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A Model for Calculating Shock Loading and Release Paths for Multicomponent Geologic Media

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A MODEL FOR CALCULATING
SHOCK LOADING AND RELEASE PATHS
FOR MULTICOMPONENT GEOLOGIC MEDIA

ABSTRACT

A model has been devised to calculate shock Hugoniot and release paths off the Hugoniot for multicomponent rocks containing silicate, carbonate, and water. Hugoniot equations of state are constructed from relatively simple measurements of rock properties including bulk density, grain density of the silicate component, and weight fractions of water and carbonate. Release paths off the composite Hugoniot are calculated by mixing release paths off the component Hugoniot according to their weight fractions. If the shock imparts sufficient energy to the component to cause vaporization, a gas equation of state is used to calculate the release paths. For less energetic shocks, the rock component will unload like a solid or liquid, taking into account the irreversible removal of air-filled porosity.

INTRODUCTION

Underground nuclear explosions have been conducted in a large variety of geological settings. Most commonly, the detonations take place in silicate rocks. Some rocks contain carbonates. Most rocks have associated porosity and are fully or partially saturated with water.

In modeling the phenomenology of underground nuclear explosions with finite difference codes such as SOC¹ and TENSOR,² it is necessary to define the pressure, density, and energy states (PVE) that are attained by the surrounding rock over the entire pressure range experienced. This includes both the loading paths and the appropriate PVE unloading paths from the Hugoniot. The Hugoniot curve is formed by a locus of shock states in the pressure-volume plane. If the shock adds sufficient energy to the material to cause it to vaporize, a gas equation of state is required to calculate the unloading paths off the Hugoniot for each of the components of the rock present in the vapor state.

The computation of the equation of state draws on the knowledge of several branches of physics and chemistry. Much of the PVE-state surface is inaccessible to controlled experiments so that input to these regions are obtained from theory. In some regions it is not possible to give rigorous theoretical treatment and, where theories give different results, it is necessary to exercise judgment in selecting the most accurate one. Single shock Hugoniot curves can be obtained by direct measurement but, even here, extrapolations need to be made to extend them into the extremely high-pressure regime inaccessible to experiments.

In an underground nuclear explosion, all of the energy is released in less than a microsecond. At this instant, the energy is concentrated in a small volume of extremely high temperature, high pressure material which generates a strong shock wave that propagates through the surrounding rock, distributing the energy as it decays. Close in, the rock is completely vaporized, and this vaporized rock itself becomes the primary working gas. The gas expands forming a cavity by displacing the surrounding rock. In this region, a gas equation of state is used to calculate the adiabatic release paths off the Hugoniot for each element of the vaporized rock. For the region farther from the explosion center, where not enough energy is available for vaporization, release paths from the Hugoniot are calculated, taking into account the irreversible removal of air-filled porosity.

Using complex theoretical models and associated computer codes, a gas equation of state can be calculated for any specific mixture of chemical compounds. In nature, an almost infinite variety of mixtures of different weight fractions of silicates, carbonates, and water can exist. The process of putting the results of one set of calculations for a given mixture in a form acceptable to our finite difference codes is a long and tedious one and does not lend itself to computer algorithms.

In this paper we describe a model for the construction of pressure-volume loading curves (Hugoniots) through the entire range of pressures that might be experienced in the rock surrounding an underground nuclear explosion (10^{-1} to 10^9 MPa). The composite rock can be comprised of any ratio of silicate, carbonate, or water.

GAS EQUATIONS OF STATE

State points above a temperature of 1 eV (1.16×10^4 K) were calculated for each component using the Lawrence Livermore National Laboratory (LLNL) Ionization Equilibrium Equation of State code (IEEOS).³⁻⁷ The IEEOS is based on classical theory and can accommodate a mixture of up to 10 elements. In the thermochemical region, where equations governing the system are known and some data is available, the TIGER⁸ code was used. The TIGER code can handle some aspects of non-ideal gas behavior and more than one condensed phase. As input, TIGER requires the following: 1) co-volumes of gas species for the Kintakowsky-Wilson equation of state, 2) enthalpies of formation of the compounds, 3) absolute entropy at the reference temperature (298 K), and 4) specific heats at constant pressure as a function of temperature for all species present. The IEEOS code requires all the ionization potentials for each element present.

HUGONIOT EQUATIONS OF STATE

The model used to calculate the pressure-volume (P-V) relationships (Hugoniot) for each component is an extension of the work by Butkovich.⁹ The Rankine-Hugoniot condition is used which relates measurements of shock velocity U_s and particle velocity U_p through equations derived from the laws of conservation of mass and momentum given in Eq. (1).

$$\frac{P - P_0}{V_0} = U_s U_p \quad \text{and} \quad \frac{V}{V_0} = \frac{U_s - U_p}{U_s} \quad (1)$$

Experimentally determined variables U_s and U_p associated with a single shock are found to be linearly related over large pressure ranges. Using this, linear fits were made to the data where the data existed in the form

$$U_s = a + b U_p \quad (2)$$

and were extrapolated. Butkovich constructed a model which reproduced shock and compressibility data on a large variety of partially to fully water-saturated silicate rocks, using easily measurable rock properties such as bulk density, grain density, and weight fraction of water.

