CBP Software Description Chapter

THAMES

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Goal and Objectives of the Cementitious Barriers Partnership (CBP)

The goal of the Cementitious Barriers Partnership (CBP) is to develop a reasonable and credible set of tools to predict the structural, hydraulic and chemical performance of cement barriers used in nuclear applications over extended time frames (e.g., >100 years for operating facilities and >1000 years for waste management).

The set of simulation tools and data developed under this project will be used to evaluate and predict the behavior of cementitious barriers used in near surface engineered waste disposal systems, e.g., waste forms, containment structures, entombments and environmental remediation, including decontamination and decommissioning (D&D) activities. The simulation tools will also support analysis of structural concrete components of nuclear facilities (spent fuel pools, dry spent fuel storage units, and recycling facilities, e.g., fuel fabrication, separations processes). Simulation parameters will be obtained from literature sources and experimentally measured under this project as necessary to demonstrate application of the simulation tools to three prototype applications (i.e., waste form in concrete vault, high level waste tank grouting, and spent fuel pool).

Characterizing the properties and reducing the uncertainty in understanding the mechanistic behavior of cementitious barriers is necessary to evaluate and improve system designs. Uncertainty reductions require coupling multi-scale and multi-physics processes, including physical-chemical evolution and transport phenomena applied to heterogeneous materials with changing boundary conditions. Uncertainty evaluation will be included with simulations at both the phenomenological and integrated system level.

Through the CBP, conceptual models and computational tools will be developed or modified to improve the assessment of the long-term structural, hydraulic, and chemical performance of cementitious materials under dynamic environmental exposure conditions and in response to changes in material properties induced by (i) aging, (ii) chloride attack, (iii) sulfate attack, (iv) carbonation, (v) oxidation, and (vi) primary constituent leaching. Recommendations will be made on testing and test methods to characterize cementitious materials for the purposes of model calibration and comparative evaluations. A methodology for quantifying assessment uncertainty as a consequence of conceptual model, computational, parameter estimation and data uncertainties, and approaches for reducing uncertainty through inclusion of new information as it becomes available.

Overview

THAMES[1] software is in the beginning stages of development. It leverages thermodynamic predictions of equilibrium phase assemblages in aqueous geochemical systems to construct 3-D virtual microstructures of a cementitious binder at different times during the hydration process or during degradation phenomena. These virtual microstructures can then be used directly to calculate important engineering properties of a concrete made from that binder at prescribed

[1] THAMES is an acronym for Thermodynamic Hydration And Microstructure Evolution Simulator.

times. In this way, the THAMES model will provide a way to calculate the time evolution of important material properties such as elastic stiffness, compressive strength, effective DC conductivity, and permeability.

The basic idea in using *equilibrium* thermodynamics to guide the *nonequilibrium* development of microstructure is to approximate changes in the system as a sequence of quasi-static (i.e., reversible) changes of state during "small" time intervals. In mature concrete, dissolution of the initial cement phases is so slow—due to decreased surface area and diffusion barriers set up by hydration products—that one can get a good estimate of the solution composition by assuming the solution to be in equilibrium with all of the hydration product phases that are present at the time. This calculation of multiphase chemical equilibrium is readily accomplished using any of a number of environmental geochemistry programs such as PHREEQC (PHREEQC 2008), CHESS (CHESS 2008), GEMS (GEMS 2008) or ORCHESTRA (Meeussen 2003), although there can be differences among programs and errors in the programs. The equilibrium solution composition and number of moles of each solid phase represents the initial conditions for the system. The driving force for subsequent state changes are small excursions of the pore solution composition from equilibrium with the existing phases, due to continuous but slow dissolution of cement phases, by the exchange of ions with external groundwater, by gradual changes in temperature, and/or by degradation reactions. Even relatively fast changes, like a sudden ingress of external sulfate ions, often can be well-approximated by an assumption of thermodynamic control on the formation of reaction products (Lasaga 1981, Lothenbach and Winnefeld 2006).

The feasibility of this idea already has been demonstrated for simulating the hydration of cement paste (Lothenbach and Wieland 2006; Lothenbach and Winnefeld 2006; Guillon 2008). A number of physical parameters of the initial paste, such as solid surface area, phase composition, and water-solid mass ratio, are used to generate a semi-empirical description of the rate of dissociation of each cement clinker phase (Parrott and Killoh 1984, Tomosawa 1997). These dissolution rates enable one to determine the (non-equilibrium) solution composition at any time, which in turn is used to compute the new equilibrium solution composition and the change in number of moles of each hydration product phase. Predictions of solution composition, pH, mole fractions of hydration product phases, and total capillary porosity have been validated against experiment for several different cement compositions (Lothenbach and Wieland 2006; Lothenbach and Winnefeld 2006).

THAMES is being built around a thermodynamic engine, which rapidly predicts the bulk phase volumes as a function of time in cement paste microstructures that are evolving by hydration or degradation phenomena. However, the bulk information alone is insufficient to make accurate predictions of transport properties and mechanical properties; microstructure information is also required. That is, a successful model must predict not only the overall phase quantities, but also how these phases are distributed in space. Therefore, the complete THAMES software will include a module for generating a representative 3-D initial microstructure (GENMIC), a module for simulating microstructure changes (THAMES) guided by the thermodynamic calculations (e.g., GEMS), and a module for calculating the elastic moduli, DC conductivity/diffusivity, and permeability on the predicted cement paste and mortar/concrete microstructure (CONCPROPS). The following sections describe the conceptual models,

limitations, validation requirements, and potential development opportunities for these modules.

Explanation of Conceptual Models and Theory

The overarching conceptual model of THAMES is the abstraction of the 3-D microstructure of a cementitious material as a scalar function M(**r**,t) of **r**, the position vector relative to an arbitrary origin of space and t, the time relative to an arbitrary origin of time. For any given **r** and t, the function M gives an integer identifying the phase occupying that point in space and time. A THAMES simulation begins with input of statistical data on the mass fractions and spatial distribution of phases within the microstructure that is sufficiently detailed to enable the creation of a representative volume element (RVE) of an initial microstructure, M(**r**,0) that is consistent with the input statistical data. A module called GENMIC accomplishes this task, discretizing the RVE onto a three-dimensional cubic lattice, using random parking of digitized particle shapes and a Gaussian filter to distribute the clinker phases.

