THE DYNAMIC RESPONSE OF POROUS CALCIUM
CARBONATE MINERALS*

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ABSTRACT

A theoretical study of the shock-loaded response of calcium carbonate materials is presented in which both dry and water-saturated samples with porosities up to 50 percent are considered. Data are presented for the unloading response from 15.0 and 18.5 GPa, and calculations from a mixture model using a Mie-Grüneisen equation of state with volume-dependent parameters are compared to both the Hugoniot and the isentropic unloading response.

INTRODUCTION

When porosity is present in mineral samples, shock loading results in greatly elevated temperatures and energies. It is recognized^[1,2] that Hugoniot data from initially porous samples provide a method for the experimental probing of a more expanded region of the equation-of-state surface of the constituent mineral.

When a second substance, such as water, is introduced into the pores of the material, the high pressure constitutive response becomes more complex. The methods of mixture theory must be brought to bear, and attendant questions regarding mechanical and thermal interaction between components must be addressed.

The materials of interest in the present investigation are porous samples of the mineral calcium carbonate, in both a dry porous form and containing water to various degrees of saturation. This mineral is the primary constituent of limestone, marble and chalk, and as such, constitutes a significant portion of the earth's surface material.

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The most extensive high-pressure study of this mineral has been reported by Kalashnikov, et al.^[3]. Their work provides Hugoniot data to nearly 100 GPa for dry crystalline calcite, two porous calcites (chalk) tested in both the dry and water-saturated condition, and two other minerals of dolomitic composition. Their study also includes a preliminary analysis using a mixture theory.

The present study focuses on a more detailed application of mixture theory to this problem. The theory is compared with the data of Kalashnikov, et al.^[3]. Recent high pressure shock and release measurements on porous calcite are also reported and preliminary comparisons with these data are made.

THEORY

Wet calcium carbonate is a mixture of three constituents, solid calcium carbonate, water, and void. It is modeled by using a theory of immiscible mixtures proposed by Drumheller and Bedford^[4]. A constituent of this mixture is labelled C_ξ , where $\xi = s, f, \text{ or } v$ for solid, fluid, or void. The intrinsic mass density of C_ξ , $\bar{\rho}_\xi$, is the ratio of the mass of C_ξ divided by the portion of the mixture volume occupied by C_ξ . The volume fraction of C_ξ , ϕ_ξ , is the ratio of the volume occupied by C_ξ over the volume occupied by the mixture. The ϕ_ξ always satisfy the condition

$$\sum \phi_\xi = 1 \quad (1)$$

where the summation sign implies a sum over all constituents C_ξ . The partial mass density of C_ξ is denoted by ρ_ξ and is given by

$$\rho_\xi = \phi_\xi \bar{\rho}_\xi. \quad (2)$$

In situations where the C_ξ have independent motions, balance of mass and momentum equations are required for each constituent. In this analysis it is assumed that all the C_ξ have identical motions. As a result the summed balance of mass and momentum relations for the mixture are sufficient to specify the solution to the problem. These relations are identical to the traditional continuum relations in which the density ρ and the pressure P are identified with the mixture mass density $\rho = \sum \rho_\xi$ and the constituent pressures P_ξ , so that $P = P_\xi$. Because of the assumption of equal pressures between the C_ξ , $P_\xi = 0$ when void is present.

It is assumed that C_s has an equilibrium pressure given by the Mie-Grüneisen relation

$$P_s = \frac{\bar{\rho}_{s0} c_{s0}^2 \eta_s}{(1 - s_s \eta_s)^2} \left[1 - \frac{1}{2} \Gamma_{s0} \eta_s \right] + \bar{\rho}_s \Gamma_s e_s \quad (3)$$

and

$$\bar{\rho}_s \Gamma_s = \bar{\rho}_{s0} \Gamma_{s0} (1 - \eta_s)^n \quad (4)$$

where $\eta_s = 1 - \bar{\rho}_{s0}/\bar{\rho}_s$ and e_s is the specific internal energy. The material constants $\bar{\rho}_{s0}$, c_{s0} , Γ_{s0} , and n are intrinsic properties of the calcite mineral. A variable Grüneisen parameter Γ_s is assumed ($n = 0$ corresponds to the common assumption that $\bar{\rho}_s \Gamma_s = \bar{\rho}_{s0} \Gamma_{s0}$). Equation 4 is equivalent to that proposed by Al'tshuler^[1].

The C_f has an equilibrium pressure given by a tabular equation of state^[5] based on Hugoniot data for water to 100 GPa.

