User Guide for THAMES Input

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1 Introduction

THAMES is a program for simulating 3D microstructure development during cement binder hydration, leaching, or sulfate attack. It uses equilibrium thermodynamic calculations to determine the types and amounts of various solid phases that are in chemical equilibrium with a pore solution. Briefly, this requires a partitioning of the system into that which is kinetically controlled and that which is thermodynamically controlled. The kinetically controlled part is usually composed of the cement clinker phases or any others that gradually dissolve during cement hydration. The thermodynamically controlled part is usually the pore solution and any solid hydration products that can potentially precipitate during the process. More detailed information on the system description can be found elsewhere [1].

The user is expected to know how to work with GEMS-Selektor to generate the various thermodynamic system data files that are required for the GEM3K library that is linked to THAMES. More information on the contents of the thermodynamic data data files and how to generate them may be found in the online documentation for GEM-Selektor [2].

2 Launching THAMES

The current version of THAMES is launched from the command line with a command similar to this, assuming that your current working directory contains the executable:

```
nohup ./thames < input.txt >& output.txt &
```

where `input.txt` is the top-level input data file and `output.out` is a file to which standard output will be written.

3 The Top-Level Input File

The top-level input file is really just a list of other input file names that THAMES will read at the beginning of its execution. An example input file is given below, followed by a line-by-line description.

```
1
solution-dat.lst
solution-dbr.dat
gem3k-dat.lst
gem3k-dbr.dat
job1-ccr168-chemistry.xml
ccr168_45.img.thames
phasemod.txt
parameters.xml
myjob
```

- The first line is a numerical code that tells THAMES which kind of a simulation is to be performed. Choices are:
  - 1 = Quit program
  - 2 = Hydration
  - 3 = Leaching with neutral water
  - 4 = External sulfate attack
- The next two lines are the names of the thermodynamic data files for just the pore solution. The upper bound metastibility contraints for all DC solid phases must be set to a very small number such as 1×10^{-30}, while the constraints for all DC solute components are set to a large number such as 1×10^{6}. Furthermore, all the DC names must be unique in this file. Otherwise, these two files are identical to the data files described on the fourth and fifth lines. Therefore, usually one will generate the whole-system files from GEM-Selektor and then make copies to edit for the solution data files.
- The fourth and fifth lines are the names of the thermodynamic data files for the entire system, including the solid hydration products that may precipitate. The DC names need not be unique in this file, but one may still wish to set the upper bound metastability constraint to be exceedingly low for some solid phases, such as quartz, that are known to not precipitate during cement hydration.
- The next line is the name of the XML-formatted "THAMES phase definition file" that defines the behavior of each phase, such as whether it is part of the kinetic partition or the thermodynamic partition, the degree of randomness of its growth shape, and the correspondence between THAMES-defined phases in the microstructure and the GEM-defined phases in the thermodynamic data files. This file is somewhat complicated and will be described more fully in Section 4.
- The next line contains the name of the 3D initial microstructure file. After a short header section that defines the size of the system, the main body

of this file is a sequence of rows with one whole number on each row, with the whole number being the integer identification number of the THAMES phase at a particular location in the microstructure. This file will be described more fully in Section 5.

- The eighth line is the name of a file that contains the Young's modulus, in GPa, and Poisson ratio of each phase in the microstructure. It is used only for computing effective elastic moduli of the system or for computing the volumetric expansion under sulfate attack. An example line from the file might be

  ```
  2 C3S 117.6 0.314
  ```

  where the first entry is the microstructure identification number for the phase recognized by THAMES and the second entry is the THAMES name of the phase. Both of these items are given in the THAMES phase definition file. The third and fourth entries are the Young's modulus (GPa) and Poisson's ratio, respectively.

- The ninth line is the name of the XML-formatted file that defines the individual times, in days, at which the system's state is to be evaluated and updated. After a short header defining the XML file and schema location, a typical line in the file might be

  ```
  <calctime>0.0174494</calctime>
  ```

  At the very end of the file is another line that determines the time intervals at which the full 3D microstructure is to written to a file. For example,

  ```
  <image_frequency>1.0</image_frequency>
  ```

  means that a microstructure is to be written for each day of simulation time.

- The last line is the root name of all output files that will be created by the simulation. It can be any string you wish.

