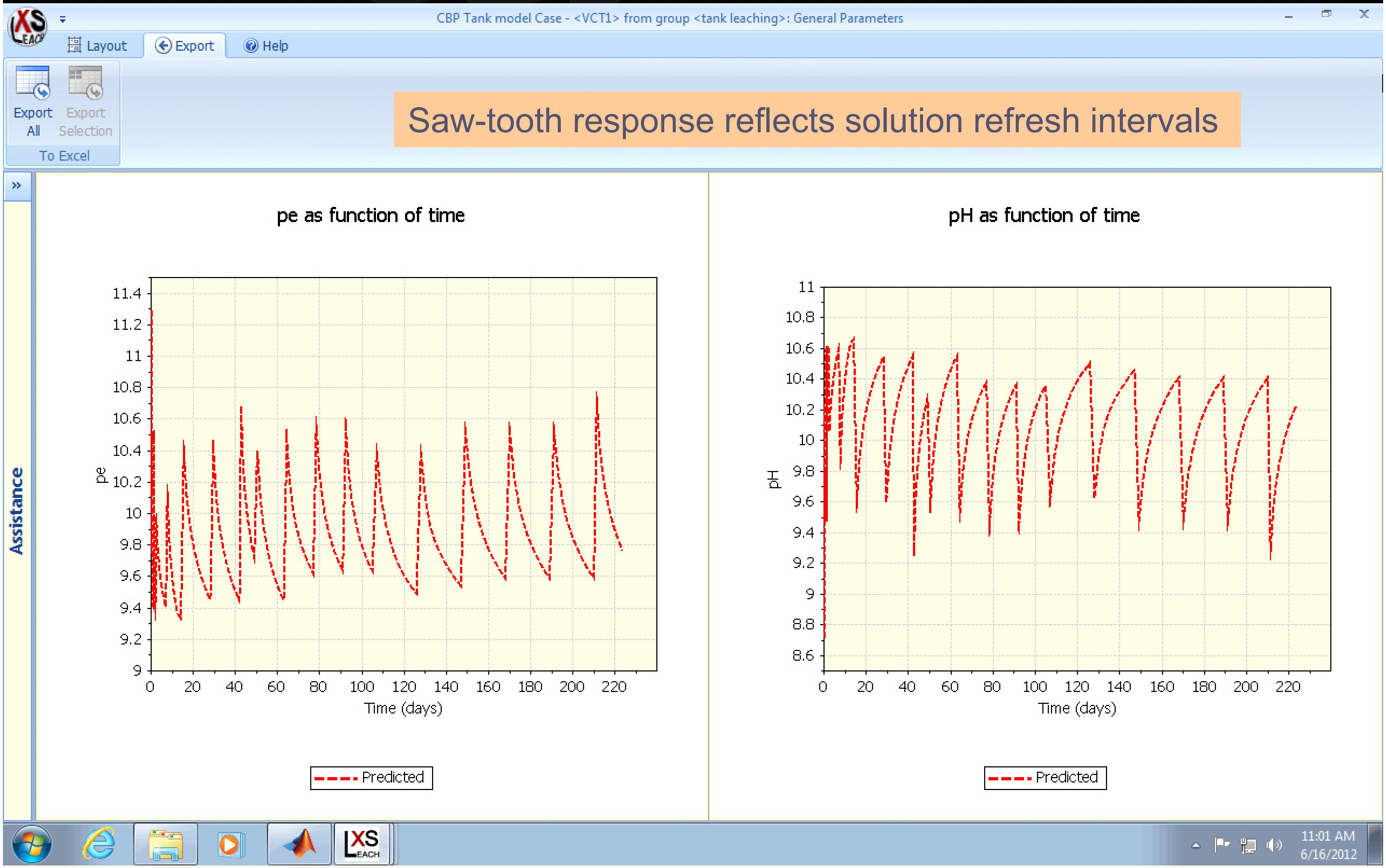
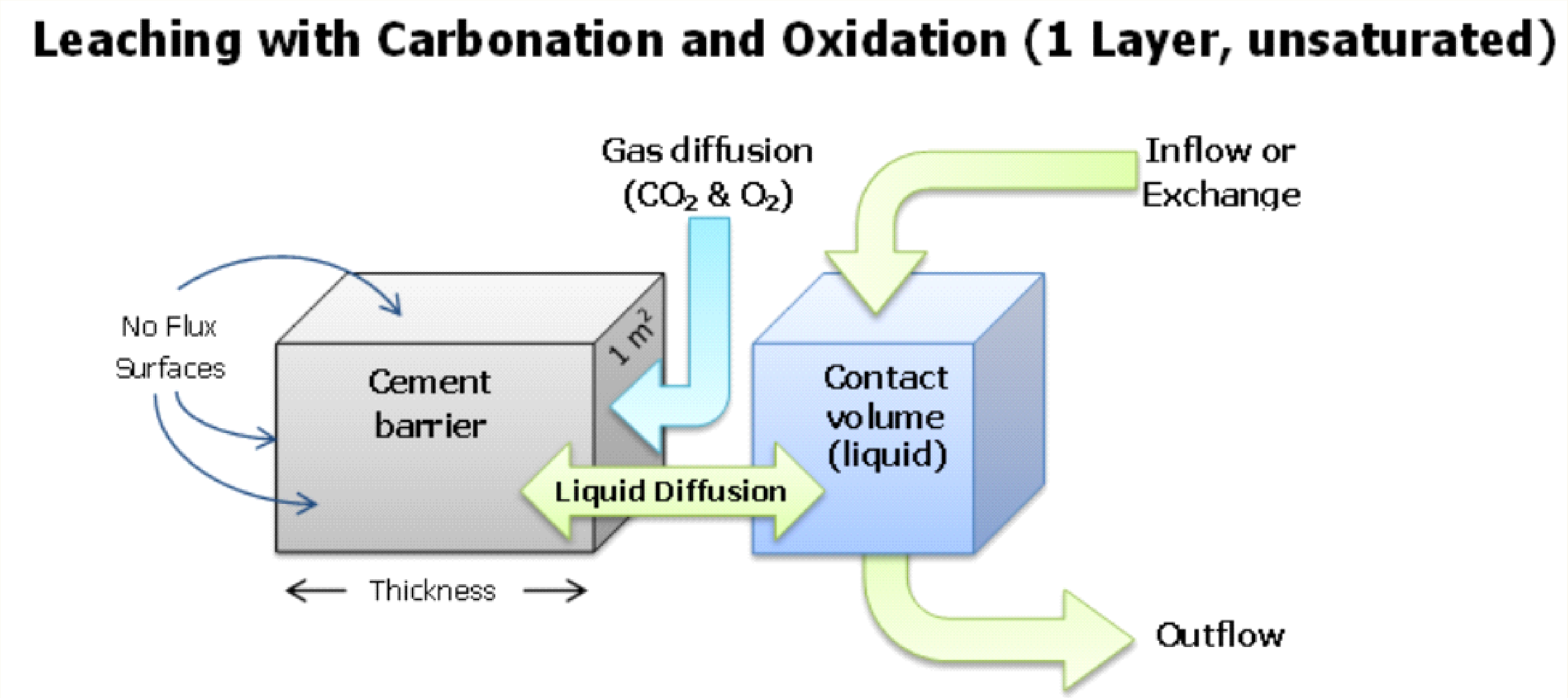
Saw-tooth response reflects solution refresh intervals

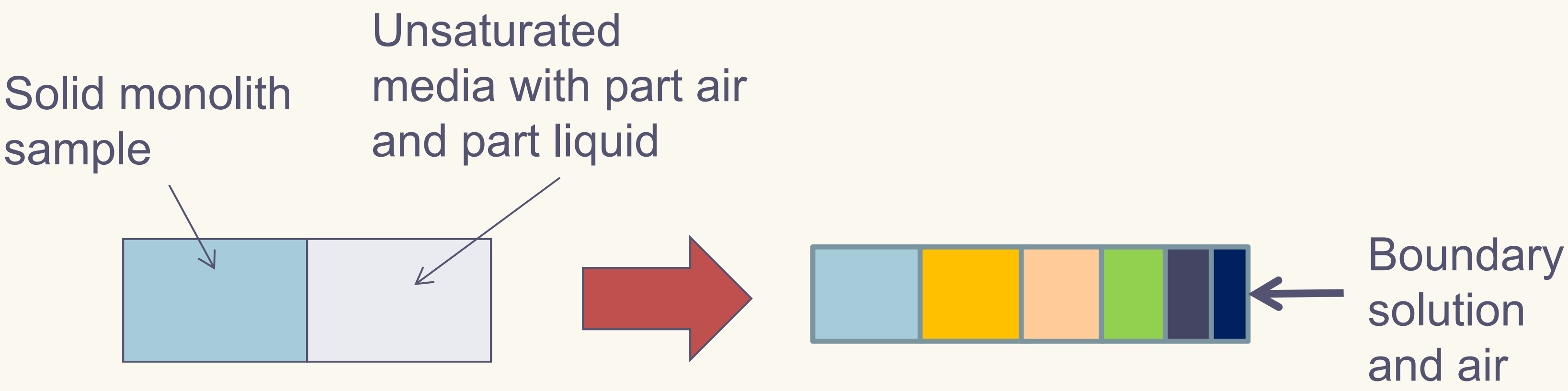


Prediction Scenario – Leaching with Carbonation and Oxidation



Prediction Scenario – Leaching with Carbonation and Oxidation

Default Template



Actual problem

1D idealization (1 m divided into 140 nodes using polynomial meshing scheme)

Prediction Scenario – Leaching with Carbonation and Oxidation

Tailoring to specific test scenarios:

Solution Phase (initial and at refresh intervals)

