International Journal of Fracture **115**: L49–L54, 2002.

EXTRACTION OF ELASTIC MODULI FROM GRANULAR COMPACTS

T. I. Zohdi
Department of Mechanical Engineering
6195 Etcheverry Hall
University of California, Berkeley, CA, 94720-1740, USA
e-mail: zohdi@newton.berkeley.edu, fax. 510-642-5539

P. J. M. Monteiro and V. Lamour
Department of Civil and Environmental Engineering
725 Davis Hall
University of California, Berkeley, CA, 94720-1740, USA
e-mail: monteiro@ce.berkeley.edu, fax. 510-643-8928

Abstract: The precipitation of crystals in certain solid nucleation processes can lead to subcritical failure. An important case is that of ettringite crystals in hardened concrete which, when exposed to sulfate attack, can lead to cracking of the structure. In order to conduct micromechanical modeling of this deterioration process, it is necessary to know the elastic moduli of ettringite. However, due to the difficulty in obtaining crystals large enough to conduct mechanical tests, the elastic moduli of ettringite remain unknown. The focus of this communication is to report estimates on the elastic moduli of ettringite, which are determined by solving an inverse formulation, where only the experimentally measured effective responses of porous ettringite compacts are known. The inverse solution is obtained by using a probabilistic genetic search algorithm.

1. Introduction. Ettringite crystals are precipitated during the early hydration of cement (Figure 1). These crystals have great importance in the rheology and early hardening of concrete. After the first few weeks, the ettringite crystals, depending on the amount of tricalcium aluminate, tend to convert to monosulfoaluminante hydrates until a thermodynamical equilibrium is achieved. When concrete is exposed to sulfate attack, the monosulfoaluminate hydrate converts back to ettringite which in presence of water leads to expansion and cracking (Figure 2). Expansive cements, on the other hand, take advantage of ettringite growth and expansion to produce concrete less prone to cracking (Figure 3). There is great interest to perform micromechanical modeling of these complex mechanisms, however it is necessary to determine the elastic moduli of the ettringite crystals. Unfortunately, ettringite is seldom found in nature and the few large crystals often contain substitution of both the anions and cations into their structure. Ettringite crystals synthesized in laboratory are too small to perform mechanical characterization in a single crystal. Therefore, we measured the elastic moduli of compacted ettringite samples with known porosity and used an inverse scheme to estimate the moduli of the compact with zero porosity. In laboratory experiments, aggregates of ettringite forming the tested compacts exhibited negligible relative sliding, in the infinitesimal

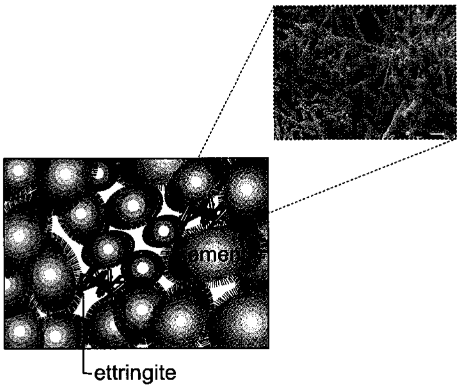

Figure 1: Early hydration of cement paste: The precipitation of ettringite is responsible for the setting of concrete. Many of the needle-shaped prismatic crystals of ettringite will eventually convert to monosulfate hydrate. The precipitation of ettringite at early ages does not generate stresses because the high porosity of the matrix can accommodate any volumetric change.

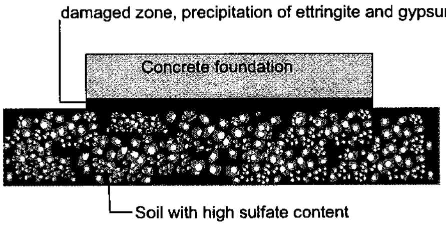

Figure 2: Concrete exposed to external sulfate attack: The monosulfate hydrate that is formed after the few weeks of hydration is stable under normal environmental conditions. However, when concrete is exposed to sulfate attack, the monosulfate hydrate is converted back to ettringite. This reaction is expansive and the low-porosity matrix of mature concrete cannot accommodate the stresses and cracks. The diffusion of sulfates will be much faster once the matrix is cracked and the deterioration process accelerates.

strain range, under applied macroscopic pressure, thus making the characterization of the aggregate as a poroelastic material reasonable.