4 THAMES Phase Definition File

The THAMES phase definition file is an XML file, the form of which is validated against the schema definition file defined at the end of the second line of the file:

```
<chemistry_data xmlns:xs="http://www.w3.org/2001/XMLSchema-instance"
xs:noNamespaceSchemaLocation="/Users/username/thames_wd/chemistry.xsd">
```

This file has two basic sections. The first section containes several entries that pertain to the entire simulation, and the second section specifies the definition and behavior of each phase that THAMES recognizes.

4.1 System-wide parameters

The first six lines are the system-wide parameters:

```
<numentries>22</numentries>
<blaine>408.0</blaine>
<refblaine>385.0</refblaine>
<wcRatio>0.45</wcRatio>
<temperature>298.15</temperature>
<reftemperature>296.15</reftemperature>
```

where `numentries` is the number of microstructure phases recognized by THAMES—and also the number of subsequent `phase` code blocks in the remainder of this file. The entry `blaine` is the Blaine fineness of the cement powder ($m^2\,kg^{-1}$), which is used by the kinetic dissolution model for the portland cement clinker components. The `refblaine` entry is used to calibrate the kinetic model and should not be changed by the user. The `wcRatio` parameter is the water-cement mass ratio of the binder being simulated. The `temperature` entry is the system temperature (K), and `reftemperature` is a reference temperature used by the GEMS library and by the THAMES kinetic model. It should not be changed by the user.

4.2 THAMES phase definitions

As described earlier, THAMES defines phases that are to be kinetically controlled by some internal kientic model of dissolution or growth, and also phases that are controlled by thermodynamic equilibrium. The change in amount of a kinetically controlled phase during a particular time interval is determined by a kinetic rate equation such as the model by Parrot and Killoh [4, 3]. In contrast, the change in amount of a thermodynamically controlled phase during that same interval the amount required to reach chemical equilibrium with the pore solution.

4.3 Kinetically controlled phases

We document the meaning of each line of a kinetically controlled phase input block using XML comments here. An XML listing is first provided, followed by the explanation of each line.

```
<phase>
 <thamesname>C3S</thamesname>
 <id>2</id>
 <porosity>0.0</porosity>
 <gemphase_data>
   <gemphasename>Alite</gemphasename>
```

```
    <gemdcname>C3S</gemdcname>
  </gemphase_data>
  <interface_data>
    <randomgrowth>0.0</randomgrowth>
    <growthtemplate>2</growthtemplate>
    <growthtemplate>12</growthtemplate>
    <growthtemplate>19</growthtemplate>
    <growthtemplate>20</growthtemplate>
    <affinity>
      <affinityphaseid>2</affinityphaseid>
      <affinityvalue>1</affinityvalue>
    </affinity>
  </interface_data>
  <impurity_data>
    <k2ocoeff>0.00087</k2ocoeff>
    <na2ocoeff>0.0</na2ocoeff>
    <mgocoeff>0.00861</mgocoeff>
    <so3coeff>0.007942</so3coeff>
  </impurity_data>
  <kinetic_data>
    <type>kinetic</type>
    <scaledmass>54.46</scaledmass>
    <k1>1.5</k1>
    <k2>0.05</k2>
    <k3>1.1</k3>
    <n1>0.7</n1>
    <n3>3.3</n3>
    <Ea>41570.0</Ea>
    <critdoh>2.0</critdoh>
  </kinetic_data>
  <display_data>
    <red>162.0</red>
    <green>117.0</green>
    <blue>95.0</blue>
    <gray>220.0</gray>
  </display_data>
</phase>
```

Each phase definition is begun and ended by the `<phase>` ... `<\phase>` identifiers.

- `thamesname` is the ASCII character string that THAMES uses to identify a particular microstructure phase.
- `id` is the whole number identifier for the phase in the microstructure. These are the numbers used in the microstructure input file.

- `porosity` is the *internal* porosity associated with the phase. This includes and porosity that is too small to be resolved at the scale of the model. `C3S` has no internal porosity and so its value is 0 in this example. But other phases like C–S–H have gel porosity that could be included in this value. The porosity is the volume fraction of the phase at the bulk scale which is porous