Generally, an initial microstructure M(**r**,0) contains a collection of mineral phases that are not at thermodynamic equilibrium with the aqueous solution in the capillary pores. As a result, interactions between the solution and the solid phases will take place, with some phases partially dissolving and other phases precipitating as the system tends toward an equilibrium state. The goal of THAMES is to capture the trajectory of microstructural changes and determine the M(**r**,t) function during this process. For any collection of components and a sufficiently comprehensive thermodynamic database, one can determine a particular subspace of the range of M(**r**,t $\rightarrow\infty$) to which the equilibrium state must belong, i.e., the equilibrium mass fractions of each phase. The role of the GEMS module (see description below) is to identify that subspace. However, this thermodynamic constraint does not specify the spatial distribution of those phases, nor does it indicate how the initial microstructure changes continuously along a path toward that equilibrium state.

Therefore, the THAMES software assumes that the path toward equilibrium can be partitioned into a sequence of quasi-static changes in microstructure subject to time-dependent boundary conditions on the chemical composition of the pore solution. This sequence is constructed by assuming that, during a suitably small time interval Δt, (a) each phase that is unstable with respect to dissolution will dissociate according to a prescribed rate law; (b) the partial dissolution of those phases establishes an initial condition on the solution composition for that time interval; (c) subject to that initial condition, a thermodynamic calculation determines the solution speciation and the mass fractions of solid phases that are in equilibrium with the pore solution at the end of the time interval Δt; and (d) a set of customized rules for each phase determines how to add or subtract phase volumes from the microstructure to obtain realistic spatial distributions of those phases that are consistent with experimental observation. The new state of microstructure, M(**r**, t+Δt), then serves as the starting microstructure for the next time interval, and the process is repeated until a desired end time is reached.

One of the key tenets of materials science is that structure, together with chemistry, determines the properties of any material. If the microstructure of a cementitious material is resolved with sufficient accuracy, then that structure can be used to calculate engineering properties of the

material using computational mechanics and composite theory. In the THAMES software, therefore, the output of the microstructure calculations at any time, i.e., the 3-D lattice approximation of M(**r**,t) can be used as a finite element or finite difference mesh to estimate properties including linear elastic moduli, DC conductivity, and permeability of the material using established algorithms developed and validated at NIST. This collection of models for calculating engineering properties comprises the CONCPROPS module of the THAMES software, which works at the cement paste and mortar/concrete levels.

Hardware and Software Requirements

THAMES is comprised of software modules written in the C and C++ programming languages. It can be compiled and run on any platform with a C/C++ compiler in principle. The development version of THAMES has been used with Unix/Linux[2] and Mac OS X, both of which have the GNU gcc compiler. MS Windows platforms furnished with a Linux virtual machine or a commercial C/C++ compiler also could be viable, although it has not been verified.

Several of the programs within the CONCPROPS module are available in both serial and parallelized versions, but the programs in all the other modules are now available only in serial form. Parallelizing all of the programs, which would enable much larger microstructures to be simulated, would require libraries for the Message Passing Interface (MPI) protocol to be installed. In the latter case, the parallelized version would be beneficial if multiple processors or multi-core processors are available, and linked via ethernet or higher-speed network (e.g. myrinet) connections.

Program Execution Mode(s) and User/Program Interface Information

Currently, the development version of the THAMES software operates exclusively in command-line mode. A graphical user interface (GUI), probably based on Java applets, could be developed at some point during the CBP project if found necessary.

System Performance

On a computer with a 2.33 GHz 2-core processor, the GENMIC module can create a 100 μm^3 volume of cement paste (10^6 pixels) in about 20 minutes. Simulating 3 years of hydration of this microstructure with the THAMES and GEMS modules requires about one or two hours. Calculation of concrete properties, such as effective elastic moduli, with the CONCPROPS module currently requires less than an additional hour of computational time. Larger cement paste volumes require proportionally longer computational times, scaling roughly linearly with system volume.

[2] Certain computer programming languages and operating systems, either commercial or open source, are identified to adequately specify program compilation procedures. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the items identified are necessarily the best available for the purpose.

Input Data Description

The input data required to begin a simulation with THAMES are the set of statistical parameters and functions that are sufficient to create a 3-D approximation of the initial microstructure on a cubic lattice. Generally, the input requirements will include (1) the frequency with which to output the state of the lattice microstructure and to calculate selected properties; (2) the particle size distribution of each distinct component (cement, gypsum, fly ash , etc.) tabulated as a probability density function; (3) the shape distribution of each distinct component, catalogued in a database of spherical harmonic coefficients for individual particles; (4) the mass fractions of each phase, including pore solution, in the initial microstructure; (5) the surface area fractions of each solid phase; (6) a two-point correlation function for each solid phase in the cement clinker; and (7) a database of thermodynamic functions and thermophysical properties of cementitious phases. This database can be embedded in the GEMS module and, therefore, technically, may not be considered as an input. For simulating mortar or concrete, additional input parameters are required including (8) the aggregate mass fraction; (9) the aggregate grading, that is, the mass fraction of aggregate particles retained in each of a stack of sieves; and (10) the aggregate shape distribution, catalogued in the same way as for cement particles. To calculate engineering properties in the CONCPROPS module, one must also input the relevant physical properties of each phase in the microstructure, including (11) bulk modulus of each phase, (12) the shear modulus of each phase, (13) the effective diffusivity of ions through the phase relative to their diffusivity in bulk pore solution, and (14) the liquid or gas permeability of each phase. More detailed descriptions of many of these parameters are given in the following sections.

As part of the development of THAMES during the lifetime of the CBP project, the software will be extended to allow the possibility to make changes to the pore solution composition at prescribed times. This will be done to simulate the influence of the ingress of external agents, such as sulfates and chlorides. When this is accomplished, additional input will be required in the form of a table of time-dependent boundary conditions on the pore solution chemistry, specifically the elemental molal concentration of certain components.