2. Inverse problem formulation. The compacts are modeled as a poroelastic material, which on the microscale is characterized by spatially variable, two-phase elasticity tensors, $\mathbb{E}$, while the macroscale response is described by a relation between averages, $\langle\boldsymbol{\sigma}\rangle_\Omega = \mathbb{E}^* : \langle\boldsymbol{\epsilon}\rangle_\Omega$, where $\langle\cdot\rangle_\Omega \stackrel{\text{def}}{=} \frac{1}{|\Omega|}\int_\Omega \cdot\, d\Omega$, where $\boldsymbol{\sigma}$ and $\boldsymbol{\epsilon}$ are the stress and strain tensor fields within a statistically representative volume element (RVE) of volume $|\Omega|$. Direct numerical simulation of compacted the ettringite powder is of extreme computational complexity, due to the fact that the irregular microstructure, namely the gap space, must be resolved by the discretization mesh. Therefore, it is advantageous to use analytical effective property approximations. For the present analysis we employ the widely used Hashin and Shtrikman bounds

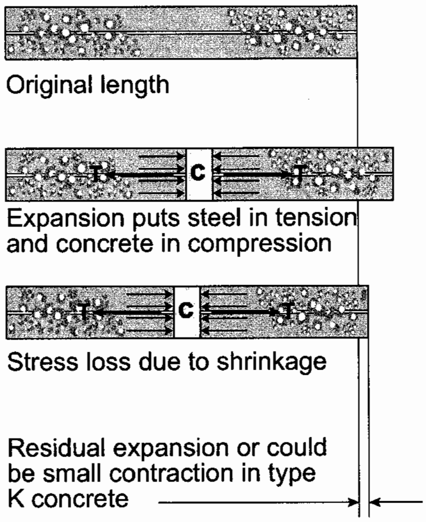

Figure 3: Expansive Concrete: Cracking caused by drying shrinkage of concrete is prevalent in reinforced concrete structures. Shrinkage-compensating cements, when properly restrained by reinforcement, can generate chemical precompression in the concrete which can compensate the tensile stresses created by the drying shrinkage. Most expansive cements employ the controlled expansion of ettringite at early ages by modifying the composition of traditional portland cement.

(1962, 1963) for isotropic materials with isotropic effective responses, which are, for the effective bulk modulus,

$$\kappa^{*,-} \stackrel{\text{def}}{=} \kappa_1 + \frac{v_2}{\frac{1}{\kappa_2-\kappa_1} + \frac{3(1-v_2)}{3\kappa_1+4\mu_1}} \leq \kappa^* \leq \kappa_2 + \frac{1-v_2}{\frac{1}{\kappa_1-\kappa_2} + \frac{3v_2}{3\kappa_2+4\mu_2}} \stackrel{\text{def}}{=} \kappa^{*,+}, \tag{1}$$

while for the effective shear modulus,

$$\mu^{*,-} \stackrel{\text{def}}{=} \mu_1 + \frac{v_2}{\frac{1}{\mu_2-\mu_1} + \frac{6(1-v_2)(\kappa_1+2\mu_1)}{5\mu_1(3\kappa_1+4\mu_1)}} \leq \mu^* \leq \mu_2 + \frac{(1-v_2)}{\frac{1}{\mu_1-\mu_2} + \frac{6v_2(\kappa_2+2\mu_2)}{5\mu_2(3\kappa_2+4\mu_2)}} \stackrel{\text{def}}{=} \mu^{*,+}, \tag{2}$$

where ($\kappa_2 \geq \kappa_1$) and ($\mu_2 \geq \mu_1$) are the bulk and shear moduli for phases one and two and where v_2 is the second phase volume fraction. Such bounds are the tightest possible on isotropic effective responses, with isotropic two phase microstructures, where only the volume fractions and phase contrasts of the constituents are known. In the present analysis, the pore phase, i.e. the gap space between the individual grains in the compacts, is modeled as $\kappa_{pore} = \delta \times \kappa_{matrix}$ and $\mu_{pore} = \delta \times \mu_{matrix}$, where $\delta << 1$. We remark that, in the development of the Hashin-Shtrikman bounds, one must be cognizant of the fact that the second phase is considered to be the stiffer of the two phases. The inverse problem is to extract matrix properties of a porous solid where only the effective responses and pore volume fraction are known. Specifically, this is formulated as an optimization (inverse) problem to determine the bulk and shear properties of the crystals without porosity where pore volume fractions (v_1), and the mechanical properties of matrix materials (κ_2, μ_2) are sought to minimize the following cost function

$$\Pi = (\tfrac{\kappa^*}{\kappa^{*,M}} - 1)^2 + (\tfrac{\mu^*}{\mu^{*,M}} - 1)^2, \qquad (3)$$

