REVIEW OF APPROACHES TO COUPLING PHYSICAL, STRUCTURAL AND CHEMICAL MECHANISMS

Cementitious Barriers Partnership

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FOREWORD

The Cementitious Barriers Partnership (CBP) Project is a multi-disciplinary, multi-institutional collaboration supported by the United States Department of Energy (US DOE) Office of Waste Processing. The objective of the CBP project is to develop a set of tools to improve understanding and prediction of the long-term structural, hydraulic, and chemical performance of cementitious barriers used in nuclear applications.

A multi-disciplinary partnership of federal, academic, private sector, and international expertise has been formed to accomplish the project objective. In addition to the US DOE, the CBP partners are the United States Nuclear Regulatory Commission (NRC), the National Institute of Standards and Technology (NIST), the Savannah River National Laboratory (SRNL), Vanderbilt University (VU) / Consortium for Risk Evaluation with Stakeholder Participation (CRESP), Energy Research Center of the Netherlands (ECN), and SIMCO Technologies, Inc.

The periods of cementitious performance being evaluated are >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 also will support analysis of structural concrete components of nuclear facilities (spent-fuel pools, dry spent-fuel storage units, and recycling facilities such as fuel fabrication, separations processes). Simulation parameters will be obtained from prior literature and will be experimentally measured under this project, as necessary, to demonstrate application of the simulation tools for three prototype applications (waste form in concrete vault, high-level waste tank grouting, and spent-fuel pool). Test methods and data needs to support use of the simulation tools for future applications will be defined.

The CBP project is a five-year effort focused on reducing the uncertainties of current methodologies for assessing cementitious barrier performance and increasing the consistency and transparency of the assessment process. The results of this project will enable improved risk-informed, performance-based decision-making and support several of the strategic initiatives in the DOE Office of Environmental Management Engineering & Technology Roadmap. Those strategic initiatives include 1) enhanced tank closure processes; 2) enhanced stabilization technologies; 3) advanced predictive capabilities; 4) enhanced remediation methods; 5) adapted technologies for site-specific and complex-wide D&D applications; 6) improved SNF storage, stabilization and disposal preparation; 7) enhanced storage, monitoring and stabilization systems; and 8) enhanced long-term performance evaluation and monitoring.

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LIST OF ABBREVIATIONS AND ACRONYMS

ADE	Advective-Dispersive Equation or Advective-Diffusive Equation
ASR	Alkali-Silica Reaction
DEF	Delayed Ettringite Formation
DSA	Direct Substitution Approach
FHWA	Federal Highway Administratio
HMW	Harvies, Moller and Weare implementation of Pitzer’s ionic interaction model
IX	Ionic Exchange
LEA	Local Equilibrium Assumption
opc	ordinary Portland cement
OS	Operator Splitting
REV	Representative Elementary Volume
SIA	Sequential Iterative Approach
SNIA	Sequential Non Iterative Approach
THM	Thermo-hydro-mechanical

LIST OF NOMENCLATURE

a	Material constant in the hydration model
A_{ij}	Stoechiometry coefficient matrix
A_o	Initial affinity of the hydration reaction
b	Biot pressure coupling parameter
B_{ij}	Stoechiometry coefficient matrix
C_i	Concentration of species i in solution
c_s^i	Concentration of species i in solid phase
C_{pi}	Heat capacity of phase i
d	Damage parameter
D_i	Diffusion coefficient of species i in solution
D_v	Diffusion coefficient of water vapor in the gas phase
$\boldsymbol{D}^*$	Hydrodynamic dispersion tensor
E_a	Energy of activation
$\boldsymbol{E_o}$	Elasticity tensor
f_i^{sx}	Function describing the amount of sorbed species i as a function of variable x
f_k	Source/sink term in the energy conservation equation
f_ξ	Source term to model the heat of hydration
F	Faraday constant
$\boldsymbol{g}$	Gravitational acceleration vector
H	Relative humidity
$\boldsymbol{I}$	Identity tensor
$\boldsymbol{j_i}$	Flux of species $\boldsymbol{i}$
$\boldsymbol{j_i}^{diff}$	Diffusive contribution to the flux of species $\boldsymbol{i}$
$\boldsymbol{j_i}^{\mathrm{adv}}$	Advective contribution to the flux of species $\boldsymbol{i}$
k	Permeability
K	Unsaturated hydraulic conductivity
K_m	Equilibrium constant of mineral m
K_i	Equilibrium constant of secondary species i
$L(.)$	Transport operator
M_w	Molar mass of water
n_v	Number of vapor molecule in the gas phase volume V^g
n_o	Material constant in the hydration model

LIST OF NOMENCLATURE (contd)

$\bar{n}$	Material constant in the hydration model
N	Number of species in solution
N_x	Number of secondary species in solution
N_p	Number of immobile species
N_c	Number of main species (components) in solution
p	Average pressure
p_i	Pressure in phase i
p_k	Concentration of species k in mineral form
Q_ξ	Material parameter in the heat of hydration model
r_i	Source/sink term for the homogeneous reaction
R	Ideal gas constant
s_i	Concentration of species i sorbed on the solid matrix
S	Saturation
t	time
T	Temperature
T^{ref}	Reference temperature
$\mathbf{u}$	Displacement vector
u_i	Total soluble concentration of species i
$\boldsymbol{v}i$	Velocity vector of fluid i (i = gas, liquid water, vapor)
V_g	Volume of the gas phase
V_d	Ageing parameter
w	Water content
w_i	Total concentration of species i
w^s	Solid phase content
x, y, z	Position
x_i	concentration of secondary species
z_i	valence number of species i
Z	Gravitational potential

LIST OF NOMENCLATURE (contd)

$\boldsymbol{\alpha}$	Dynamic dispersivity tensor
α^T	Thermal dilatation coefficient
α_ξ	Thermal expansion parameter associated with the heat of hydration
β_i	Mole fraction
ε	Total strain
ε^e	Elastic strain
ε^{ch}	Strain caused by the heat released during the hydration of cement
ε^o	Autogeneous strain
ε^T	Strain caused by thermal expansion
φ	Porosity
γ_i	Chemical activity coefficient of species *i*
$\mathit{\Gamma}$	Moisture potential
λ	Capillary potential
λ_{eff}	Effective thermal conductivity
μ_i	Dynamic viscosity of phase *i*
$\dot{\mu}_{l\to v}, \dot{\mu}_{v\to l}$	Water vaporization/condensation terms
v^{ij}	Stoechiometry coefficient
ρ_i	Density of phase *i*
σ	Total stress tensor
σ'	effective stress tensor
ξ	Degree of hydration
ξ_∞	Maximum degree of hydration
ψ	Electrodiffusion potential

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ABSTRACT

This chapter reviews approaches used to model coupling between different degradation mechanisms affecting concrete structures. Two main categories of models were identified: reactive transport modeling and thermo-hydro-mechanical models.

Reactive transport models are concerned with the transport of chemical species in porous materials and the multiple interactions they can have with the solid matrix. These models couple transport equations with complex chemical models. They ignore the mechanical aspects of deleterious chemical reactions such as crack formation upon sulfate attack.

On the other hand, there are models that couple fluid transport with thermal and mechanical equations, called thermo-hydro-mechanical (THM) models. These models can be used to simulate crack formation caused by drying shrinkage or heat release during the hydration of cement. However, classic THM models do not incorporate the transport of species in the fluid phases and the chemical exchange with the solid minerals.

Reactive transport models incorporating mechanical considerations, or THM models dealing with detailed transport and chemistry relationships, are nearly non-existent. Given the mechanisms and time scales involved in nuclear waste storage problems, models incorporating detailed reactive transport with a THM framework could be used to provide a global durability assessment for those structures.