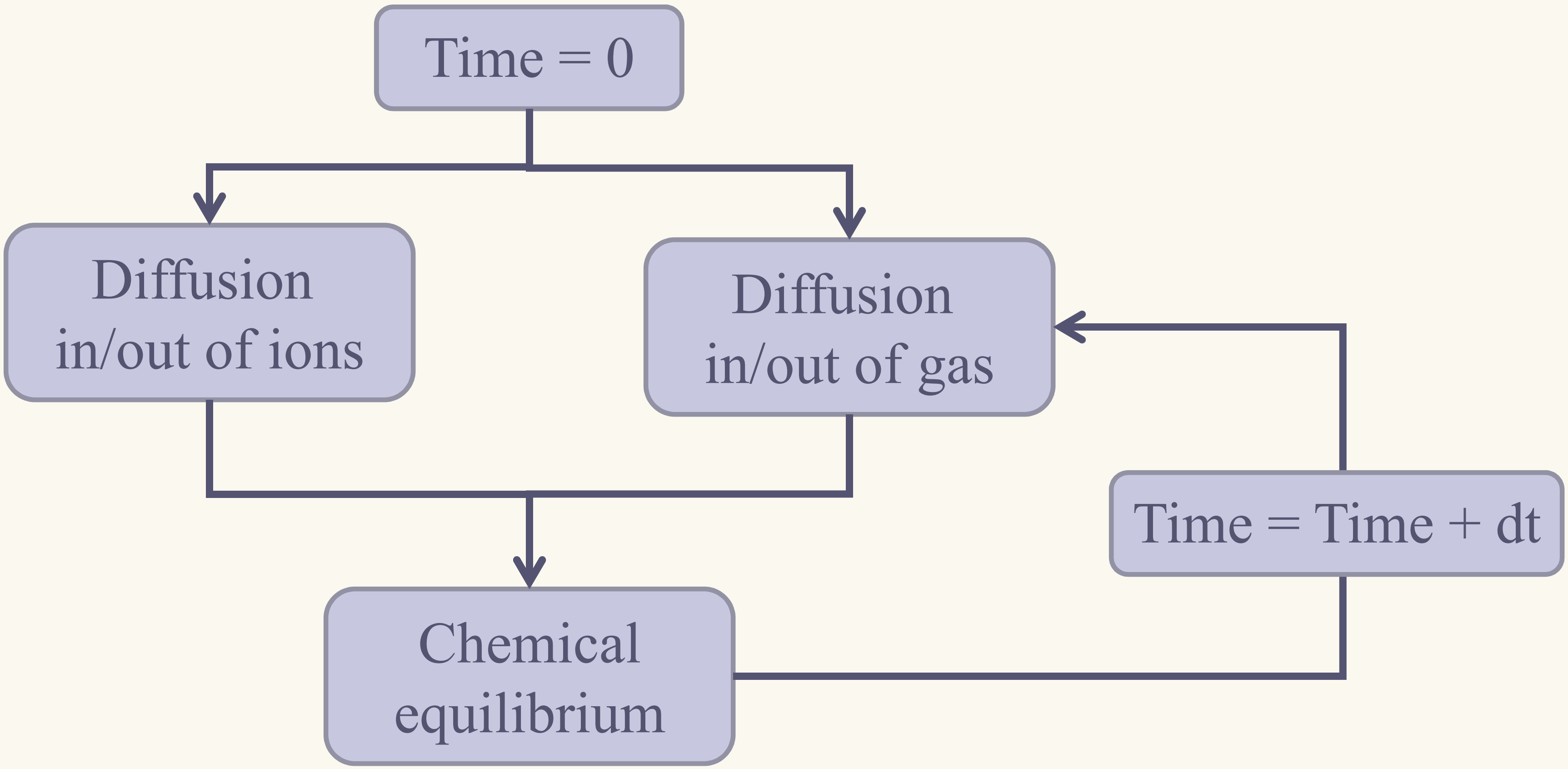
- Liquid to surface area ratio
- Refresh scheme
  - Intermittent wetting
  - Refresh at predefined rate or Continuous flow
- Solution chemistry (preset or user defined)

Solid Phase (homogeneous or layers by node)

- Sample dimensions
- Number of nodes
- Saturation
- Chemical composition
- Mineralogical composition
- Physical properties (porosity, tortuosity)

Gas Phase (composition at boundary)

Leaching with Carbonation and Oxidation Model Framework



Diffusion and Chemical Reactions

- Governing Equation for Dissolved Phase Diffusion

$$\frac{\partial(w_l c)}{\partial t} = \frac{\partial}{\partial x}\left(\frac{D_{0l} w_l}{\tau}\frac{w_l^{7/3}}{\phi^{7/3}}\left(\underbrace{\frac{\partial c}{\partial x}}_{\text{concentration gradient}}\right)\right)$$

D_{0l} – Free solution diffusivity (m^2/s)

w_l – Liquid filled space (m^3/m^3)

Millington and Quirk (1961)

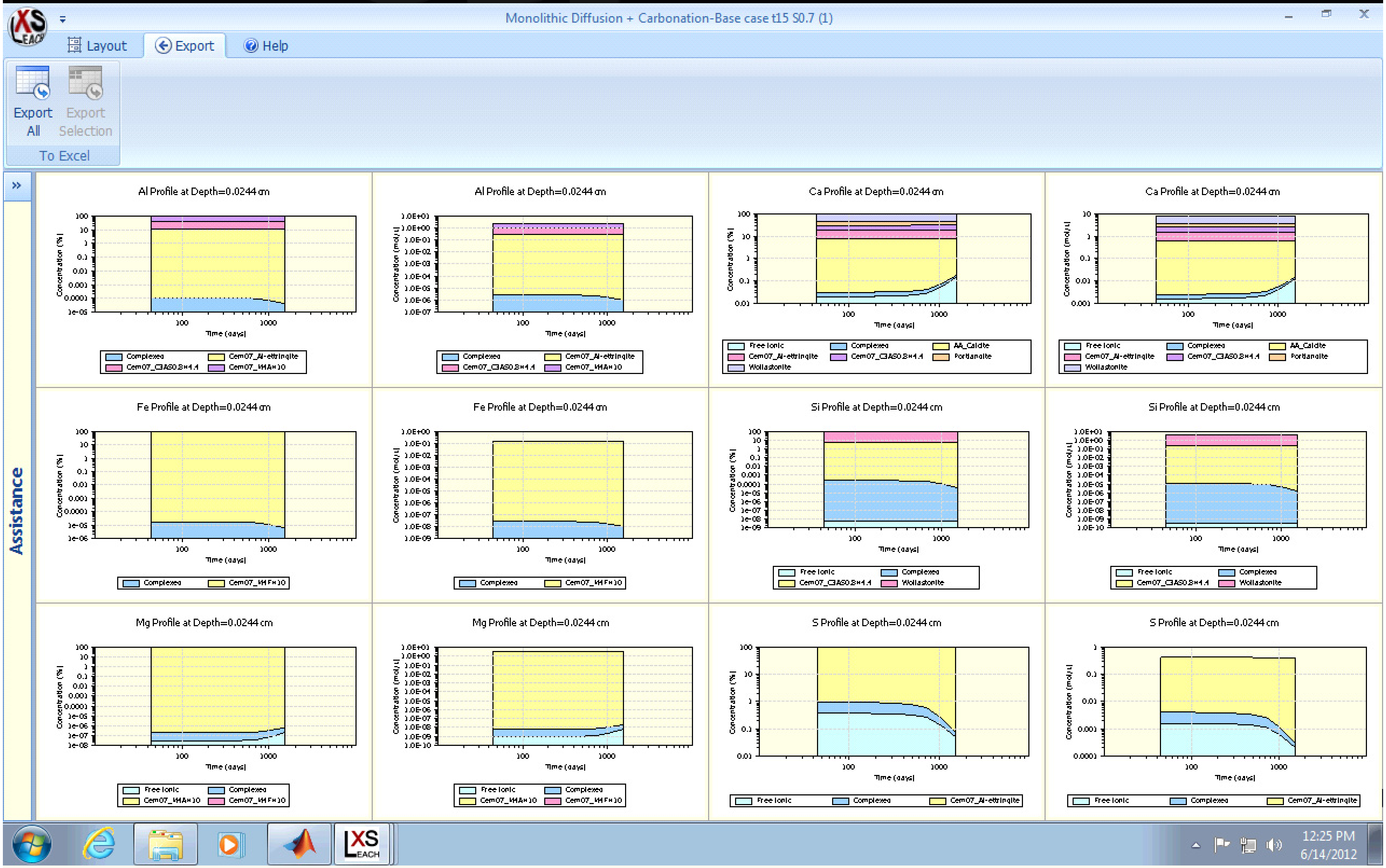
- Governing Equation for Gas Phase Diffusion

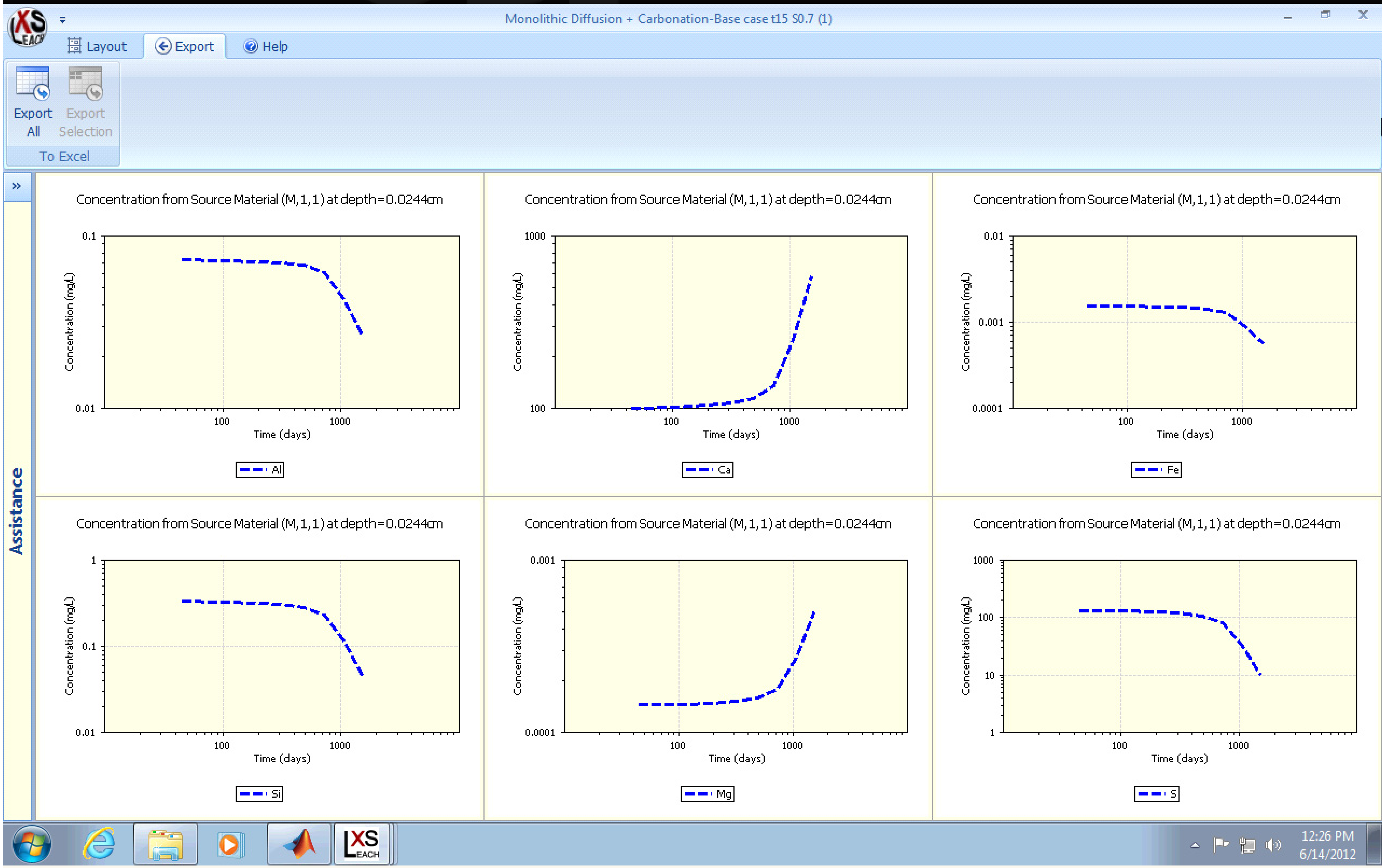
$$\frac{\partial(w_v c)}{\partial t} = \frac{\partial}{\partial x}\left(\frac{D_{0g} w_v}{\tau}\frac{w_v^{7/3}}{\phi^{7/3}}\left(\underbrace{\frac{\partial c}{\partial x}}_{\text{concentration gradient}}\right)\right)$$