where κ^* and μ^* are the effective responses produced by a trial microstructure, which can be considered as a trial vector, (κ_2, μ_2), and where $\kappa^{*,M}$ and $\mu^{*,M}$ are the measured effective responses and the pore phase volume fraction ($v_1 = 1 - v_2$) is known. Our objective is to match measured macroscale effective bulk and shear moduli (to drive Π to zero) using convex combinations of the Hashin-Shtrikman bounds as approximations for the effective moduli $\kappa^* \approx \theta\kappa^{*+} + (1-\theta)\kappa^{*-}$ and $\mu^* \approx \theta\mu^{*+} + (1-\theta)\mu^{*-}$ where $0 \leq \theta \leq 1$. The values of θ vary with volume fraction. It is important to calibrate the values for hydration product also exposed to similar compaction. Fortunately, the elastic moduli of calcium hydroxide are known and Beaudoin (1983) measured Young's modulus of their compacts with known porosities. The values for θ were used to generate a $\theta - v_2$ curve-fit. The results are shown in Table 1. The curve-fit was

$$\theta = 0.0281e^{3.5336v_2}, \qquad (4)$$

which had a nearly perfect regression value $R^2 = 0.9928$ (perfect is $R^2 = 1.0$). The range of the curve-fit was $0.646 \leq v_2 \leq 0.8257$. This $\theta - v_2$ relation was used to select θ values for the genetic search algorithm described in the next section.

v_{pore}	v_2	E^* (GPa)	θ^{opt}
0.174	0.825	15.290	0.517
0.195	0.804	13.830	0.488
0.218	0.781	11.700	0.434
0.246	0.753	10.490	0.413
0.316	0.683	6.682	0.306
0.354	0.646	5.605	0.279

Table 1: Measured effective properties for various pore volume fractions for Calcium Hydroxide and the computed optimal θ to match the measured effective response. The value of κ_2 and μ_2 were known to be $\kappa_2 = 38\ GPa$ and $\mu_2 = 16\ GPa$.

3. Probabilistic nonconvex minimization. The main difficulty with the formulation in Equation 3 is that since the Hashin-Shtrikman bounds are nonconvex, the resulting objective function is nonconvex, i.e. the inverse problem's Hessian is not positive definite (invertible) throughout variable search space. In other words, there are local minima in which a gradient search method can become trapped. An appropriate family of methods for nonconvex optimization, based on the probabilistic principles of natural selection, are genetic algorithms, which stem from the work of John Holland and collaborators in the late 1960's (Holland 1975). For a recent survey of the state of the art, see Goldberg and Deb (2000). In Zohdi (to appear) a general genetic algorithm was developed, where the key feature was the development of a "genetic string", which contains microstructural design information. Adopting these ideas for the problem at hand, we have the following survival of the fittest algorithm: (I) Randomly select N starting genetic strings: $\mathbf{\Lambda}^i \stackrel{\text{def}}{=} (\kappa_2^i, \mu_2^i)$, $(i = 1, ..., N)$, (II) Compute fitnesses $(\Pi(\mathbf{\Lambda}^i))$ of each genetic string $(i = 1, ..., N)$ (III)Rank the genetic strings $\mathbf{\Lambda}^i$, $(i = 1, ..., N)$ (IV) Mate nearest pairs and produce offspring $(i = 1, ..., N)$: $\boldsymbol{\lambda}^i \stackrel{\text{def}}{=} \Phi^i \mathbf{\Lambda}^i + (1 - \Phi^i)\mathbf{\Lambda}^{i+1}$ and $\boldsymbol{\lambda}^{i+1} \stackrel{\text{def}}{=} \Phi^{i+1}\mathbf{\Lambda}^{i+1} + (1 - \Phi^{i+1})\mathbf{\Lambda}^{i+1}$, $0 \leq \Phi^i = random \leq 1$, different for each component, (V) Enforce constraints (if active): $\kappa_2^- \leq \kappa_2^i \leq \kappa_2^+$ and $\mu_2^- \leq \mu_2^i \leq \mu_2^+$, (VI)Kill off bottom M¡ N strings (optional: keep top K parents) and (VII) Repeat with top gene pool plus M new ones: $\mathbf{\Lambda}^i = \boldsymbol{\lambda}^i$, $(i = 1, ..., N)$. The most fit genetic string is that with the smallest objective function value. Typically, the algorithm produces an optimal genetic string only after a few generations. Keeping the top K parents typically allows faster rates of convergence.