1.0 INTRODUCTION

Modeling the behavior of concrete structures over very long time periods in order to assess the durability of nuclear waste storage structures involves many different phenomena ranging from chemical interactions to crack formation. Concrete durability analyses over short durations (e.g., <100 years) usually focus on specific problems that can studied with a limited set of parameters. However, the durability of nuclear storage structures is a problem that extends over thousands (up to 10,000) of years. Many problems that are uncoupled over a few years can become coupled together over such a long time interval. For instance, the leaching of calcium and hydroxide ions from materials in contact with low pH groundwater can be considered harmless over 100 years if the concrete mixture was designed correctly. However, over 10,000 years, it is possible that the decalcification of the solid matrix will have an impact on the overall performance of the structure and a durability analysis for such cases must consider chemical and mechanical aspects.

This chapter reviews approaches used to model coupling between different degradation mechanisms affecting concrete structures. Two main categories of models were identified: reactive transport and thermo-hydro-mechanical models.

Reactive transport models are concerned with the transport of chemical species in porous materials and the multiple interactions they can have with the solid matrix. These models couple transport equations with complex chemical models. They ignore the mechanical aspects of deleterious chemical reactions such as crack formation upon sulfate attack.

On the other hand, there are models that couple fluid transport with thermal and mechanical equations, called thermo-hydro-mechanical (THM) models. These models can be used to simulate crack formation caused by drying shrinkage or heat release during the hydration of cement. However, classic THM models do not incorporate the transport of species in fluid phases and chemical exchange with the solid minerals.

A global durability prediction approach would couple reactive transport and THM models. As the review showed, only limited attempts at such a global model have been made so far.

2.0 COUPLING TRANSPORT AND CHEMISTRY

The interest in ionic transport modeling dates back to the 1970s. At the time, the new awareness of environmental problems led to the development of models dedicated to predicting the rate of ingress of contaminants in groundwater. Leaching of contaminants from a material of interest and transport of leached species within the subsurface to groundwater sources were the main focus of these early models. Thus, hydrogeology and environmental sciences have been the primary fields interested in this type of modeling. Performance assessment models developed under the US DOE Office of Environmental Management focus on near-field release (i.e., leaching from the source material) and far-field (i.e., subsurface transport) approaches. Later, similar approaches have been used in civil engineering to address the durability of cementitious materials (e.g., reinforcement corrosion via carbonate and chloride ingress).

The early model approaches consisted of single-species transport using an advection-diffusion equation (ADE) that incorporated a very simplified term to account for all chemical reactions. This type of model is known today as the "K_d" approach (Fetter 1999). The lumped chemistry of the K_d approach may be applicable when species concentrations are quite low, the geochemistry of the system is unknown or not considered in detail, and interaction of the diffusing species is relatively unaffected by external influences. These conditions typically are not the case for cementitious materials but are encountered in waste forms which can contain dissolved salts (nitrates, nitrites, sulfates, aluminates, carbonates, phosphates, borates, oxalates, chlorides, fluorides, etc.), numerous radionuclides species, industrial chemicals, etc.

Figure 1 illustrates the complex system of issues to be covered when dealing with coupled chemical reaction

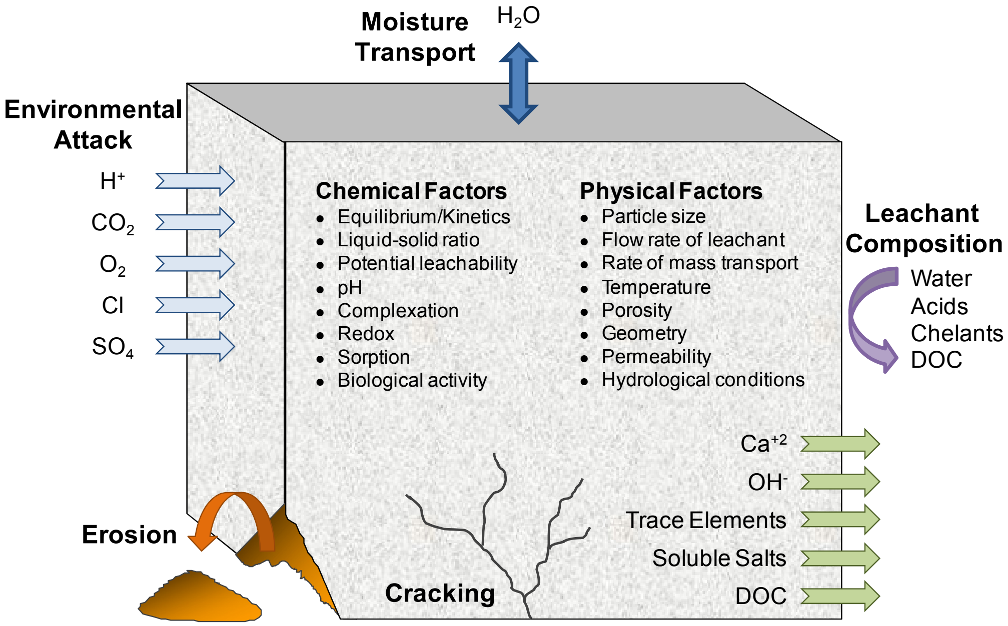

Figure 1. Factors Affecting the Rate of Leaching from Solid Materials Including Cementitious Waste Forms and Concrete Waste Containment Structures (adapted from Garrabrants et al. 2005).

and transport solid wastes such as cementitious materials. All aspects of relevance are covered here ranging from physical properties like temperature variation and mechanical influences to chemical aspects covering a full suite of major, minor and trace elements affecting the release of species of interest. In order to describe these complex physio-chemical phenomena, diffusion/advection equations have been coupled with increasingly complex chemical models describing multiple ionic transport equations with simultaneous reactions.

The relevant transport equations are briefly reviewed in the next section. A more complete description can be found in the chapters concerned with the hydraulic properties and the chemical degradation mechanisms. This is followed by a description of basic chemical reaction modeling. The coupling between linear transport models and chemistry is then reviewed. Finally, the last section is dedicated to the coupling between nonlinear transport equations and chemistry.

2.1 General Overview of Ionic Transport

The transport of ionic species in porous materials is the result of two main mechanisms: diffusion and advection[1]. Diffusion results from the random motion of dissolved species in the solution while

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[1] Cementitious materials are porous and contain pore fluid as the result of residual mixing water and/or contact with moisture from the environment. Moisture and dissolved contaminants and corrodents migrate through this pore solution. If the aqueous pore solution is not continuous in the pores, transport of soluble species is for practical purposes zero. However, in this case transport of gaseous species through the unsaturated pores becomes very important. Solid state diffusion and conductance are not considered here.

advection is the contribution from the solvents's own movement. The complete flux expression is the sum of both terms (Helfferich 1961):

$$\mathbf{j}_{\boldsymbol{i}}=\mathbf{j}_{\boldsymbol{i}}^{diff}+\mathbf{j}_{\boldsymbol{i}}^{adv} \qquad (1)$$

where: $\mathbf{j}_{\boldsymbol{i}}$ is the flux of species ***i*** and the subscript "diff" and "adv" stand for the diffusion and advection contribution respectively.

The diffusion part of Equation (1) is related to the gradient of the electrochemical potential (Bockris 1970). The final expression is (Samson 2007):

$$\mathbf{j}_{\boldsymbol{i}}^{diff} = \underbrace{-D_i\,\mathrm{grad}(c_i)}_{\text{diffusion}} - \underbrace{\frac{D_i z_i F}{RT} c_i\,\mathrm{grad}(\psi)}_{\text{elect. coupling}} - \underbrace{D_i c_i\,\mathrm{grad}(\ln\gamma_i)}_{\text{chemical act.}} - \underbrace{\frac{D_i c_i \ln(\gamma_i c_i)}{T}\,\mathrm{grad}(T)}_{\text{temperature coupling}} \qquad (2)$$

where: c_i is the concentration, D_i is the diffusion coefficient, z_i is the valence number of the species, F is Faraday constant, R is the ideal gas constant, T is the temperature, Ψ is the diffusion potential, and γ_i is the chemical activity coefficient. The term involving the diffusion potential is responsible for maintaining electroneutrality in the solute despite the differences in diffusion coefficient of each individual species. The chemical activity term accounts for the non-ideal behavior of diffusion for high concentrations.