D_{0g} – Gas diffusivity in air (m^2/s)

w_v – Void space (m^3/m^3)

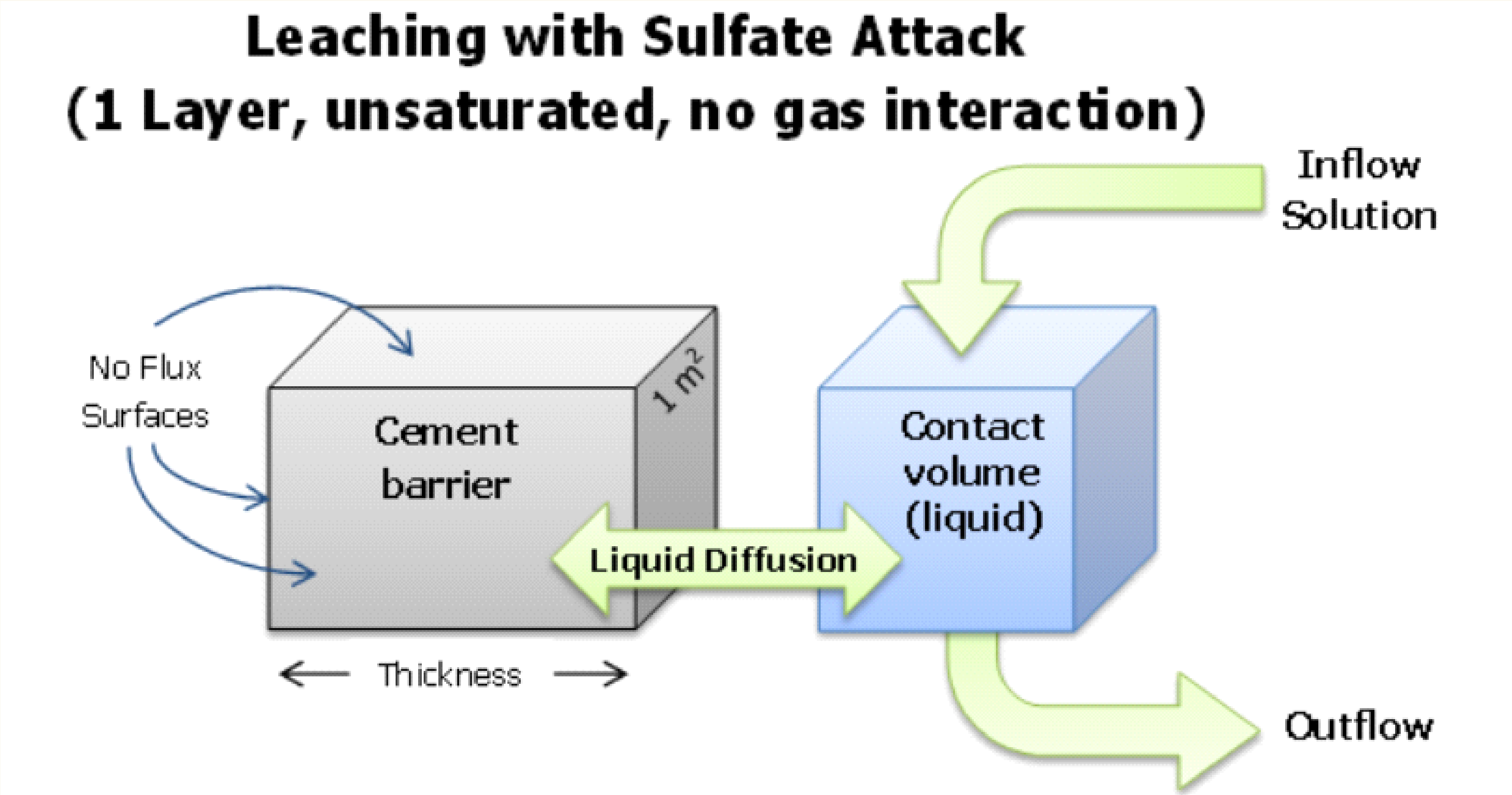
- Chemical Reactions
  - Potential solid phases: Identified by comparing results of pH-dependent leaching tests and simulations with different solid phase mineral sets using LeachXS/ORCHESTRA (by ECN)


Monolithic Diffusion + Carbonation-Base case t15 S0.7 (1)
Layout
Export
Help
Export All
Export Selection
To Excel
Assistance
Al Profile at Depth=0.0244 cm
Ca Profile at Depth=0.0244 cm
Fe Profile at Depth=0.0244 cm
Si Profile at Depth=0.0244 cm
Mg Profile at Depth=0.0244 cm
S Profile at Depth=0.0244 cm
Concentration (%)
Concentration (mol/L)
Time (days)
Free Ionic
Complexed
Cem07_Al-ettringite
Cem07_C3AS0.8H4.4
Cem07_M4AH10
Cem07_M4FH10
AA_Calcite
Portlandite
Wollastonite
12:25 PM
6/14/2012


Monolithic Diffusion + Carbonation-Base case t15 S0.7 (1)
Layout
Export
Help
Export All
Export Selection
To Excel
Assistance
Concentration from Source Material (M,1,1) at depth=0.0244cm
Concentration (mg/L)
Time (days)
Al
Ca
Fe
Si
Mg
S
12:26 PM
6/14/2012

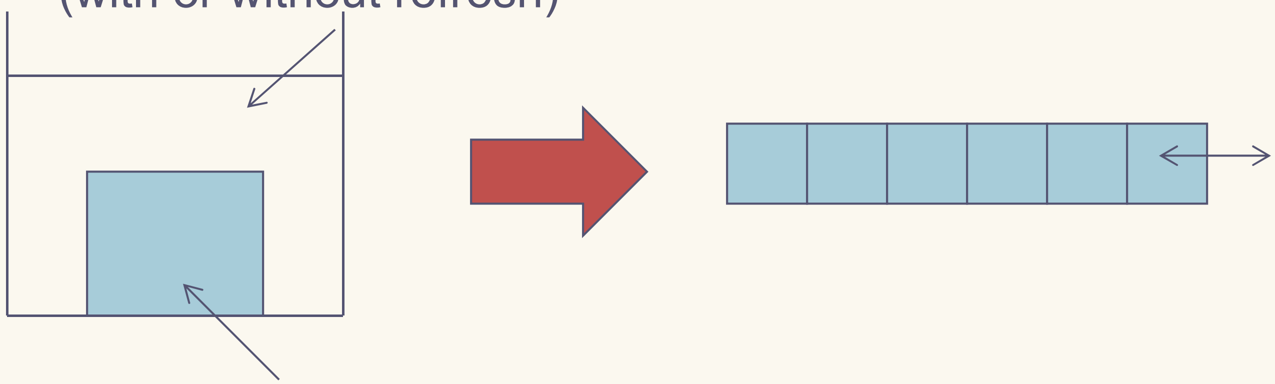

Monolithic Diffusion + Carbonation-Base case t15 S0.7 (1)
Layout
Export
Help
Export All
Export Selection
To Excel
Assistance
Al Profile at Time=1.53E+03 days
Al Profile at Time=1.53E+03 days
Ca Profile at Time=1.53E+03 days
Ca Profile at Time=1.53E+03 days
Fe Profile at Time=1.53E+03 days
Fe Profile at Time=1.53E+03 days
Si Profile at Time=1.53E+03 days
Si Profile at Time=1.53E+03 days
Mg Profile at Time=1.53E+03 days
Mg Profile at Time=1.53E+03 days
S Profile at Time=1.53E+03 days
S Profile at Time=1.53E+03 days
Depth (cm)
Concentration (%)
Concentration (mol/L)
12:29 PM
6/14/2012