Specific inputs for each module of THAMES will be listed in tabular form in the detailed description of those modules.

Output Descriptions

The output of the THAMES software consists of (a) the three-dimensional state of the lattice approximation to the microstructure RVE, given by the integer phase identification number at each lattice site, at times prescribed by the user and (b) values of selected properties prescribed by the user. Both of these outputs are in the form of regular ASCII text files.

Detailed Example(s)

No detailed examples are available at this time because the development of the THAMES model is not yet finished.

Program Structure

THAMES software is comprised of four interacting modules:

(1) A generator for the initial 3-D microstructure of a cementitious paste (GENMIC).

(2) A Gibbs free energy minimizer (GEMS) including a thermodynamic database customized for cementitious phases.

(3) A lattice-based model for simulating the microstructure state as a function of time (EVOLVER).

(4) A module for calculating the mechanical and transport properties of cement paste, mortar, or concrete based on the cement paste microstructure and constituent phase properties (CONCPROPS).

The relationship between these modules is shown schematically in Figure 1. In the following subsections, the conceptual models and required inputs and outputs of each module are enumerated.

Detailed Explanation of Computational Algorithms and Methods

THAMES is composed of four primary modules. Interactions among the modules are shown in Figure 1. A discussion of the algorithms and methods is deferred until the next section, which explains the details of each of these four computational modules.

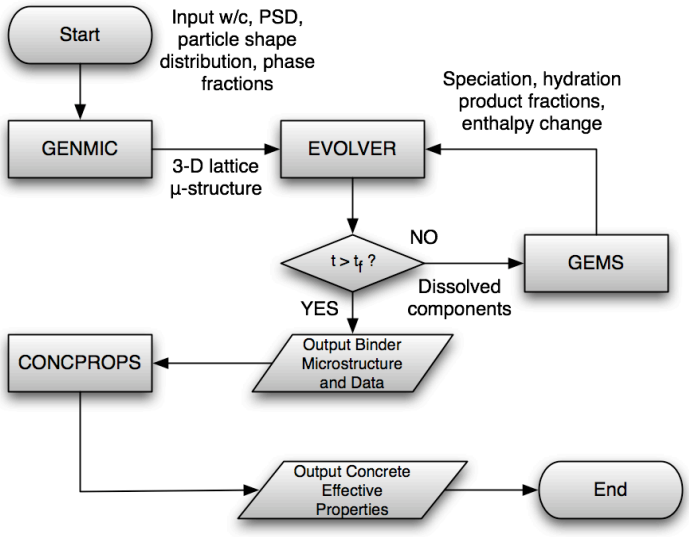

Figure 1. Flow chart showing THAMES structure and relation of GENMIC, GEMS, and EVOLVER modules.

Detailed Explanations of Program Modules

Program Element 1: GENMIC

Identification
The name of the element is GENMIC, which is descriptive of its purpose of generating initial 3-D microstructures on a computational lattice.

Type
GENMIC is one of four modules in THAMES.

Purpose
GENMIC is used to create a realistic representation of a 3-D cementitious paste microstructure on a computational lattice.

Function
The GENMIC module uses random parking algorithms to populate a 3-D lattice with particles that follow the prescribed particle size distribution. The particles can assume shapes taken from a database of shapes obtained by spherical harmonic (SH) analysis of tomographic images of real particles. After the particles have been placed to achieve a desired mass fraction of solids, a Gaussian filter is used to distribute the major clinker phases among the particles using two-point correlation functions obtained on segmented micrographs of the cement powder. The difference between the target and actual volume fraction of phases is generally 0.01. The uncertainty in the surface area fractions of each clinker phase is generally 0.001.

Subordinates
GENMIC is a self-contained module, consisting of a number of subroutines for accomplishing the separate tasks of particle placement (subroutine `create`), clinker phase distribution (subroutine `distrib3d`), and surface area adjustment (subroutine `sinter3d`).

Dependencies
GENMIC is used once to generate an initial microstructural state for a simulation. It has no dependencies on the other THAMES modules.

Interface
GENMIC requires input of mix formulation parameters, including volume fraction of solids, volume fractions of clinker phases, gypsum, etc., and autocorrelation functions to use for distributing the clinker phases in 3-D space among the cement particles. All of these data are contained in ASCII text files. The program can be executed from the command line.

Resources
There are no primary external resource elements for GENMIC.

Processing
The GENMIC module uses the input value of the target volume fraction of solids, together with an input probability density function for the particle size distribution, and uses a random parking algorithm with no overlaps to place particles according to the size distribution until the target volume fraction is reached. If the particles are to have realistic shapes, then the spherical harmonic (SH) coefficients for a representative ensemble of particle shapes must be available.

The SH coefficients for each particle must be stored in separate ASCII text files which will be read by GENMIC and used to place the shape with specified volume and arbitrary orientation. After the particles are placed, the input autocorrelation functions are used to partition the structure into silicates and aluminates, after which this partitioning is refined to the individual four major clinker phases of portland cement. After the partitioning of phases, the surface areas of each phase are adjusted using a sintering algorithm, which conserves volume but changes the shape of the phase domains. Further details may be found in Bentz (1997). The required input data are summarized in Table 1. At the conclusion of GENMIC, the lattice is stored as a 3-D array, with an integer identification number at each lattice site to specify the phase located there.