Most models found in the literature are based on a simplified version of Equation (2). The vast majority of models dedicated to contaminant transport in groundwater neglect the electrical coupling, chemical activity effects, and temperature coupling terms. In most cases, they only consider the diffusion term. The corresponding equation is called the Fick's diffusion relationship:

$$\mathbf{j}_{\boldsymbol{i}}^{diff} = -D_i\,grad(c_i) \qquad (3)$$

Recent models specifically dedicated to transport in cementitious materials considered the electrical coupling term to account for the highly charged pore solution of those materials (e.g., Samson 2007b, Truc 2000).

The advection term can be written as (Bear 1991):

$$\mathbf{j}_{\mathbf{i}}^{adv} = c_i\mathbf{v} \qquad (4)$$

where: **v** is the fluid velocity vector. The fluid moves in a porous material under the action of external pressure, gravity and capillary forces (Fetter 1999). In saturated materials, the capillary effects are non-existent. The driving forces are limited to gravity and pressure gradients.

In that case, the fluid obeys Darcy's generalized law (Bear 1988):

$$\mathbf{v} = -\frac{k}{\mu}\left(\mathrm{grad}(p_l) - \rho_l\mathbf{g}\right) \qquad (5)$$

where: k is the liquid permeability of the material, μ is the dynamic viscosity of the liquid phase, p_l is the liquid pressure, ρ_l is the fluid density and **g** is the gravity acceleration vector.

In unsaturated materials, the pore water is under a negative pressure caused by surface tension (Fetter 1999), called the capillary potential. The total moisture potential is the sum of the capillary and gravitational potentials (Fetter 1999):

$$\Gamma = \lambda + Z \qquad (6)$$

where: Γ is the total moisture potential, λ is the capillary potential, and Z is the gravitational potential.

In that case, moisture movement in porous materials can be modeled on the basis of the Buckingham flux law:

$$\mathbf{v} = -K(\lambda)\,\mathrm{grad}(\Gamma) \tag{7}$$

where: $K(\lambda)$ is the unsaturated hydraulic conductivity.

Because of heterogeneities at the pore level, the flow of a fluid in a porous network induces a phenomenon called mechanical dispersion that spreads the dissolved species in the solution. This is discussed at length in (Bear 1991, Fetter 1999). This effect is modeled as a term that is added to the diffusion coefficient to yield the dispersion coefficient:

$$\mathbf{D}_i^* = \mathrm{D}_i\mathbf{I} + \boldsymbol{\alpha}\mathbf{v} \tag{8}$$

where: $\mathbf{D}_i^*$ is the dispersion tensor, $\mathbf{I}$ is the identity tensor, and $\boldsymbol{\alpha}$ is the dynamic dispersivity tensor, which has longitudinal and transverse components.

The dynamic dispersivity depends on the fluid velocity and its impact on the dispersion coefficient can be estimated from the Peclet number $P_e = \mathbf{v}L/D_i$, where L is the characteristic flow length. For low Peclet values ($P_e < 1$), the diffusion is dominant and the mechanical dispersion can be neglected. However, for high P_e values (>10), dispersion dominates. The latter case is especially important from a modeling standpoint. When dispersion dominates, the individual diffusion coefficients can be neglected, which results in each species having the same dispersion coefficient. This allows several simplifications to the transport model and has been used extensively in hydrogeology, as will be shown in Sections 2.3 and 2.4.

When the flux relationships are known, they are substituted in the mass conservation equation (Bear 1991):

$$\frac{\partial(w^s c_i^s)}{\partial t} + \frac{\partial(wc_i)}{\partial t} + \mathrm{div}(w\mathbf{j_i}) + r_i = 0 \tag{9}$$

where: w is the water content, w^s is the solid phase content, c_i^s is the content of species i in the solid phase, and r_i is a source/sink term. The term r_i accounts for the rate of formation or elimination of species i from chemical reactions occurring solely within the pore solution while the term involving c_i^s accounts for the exchange between the solid and aqueous phases. These different types of chemical reactions are outlined in the next section.

2.2 General Overview of Chemical Reactions

In a comprehensive review on the modeling of chemical reactions in porous media, Rubin (Rubin 1983) divided the reactions in two main categories: sufficiently fast and reversible, and insufficiently fast and/or irreversible. If the rate of reaction is large with respect to the ionic and fluid transport processes, then it belongs to the sufficiently fast category.
In this particular case, it is assumed that the local chemical equilibrium (LEA) is preserved throughout the porous system. As emphasized by Steefel (Steefel 1994), LEA has long been one of the most fundamental tenets of hydrothermal and metamorphic geochemistry and petrology.

The same can be said about cementitious materials, where LEA is assumed in most, if not all, reactive transport models. A few dimensional analyses support this assumption. Barbarulo et al. (Barbarulo 2000) performed a dimensional analysis that validated LEA in fluid saturated cementitious materials. In (Samson 2007b), a similar analysis was made based on the Damköhler number for diffusion and advection. In both cases, the local equilibrium assumption was validated.

All reactions falling under the sufficiently fast category are modeled through chemical equilibrium equations (Rubin 1983), which are algebraic, as opposed to the partial differential equations used in transport models. Since the equilibrium is expressed, in most cases, through chemical activity, algebraic relations giving the chemical activity coefficients must also be considered while modeling the chemical reactions. The resolution of a transport problem involving chemical reactions is thus called a mixed problem, because it involves algebraic and partial differential equations.

The chemical reactions were then divided by Rubin (1983) into two sub-categories: homogeneous and heterogeneous. The homogeneous reactions are those involving a single phase. This sub-category includes all the complexation reactions, i.e., the formation of products occurring in the aqueous phase. For example, the reaction:

$$\mathrm{Ca^{2+}}_{\mathrm{(aq)}} + \mathrm{OH^-}_{\mathrm{(aq)}} \rightleftharpoons \mathrm{CaOH^+}_{\mathrm{(aq)}} \tag{10}$$

is a homogeneous reaction since it only occurs in the aqueous phase. In this reaction, Ca^{2+} and OH^- are called the primary species and $CaOH^+$ is called the secondary species (Steefel 1994). The general equilibrium relationship for that type of reaction is written as:

$$K_i = \frac{1}{\gamma_i x_i} \prod_{j=1}^{Nc} (\gamma_j c_j)^{\nu_{ij}} \tag{11}$$

> *where:* K_i is the equilibrium constant, x_i is the concentration of the secondary species, γ is the chemical activity coefficient, N_c is the number of components forming the secondary species, c_j is the concentration of the primary species, and v_{ij} is the number of moles of primary species *j* in one mole of secondary species *i*.

Contrary to the previous category, the heterogeneous reactions involve at least two phases (Rubin 1983). Rubin distinguishes two types of heterogeneous reactions: surface and classical ones. Surface reactions are either adsorption, in which ions are attracted to the surface of the pore network under the influence of electrostatic forces (Bockris 1970), or ion exchange, in which two or more ionic species are exchanged between the surface of the solid and the aqueous phase (Appelo 1996). The classical reactions are precipitation, dissolution, oxidation and reduction. The dissolution of portlandite belongs to this category since it involves the aqueous and the solid phase:

$$\mathrm{Ca^{2+}}_{\mathrm{(aq)}} + 2\mathrm{OH^-}_{\mathrm{(aq)}} \rightleftharpoons \mathrm{Ca(OH)}_{2\mathrm{(s)}} \tag{12}$$

Similar to the complexation reaction (Equation (11)), the equilibrium of a mineral *m* can be expressed as a function of a constant K_m (Xu 1999):

$$K_m = \prod_{i=1}^{N} c_i^{\nu_{mi}} \gamma_i^{\nu_{mi}} \tag{13}$$

> *where:* *N* is the number of species entering the composition of the mineral *m*, c_i is the concentration of species *i* in solution and v_{mi} is the number of moles of species *i* in one mole of mineral *m*.

It should be noted that contrary to Equation (11), the reaction product of dissolution/precipitation reactions is not part of the equilibrium relationship (13), because the solid has an activity coefficient equal to one (Stumm 1996). This peculiarity of the dissolution/precipitation mechanism induces the formation of mineral fronts inside the porous material, as discussed in (Rubin 1983). Such fronts can be observed in calcium leaching (e.g., Mainguy 2000) and sulfate attack cases (e.g., Maltais 2004).