Prediction Scenario – Leaching with Sulfate Attack



Sulfate Attack Scenario

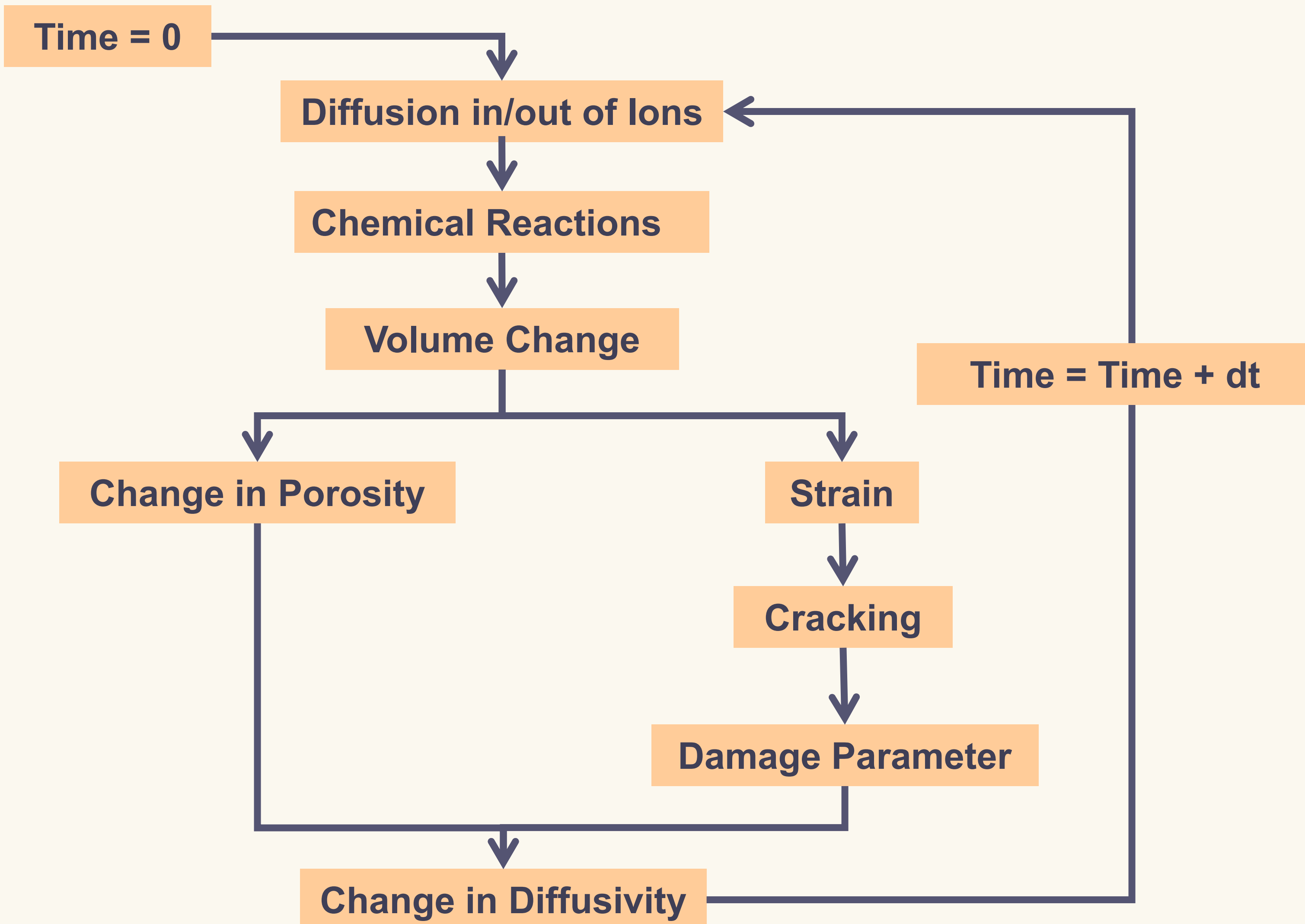
Default Template



Actual problem

1D idealization (0.2 m divided into 100 nodes using uniform meshing scheme)

Numerical Model Framework



Diffusion and Chemical Reactions

Governing Equation for Diffusion

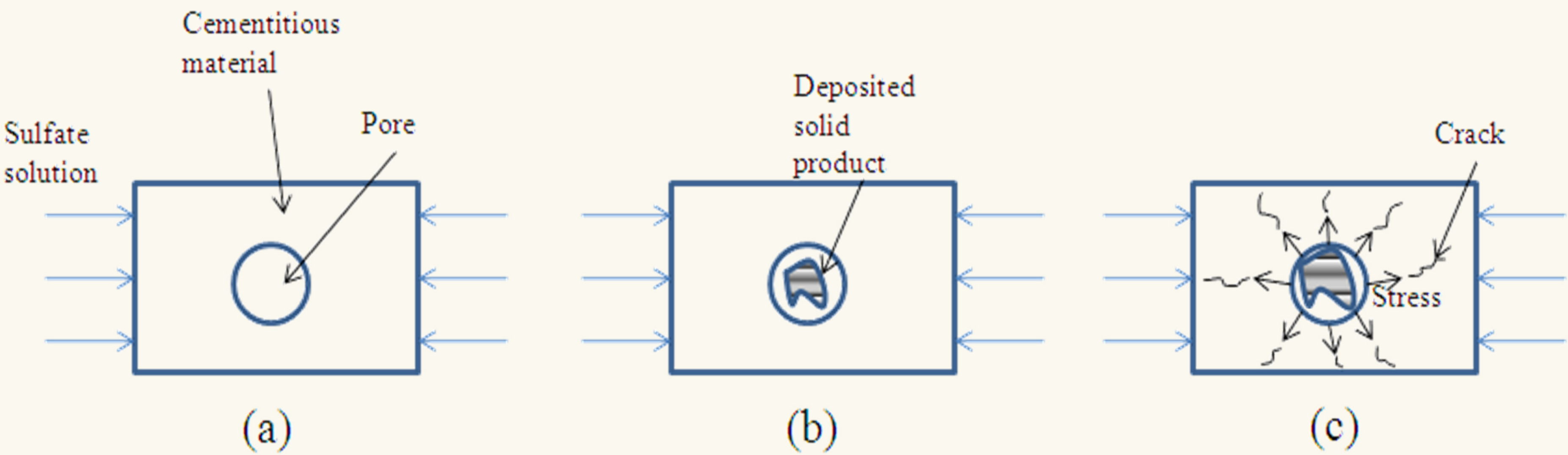
(saturated porous material under isothermal condition)

$$\frac{\partial(\phi c)}{\partial t} = \frac{\partial}{\partial x}\left(\frac{D_0 \phi}{\tau}\left(\underbrace{\frac{\partial c}{\partial x}}_{\text{concentration gradient}}\right)\right)$$

Chemical Reactions

- Potential solid phases: Identified by comparing results of pH-dependent leaching tests and simulations with different solid phase mineral sets using LeachXS/ORCHESTRA (by ECN)

Strain Development Mechanism



- Volume Change: $\overline{\Delta V_s} = (V_{\text{products}} - V_{\text{reactants}}) - b\varphi$

Fraction of porosity available (Tixier and Mobasher, 2003)

- Strain: $\varepsilon = \dfrac{\overline{\Delta V_s}}{3}$

(homogeneous and isotropic material)

- Porosity Change: $\varphi_{\text{new}} = \varphi_{\text{original}} - (V_{\text{products}} - V_{\text{reactants}})$
- Diffusivity Change: $H_D(\varphi) = \exp((\varphi_{\text{original}} - \varphi_{\text{new}}) * 4.3 / \text{paste volume})$

(Samson and Marchand, 2007)

Damage Accumulation due to Cracking

- Nonlinear Ascending Region

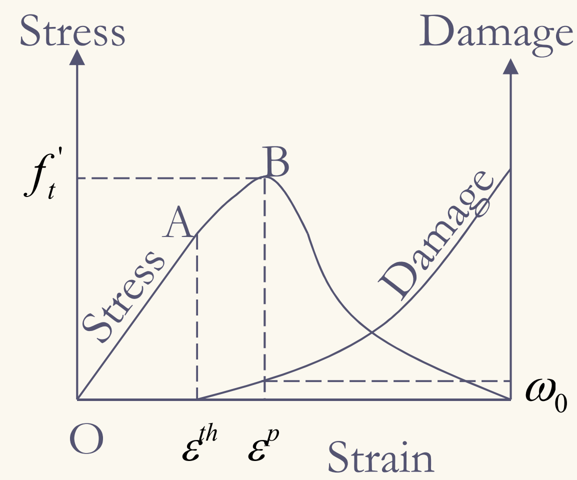
(Karihaloo, 1995, Budiansky and O'Connell, 1976)

Crack density parameter

$$C_d = k\left(1 - \frac{\varepsilon^{th}}{\varepsilon}\right)^m$$

Damage parameter

$$\omega \approx \frac{16}{9} C_d$$



- Nonlinear Descending Region

(Nemat-Nasser and Hori, 1993)

Fracture Mechanics

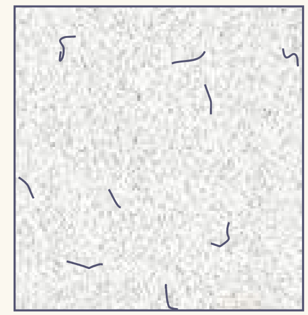
$$\frac{\sigma}{f_t'} = \sqrt{\frac{\tan(\pi\omega_0/2)}{\tan(\pi\omega/2)}} \text{ and } \frac{w}{w_0} = \frac{\sigma}{f_t'}\left(\frac{\log(\sec(\pi\omega/2))}{\log(\sec(\pi\omega_0/2))}\right) - 1$$

Change in Diffusivity due to Cracking

- Mean Field Regime

Assumption: randomly oriented penny-shaped cracks scattered in a homogeneous matrix (Salganik, 1974)

$$D = \frac{D_0}{\tau}\left(\mathbf{1} + \frac{\mathbf{32}}{\mathbf{9}} C_d\right)$$