Table 1. Input parameters for GENMIC module

Input Property	**Meaning**	**Other Information**
Lattice dimensions	x, y, z (number of lattice sites in each dimension)	
Lattice spacing	Physical distance between lattice points	Units of μm
Unsigned integer values representing phases	Phases: Saturated porosity, alite, belite, tricalcium aluminate, etc.	Typical values 0, 1, 2, .., catalogued in a phase db file
Density of each phase	Mass per unit volume	Units of g/cm^3, catalogued in a phase db file; value from cemdata07 GEMS db
Molar volume of each phase	Volume occupied by one mole of phase	Units of cm^3/mole, catalogued in a phase db file; value from cemdata07 GEMS db
Particle size distribution	Probability density function	Two-column ASCII file
Particle shape distribution	Pointer to collection of SH coefficients for different shapes	SH coefficients for each shape stored in separate ASCII file
Target mass fractions of cement clinker minerals	Mass es of alite, belite, tricalcium aluminate, and ferrite phases per unit mass of clinker	Sum normalized to 1
Target surface area fractions of cement clinker minerals	Surface areas of alite, belite, tricalcium aluminate, and ferrite phases per unit surface area of clinker	Sum normalized to 1
Two-point correlation functions for each clinker	Separate functions for alite, belite, tricalcium aluminate, and ferrite phases	Two-column ASCII file, assumes isotropic

Input Property	Meaning	Other Information
phase		homogeneous medium
Target mass fraction of calcium sulfate in cement	Mass of gypsum, bassanite, and anhydrite per unit mass of cement	
Target mass fractions of supplementary cementitious materials (e.g. silica fume, slag, fly ash, limestone)	Mass of supplementary cementitious material per unit mass of cementitious material	
Target mass fractions of fly ash constituents	Masses of aluminosilicate glasses, tricalcium aluminate, etc, per unit mass of fly ash	Sum normalized to 1 (fly ash only)
Target mass fraction of water	Mass of water in cement paste per unit mass of cement paste	Can be inferred from water-cement mass ratio
Flocculation parameter	Number of particle agglomerates in microstructure	

Data
There are no major internal data elements in GENMIC.

Descriptions of Required External Databases and Programs
The SH coefficients of hundreds of real-shaped particles for a given cement are generally stored in a folder on the computer running the GENMIC module. Other than the input files already described, no external databases or programs are required.

Verification and Validation
The ability of GENMIC to accurately reproduce desired w/c, cement phase volume fraction, surface area fraction, and spatial distribution, and cement particle size and shape distribution has been extensively verified and validated in the literature (Bentz and Stutzmant 1994, Bentz 1997, Bullard and Garboczi 2005, Bentz et al 2006). Further verification and validation is needed for cements containing fly ash or other waste-stream materials to ensure that the simulated distributions of phases in those materials are sufficient to accurately describe subsequent hydration and property development. Experimental characterization of waste-stream materials needs to be developed to serve as input to improved versions of GENMIC.

Program Element 2: GEMS

Identification
The name of the element is GEMS.

Type
GEMS is one of four modules in THAMES.

Purpose
GEMS is used to make calculations of equilibrium solution compositions and phase assemblages in cementitious microstructures. These calculations are used to determine how the 3-D microstructure should be modified at each time increment of hydration to be consistent with thermodynamic calculations.

Function
The GEMS module is basically identical to the GEMIPM2K standalone version of the GEMS application developed by Dmitrii Kulik (Kulik and Kersten 2001, Kulik and Kersten 2002). It is being embedded in THAMES as a module than can be called by the EVOLVER module and which can return calculated phase assemblages in tabular form to the EVOLVER module.

Subordinates
The GEMS module has no major subordinate entities.

Dependencies
The GEMS module depends on the EVOLVER module for prescribing the boundary conditions on the solution composition at each time increment for which a thermodynamic calculation is required.

Interface
The GEMS module has no user interface. All of its calculations are internal to the THAMES program.

Resources
Originally developed for environmental geochemistry applications, the external resources for GEMS consist of thermodynamic databases, supplemented with a cementitious material database, called cemdata07, which contains thermodynamic data on important cementitious phases that are missing from the standard databases, e.g., SUPCRT.

Processing
The GEMS module is based on the GEMIPM2K program for minimizing the Gibbs free energy of multicomponent, multiphase aqueous systems (GEMS 2008). The GEMS module requires input of the equivalent oxide mass fractions in the cement, as well as the elemental mass fractions of the capillary pore solution. After minimizing the free energy of the system subject to these boundary conditions, the GEMS module outputs the volume and mass fractions and compositions of each phase in the microstructure, the enthalpy change, and the speciation of the pore solution. The volume fractions are used as input to EVOLVER for the next time step of microstructure development. The inputs required by the GEMS module are given in Table 2.

Data
There are no major internal data elements in GEMS.

Descriptions of Required External Databases and Programs
No external databases or programs are required besides those listed in the Resources section.

Verification and Validation
The GEMS module and database have been carefully verified and validated in the literature for regular OPCs (Lothenbach and Winnefeld 2006, Lothenbach and Matschei 2008), for sulphate-

resisting OPCs (Lothenbach and Wieland 2006), for OPC/limestone blends (Lothenbach and LeSaout 2008), for certain alkali-activated slags (Gruskovnjak, Lothenbach, and Holzer 2006), and for super-sulphated slag cements (Gruskovnjak, Lothenbach, and Winnefeld 2008). Further verification and validation are needed for cements containing additions of slag, fly ash, or other chemicals/minerals, such as can often be found in Saltstone waste forms.

Summary of Model Limitations

The cemdata07 database in GEMS contains very limited data on the calcium silicate hydrate (C–S–H[3]) gel formed in the presence of pozzolans and on the binding of alkali and transition metal cations. These are subjects of ongoing research at EMPA and the Paul Scherrer Institute, Swiss institutions where the cemdata07 database and C-S-H solid solution model, respectively, were developed.

The current kinetic module for cement hydration was originally developed by Parrott and Killoh for ordinary portland cement (OPC) pastes (Parrott and Killoh 1984) and provides empirical equations for the rate of dissolution of the major clinker phases as a function of water-cement mass ratio (w/c), cement fineness as measured by the Blaine air permeability test, and temperature. This kinetic model will not be applicable in cement blends containing ground granulated blast furnace slag (GGBFS) or fly ash. Currently there is no reliable kinetic model for blended cements, so developing one will be an important subject of research.

Program Element 3: EVOLVER

Identification

The name of the element is EVOLVER, which is descriptive of its task of simulating the evolution of 3-D microstructure of cementitious concrete binders.