Heterogeneous reactions also include sorption. This class of chemical reaction includes all reactions involving ions in the pore solution and the surface of the solid matrix, such as ion exchange and surface complexation. Ion exchange is mostly associated with the interaction of cations in the pore solution exchanged with cations in the solid:

$$\mathrm{Na^+}_{\mathrm{(aq)}} + \mathrm{K\text{-}X}_{\mathrm{(s)}} \rightleftharpoons \mathrm{K^+}_{\mathrm{(aq)}} + \mathrm{Na\text{-}X}_{\mathrm{(s)}} \tag{14}$$

> *where:* X represent the solid matrix.

The equilibrium relationship for two cations *a* and *b* can be written as (Appelo 1996):

$$K_{a/b} = \frac{\beta_a^{1/z_a}}{\beta_b^{1/z_b}} \frac{\gamma_b^{1/z_b} c_b^{1/z_b}}{\gamma_a^{1/z_a} c_a^{1/z_a}} \tag{15}$$

where: β is the equivalent mole fraction of the exchangeable cations, with $\Sigma\beta_i = 1$.

The modeling of other types of heterogeneous chemical reactions such as oxidation and reduction and surface complexation can be found in textbooks (Bethke 2008, Stumm 1996).

All chemical equilibrium calculations involve chemical activity. Several models exist to calculate chemical activity coefficients. Classical electrochemical models like the Debye-Hückel or extended Debye-Hückel relationship are valid for weak electrolytes for which the ionic strength is on the order of 100 mmol/L, while the Davies correction can be used to describe the behavior of more concentrated solutions, i.e., with ionic strengths up to 300 mmol/L (Pankow 1994). Pore solutions extracted from hydrated cement systems are in the 300 mmol/L (Hidalgo 2001) to 900 mmol/L range (Reardon 1992). As reported in (Zemaitis 1986), many models were developed to estimate the activity coefficients for highly concentrated solutions. One of the most commonly used approaches is the implementation of Pitzer's ionic interaction model proposed by Harvie, Moller and Weare (Harvie 1984). Pitzer's model was used by Reardon (Reardon 1990) to model the hydrated paste/solution chemical equilibrium.

2.3 Linear Transport Equations Coupled with Chemistry

The early models dedicated to reactive transport in porous materials basically attempted to substitute the chemical equilibrium relationships such as Equations (11) and (13) in the mass conservation Equation (9). This is called the Direct Substitution Approach (DSA), where the transport equations can be expressed according to different formulations (Kirkner 1988). The next paragraphs summarize three different formulations of the DSA, as described by Kirkner and Reeves. The different formulations were devised assuming saturated materials and a linear transport operator, i.e., electrical coupling and chemical activity effects were neglected. While the saturated assumption could be extended to unsaturated cases, it will be shown that DSA works only if a linear transport model with a uniform dispersion coefficient is used.

The N reactive species in solution are divided in N_c components and N_x secondary (or complex) species. The equations governing the transport of the N_c components and N_x secondary species are:

$$\frac{\partial \phi c_j}{\partial t} + div\,(c_j \mathbf{v} - \phi \mathbf{D}^* \, grad\, c_j) = r_j^c \qquad j = 1,\ldots,N_c \tag{16}$$

$$\frac{\partial \phi x_i}{\partial t} + div\,(x_i \mathbf{v} - \phi \mathbf{D}^* \, grad\, x_i) = r_i^x \qquad i = 1,\ldots,N_x \tag{17}$$

where: ϕ is the porosity and the reactions terms in Equation (9) have been lumped in the r_j^c and r_i^x terms.

The subscript i of the dispersion tensor has been omitted since it is assumed that the mechanical dispersion dominates over diffusion, which leads to all species having the same dispersion coefficient. In Equations (16) and (17), the porosity replaces the water content of Equation (9) because of the saturated pores assumption.

The authors then introduced the total soluble concentration u_j of each species as:

$$u_j = c_j + \sum_{i=1}^{N_x} A_{ij} x_i \tag{18}$$

where: A_{ij} is a stoechiometry coefficient matrix linking the main species to the complexes.

Substituting Equation (11) in (18) gives:

$$u_j = c_j + \sum_{i=1}^{N_x} A_{ij} K_i \prod_{k=1}^{N_c} C_k^{A_{ik}} \tag{19}$$

The reaction rates r_j^c are defined as:

$$r_j^c = r_j^{c(aq)} + r_j^{c(s)} + r_j^{c(p)} \tag{20}$$

where:

$$r_j^{c(aq)} = -\sum_{i=1}^{N_x} A_{ij} r_i^x \tag{21}$$

reaction rate of *j* due to complexation

$$r_j^{c(s)} = -\frac{\partial \phi S_j}{\partial t} \tag{22}$$

reaction rate of *j* due to soprtion or 1X

$$r_j^{c(p)} = -\sum_{i=1}^{N_p} B_{ij} \frac{\partial \phi P_i}{\partial t} \tag{23}$$

reaction rate of *j* due to diss./prec.

In Equations (21) to (23), s_j corresponds to the concentration of the main species *j* sorbed on the solid phase, p_i is the concentration of mineral *i*, N_p is the number of immobile species, and B_{ij} is a stoechiometry coefficient matrix. Kirkner and Reeves showed that it is possible to write the sorbed concentrations as:

$$s_j = f_j^{sc}(c_1, c_2, \ldots, c_{N_c}) \tag{24}$$

Using Equation (19), it is possible to write Equation (24) as a function of the total concentration u_j:

$$s_j = f_j^{su}(u_1, u_2, \ldots, u_{N_c}) \tag{25}$$

Summing the mass conservation Equations (16) and (17) and using the total concentration u_j (Equation (19)) eliminates the reaction rates $r_j^{c(aq)}$. This operation is possible because all species have the same dispersion coefficient. Substituting the rate expressions (22) and (23), and the sorption function (25) in the summed conservation equations yield:

Formulation A:

$$\frac{\partial(\phi u_j)}{\partial t} + \frac{\partial(\phi f_j^{su})}{\partial t} + \sum_{k=1}^{N_p} B_{kj} \frac{\partial(\phi p_k)}{\partial t} + \\ + L(u_j) = 0 \quad j = 1, \ldots, N_c \tag{26}$$

where: L(.) is the linear transport operator:

$$L(.) = \mathrm{div}[(.)\mathbf{v} - \phi \mathbf{D}^* \,\mathrm{grad}(.)] \tag{27}$$

The complexation reactions are implicitly included in the mass conservation equation as part of the definition of u_i (Equation (19)).

It is possible to further simplify the transport equations by introducing the total concentration w_j as the main variable:

$$w_j = u_j + s_j + \sum_{k=1}^{N_p} B_{kj} p_k \qquad j = 1, \ldots, N_c \tag{28}$$

From this definition, it is possible to write all the concentration variables as a function of the total concentration variable (Kirkner 1988):

$$c_j = f_j^{cw}(w_1, \ldots, w_{N_c}) \qquad j = 1, \ldots, N_c \tag{29}$$

$$p_j = f_j^{pw}(w_1, \ldots, w_{N_c}) \qquad j = 1, \ldots, N_p \tag{30}$$

$$u_j = f_j^{uw}(w_1, \ldots, w_{N_c}) \qquad j = 1, \ldots, N_c \tag{31}$$

$$s_j = f_j^{sw}(w_1, \ldots, w_{N_c}) \qquad j = 1, \ldots, N_c \tag{32}$$

Based on these functions, it is possible to write Equation (26) as:

Formulation B:

$$\frac{\partial(\phi w_j)}{\partial t} + L[f_j^{uw}(w_1, \ldots, w_{N_c})] = 0 \tag{33}$$

or alternatively:

Formulation C:

$$\frac{\partial(\phi w_j)}{\partial t} + L(w_j) = L[f_j^{sw}(w_1, \ldots, w_{N_c})] + \sum_{k=1}^{N_p} B_{kj} L[f_k^{pw}(w_1, \ldots, w_{N_c})] \tag{34}$$

These different formulations have been used in the literature to solve reactive transport problems. Valocchi et al. (1981) used formulation A (Equation (26)) in their model, which considered ion-exchange reactions but did not include complexation nor dissolution/precipitation. Miller and Benson (1983) and Jennings et al. (1982) also used a formulation similar to A while considering complexation and ion exchange.