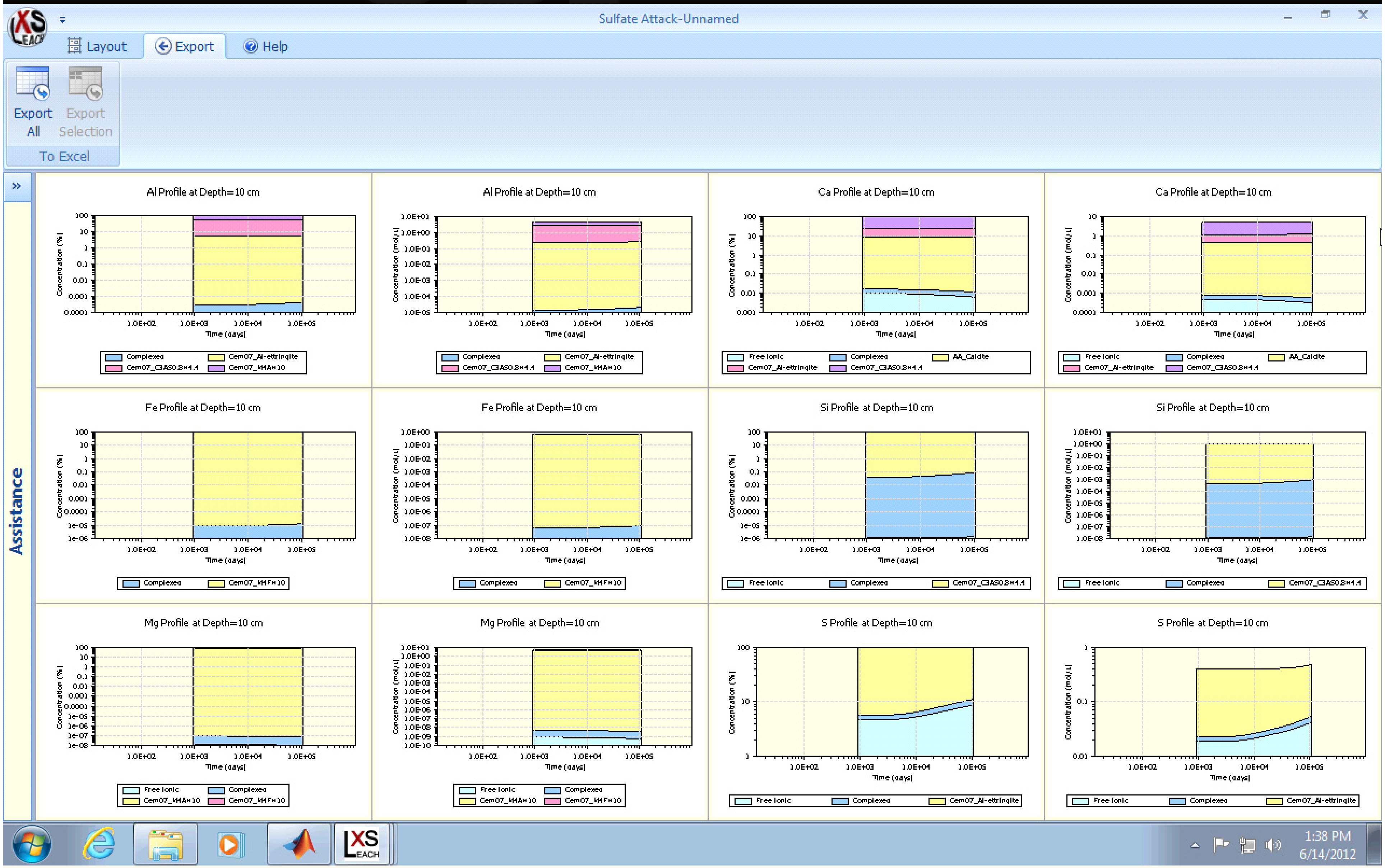
Dilute concentration of cracks

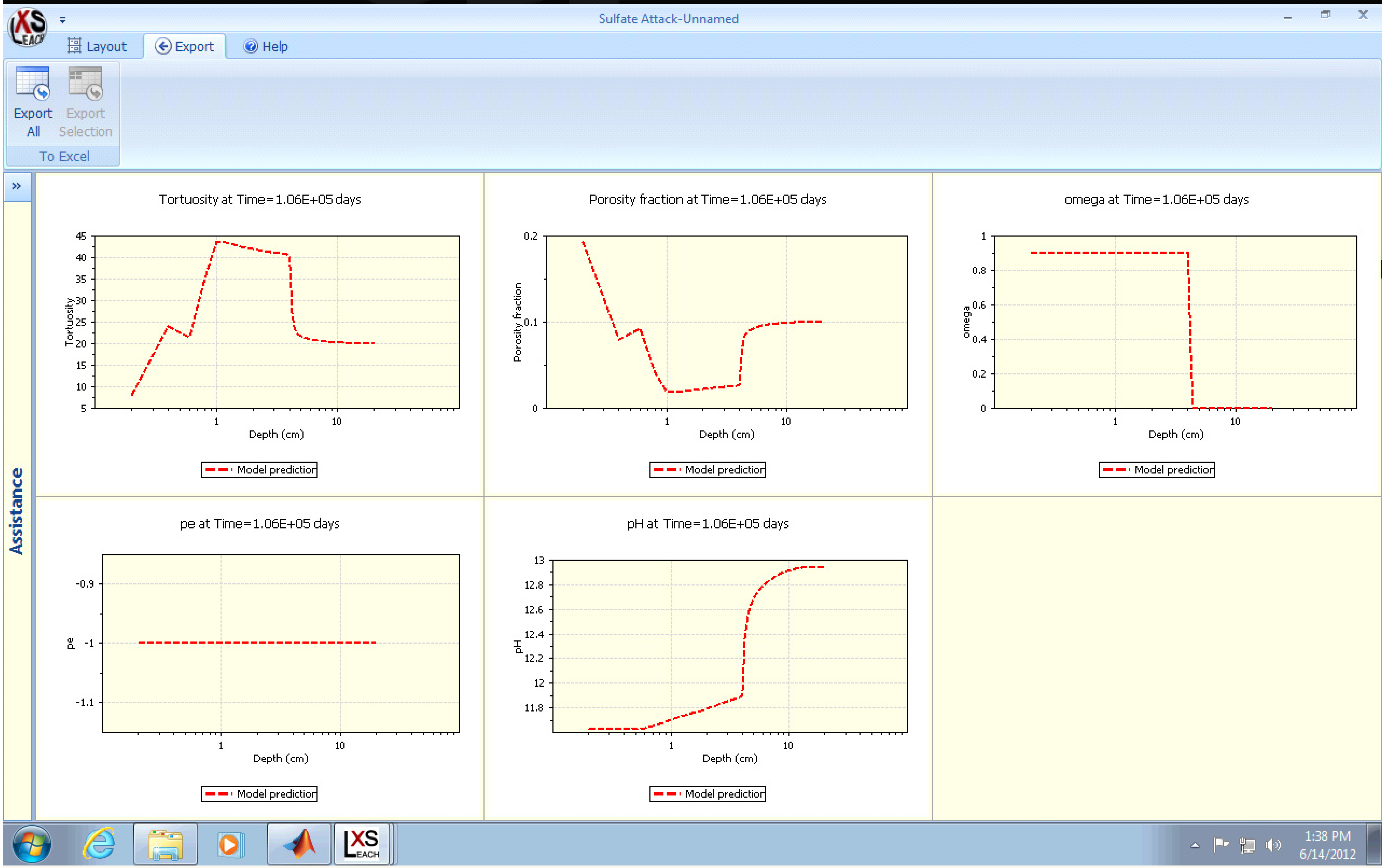
- Percolation Regime

(Stauffer, 1985 and Krajcinovic *et al*., 1992)

$$D = \frac{D_0}{\tau}\left(\mathbf{1} + \frac{\mathbf{32}}{\mathbf{9}} C_d\right) + \frac{D_0}{\tau}\frac{\left(C_d - C_{dc}\right)^2}{\left(C_{dec} - C_d\right)}$$

Spanning cluster of cracks and macro-cracks

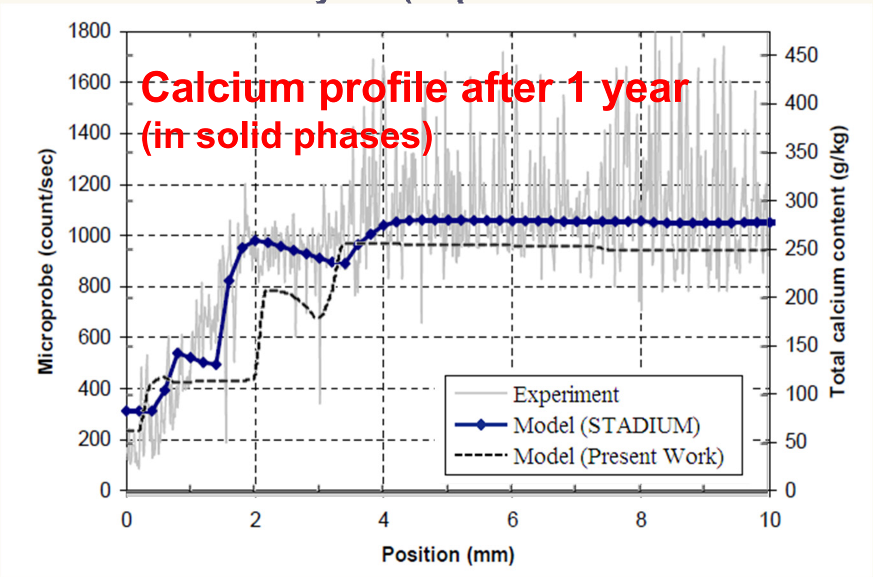

Sulfate Attack-Unnamed
Layout
Export
Help
Export All
Export Selection
To Excel
Assistance
Al Profile at Depth=10 cm
Al Profile at Depth=10 cm
Ca Profile at Depth=10 cm
Ca Profile at Depth=10 cm
Fe Profile at Depth=10 cm
Fe Profile at Depth=10 cm
Si Profile at Depth=10 cm
Si Profile at Depth=10 cm
Mg Profile at Depth=10 cm
Mg Profile at Depth=10 cm
S Profile at Depth=10 cm
S Profile at Depth=10 cm
Time (days)
Free Ionic
Complexed
1:38 PM
6/14/2012