Type

EVOLVER is one of four modules in THAMES.

Purpose

The EVOLVER module operates directly on the 3-D lattice that is output by the GENMIC module, as depicted in Figure 1. It modifies the lattice sequentially by changing the value of the phase identification number a selected lattice sites to simulate growth or dissolution of phases consistent with the calculations of the GEMS module for that time increment.

Table 2. Input parameters for GEMS module

Input Property	Meaning	Other Information
Temperature	System temperature	Units of °C
Pressure	System hydrostatic pressure	Units of bars
Number of independent components (ICs)	Maximum number of components that form the basis set for describing all phases in the system	Typically between 4 and 8. Used for memory allocation
Number of	Maximum number of DCs, i.e., the	Typically between 20 and 30. Used for

[3] Conventional cement chemistry notation is used here, e.g., C = CaO, S = SiO_2, H = H_2O.

Input Property	Meaning	Other Information
dependent components (DCs)	individual phases and pore solution species	memory allocation
Number of phases	Max number of phases that can coexist	Typically between 10 and 20. Used for memory allocation
Number of solid solution (SS) phases	Max number of SS phases that can coexist	Must be less than the number of phases. Typically between 4 and 8. Used for memory allocation.
Number of DCs in SS phases	Max number of DCs needed to characterize SS phase compositions	Must be less than the number of DCs. Typically between 15 and 20. Used for memory allocation.
Names of Ics	Text identifying ICs	Character strings in single quotes, separated by space
Molar masses of ICs	Molar masses of ICs	Real-valued, separated by a space; units of g/mole
Names of phases	Text identifying phases	Character strings in single quotes, separated by space
Number of DCs in each phase	Minimum number of DCs required to characterize each phase's composition	Vector of unsigned integers, separated by space
Stoichiometry matrix for Ics	Matrix that specifies the composition of each IC	One column for each IC, one row for each DC. Each element ij is the molar stoichiometric coefficient of the i-th DC in the j-th IC
Molar volumes of DCs	Molar volume of each DC, including solutes	Units of J/bar
Molar Gibbs free energy function coefficients for each DC	Molar Gibbs free energy of each DC, including solute species, at reference temperature	Units of J/mole

Function

The EVOLVER module keeps a running track of the volume fraction of each phase and an updated list of all of the lattice sites that lie on an interface between phases. The different interfaces are categorized by the phases that they separate. During a given time increment, EVOLVER uses kinetic equations (Parrott and Killoh 1984) to determine the boundary conditions on the pore solution elemental composition. These boundary conditions are passed to the GEMS module, which returns a list of target volume fractions for the system at the end of that time increment. EVOLVER compares for each phase the current volume fraction with the target volume fraction calculated by the GEMS module for that same time increment. The volume fractions are adjusted accordingly by modifying the phase identification numbers at

selected points along the interface of each phase to simulate either growth or dissolution of the phase.

Subordinates

EVOLVER contains subroutines for sorting the lists of interface sites according to various criteria, generically termed affinities. It also contains subroutines for modifying the interface sites depending on whether growth or dissolution of a given phase is required. These subroutines are all internal to the EVOLVER module.

Dependencies

The EVOLVER module depends on the GEMS module to provide a list of phase volume fractions during each time increment subject to the boundary conditions on the elemental composition of the pore solution that the EVOLVER module provides to the GEMS module.

Interface

The EVOLVER module has no user interface. It accesses the GEMS module during each time increment to retrieve an updated list of phase volume fractions, but this is internal to the program.

Resources

EVOLVER requires no external resources. It requires an input file, as ASCII text, that provides information on the growth morphology of each phase, which is used to determine the rules for modifying the phase identification numbers at interface sites to achieve different morphologies.

Processing

The EVOLVER module operates directly on the 3-D lattice that is output by the GENMIC module, as depicted in Figure 1. During each time step, EVOLVER computes the surface area of each phase, degree of saturation of the capillary pore volume, and the local environment of each lattice site (i.e., the phases occupying itself and its nearest neighbors) to generate a list of interfaces and a list of potential growth and dissolution sites of each phase, sorted by the affinity of the site, which depends on the phase and the local environment of the interface site. The interface sites are stored as vectors, which are standard containers in the C++ Standard Template Library (STL). Microstructure evolution is accomplished by changing the state (phase) of selected lattice sites according to the sorted lists of growth/dissolution sites. A degree of random deviation from the sorted list is allowed for each phase. That is, each growing phase has a finite probability that it may grow at a site other than that at which it attains maximum affinity. As mentioned earlier, the affinity at each interface site is determined using user-specified growth morphology types. The possible morphology types are:

(1) Driven by decreasing mean curvature; dissolution occurs at sites of highest mean curvature and growth occurs at sites of lowest mean curvature. This produces compact, equiaxed growth morphologies.

(2) Random; growth or dissolution occurs with equal probability at any location along the existing interface. This produces a compact morphology with considerable surface roughness.

(3) Driven by increasing mean curvature. This produces compact but non-equiaxed shapes and can be tailored to produce acicular or tabular morphologies.

The inputs required by the EVOLVER module are given in Table 3.

Table 3. Input parameters for EVOLVER module

Input Property	**Meaning**	**Other Information**
Initial microstructure file	3-D cubic lattice populated with integers identifying the phases	Output from GENMIC module, header contains the x, y, and z dimensions of the lattice and the lattice spacing
Lattice spacing	Physical distance between lattice points	Units of μm
List of phase IDs	Phases: Saturated porosity, alite, belite, tricalcium aluminate, etc.	Typical values 0, 1, 2, .., catalogued in a phase db file, must coincide with values used to create initial microstructure
Phase densities	Mass per unit volume	Units of g/cm^3, catalogued in a phase db file; value from cemdata07 GEMS db
Phase molar volumes	Volume occupied by one mole of phase	Units of cm^3/mole, catalogued in a phase db file; value from cemdata07 GEMS db
Growth "templates" for each phase	A list of phases (integer IDs) upon which a precipitating phase can favorably grow	Used for determining nucleation sites for new phases; catalogued in a phase db file
Affinities for each pair of phases	Empirical integer factors; represents rankings of interface free energies	Catalogued in a phase db file
Random growth factor	Real-valued parameter that gives probability that a growing phase can grow at a site other than the site having maximum affinity for the phase	Real number on [0,1]
Target volume fractions	Output from GEMS module at each time step, gives the equilibrium volume fraction of each phase at a given time step	Used to determine how many lattice sites need to change state to cause updated microstructure to agree with target volume fractions
Output frequency	How often to output the microstructure lattice in the form of an ASCII file	Units of hours

Data
There are no major internal data elements in EVOLVER.