Although the chemical reactions are included in formulations B and C, the total concentration they provide cannot be used directly and must be converted back to the c_i and x_i variables. To do so requires solving the algebraic chemical expressions separately. This is discussed for instance in (Cederberg 1985). These formulations hint at the operator splitting approaches presented in the following section. However, they are considered under the DSA category because the transport equations still need to be solved simultaneously (Yeh 1989).

It must be noted that all papers cited previously only consider complexation and sorption reactions. As mentioned in (Kirkner 1988), the discontinuities (fronts) induced by the presence of dissolution/precipitation reactions require a special treatment. Some aspects are discussed in (Kirkner 1984). Most notably, the discontinuities associated with the precipitate content require the use of Dirac-type interpolation in a finite element formulation, which differs from the classical C^o shape functions (Zienkiewicz 1989). Lichtner (1985) presented a model dealing with dissolution/precipitation reactions like a moving front problem. The approach includes specific mass conservation equations at the front locations, which must be added to the mass conservation equations.

2.4 Operator Splitting Approaches

One of the first models that separated transport and chemistry was developed by Grove and Wood (1979). The model was used to predict transport of calcium, magnesium, and sulfate in groundwater. The transport Equations (linear ADE, see Equation (27)) are first solved without considering any reaction terms. Next, the chemical reactions are solved using the concentration estimated by the transport step as initial guess. After this, the algorithm goes to the next time step and solves the next transport/chemistry sequence.

But what really triggered interest for splitting transport and chemistry in reactive transport models was the very influential paper published by Yeh and Tripathi in 1989 (Yeh 1989). Their main argument for splitting transport and chemistry was a reduction of CPU time. It also allows avoiding most of the problems associated with the dissolution/precipitation reactions. Although their arguments were criticized later (Saaltink 2001) because they were theoretical and did not reflect actual calculation results, the paper was so highly regarded that DSA almost completely disappeared from that point on. Since then, splitting approaches have been adopted as the preferred method to model reactive transport problems despite the implicit numerical error that they introduce in the calculations (Kanney 2003, Jacques 2006). The possibility of coupling existing transport and chemical models together proved too attractive compared to the numerical problems and computational burden associated with the fully coupled Direct Substitution Approach.

The operator splitting approaches are divided in two main categories:

- Sequential Iterative Approaches (SIA) and
- Sequential Non-Iterative Approaches (SNIA).

In the iterative approach, iterations are performed between the transport and chemistry until convergence is reached. In the SNIA, transport and chemistry are solved sequentially without iterations. The model described at the beginning of this section (Grove 1979) belongs to the SNIA category.

The SIA method consists mainly in expressing the formulations given in Section 2.3 so that the transport equations can be solved individually before chemistry is considered on a node per node basis (Yeah 1989). For instance, Walsh et al. (1984) used transport equations corresponding to formulation C (Equation (34)) solved using an explicit time stepping scheme. This linearizes the transport equations, which can be solved individually. The total concentrations are then separated into the solute, sorbed, and mineral components upon solving the chemical equilibrium equations. In (Engesgaard 1992), a model dealing with complexation, precipitation/dissolution, and oxidation/reduction was presented. The transport equations are expressed according to formulation A (see Equation (26)), where the reaction terms are considered as explicit source/sink terms. During the first iteration, the transport equations are first solved with the reaction terms set to zero. After chemistry, the source/sink terms are estimated based on the variations in the amount of precipitate and included in the transport equations. The iterations continue until a stable solution is reached. A similar algorithm was used in (Simunek 1994).

At the other end of the operator-splitting spectrum is the SNIA, exemplified by the paper from Grove and Wood (1979) summarized at the beginning of this section. SNIA can be selected over SIA for some reasons. Since it completely decouples transport and chemistry, it can prove easier to implement different transport and chemistry schemes in a single simulation platform. Removing the iterations between transport and chemistry can potentially reduce calculation times. However, as mentioned in (Steefel 1994b), SNIA requires a smaller time step than SIA to achieve the same level of accuracy. Strategies to reduce the operator-splitting error in SNIA, by controlling the grid spacing and time step, are discussed in (Jacques 2006). Comparisons between SNIA and SIA are provided in (Steefel 1994b, Walter 1994, Xu 1999). In most cases, SNIA tends to use less CPU time to get the same results. But the performances of SNIA are dependent on the type of chemical reactions. In (Xu 1999), the results showed numerical dispersion when ionic exchange simulations were performed with this algorithm. The dispersion resulted in less sharp concentration fronts than with the SIA algorithm.

Although all references cited previously were concerned with contaminant transport in groundwater, some papers have been specifically devoted to concrete barriers. In recent papers (De Windt 2004, Trotignon 2007), the authors used a SIA algorithm to simulate the long term durability of a concrete slab in contact with soil. In both papers, the simulations were performed on the layered concrete/soil system. In (Marty 2009), a similar problem was considered using a SNIA algorithm.

2.5 Nonlinear Transport Equations Coupled With Chemistry

All the papers cited in Sections 2.3 and 2.4 were based on linear equations based on the transport operator, Equation (27). This allows introducing the total soluble concentration given by Equation (19) into the mass transport equation. Following this, it is possible to eliminate the source/sink terms associated with the complexation reactions, which gives Equation (26), based on the total soluble concentration. This is possible when the fluid phase flow in the pore network induces a dispersion factor that is strong enough to overcome the individual self-diffusion coefficient of the soluble species.

In the case of concrete, the permeability of the material is so low that high velocity flows are never encountered, except in macro cracks. In that case, the coupling terms in the flux expression (2) may have a significant influence on the transport of ions. But the difficulties involved with solving these terms have led to the development of models dedicated to concrete that were still using ADE-type equations similar to Equation (16) for long-term durability predictions. For example, most of the models dedicated to chloride ingress are still based on a single ADE equation, as reviewed in the chapter on chemical degradation (see for instance references Saetta 1993, Nagesh 1998, and Martín-Pérez 2001). As mentioned previously, multi-ionic models based on the splitting-operator approach have been used to assess the long term durability of concrete barriers in contact with groundwater (De Windt 2004, Trotignon 2007, Marty 2009).

Some multi-ionic models dedicated to species ingress in concrete have been developed considering the electrical coupling term in Equation (2). The model presented by Truc et al. (2000) takes the electrical coupling into account to model the ingress of chloride in concrete structures. The binding of chloride on the hydrated cement paste is approximated by a relationship similar to Equation (24). Samson and Marchand presented a multi-ionic model based on Equation (2) that was used to model chloride (Samson 2007) and sulfate ingress (Samson 2007b) cases. Their model uses a SNIA algorithm to couple transport with the chemical equilibrium relationships. In (Samson 2007b), the authors showed that neglecting the electrical coupling may lead to erroneous predictions of sulfate ingress rate. That type of model is able to consider the different self-diffusion coefficients of the considered species while maintaining the electroneutrality of the solution. However, the extensive computational time needed to solve the transport equations, coupled with the absence of self-diffusion data for secondary species (Li 1974), forced the authors to neglect homogeneous complexation reactions. No study could be found to assess the impact of this on long-term durability simulations.

3.0 THERMO-HYDRO-MECHANICAL MODELS

Many degradation phenomena observed on concrete structures are directly related to water content and temperature gradients in the material. Some of these degradation phenomena occur at early ages, such as drying shrinkage and heat of hydration-induced crack formation. In other cases, the damage may occur later in the life of the structure, even though the material has gained strength from the hydration process. This is the case for instance for structures exposed to freezing and thawing cycles and the long-term deformations induced by creep.