4.3.1 GEM phase data

This block sets up the correspondence between the THAMES phase in the microstructure and the phase name(s) and dependent component name(s) linked to that phase in the GEM chemical system definition, which can be found in the DBR data file. In the current example, the GEM phase name is `Alite` and the dependent component is `C3S`. However, users may wish to associate multiple GEM phases and dependent components with a single THAMES phase. As an example, the user may wish to define a single microstructure phase for AFt, so the THAMES name could be `AFt` and have a unique microstructure identifier. However, the GEM chemical system definition includes multiple phases and dependent components that can be associated with AFt. The block below shows how to include all the types known to the GEM chemical system definition (DBR).

```
<gemphase_data>
  <gemphasename>ettringite-Al</gemphasename>
  <gemdcname>ettringite</gemdcname>
  <gemdcname>Fe-ettringite</gemdcname>
</gemphase_data>
<gemphase_data>
  <gemphasename>ettringite-Fe</gemphasename>
  <gemdcname>1ettringite</gemdcname>
  <gemdcname>1Fe-ettringite</gemdcname>
</gemphase_data>
<gemphase_data>
  <gemphasename>SO4_CO3_AFt</gemphasename>
  <gemdcname>tricarboalu</gemdcname>
  <gemdcname>2ettringite</gemdcname>
</gemphase_data>
<gemphase_data>
  <gemphasename>CO3_SO4_AFt</gemphasename>
  <gemdcname>1tricarboalu</gemdcname>
  <gemdcname>3ettringite</gemdcname>
</gemphase_data>
<gemphase_data>
  <gemphasename>ettringite</gemphasename>
  <gemdcname>4ettringite</gemdcname>
</gemphase_data>
```

In this case there are five GEM phases that all can be identified as AFt. Moreover, each of these phases is modeled as a solid solution with two end-members that are each dependent components, so each GEM phase has two DC entries. Check the DBR file to ensure that the phase names and DC names are typed exactly as they appear in the DBR file.

4.3.2 Interface data

This block is identified by the `<interfacedata>` ... `<\interfacedata>` identifiers. The block defines roughly the growth morphology and the locations where the phase can grow.

- `randomgrowth` is a number on $[0, 1]$ that determines how much randomness there is to the growth process of a phase. When a phase is eligible to grow, THAMES creates a list of all the sites in the microstructure where growth of that phase is allowed, and then orders the list in descending order of the energetic favorability of that site for growth. The energetic favorability is determined by the "affinity" of the growing phase for each of the phases in its neighboring sites. Suppose that n voxels of the phase need to grow during a given iteration. If `randomgrowth` $= 0$, then the first voxel will be placed at the location of the first member of the growth list (energetically most favorable), the second will be placed in the second member, and so on until all n voxels have been placed. However, if the `randomgrowth` parameter is $r > 0$, then a fraction r of the list members will be randomly shuffled in pairs to create a disordered list. The growing voxels are then assigned from the top of the list as before.

- `growthtemplate` is a THAMES phase identification number. There may be multiple growth templates defined for any given phase. When constructing the list of sites at which a given phase can grow, THAMES will add an empty site to that list if one or more of the neighboring sites is occupied by a phase that belongs to the list of growth templates. One should always define the phase itself as one of its own growth templates.

- `affinityphaseid` and `affinityphasevalue` provide a way to specify with more detail the local energetic favorability of a potential growth site. The `affinityphasevalue` is positive if a growing phase has an affinity for growing next to the phase with the corresponding `affinityphaseid`, and is negative if the two phases are not energetically disposed to grow next to each other. The notion of "affinity" might be imagined as a rough proxy for wettability according to the Young-Dupré equation, so that the affinity will be negative if the contact angle between the two phases is greater than $90°$ and is positive if the contact angle is less than $90°$.

  A phase with negative affinity for a growing phase should not be a member of the growing phase's growth templates. And among all the growth

templates, the default affinity is zero so that one needs to identify only those phases in the list of growth templates that have a positive affinity.

4.3.3 Impurity data

Each phase in cement clinker generally contains impurities that dissolve into the pore solution as the phase itself dissolves. The kinetic model in THAMES for clinker phase dissolution currently recognizes four impurities, defined on an oxide basis, that can exist in each clinker phase, namely K_2O, Na_2O, MgO, and SO_3. The impurity levels are defined on a mass fraction basis as described by Lothenbach and Winnefeld [3]. The data are entered in the XML block identified by `<impurity_data>` ... `<\impurity_data>`.