The present work extends the model to include the effect of the carbonate component and thermal heating using the Mie-Grüneisen equation.

The required input parameters are:

Z = weight fraction of water (H_2O),

C = weight fraction of carbonate ($CaCO_3$),

ρ_C = bulk density of composite material,

ρ_{GS} = grain density of silicate component,

ρ_{GC} = grain density of carbonate component,

ψ_i = initial air-filled porosity.

Calculated, inferred, or default parameters are:

Γ_0 = Grüneisen parameter where $\Gamma_0 = \frac{\Gamma}{V}$ (0.5 is default),

S = weight fraction of silicate ($S = 1 - Z - C$),

ρ_{GC} = grain density of carbonate (2.712 g/cm³) is default for $CaCO_3$.

The P-V curves for each of the three components are calculated from linear fits to their U_s vs U_p data. The coefficients a and b in Eq. (2) that best fit the data are used. Equations (1) and (2) are solved for V in terms of P , using the coefficients a and b from Eq. (2). The resulting equations are

$$V = \left[\frac{a(b+1) + R(b-1)}{b(a+R)} \right] V_G \quad (3)$$

where

$$R = \left(a^2 + 4bPV_G \right)^{1/2} \quad (4)$$

Here V_G is the reciprocal of the grain density for a particular component. At atmospheric pressure (0.1 MPa), silicate rocks have a range of grain densities between 2.3 and 2.8 g/cm³, depending upon their mineral composition. The carbonate ($CaCO_3$) grain density is 2.712 g/cm³ and the water density is 0.998 g/cm³.

For the silicate component, empirical fits were obtained for U_s vs U_p Hugoniot data for grain densities between 2.3 and 2.8 g/cm³ (see Ref. 9).

$$\left. \begin{aligned} a &= 0.3427\rho_{GS} - 0.432 \\ b &= 4.598 - 1.568\rho_{GS} \end{aligned} \right\} \quad \text{for } P < P = \rho_{GS}(0.0028\rho_{GS} + 0.112)$$

$$\left. \begin{aligned} a &= 0.235 \\ b &= 1.60 \end{aligned} \right\} \quad \text{otherwise.}$$

The values of the coefficients a and b and used in Eqs. (3) and (4), give P in Mbars (10^5 MPa) and V in cm³/g.

A fit to the available data for grain density CaCO₃ provides

$$\begin{aligned} a &= 0.380 \\ b &= 1.425 \end{aligned}$$

For the water component, the U_s vs U_p relationship was obtained by fitting the available data. The extrapolated region was fitted to results obtained theoretically by Bjork et al.¹⁰ The fit is in the form of three straight line segments with the parameters shown in Table 1.

The P - V points are calculated by substituting a selected Hugoniot pressure P_H into Eq. (4), solving for R , and using this value in Eq. (3) to obtain the corresponding V . The result is a curve defining a locus of shock

TABLE 1. Values of coefficients for straight-line segments for water.

a	b	U_p (m/s)	Corresponding
			pressure range (MPa)
0.176	1.65	$\leq 2.6 \times 10^4$	$< 1.5 \times 10^4$
0.320	1.14	$> 2.6 \times 10^4$ and $< 10^5$	$> 1.5 \times 10^4$ and $< 1.5 \times 10^5$
0	1.294	$> 10^5$	$> 1.5 \times 10^5$

states for a non-porous component. If the component is porous, then the non-porous curve is adjusted using the Mie-Grüneisen equation

$$P = P_H + \Gamma(E - E_H) \quad , \quad (5)$$

where

$$\frac{\Gamma_0}{V_H} = \Gamma = \text{constant} \quad ,$$

where the subscript H refers to the values of the variables on the non-porous Hugoniot. This equation calculates a pressure greater than P_H to compress porous material from V_f to V , where $V_f = V_G/(1 - \phi)$ and where V_G is the specific volume of the porous component. The relationship below derived from Eq. (6), is used.

$$P = \frac{1 - \frac{\Gamma}{2}(V_G - V)}{1 - \frac{\Gamma}{2}(V_f - V)} \quad (6)$$

where

$$P = FP_H \quad .$$

Figure 1 shows a typical non-porous loading curve with adjustment for porosity.