Modeling these phenomena is performed using thermo-hydro-mechanical (THM) approaches. While many different THM models have been proposed, they are in most cases based on solving the conservation equations for the gas and fluid phases, coupled to mechanical and thermal relationships. The global THM framework is reviewed in the following section. THM models based on simplified fluid transport equations were also reviewed. Finally, the last subsection is dedicated to modeling mechanical damage induced by the cement hydration process.

3.1 General Overview

The general framework outlined in this section closely follows the description found in (Gawin 1996). Other THM models can be found in (Baggio 1995, Bary 2000, Khalili 2001, Obeid 2001, Gawin 2006, Bary 2008).

In order to simulate moisture transfer, most THM models found in the literature are based on separate mass conservation equations for the gas, water vapor and liquid vapor phases. This type of model has also been reviewed in the chapter dedicated to hydraulic properties. The mass conservation equations for the fluid phases, under the assumption of a rigid solid matrix, can be expressed as (Mainguy 2001):

Liquid phase:

$$\frac{\partial(\phi S\rho_l)}{\partial t} + \mathrm{div}\big(\phi S\rho_l \mathbf{v}_l\big) + \mu_{l\to v} = 0 \qquad (35)$$

Vapor phase:

$$\frac{\partial\big(\phi\rho_v(1-S)\big)}{\partial t} + \mathrm{div}\big(\phi(1-S)\rho_v\mathbf{v}_v\big) - \mu_{l\to v} = 0 \qquad (36)$$

Dry air phase:

$$\frac{\partial\big(\phi\rho_a(1-S)\big)}{\partial t} + \mathrm{div}\big(\phi(1-S)\rho_a\mathbf{v}_a\big) = 0 \qquad (37)$$

where: the subscript *l*, *v* and *a* stand for the liquid, vapor and dry air phases respectively, ϕ is the porosity, *S* is the saturation of the liquid phase, ρ is the density, **v** is the velocity (flow) vector, and $\mu_{l\rightarrow v}$ is a source term accounting for the condensation/vaporization at the liquid/gas interface.

In most THM models, the coupling with mechanics allows consideration of cases where the solid matrix assumption is not valid. In this case, terms involving the deformation of the matrix are added to the mass transport Equations (35) to (37). In order to keep the model to a reasonable size, it is possible to combine the liquid and vapor phase conservation equations to eliminate the condensation/vaporization term. Also, relationships between vapor pressure, water content, saturation and capillary pressure can be used so that the resulting equation is based on a single state variable. This approach was used in (Baggio 1995, Gawin 1995, Gawin 2002, and Gawin 2006). The following paragraphs give the basic conservation equations considered in most THM models (Gawin 1995).

Water species (liquid + vapor):

The mass conservation equation for the combined liquid and gaseous water is given by:

$$\begin{aligned}\phi\frac{\partial\big((1-S)\rho_v\big)}{\partial t} + \phi\rho_l\frac{\partial S}{\partial t} + \alpha(1-S)\rho_v\frac{\partial(\mathrm{div}\,\mathbf{u})}{\partial t} + {} \\ + bS\rho_l\frac{\partial(\mathrm{div}\,\mathbf{u})}{\partial t} + \mathrm{div}(\rho_v\mathbf{v}_g) \\ + \mathrm{div}(\rho_l\mathbf{v}_l) + \mathrm{div}(\rho_g\mathbf{v}_v^d) = 0\end{aligned} \qquad (38)$$

where: **u** is the displacement vector of the solid matrix, the subscript *g* refers to the gas phase, α is Biot's constant, $\mathbf{v}_g$ is the bulk velocity of the gas phase and $\mathbf{v}_v^d$ is the flow of vapor due to diffusion.

Constitutive relationships provide the flow equations for the different phases. For the liquid phase, the flow equation corresponds to Darcy's law:

$$\mathbf{v}_l = -\frac{k_l}{\mu_l}\big(\mathrm{grad}(p_l) - \rho_l\mathbf{g}\big) \qquad (39)$$

where: k_l is the liquid permeability of the material, μl is the dynamic viscosity of the liquid phase, ρ_l is the liquid pressure, and **g** is the gravity acceleration vector.

A similar expression is used for the gas phase flow:

$$\mathbf{v}_g = -\frac{k_g}{\mu_g}\big(\mathrm{grad}(p_g) - \rho_g\mathbf{g}\big) \qquad (40)$$

Finally, the flow of vapor due to diffusion can be expressed as (Whitaker 1977):

$$\mathbf{v}_v^d = -D_{\mathrm{v}}\ \mathrm{grad}\left(\frac{\rho_v}{\rho_g}\right) \qquad (41)$$

where: D_{v} is the diffusion coefficient of vapor.

In order to express Equation (38) as a function of a single state variable for water, most models rely on the definition of capillary pressure p_c, which relates liquid and gas pressures (Bear 1988):

$$p_c = p_g - p_l \tag{42}$$

and Kelvin's relationship (Kaviany 1995):

$$p_c = -\frac{\rho_l RT}{M_w}\ln\left(\frac{p_v}{p_v^s}\right) = -\frac{\rho_l RT}{M_w}\ln(H) \tag{43}$$

where: R is the ideal gas constant, T is the temperature, M_w is the molar mass of water, p_v^s is the saturated vapor pressure, and H is the relative humidity.

Also, the ideal gas law can be used to relate the vapor density of Equation (41) to the vapor pressure:

$$\frac{\rho_v}{M_w} = \frac{n_v}{V^g} = \frac{p_v}{RT} \tag{44}$$

where: n_v is the number of vapor molecule in the gas phase volume V^g.

Substituting relationships (42)–(44) in the flow Equations (39)–(41) allows expressing the water species conservation equation as either liquid pressure, vapor pressure, or capillary pressure. If the relationship between saturation or water content and capillary pressure is known, such as Van Genuchten's relationship (Van Genuchten 1980), it is possible to use these state variables instead.

A comprehensive discussion on the choice of the state variable can be found in (Gawin 2006). The authors suggest using the pressure variables instead of saturation or water content because these variables are not continuous at the interface between two materials having different porosities and moisture retention characteristics. It is thus not possible with these variables to solve problems where different material layers (material interfaces) are present.

Dry air:

The mass conservation equation for dry air is given by (Gawin 1995):

$$\phi\frac{\partial\big((1-S)\rho_a\big)}{\partial t} + \alpha(1-S)\rho_a\frac{\partial(\operatorname{div}\mathbf{u})}{\partial t} + \operatorname{div}(\rho_a\mathbf{v}_g) - \operatorname{div}(\rho_g\mathbf{v}_v^d) = 0 \tag{45}$$

Similar to the water species relationship, flow Equations (40) and (41) are substituted in (45) to yield the full dry air conservation relationship.

Energy conservation:

The evolution of temperature in the porous material is calculated from the energy balance relationship. Most authors assume that the different phases (solid matrix, liquid and gas) of the material are in thermal equilibrium. In these conditions, the energy balance equation is given by (Gawin 1995):

$$\rho C_p\frac{\partial T}{\partial t} + \big(C_{pl}\rho_l\mathbf{v}_l + C_{pg}\rho_g\mathbf{v}_g\big)\operatorname{grad}(T) - \operatorname{div}\big(\lambda_{\text{eff}}\operatorname{grad}(T)\big) + \sum_k f_k = 0 \tag{46}$$

where: ρ is the average density of the material, C_p is the specific heat, λ_{eff} is the effective thermal conductivity, and f_k represents the various sink or source terms that affect temperature.

Many different phenomena may contribute to the term f_k in Equation (46). Gawin (2002) reported terms associated with phase change (evaporation) and dehydration of water. In (Ulm 1995, Ulm 1998, Gawin 2006), the modeling of the heat generated during the hydration of concrete and its coupling with mechanics is discussed (see Section 3.3).

In (Khalili 2001), the authors devised a THM model without assuming thermal equilibrium between the solid, liquid, and gas phases. In that case, three separate energy balance equations similar to (46) were considered for each phase, with thermal exchange terms between the phases being added.