Descriptions of Required External Databases and Programs
No external databases or programs are required besides those listed in the Resources section.

Verification and Validation
The THAMES module is used to simulate the development of microstructure in a hydrating cement paste. It has not been verified or validated at any significant level. However, the verification and validation procedure for THAMES on OPCs will be identical to that used for verifying and validating NIST's CEMHYD3D model (Bentz 1997). The experimental data used to validate CEMHYD3D are extensive and cover a wide range of OPCs with differing phase distributions, alkali contents, w/c ratios, powder finenesses, and curing conditions (Bentz 1995, Bentz 1997, Bentz and Remond 1997, Bentz, Snyder and Stutzman 1997, Bentz and Feng 2000, Bentz 2005, Bentz 2006, Bullard and Stutzman 2006). These same data sets will be used to systematically verify and validate the THAMES module on OPCs. Further validation work will be needed for cements containing slag, fly ash, or Saltstones**.** Such testing may reveal that modifications are required in the code to better capture the growth morphology of hydration products, but most of the anticipated modifications will need to be made in the thermodynamic database for the GEMS module.

Summary of Model Limitations
EVOLVER currently simulates only hydration and microstructure evolution of ordinary portland cement binders. It is not yet able to simulate the effects of slag, fly ash, or other waste stream materials on the hydration and microstructure development, although this limitation is due primarily to limitations in the cemdata07 database used by GEMS. EVOLVER cannot yet directly simulate degradation mechanisms such as alkali-silicate reactions (ASR), sulfate attack, chloride ingress, or freeze-thaw cycling, nor the initiation/evolution of damage associated with those degradation phenomena. However, it could be extended to capture these phenomena with sufficient research and development.

EVOLVER has no intrinsic limitations on the size or resolution of its computational domain, i.e., the lattice. These limitations are set by the memory capacity of the computer. On a single processor desktop computer, cement paste microstructures with up to 500 lattice sites in each dimension can typically be simulated, although the execution time will scale with the number of lattice sites to the 2/3 power. Parallel versions of THAMES, which have not yet been developed, could work with larger systems and/or have much faster run times.

The current kinetic module for cement hydration was originally developed by Parrott and Killoh for OPC pastes (Parrott and Killoh 1984) and provides empirical equations for the rate of dissolution of the major clinker phases as a function of water-cement mass ratio (w/c) , cement fineness as measured by the Blaine air permeability test, and temperature. This kinetic model will not be applicable in cement blends containing ground granulated blast furnace slag (GGBFS) or fly ash.

Program Element 4: CONCPROPS

Identification
The name of the element is CONCPROPS, which is descriptive of its task of calculating the resultant properties of concrete materials.

Type
CONCPROPS is one of four modules in THAMES.

Purpose
The CONCPROPS module operates directly on the 3-D lattice that is output by the EVOLVER module at prescribed times, as depicted in Figure 1. It calculates engineering properties, such as linear elastic moduli, compressive strength, and DC conductivity of concrete materials made from the cementitious binders simulated by the THAMES program.

Function
The CONCPROPS module is a collection of models developed at NIST for calculating the effective (composite) mechanical and transport properties of cement paste, mortar, or concrete, based on the microstructure of the cement paste binder. Using the 3-D lattice microstructure output from EVOLVER at a particular age, the CONCPROPS module adopts the same lattice as a finite element/finite difference mesh to calculate the effective linear elastic moduli, the compressive strength, or the effective DC conductivity/diffusivity. The finite element models use a conjugate gradient method to minimize energy of the lattice subject to imposed boundary conditions, e.g., applied strain or concentration gradient, and then uses computation of the mean values of the material response, e.g., elastic stress field or diffusive flux, to infer the effective linear property of the composite. Table 4 lists the input parameters required by the CONCPROPS module.

Table 4. Input parameters for CONCPROPS module.

Input Property	Meaning	Other Information
Cement binder microstructure	3-D lattice of hydrated cement microstructure output from THAMES module.	ASCII text file
List of phase IDs	Phases: Saturated porosity, alite, belite, tricalcium aluminate, etc	Typical values 0, 1, 2, .., catalogued in a phase db file, must coincide with values used to create initial microstructure
Phase elastic moduli	File listing the bulk and shear modulus of each phase in the hydrated cement paste	ASCII text file. All moduli given in GPa units
Phase relative conductivities	File listing the DC conductivity of each phase in the hydrated cement paste, normalized to the conductivity of bulk pore solution	ASCII text file. All quantities are dimensionless
Fine aggregate grading	Given as a sieve distribution, between 0.01 mm and 4.5 mm, in terms of mass fraction retained at each size.	Two-column ASCII text file, with first column as a sieve opening in mm, and the second column the mass fraction retained.
Coarse aggregate grading	Given as a sieve distribution, between 4.75 mm and 100 mm, in terms of mass fraction retained at each size.	Two-column ASCII text file, with first column as sieve opening in mm, and the second column the mass fraction retained.
Fine aggregate elastic moduli	Bulk and shear modulus of the aggregate particles	GPa units
Coarse aggregate elastic moduli	Bulk and shear modulus of the aggregate particles	GPa units
Fine aggregate shape distribution	Pointer to collection of SH coefficients for different shapes	SH coefficients for each shape stored in separate ASCII file
Coarse aggregate shape distribution	Pointer to collection of SH coefficients for different shapes	SH coefficients for each shape stored in separate ASCII file

Subordinates

The CONCPROPS module consists of several subordinate programs, each of which is responsible for calculating a different engineering property. The program `elastic` calculates the effective linear elastic moduli and compressive strength of the concrete. It uses a finite element model of the cement binder microstructure (subroutine `cpelas`) to compute the linear elastic moduli of the binder. These moduli are then used in a calculation (subroutine `concelas`) based on differential effective medium theory (D-EMT) to compute the linear elastic moduli of the concrete (including coarse and fine aggregate components as well as air voids). The linear elastic moduli of the concrete are used to estimate the compressive strength of a cube of the material using an empirical relation (Neville 1973).