The traditional balance of energy relation is used to describe the conservation of the mixture energy, where this energy is given by $e = \sum \rho_\xi e_\xi / \rho$. Two possible thermal states are considered. In the first case the temperatures of the water and the solid are equal. In the second case the energy in the water is given by

$$\rho_f \dot{e}_f = \phi_f P_f \frac{\dot{\rho}_f}{\rho_f}. \quad (5)$$

This second condition implies that the dissipative heating of the mixture occurs within the solid and does not influence the water. In addition, local heat transfer between the solid and the water is neglected. Consequently all of the shock heating is produced and remains within the solid. These two cases represent reasonable extremes in the possible assumptions for the thermal behavior of the mixture. Comparison of the solutions for these two cases will illustrate the sensitivity of the model to these types of mixing assumptions.

These relations were studied using a steady-wave analysis; that is, the solution was assumed to depend only on the factor $\Omega = x - Ut$, where U is the velocity of the wave, x is the spatial position, and t is the time. For the equal-temperature case the resulting relations can be integrated to obtain jump conditions for the steady wave. When Eqn. 5 is used the equations must be integrated numerically.

RESULTS

Figure 1 contains comparisons of calculated Hugoniots to the data of Kalashnikov, et. al.^[3] and Tyburczy and Ahrens^[6] for various initial mass densities. The model parameters used in these calculations are: $\bar{\rho}_{s0} = 2710 \text{ kg/m}^3$; $c_{s0} = 3.65 \text{ km/s}$; $\Gamma_s = 0.8$; and $n = -2.25$. The porosities of these samples, which can be

Figure 1: Comparison of theory to Hugoniot Data^[3,6] for dry porous and water-saturated calcite.

Figure 2: Calculated temperatures for water-saturated calcite (100 GPa).

computed from the listed initial densities range from zero to approximately fifty percent. With the exception of the water-saturated sample ($\rho_0 = 2200 \text{ kg/m}^3$), all of these data are for dry chalk. Two calculations are shown for the water-saturated case. These curves correspond to the two thermal assumptions described in the previous section.

Good agreement is achieved for the dry samples; however, some discrepancy is observed in the comparison to the water-saturated sample. Kalashnikov, et al.^[5] have also proposed a model for water-saturated chalk. They reported better agreement for the water-saturated case; however, they did not include a description of their equation of state for water.

The calculated Hugoniot in Figure 1 for the water-saturated case are relatively insensitive to the choice between the two thermal assumptions. The temperatures of the calcite and the water for these two cases is shown in Figure 2. Temperatures corresponding to the release paths from 100 GPa are also shown. These temperatures were computed by assuming a constant specific heat for calcite of 1200 J/kg K ^[7]. The porosity of the sample results in very high temperatures, and the values of the temperatures are strongly dependent upon the thermal assumption.

In Figure 3 the calculation is compared with release isentropes obtained from shock compression and unloading experiments on dry calcite samples with initial density of 1600 kg/m^3 and a porosity of approximately 40 percent^[8]. Release paths from 15.0 and 18.5 GPa were determined from the measured wave profile data. The comparison in Figure 3 is based on the same volume dependent Grüneisen parameters used to model the Hugoniot data in Figure 1. Considering the current uncertainty in the release curves, a better fit was not attempted. However, for contrast a calculation based on constant $\rho\Gamma$ is shown in Figure 4. This assumption clearly leads to excessive volumetric expansion for the release isentropes, although virtually identical agreement with the Hugoniot data in Figure 1 can be achieved.

Figure 3: Comparison of the volume-dependent $\rho\Gamma$ theory to release data for 1600 kg/m^3 porous calcite.

Figure 4: Comparison of Hugoniot and release paths calculated from two Mie-Grüneisen forms for 18.0 GPa data shown in Figure 3.

It is concluded that an overall better fit of a temperature-independent Grüneisen equation of state to both the high-pressure Hugoniot data and the release data is provided with a Grüneisen parameter which decreases with increasing specific volume. This would seem to be inconsistent with common models for solids from which the opposite behavior is predicted. Temperatures of 2500 K were calculated for the compressed state of the 1600 kg/m³ sample. This strongly suggests that calcium carbonate may be a liquid at the Hugoniot state or on the release isentrope. Theoretical studies described by Royce^[9] predict values in the liquid range which are significantly lower than those for the solid at the same specific volume. This is consistent with the trend observed in the present analysis.

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