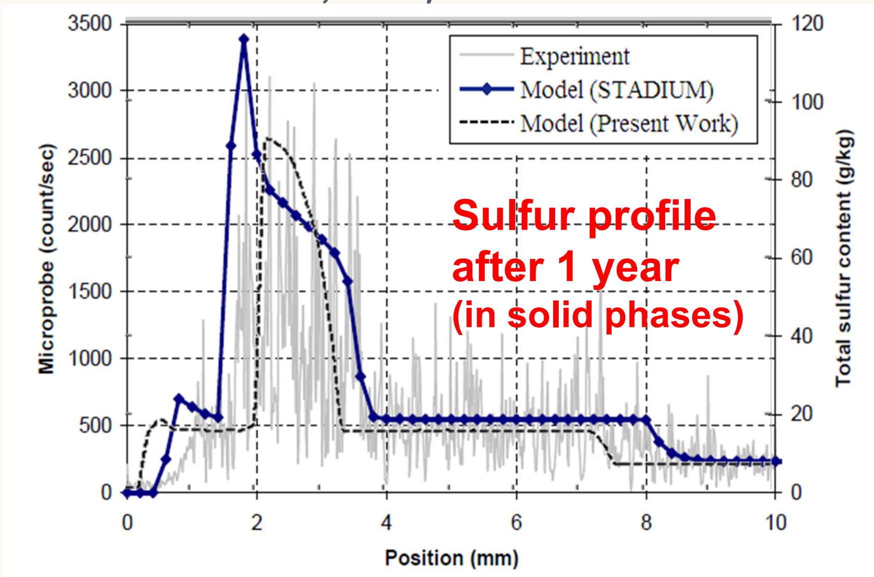

Sulfate Attack-Unnamed
Layout
Export
Help
Export All
Export Selection
To Excel
Assistance
Tortuosity at Time=1.06E+05 days
Tortuosity
Depth (cm)
Model prediction
Porosity fraction at Time=1.06E+05 days
Porosity fraction
Depth (cm)
Model prediction
omega at Time=1.06E+05 days
omega
Depth (cm)
Model prediction
pe at Time=1.06E+05 days
pe
Depth (cm)
Model prediction
pH at Time=1.06E+05 days
pH
Depth (cm)
Model prediction
1:38 PM
6/14/2012

Model Calibration and Validation

- 7 cm x 20 mm CSA type 10 cement paste, porosity = 0.52, one face exposed
- 50 mmol/L of Na_2SO_4 solution at pH 10.3 in 30 L tank renewed every 7 days
- Porosity : 0.52
- Calibration parameter: tortuosity (= 35) and b (= 0.3)

Model calibrated with experimental results after 3 months and validated against experimental results after 1 year (experimental data from Samson and Marchand, 2007)



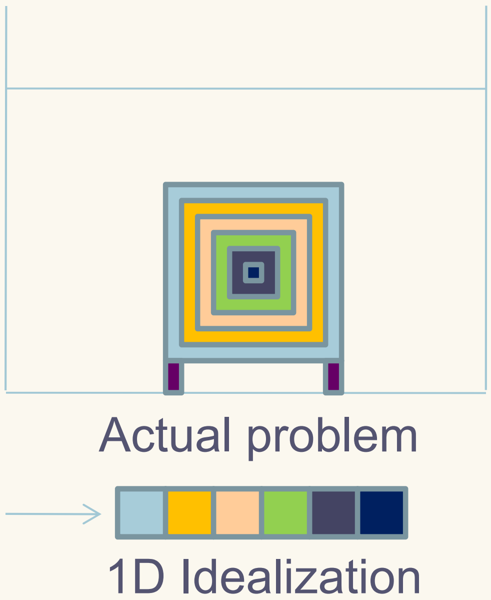


Consistent with other software which may have different applicabilities

Examples of Sensitivity Analysis

Factors Considered

- External solution – concentration of sulfate solution (0.15, 0.25, 0.35, 0.45, 0.55 moles/L)
- Structure – initial porosity (0.15, 0.2, 0.25, 0.3, 0.35, 0.4)
- Types of cement

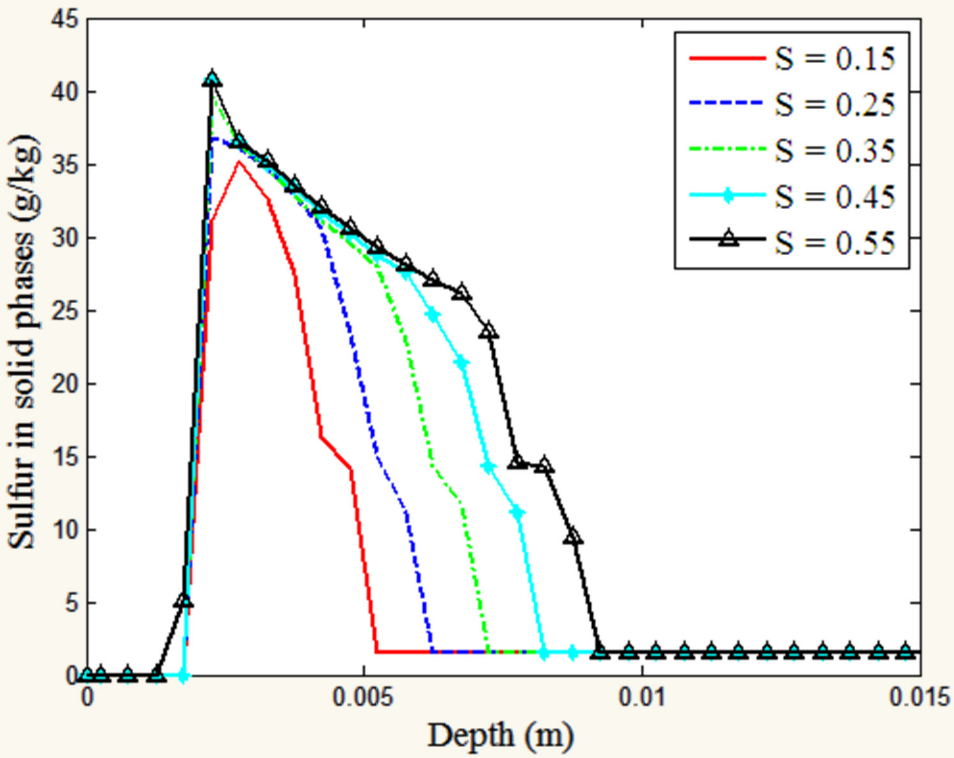


Simulation Details

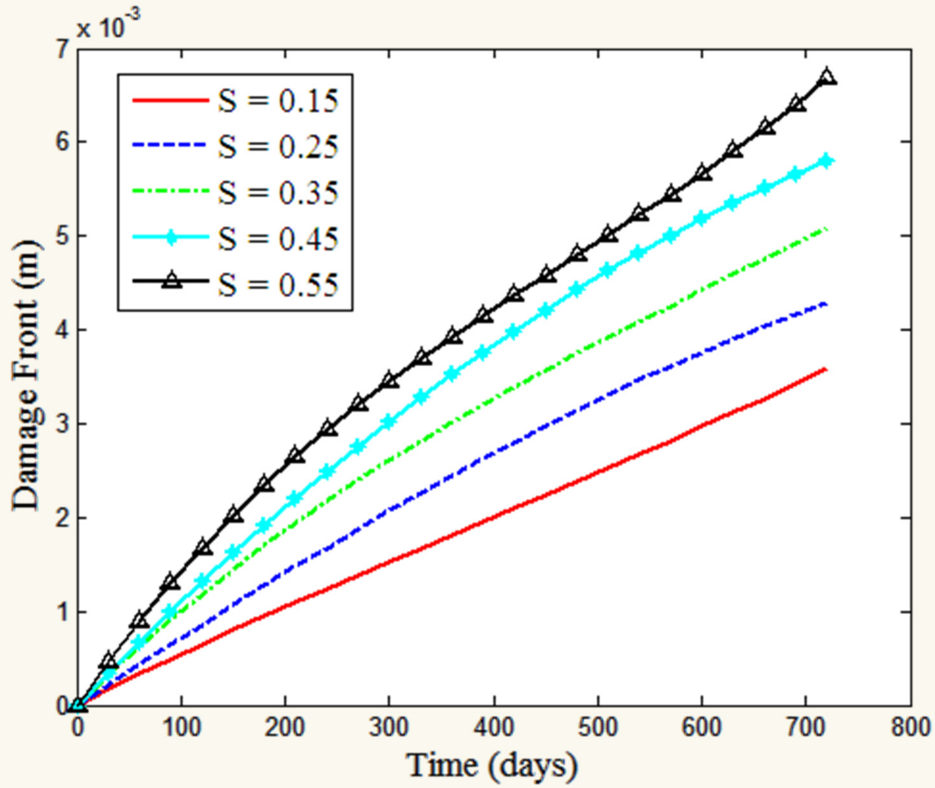
- 50 mm x 50 mm x 50 mm US type I sample, all faces exposed
- 350 mmol/L Na_2SO_4 external solution at pH 7
- Porosity : 0.25, tortuosity : 100
- Fraction of available porosity : 0.5
- Mortar - Cement : water : sand (mass ratio) = 1 : 0.5 : 3
- 7 day renewal rate of external solution for 2 years

External Solution Concentration

Sulfur Profile in Solid Phases



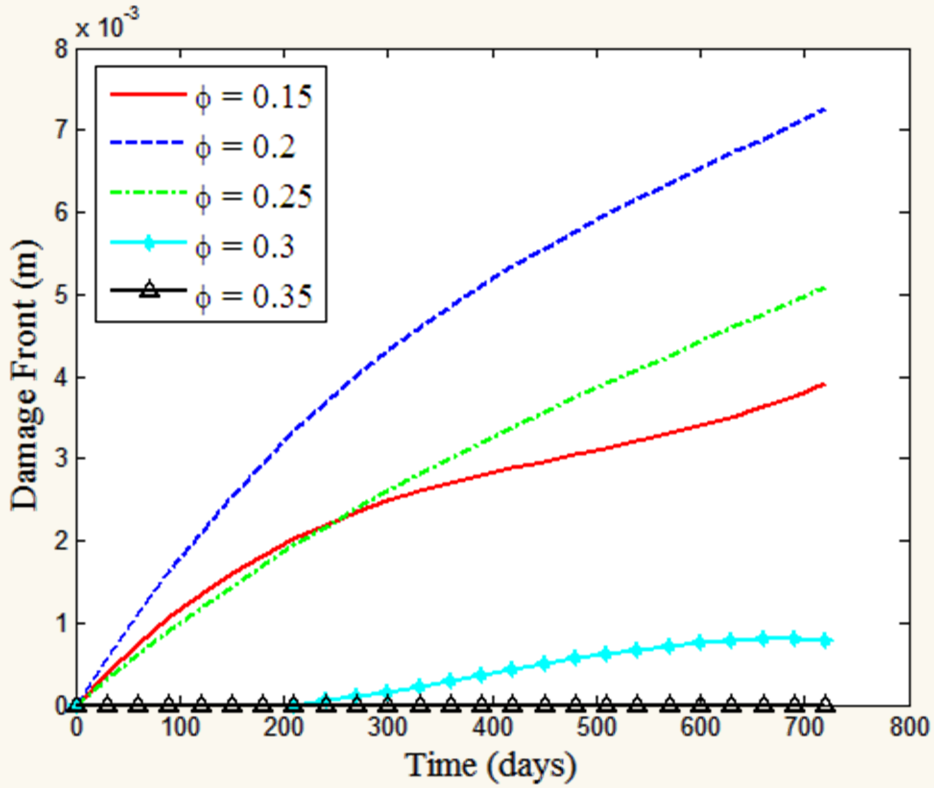
Rate of Damage Progression



- Rate of damage progression increases with increase in external sulfate solution concentration