4.3.4 Kinetic data

The block identified by `<kinetic_data>` ... `<\kinetic_data>` provides parameter values for the kinetic model of clinker phase dissolution described by Parrot and Killoh [4]. The parameters in this block are

- The `type` parameter determines how a given phase in the original system, before any hydration, is treated by the model. There are three options:
  - **kinetic** phases will dissolve at a rate determined by the internal kinetic model, which is currently based on that of Parrot and Killoh [4]. The number of moles of each independent component (IC) dissolved from these phases during a time step is transferred to the thermodynamic subsystem.
  - **soluble** phases dissolves completely during the first time interval of the simulation. All the IC moles for these phases are immediately transferred to the thermodynamic subsystem in the first time step.
  - **thermo** phases are those phases that may be present in the initial microstructure but which nevertheless should be considered part of the thermodynamic partition. These phases are not dissolved but their IC moles are still transferred to the thermodynamic subsystem.
- `scaledmass` is the mass of the phase per 100 g of solids in the original microstructure. If the microstructure was created using VCCTL software, then this value should correspond to the mass fraction of that phase that was specified to create the microstructure.
- `k1`, `k2`, `k3`, `n1`, `n3`, and `Ea`, and `critdoh` are empirical parameters determined for each phase in the Parrot and Killoh model. Refer to Lothenbach and Winnefeld [3] or to Parrot and Killoh [4] for more details.

4.3.5 Display data

The data in this section are used when creating a visualization of the microstructure. Each phase can be assigned a color defined by the 8-bit `red`, `green`, and `blue` channels (0 to 255). In addition, one can define an 8-bit monochromatic `gray` value that will be used to create phase contrast when simulating a backscattered electron (BSE) image of the microstructure. For that purpose, bright phases such as ferrite and alite should have relatively high gray values while porosity should have low gray values.

4.4 Thermodynamically controlled phases

Thermodynamically controlled phases consist of the pore solution and any solids that precipitate during hydration. These phases have the same types of data as kinetically controlled phases with two exceptions: they have neither a `<kinetic_data>` ... `<\kinetic_data>` block nor a `<impurity_data>` ... `<\impurity_data>` block.

5 THAMES Microstructure File

Microstructure files for THAMES input have a header section as shown in the following example:

```
Version: 7.0
X_Size: 100
Y_Size: 100
Z_Size: 100
Image_Resolution: 1.00
```

The `Version` parameter is not used. `X_Size`, `Y_Size`, and `Z_Size` are the number of voxels (or lattice sites) in the x, y, and z axes of the microstructure. `Image_Resolution` is the size of a single voxel in µm units.

The remainder of the microstructure file is a sequence of `X_Size`×`Y_Size`×`Z_Size` lines, each of which has the integer id of the THAMES phase occupying the voxel associated with that line. The lines are ordered so that the x coordinate varies most quickly, followed by the y coordinate and lastly by the z coordinate. As

an example of the coordinate ordering for a $3 \times 3 \times 2$ microstructure is

$$
\begin{gathered}
(0,0,0) \\
(1,0,0) \\
(2,0,0) \\
(0,1,0) \\
(1,1,0) \\
(2,1,0) \\
(0,2,0) \\
(1,2,0) \\
(2,2,0) \\
(0,0,1) \\
(1,0,1) \\
(2,0,1) \\
(0,1,1) \\
(1,1,1) \\
(2,1,1) \\
(0,2,1) \\
(1,2,1) \\
(2,2,1)
\end{gathered}
$$

5.1 Transforming a VCCTL microstructure

In the majority of cases, an initial THAMES microstructure will be based on a 3D microstructure created within VCCTL. Unfortunately, a VCCTL microstructure file cannot be read directly by THAMES, but instead must be transformed so that the phase identifiers agree. `vcctl2thames` is a short program that can perform the transformation for you.

References

[1] Bullard JW, Lothenbach B, Stutzman PE, Snyder KA (2011) Coupling thermodynamics and digital image models to simulate hydration and microstructure development of portland cement pastes. *J Mater Res* 26(4):609–622.

[2] Kulik DA, Wagner T, Dmytrieva SV, Kosakowski G, Hingerl FF, Chudnenko KV, Berner UR (2013) GEM-Selektor geochemical modeling package: Revised algorithm and GEMS3K numerical kernel for coupled simulation codes. *Comput Geosci* 17(1):1–24.

[3] Lothenbach B, Winnefeld F (2006) Thermodynamic modelling of the hydration of Portland cement. *Cem Concr Res* 36:209–226.

[4] Parrot LJ, Killoh DC (1984) Prediction of cement hydration. *Br Ceram Proc* 35:41–53.