The program `dc3d` calculates the effective DC conductivity of the cement paste binder, relative to the conductivity of bulk solution of the same composition. The program solves the Laplace equation using a finite difference method. It requires input of the transport factor (i.e., the inverse of the formation factor) of each phase present in the cementitious binder.

For calculations of cement paste permeability, a Stokes solver called `Permsolver` reads the 3-D digital image of the hydrated microstructure and calculates the flow response to a fluid pressure head as a boundary condition. The program requires input of the permeability of each phase present in the cementitious binder.

Dependencies

The CONCPROPS module has no dependencies on any other module in THAMES.

Interface

The CONCPROPS module currently is operated as a collection of separate programs, each of which is executed from the command line.

Resources

CONCPROPS requires no external resources.

Verification and Validation

The CONCPROPS module incorporates a number of models developed at NIST, many of which have been extensively validated on OPCs in recent years (Garboczi and Bentz 1992, Christensen, Mason, Bentz, and Garboczi 1992, Bentz, Detwiler, et al 1997, Bentz, Garboczi, Haecker, and Jensen 1999, Bentz, Jensen, Coats, and Glasser 2000, Garboczi and Berryman 2000, Haecker et al 2005). These models have not been systematically validated on blended cements with waste-stream materials. Such validation will need to be made.

Summary of Model Limitations

The CONCPROPS module for calculating cement and concrete properties currently is limited to calculations of linear elastic moduli (for cement paste, mortar, or concrete), thermal expansion coefficients (for cement paste, mortar, or concrete), compressive strength (semi-empirical estimates for mortar or concrete), DC conductivity / diffusivity (for cement paste, mortar or concrete), and permeability (for cement paste only). When new materials (e.g., fly ash, slag, or other waste stream materials) are added to cementitious binders, then their individual elastic moduli will need to be measured experimentally before the CONCPROPS module can make accurate calculations on them.

Summary and Conclusions

Both the current state and development needs of THAMES have been described. The complete THAMES software includes a module for generating a representative 3-D initial microstructure (GENMIC), a module for simulating microstructure changes (THAMES) guided by thermodynamic calculations (GEMS), and a module for calculating the elastic moduli, compressive strength, DC conductivity / diffusivity, and permeability on the predicted cement paste and mortar / concrete microstructure (CONCPROPS).

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Appendix I. Necessary Material Characterization Techniques

Although not technically within the scope of a detailed description of the THAMES modeling software, reference is briefly made of the important experimental measurements and characterization techniques required to obtain the necessary input for the GENMIC and CONCPROPS modules.

The usual methods of cement mineralogy characterization involve oxide analysis via X-ray fluorescence and then estimation of phase abundance via the Bogue calculations (Taylor 1997).

The Bogue calculations are notoriously inaccurate, especially for the minor clinker phases. Fortunately, these methods are gradually being supplemented with quantitative X-ray diffraction techniques based on the Rietveld method (Stutzman & Leigh 2007). However, even the quantitative XRD techniques do not give any information about how the phases are arranged in each particle, only bulk averages. Therefore, one also needs particle-level characterization of cements (Stutzman & Leigh 2000; Bentz & Stutzman 1994; Stutzman 2004) because the average spatial distribution of different clinker phases affects their reaction rates. Fly ashes and other multi-phase mineral admixtures need to be characterized in this way as well (Chancey et al. 2008; Williams et al. 2005). To understand how different mineral admixtures react together with cement over time, in hydration and in degradation, detailed characterization of their mutual reactions are very important to obtain (Feng et al. 2004). This particular interaction will be important to obtain at later ages in the CBP work, as well as more general mineral interactions over lifetimes of 100 years to 1000 years.

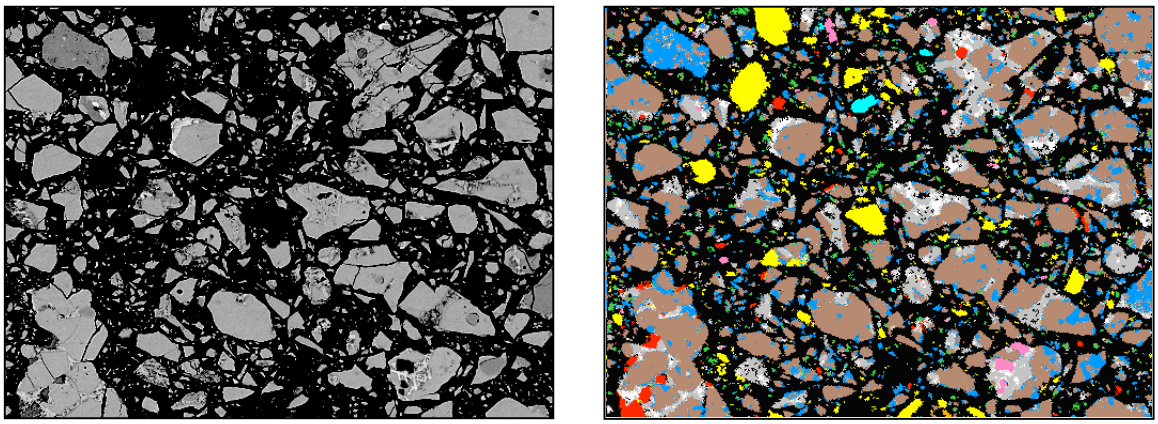

Figure 2: A polished back-scattered scanning electron micrograph of cement particles embedded in epoxy (left). The false colors in the image at the right are added based on analysis of the X-ray signals given off in the back-scattered electron process. Each color (except black) corresponds to a different mineralogical phase. Some examples are yellow = gypsum, brown = tricalcium silicate, and blue = dicalcium silicate.