4. Experimental results, inversion and discussion. The small ettringite crystals were precipitated from solution and the powder was compacted to produce pellets of known porosity. Specifically, pellets were made by compacting pure powder in a confining metallic mould with a hydraulic press. The pellet geometry was cylindrical with a diameter of 30 mm and a height of approximately 15 mm. Porosity was measured with an hydrostatic scale in ether bath. Ultrasound measurements were performed using coupled longitudinal and transversal piezoelectric transducers directly attached to the sample. The elastic moduli of the pellets were determined by measuring their primary and secondary wave velocities. The pores are formed from the gaps between the crystals. The objective now was to invert the data to obtain the values for zero porosity. The variable's ranges were $1\,\text{GPa} = \kappa_2^{(-)} \leq \kappa_2 \leq \kappa_2^{(+)} = 10^2\,\text{GPa}$, and $1\,\text{GPa} = \mu_2^{(-)} \leq \mu_2 \leq \mu_2^{(+)} = 10^2\,\text{GPa}$. The number of genetic strings was set to 1000, keeping the offspring of the top 100 parents after each generation, and additionally keeping top $K = 100$ parents after each generation. Therefore, 800 new genetic strings were infused after each generation. Typically, after under ten generations, a dominant genetic appeared for each volume fraction level. Simulations were repeatedly rerun with progressively smaller values of the porous space stiffness reduction factor (δ), forcing $\delta \to 0$. Beyond a threshold of $\delta = 0.001$ the results were insensitive, and thus the simulations can be considered "convergent" to simulations involving true voids. The total simulation time was on the order of a few seconds. The results of applying the genetic algorithm are shown in Table 2. Figure 4 depicts the close agreement between the experimental results and the theoretical predictions when the average values, computed from the results, $\kappa_2 = 47.9$ GPa and $\mu_2 = 19.9$ GPa, are assumed for ettringite. Finally, we remark that the approach is general and could be applied to other types of compacts, in particular for sintered materials.

v_{pore}	v_2	κ^* (GPa)	μ^* (GPa)	θ	κ_2 (GPa)	μ_2 (GPa)
0.413	0.586	2.968	1.968	0.223	47.101	18.653
0.291	0.708	7.370	3.587	0.343	47.110	18.530
0.250	0.749	8.581	4.534	0.397	46.403	21.442
0.248	0.752	9.819	5.209	0.400	46.393	21.493
0.242	0.757	10.316	4.687	0.408	53.713	18.178
0.238	0.761	10.490	5.308	0.414	46.849	21.145

Table 2: Computed values of κ_2 and μ_2 for ettringite using the measured effective moduli of compacted ettringite pellets.

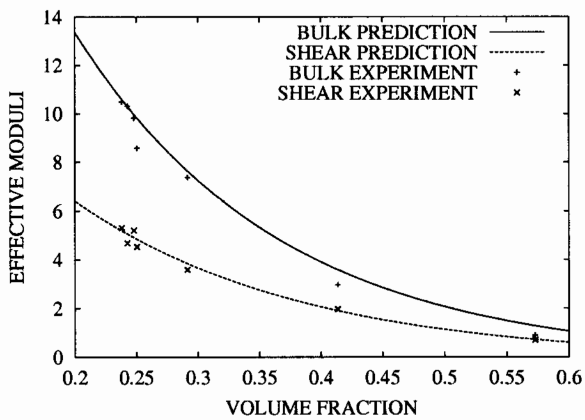

Figure 4: Experimental and theoretical results for the inverse problem involving ettringite.

Acknowledgement: Paulo Monteiro wishes to acknowledge the financial support given by NSF and the Federal Highway Administration (Award CMS-9812757). The helpful discussions with Dr. Richard Livingston are appreciated. Also, the authors wish to thank Dr. Paulo Ney de Souza for the help with graphics.

REFERENCES

1. Beaudoin, J. J. (1983) Cement and Concrete Research. **13**, 319.
2. Goldberg, D. E. and Deb, K. (2000) Special issue on genetic algorithms. *Computer Methods in Applied Mechanics and Engineering.* **186** (2-4) 121-124.
3. Hashin, Z. and Shtrikman, S. (1962). "On some variational principles in anisotropic and nonhomogeneous elasticity." *Journal of the Mechanics and Physics of Solids.* **10**, 335-342.
4. Hashin, Z. and Shtrikman, S. (1963). "A variational approach to the theory of the elastic behaviour of multiphase materials." *Journal of the Mechanics and Physics of Solids.* **11**, 127-140.
5. Holland, J. H. (1975). *Adaptation in natural and artificial systems.* Ann Arbor, Mich. University of Michigan Press.
6. Zohdi, T. I., (accepted). "On the tailoring of microstructures for prescribed effective properties." *The International Journal of Fracture.*