Initial Porosity

Rate of Damage Progression



Competing Processes

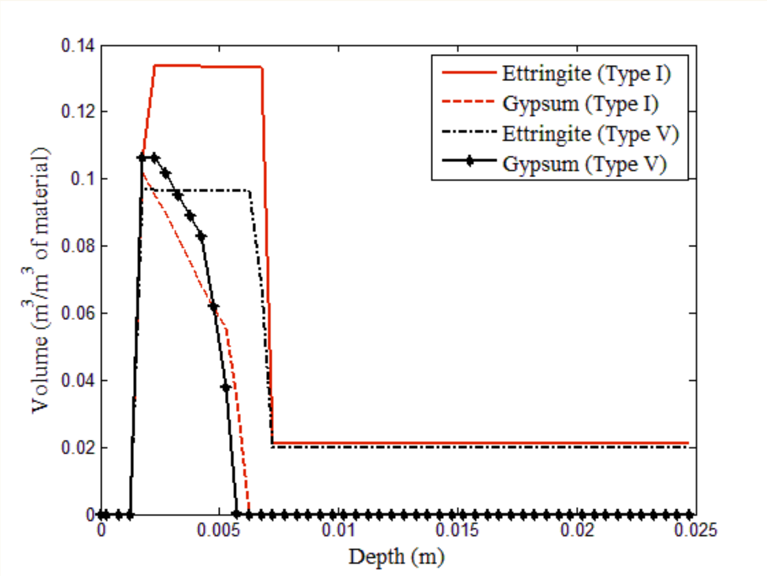
• φ ↑ ⇒

- Diffusion ↑
- Formation of solid phases ↑
- Leaching ↑
- Strain development ↓
- Solid phase present ↓
- Formation of solid phases ↓

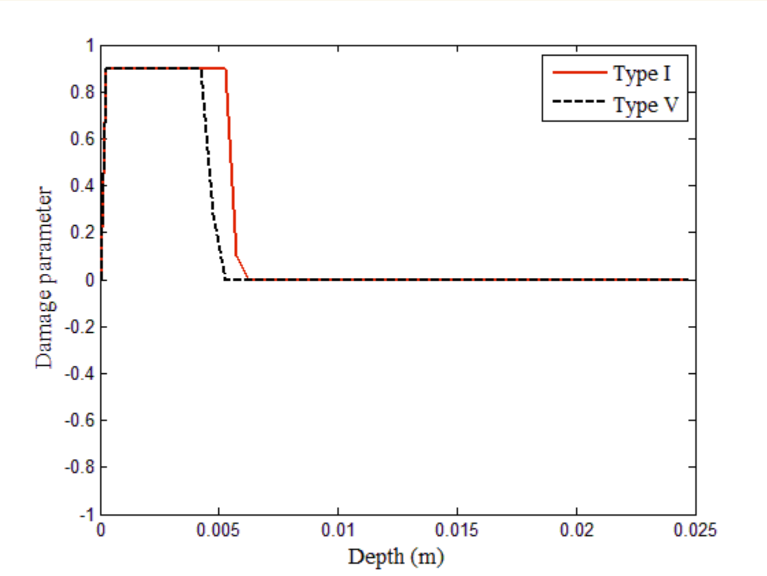
- No direct linear relationship between rate of damage progression and amount of porosity

Types of Cement

Mineralogical Changes

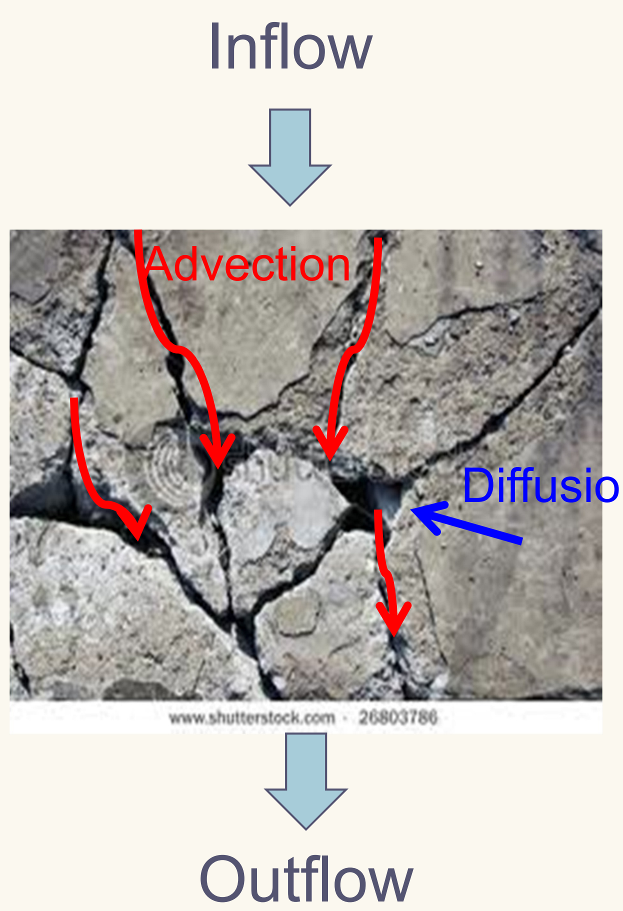


Damage Parameter

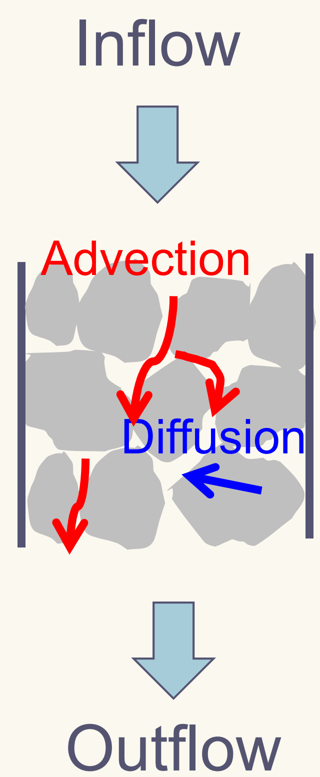


- Damage progression depends on exposure conditions and material properties

Column Percolation Scenario (M1314)