Mechanical coupling:

In many THM models, the time-dependent mass and energy conservation equations are coupled to the static linear momentum balance equation, assuming that the deformations induced by the fluids and energy transport are slow enough to be considered as a series of static mechanical problems. In that case, the linear momentum balance equation is given by (Gawin 1995):

$$\mathrm{div}(\boldsymbol{\sigma}) + \rho\mathbf{b} = 0 \tag{47}$$

where: $\boldsymbol{\sigma}$ is the total stress tensor, **b** is a body force vector, usually corresponding to gravity, and ρ is the average density of the material, expressed as a weighted average of the separate phase density:

$$\rho = (1-\phi)\rho_s + \phi S\rho_l + \phi(1-S)\rho_g \tag{48}$$

where: ρ_s is the density of the solid matrix.

The constitutive equation is expressed as a function of the effective stress $\boldsymbol{\sigma}'$, which was first introduced in soil mechanics (Gray 2001). The effective stress expression for an isotropic material is given by (Bary 2000):

$$\boldsymbol{\sigma}' = \boldsymbol{\sigma} + bp\mathbf{I} \tag{49}$$

where: b is the Biot scalar parameter, p is the average pressure and **I** is the identity tensor.

The average pressure is given by (Gawin 1995):

$$p = Sp_l + (1-S)p_g \tag{50}$$

The effective stress relationship links the pressure variations in the material resulting from moisture content variations with mechanical deformations. As an alternative to the relative stress expression, Coussy derived an incremental form of Equation (49) (Coussy 1995):

$$\mathrm{d}\boldsymbol{\sigma}' = \mathrm{d}\boldsymbol{\sigma} + (\mathrm{d}p^g - S\mathrm{d}p^c)\mathbf{I} \tag{51}$$

which in most cases yield results similar to expression (49) according to (Gray 2001).

The simplest mechanical coupling case corresponds to a linear elastic model (Gawin 1995), where the total stress tensor is related to the elastic strain by:

$$\boldsymbol{\sigma} = \mathbf{E_o} : \varepsilon^e \tag{52}$$

where: ε^e is the elastic strain contribution and $\mathbf{E}_o$ is the elasticity matrix.

The total strain $\underset{\sim}{\varepsilon}$ is given by (Gawin 1995):

$$\underset{\sim}{\varepsilon} = \varepsilon^e + \varepsilon^T + \varepsilon^o \tag{53}$$

where: ε^T is the strain caused by thermo-elastic expansion and ε^o is the autogeneous strain.

The thermal strain is written as (Cervera 1999b):

$$\varepsilon^T = \alpha_T(T - T^{\mathrm{ref}})\mathbf{I} \tag{54}$$

where: α_T is the thermal dilatation coefficient and T^{ref} is a reference temperature for which the thermal strain is null.

In (Gawin 2002), the elastic linear model was expanded to a nonlinear damage model to simulate concrete exposed to temperature above the critical point of water. In that case, the stress-strain relationship is written as:

$$\boldsymbol{\sigma} = (1-d)\mathbf{E_o} : \varepsilon^e \tag{55}$$

where: d is the scalar damage parameter (Mazars 1989). Kahalili and Loret (Khalili 2001) presented a THM model where the mechanical formulation is based on an elasto-plastic constitutive law to simulate moisture induced shrinkage. In (Baggio 1995), the authors devised a THM approach where the mechanical model is based on viscoelasticity and damage. Similar to the SNIA algorithm of reactive transport modeling, the calculations are performed in two sequential steps. The hydro-thermal simulations are performed first, and then the mechanical analysis is performed using a separate code.

The THM framework described in the previous paragraphs has been expanded theoretically in (Schrefler and Pesavento 2004). Averaging the microscopic mass balance and constitutive equations over a Representative Elementary Volume (REV), they obtained a set of conservation equations that includes interface terms that can be used to model different exchange phenomena between the various phases. The final system of equations is made of 30 equations with 30 corresponding independent variables. Although the global model could hardly be solved when all equations are considered, it provides a solid framework for devising specific applications.

3.2 Simplified THM Models

Given the complexity of the equations involved, solving THM models can prove a daunting task. Not surprisingly, simplifications have been made in some cases in order to keep the numerical problem manageable. In some other cases, the model can be simplified due to the nature of the problem to be solved.

This is the case for instance in (Bary et al. 2000). The authors present a model to simulate the damage caused by high fluid pressure on concrete structures such as dams. In that case, the material can be considered saturated and the temperature uniform, which simplifies the set of equations.

Similar to the moisture transport models reviewed in the chapter on hydraulic properties, many authors assumed that the gas pressure is constant in the porous material. This allows removing dry air from the set of equations and also simplifies the remaining water species conservation equation as shown in (Chijimatsu 2000, Obeid 2001, Bary 2008). In (Meschke 2003), the authors used a nonlinear diffusion approach similar to the approach proposed by Bazant (Bazant 1971) but based on the capillary pressure state variable instead of the relative humidity.

3.3 Adding Cement Hydration to THM Models

The THM modeling framework has been used frequently to model the relationship between the heat of hydration and the damage induced to the concrete matrix by the strong temperature gradients during the early ages of the material. Although the intensity of the hydration phenomena decreases rapidly after a few hours in the material's life, the potential microcracks in the hydrated cement paste can increase the transport properties and have detrimental effects in the future.

To consider the heat of hydration in coupled THM equations, Cervera et al. (Cervera 1999, Cervera 1999b) added a source term f_ξ to the energy conservation Equation (46) that models the heat generated by the chemical reactions when the cement is mixed with water:

$$f_\xi = Q_\xi \dot{\xi} \tag{56}$$

where: Q_ξ is a material constant and ξ is the degree of hydration.

The rate of hydration $\dot{\xi}$ is given by:

$$\dot{\xi} = \frac{k}{n_o}\Big(\frac{A_o}{k\xi_\infty} + \xi\Big)(\xi_\infty - \xi)\exp\Big(-\frac{\bar{n}\xi}{\xi_\infty}\Big)\exp\Big(-\frac{E_a}{RT}\Big) \tag{57}$$

where: A_o is the initial affinity of the hydration reaction, ξ_∞ is the maximum degree of hydration, E_a is the activation energy of the hydration process, R is the ideal gas constant, and T is the temperature. The other parameters, i.e., k, n_o, $\bar{n}$, are material constants to be determined experimentally.

The hydration degree and Equation (57) are added to the THM model as a new state variable and equation. They must be solved in addition to the other conservation equations.

The hydration process is coupled to the mechanical model by adding a component to the total strain Equation (53) called the chemical strain $\varepsilon^{\mathrm{ch}}$, which is the contribution from the self-generated heat of hydration of cement. This strain is proportional to the hydration degree:

$$\varepsilon^{\mathrm{ch}} = \alpha_\xi \xi \mathbf{I} \tag{58}$$

where: α_ξ is the thermal expansion parameter associated with the heat of hydration.

Similar models considering the hydration process were described in (Ulm 1995, Ulm 1998, Gawin 2006).

4.0 Coupled Ionic Transport and Mechanical Models

The concern over the long-term stability of concrete in contact with groundwater or contaminated water in the context of nuclear waste storage has initiated the development of models that attempt at coupling THM models with reactive transport approaches. A number of phenomena that are important in weathering and behavior of cementitious barriers and grouts are governed by a combination of chemical, physical, and mechanical processes. Important properties are: stability of cementitious phases, permeability for water, ions and gases, chemical composition (pH, redox), crack development. Examples of such interactions are: effect of chemical speciation (form) on mobility and transport rates of substances, effect of locally formed precipitates on porosity and tortuosity, stress and material damage caused by precipitation of expanding minerals, increased porosity of material by leaching of matrix components, and decreased material strength by leaching of matrix components

Understanding these effects and quantitative estimation of long terms effects requires models that can accommodate the different process descriptions.