There is no standard method of cement particle shape analysis, though some recent work addresses this issue (Bentz et al. 2006, Garboczi 2002; Taylor et al. 2006, Holzer et al. 2008; Erdoğan et al. 2008). Cement particle shape is probably not too important at later ages, where most of the cement has already dissolved and reacted (Garboczi & Bullard 2004; Bullard & Garboczi 2005). Aggregate shape and chemistry, however, significantly affect concrete properties. Aggregate shape plays a major role in fresh concrete rheology and early age mechanical properties (Douglas & Garboczi 1995), and at later ages, aggregate chemistry plays a major role in the resistance to degradation processes such as alkali-silica reactions. Both shape and chemistry need to be characterized, and the current characterization tests (e.g., ASR) are inadequate in that they often cannot distinguish between "good" performers and "bad" performers at fairly early ages (before six months). At the kind of ages required in the CBP work, 100 years to 1000 years, it is possible that aggregates that pass the usual earlier-age tests will still cause ASR problems at these long ages because they are exposed to different ionic species from the contained waste material. The proposed THAMES model does not address aggregate reactions. But the CBP concrete modeling, which will derive from THAMES, must be able to handle aggregates in some way, although not necessarily in a full 3-D manner. We note that some of the reference cases that will be addressed by the CBP work do not necessarily have aggregates, i.e., waste forms and grout.

Appendix II. Historical Development of Concrete Microstructure Models

This Appendix is presented to provide a better appreciation of the importance of accounting for the microstructure of cement-based materials using a brief historical account of the microstructure modeling of concrete. In particular, this Appendix highlights the theoretical foundations of microstructure modeling and the important breakthroughs in understanding and performance prediction that have been made possible by microstructure modeling approaches.

The first computer model of cement hydration and chemistry was described in an article entitled "The Mathematical Simulation of Chemical, Physical and Mechanical Changes Accompanying the Hydration of Cement" (Frohnsdorff et al. 1968). In this first effort, there was an attempt to very carefully model kinetics, but there was no 3-D microstructural information and no property prediction. A more successful model of this type, with a more diligent effort to empirically predict a wide range of properties but still with no 3-D microstructure calculation, has been extensively described (Parrott 1989).

While Parrott's model was in the final development stage, efforts turned to the problem of how to model the complex 3-D microstructural formation of cementitious materials. In 1981, Frohnsdorff at NIST led a successful effort to secure internal, multi-year funding for cement hydration and eventually concrete modeling research. This team effort, starting in 1981, resulted in a tricalcium silicate-only model (where tricalcium silicate is the main constituent of Portland cement) that could generate a 3-D microstructure upon which one could make a limited number of property calculations (Jennings & Johnson 1986). This model, however, contained almost no thermodynamics and kinetics. Particles of various sizes that followed a real cement particle size distribution were dispersed randomly in 3-D. Various rules were applied to these continuum spherical particles to simulate the dissolution of cement and the growth of hydration products. This model has inspired other work in the Netherlands (Ye, van Bruegel & Fraai 2003), Japan (Maekawa, Ishida & Kishi 2003), and Switzerland (Navi & Pignat 1991; Bishnoi & Scrivener 2008). The model is based on a continuum description of particles (e.g., spheres), so inherently can do only a limited job of modeling the real, random, complex nature of cement paste microstructure. Overcoming these limitations to accommodate more realistic chemistry, microstructure, and property computations required a different point of view and had three intellectual roots.

The work on the structure of amorphous semiconductors like silicon and germanium in the 1960's and 1970's was the first root. Physicists had before developed crystal physics to a high degree and had even allowed for crystal defects like dislocations. However, the problem of amorphous semiconductors, or of glass, was entirely different—there was no underlying crystal lattice. How was one to do any calculations at all? Analytical approximations were tried, with only a limited degree of success (Zallen 1983). Then models were built with several hundred atoms linked into a random network, pushing the limits of computing power at the time (Dean 1972). Algorithms were applied to these models to compute properties, which were then compared to experiment in an attempt to explain the experimental results.

The second root occurred in the 1980's. In 1984 and 1985, Wittmann, Roelfstra, and Sadouki published two important papers on numerically simulating the structure and properties of concrete in 2-D (Wittmann, Roelfstra & Sadouki 1984; Roelfstra, Sadouki & Wittmann, 1985). In these papers, 2-D models were developed for simulating the shape and arrangement of aggregates in concrete with finite elements applied to compute properties like thermal conductivity and elastic moduli.

The third root of the new modeling point-of-view was a paper showing how a random walk algorithm could be applied to models of porous materials to compute electrical and diffusive transport (Schwartz & Banavar 1989). The combination of the ideas of random walks, digital images, the application of finite elements to random structures and the existing cement paste

hydration microstructure development model (Jennings & Johnson 1986) led directly to the first NIST digital-image-based cement paste hydration model, which eventually became CEMHYD3D (Bentz 1997). Since CEMHYD3D was built on a digital lattice, almost any finite element or finite difference algorithm could be readily applied to it, so that almost any physical property could be simulated and compared to experimental results. Having a 3-D model with some chemistry and a 3-D microstructure and being able to realistically compute properties gave rise to the computational materials science of concrete.

The current state of computational materials science of concrete at NIST, which involves the computation of many other properties including microstructure formation via cement hydration, is embodied in the Virtual Cement and Concrete Testing Laboratory (VCCTL) (Bentz et al. 2006), which is being developed at NIST with the active cooperation of leading corporations and associations in the concrete field. Computer power and model effectiveness have grown together over the years so that this large, integrated software package can be designed to mimic a complete physical testing laboratory, with databases of cement and aggregates instead of bins and hoppers, material combination and concrete curing models instead of mixers and molds, a software interface instead of a cart to take materials and samples around the laboratory, and accurate models for performance prediction instead of instrumented testing machines.