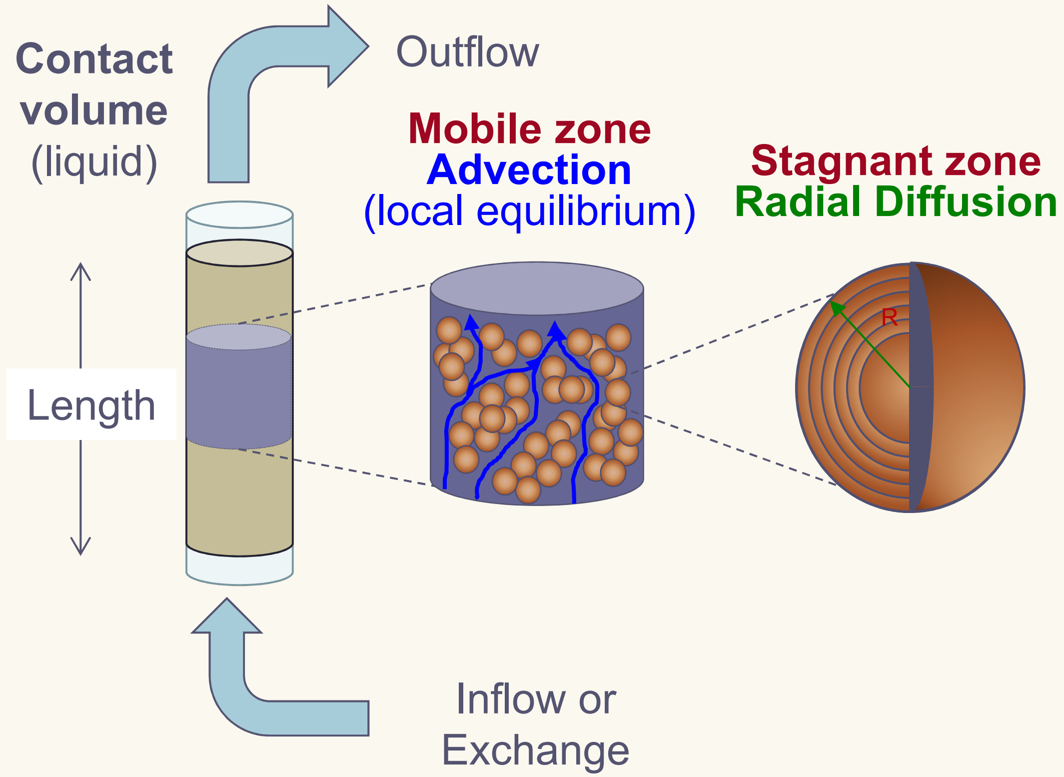


Actual problem

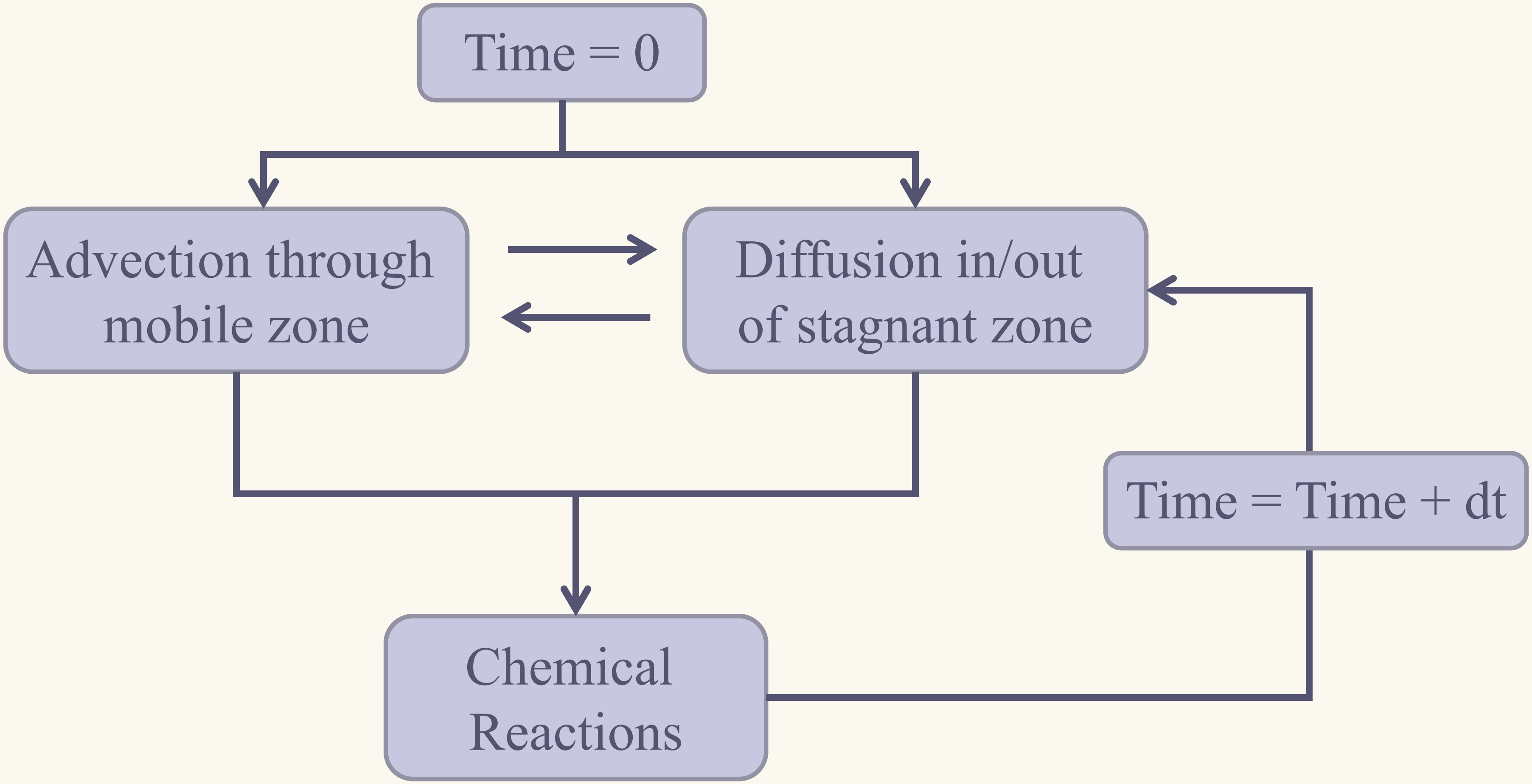


Packed bed with size reduced/compacted sample

Column Percolation Scenario (M1314)



Column Percolation Model Framework



Mass Transport Through Dual Regime and Chemical Reactions

Mass Transport

Diffusion through the spherical particle: $$\frac{\partial c_m}{\partial t} = \frac{D^m}{r^2}\left(\frac{\partial^2 c_m}{\partial r^2} + \frac{2}{r}\frac{\partial c_m}{\partial r}\right)$$

Transport through mobile phase: $$\frac{\partial c_f}{\partial t} = D^f \frac{\partial^2 c_f}{\partial x^2} - \frac{\partial}{\partial x}(q c_f) - Q$$

c_m : Concentration in immobile phase

D^m : Effective diffusivity through immobile phase

t : Time

r : Radial direction

c_f : Concentration in mobile phase

D^f : Effective diffusivity through mobile phase

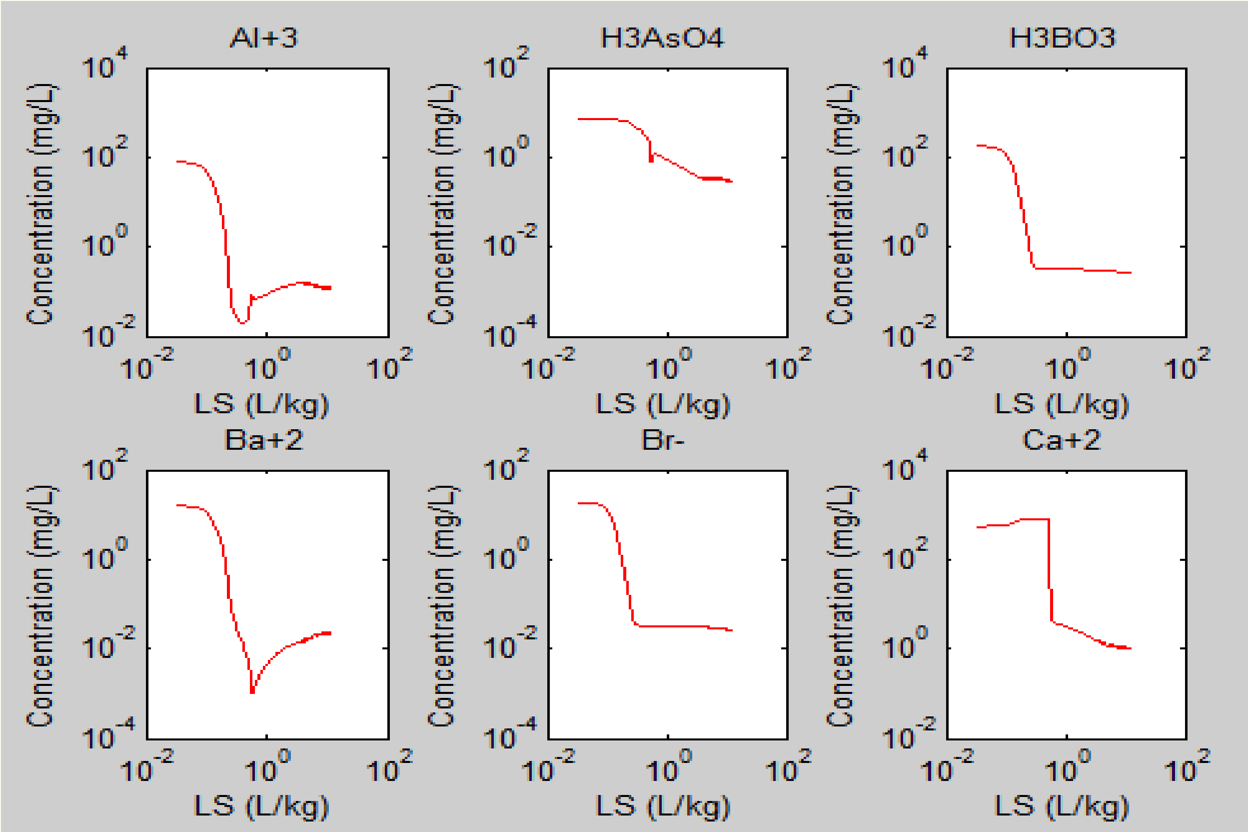
q : Volumetric water flux density

Q : Flux density of ions from the spherical particles

Chemical Reactions

- Potential solid phases: Identified by comparing results of pH-dependent leaching tests and simulations with different solid phase mineral sets using LeachXS/ORCHESTRA (by ECN)

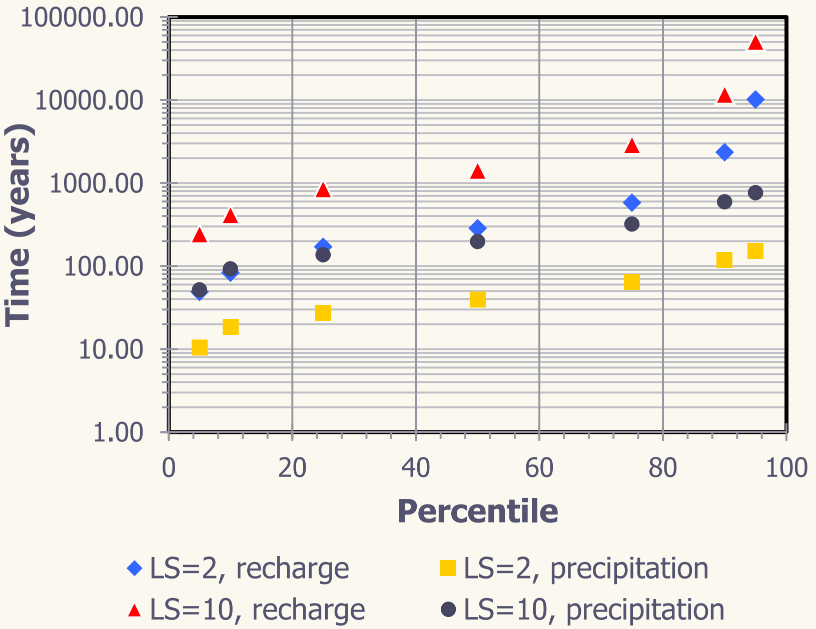
Column Percolation Scenario (M1314) – Example Outputs



- LS can be converted to equivalent time using site specific information

National Distribution of Time vs. LS

Percentiles	Time (years) to reach LS = 2		Time (years) to reach LS = 10	
	(Recharge based)	(Precipitation based)	(Recharge based)	(Precipitation based)
5	49	10	244	52
10	83	19	416	92
25	171	27	854	137
50	285	40	1425	198
75	582	64	2910	320
90	2345	119	11710	594
95	10170	153	50870	765



Information used to generate LS to time

- Site-specific precipitation rates and HELP model generated recharge rates
- Fixed landfill density (U.S. EPA, 2006)
- Site-specific landfill depth

Summary

- Three main modeling scenarios currently available
  - Monolith leaching (test and prediction cases)
  - Monolith leaching with carbonation and oxidation (prediction case)
  - Leaching with sulfate attack (prediction case)

Refinements to the current models

- Polynomial meshing scheme implementation for the prediction cases
- 3-layer (waste-cement barrier-soil) implementation

- New modeling scenarios being implemented
  - Dual regime percolation (test and prediction cases)

Significance of CBP Modeling Scenarios

- Applicability:
  - Evaluation of waste forms and treatment process effectiveness
  - Concrete vault durability and radionuclide release
  - Source term for contaminated soils/vadose zone and waste disposal scenarios
  - HLW tank integrity analysis and closure
- Flexible framework that can be easily modified to reflect various testing and field conditions
- Can be compared with available test results from the database of a large selection of materials
- Useful framework for designing future structures and maintenance scheduling for existing structures