A “complete” model should contain sub models for:

- Multi-component chemical reactions. It has a lot of advantages to use standard thermodynamic equilibrium model frameworks. In this way it is possible to use existing thermodynamic databases and easier to make use of progress made in this field,
- Mass transport processes (diffusion, convection, electrochemical coupling, heat conduction),
- Local chemical conditions (local concentrations of all physico-chemical species),
- Coupling relationships between chemistry, local pressures, porosities, strength etc.

Integration of these models needs to be tight, because chemical and physical properties change dynamically in time and place. Effectively this means that a lot of information has to be exchanged between the different sub-models during runtime, per time step. This effectively makes it necessary to integrate these models within a single framework in which all sub-models run at the same time. But so far, these efforts have been very limited. They are summarized in this section.

4.1 Simplified Transport Coupling

Most attempts to link reactive transport in cementitious materials with THM models were concerned with the decalcification of the hydrated cement paste and the impact it has on the mechanical resistance of the material and the possible damage induced to the matrix. In all the papers reviewed for this section (Gérard 1998, Ulm 1998, Kuhl 2004, Kuhl 2004b), the concentration of calcium was used as the driving mechanism behind the matrix dissolution. Accordingly, the transport of ions was limited to a single equation modeling the diffusion of calcium:

$$\frac{\partial s}{\partial t} + \frac{\partial wc}{\partial t} - \mathrm{div}\big(D_{\mathrm{ca}}\,\mathrm{grad}(c)\big) = 0 \tag{59}$$

where: c is the concentration of calcium in the pore solution of the material, s is the amount of calcium in the solid phase (as portlandite and C-S-H), w is the water content, and D_{ca} is the diffusion coefficient of calcium.

The first term on the left hand side of Equation (59) accounts for the calcium released in the pore solution upon portlandite and C-S-H dissolution. In all models cited previously, it is estimated from the C/S ratio vs. c relationship shown on Figure 2 (the experimental data in Figure 2b were taken from (Berner 1992)). Going from Figure 2a to Figure 2b is hypothetical at best since there is no direct relationship between the amount of portlandite and C-S-H and the calcium in pore solution, as emphasized by the equilibrium relationship (13).

To couple transport and matrix dissolution to the mechanical model, Gérard et al. (Gérard 1998) introduced an ageing parameter V_d [0:1] that depends on the amount of calcium dissolved. According to Figure 2, it can also be related to the calcium in solution. The ageing parameter is then incorporated in the damage model (Equation (55)) as:

$$\boldsymbol{\sigma} = (1 - V_d)(1 - d)\mathbf{E_o} : \varepsilon^e \tag{60}$$

According to this formulation, the ageing parameter contributes to reduce the mechanical properties of the material as the matrix is dissolved.

In (Gérard 1998), the authors also consider a feedback effect that modifies the transport parameters as a function of the damage level.

4.2 Multi-ionic Transport Coupling

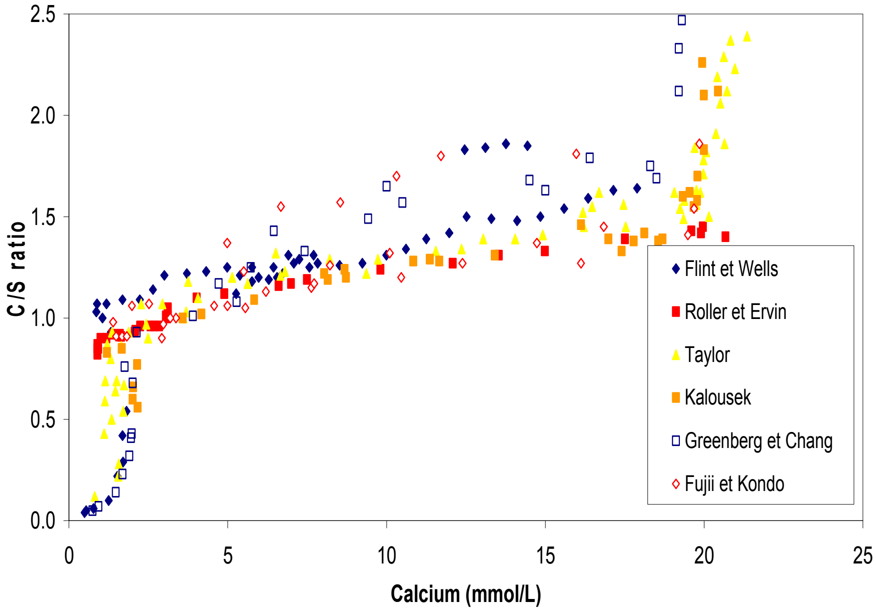
As shown in the previous section, most models attempting to couple reactive transport and THM models have been limited to simplified ionic diffusion equations. Only one model coupling multi-ionic reactive transport and damage mechanics could be found. The model, developed by Planel (Planel 2002), uses a reactive transport model based on the SIA algorithm based on linear transport equations (see Equation (27)) to simulate the precipitation of ettringite and gypsum upon exposure to groundwater containing sulfate.

The mechanical portion of this model is based on a damage model similar to Equation (55). In this case, the damage parameter is a function of the volume of ettringite that is precipitated compared to the initial porosity of the material. The dissolution of C-S-H and its impact on the pore volume is also considered.

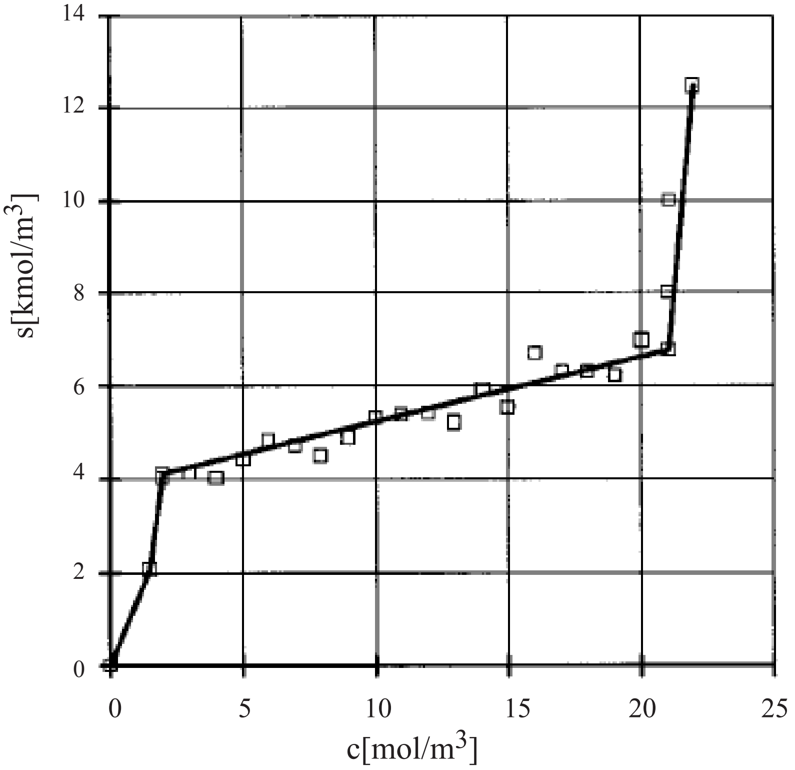
5.0 CONCLUSIONS

The review of approaches to couple physical, structural, and physical mechanisms showed two main categories of models: reactive transport and thermo-hydro-mechanical. Reactive transport models couple transport of species in the pore network with chemical reactions within the pores and with the solid matrix. On the other hand, the thermo-hydro-mechanical models focus on the impact that fluid and thermal flow have on the mechanical resistance of concrete.

The review showed that reactive transport models incorporating mechanical considerations or THM models dealing with detailed transport and chemistry relationships are nearly non-existent. Given the mechanisms and time scales involved in nuclear waste storage problems, models incorporating detailed reactive transport with a THM framework could be developed and used to provide a global durability assessment for those structures.



a. CaO/SiO$_2$ vs. Calcium in Solution (Berner 1992)



b. Solid Content s vs. Calcium in Solution (Ulm 1999)

Figure 2. Relationship Between the Calcium in Solution vs. the CaO/S$_1$O$_2$ Ratio and s.

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