When some initial air-filled porosity, ψ_i , is present in the composite rock, it is assumed to be the same in the silicate and carbonate components and is removed irreversibly by compaction. The rock is assumed to be elastic to some threshold pressure, P_T , for the onset of compaction. At pressures greater than P_T , air-filled porosity is removed exponentially to a pressure, P_m , at which all the air-filled porosity is removed. If the pressure is released from P_m or above, the release path will be that corresponding to $\psi_i = 0$. Both P_T and P_m are dependent on water content or on the initial air-filled porosity, according to the empirically determined relationships⁹ shown in Eqs. (7) and (8)

$$P_T = \frac{1}{\exp(C\psi_i + D)} \quad . \quad (7)$$

FIG. 1. Typical non-porous loading curve adjusted for porosity.

Table 2 gives the values of the parameters, C and D, as a function of the weight fraction of water, Z.

$$P_m = 6.5 \times 10^{-4} Z^{0.944} \quad \text{for } Z > 0.01$$

$$P_m = 0.05 \quad \text{for } Z < 0.01$$
(8)

The coefficients given in Eqs. (7) and (8) are for P in Mb (10^5 MPa) and v in cm^3/g .

TABLE 2. Values of parameters C and D as a function of the weight fraction of water (see Eq. 7).

Weight fraction of H_2O Z	Parameters	
	C	D
$0 < Z < 0.05$	6.579	6.908
$0.1 > Z > 0.05$	4.859	8.112
$Z > 0.1$	3.869	8.805

SHOCK LOADING AND RELEASE PROCESS

The shock compression process is assumed to occur in the following manner: From an initial state at ambient pressure, P (0.1 MPa), temperature, T (298 K), and density, ρ_0 , an element of multicomponent material undergoes a single shock compression. On shocking material to pressures greater than P_m , all air-filled porosity present is removed irreversibly. On shocking a material to very high pressures, a large increase in internal energy in the form of mechanical $P\Delta V$ work is added to the shocked material. Depending upon its compressibility, each component will receive a different increment of the added energy. Phase changes can occur in one component at a given shock pressure but not in the others.

The "waste heat concept"¹¹ is useful for estimating peak shock pressures where it is necessary for phase changes to occur in the various components being considered. In this concept the total energy acquired is

divided into available energy and "waste heat," where the "waste heat" is defined to be the net energy per unit mass which remains in the material after it expands adiabatically to its initial pressure.

Partial vaporization of the water component can begin on unloading from a peak shock pressure above about 10^4 MPa.⁵ A value of 2800 cal/g was derived by G. H. Higgins¹² as a good estimate for the increase in the internal energy required to totally vaporize $\text{SiO}_2\text{-H}_2\text{O}$ mixtures.¹³ This occurs for shocks with peak pressures above about 1.5×10^5 MPa, depending upon the grain-density compressibility of the silicate rock component.

For the CaCO_3 component, decomposition will occur with a change of enthalpy of about 400 cal/g.¹⁴ For non-porous CaCO_3 , this would occur upon release from peak shock pressures greater than about 5×10^4 MPa. Total vaporization of the carbonate component occurs with changes in enthalpy of about 4000 cal/g (Ref. 14); that is, when this amount of energy is available, the CaO component of the decomposition products $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$ is totally vaporized. This would occur for shock pressures above about 2.5×10^5 MPa for non-porous CaCO_3 . Any additional energy added to the system, by shock loading to pressures higher than necessary to vaporize any of the components, would appear as superheat in the vapor, increasing the pressure in the gas phase.

Release paths from specified points on the Hugoniot are calculated for each component in the following manner. If the peak shock pressure is at or below P_m , the porous rock behaves elastically. If the peak shock pressure is at or above P_m , all the porosity has been removed irreversibly, and the material unloads along the porosity adjusted grain density Hugoniot curve. However, if the peak shock pressure is at or above P_v , the pressure at which the onset of vaporization or decomposition to a gaseous state occurs, then the release path is calculated from the gas equation of state.

For $P_H > P_v$, the release path from any point on the Hugoniot (P_H , V_H , and E_H) is obtained by numerically integrating volume changes ΔV and energy changes $\Delta E = P\Delta V$. Each succeeding P is obtained by interpolation of the gas equation of state.

Figure 2 shows the gas equation of state for SiO_2 obtained by merging the IEEOS and TIGER code's calculational results and plotted as lines of constant density in the specific energy-pressure plane. When the results

FIG. 2. Gas equation of state for SiO_2 .

extend into the extremely high energy-density region, a radiation correction must be applied to the results.¹⁵ There is energy and momentum associated with a radiation field, and the equation of conservation of energy and momentum should include the contribution of the matter and its radiation field. The radiative contribution is negligible compared to that of matter, except at extremely high temperatures ($>1 \text{ keV} \approx 10^7 \text{ K}$) and at lower densities ($<1.0 \text{ gm/cm}^3$) where the radiative contribution becomes significant above 0.1 keV . Also shown in Fig. 2 is a typical shock Hugoniot for a grain density (non-porous) silicate rock along with representative release paths.

Figure 3 shows the radiation corrected gas equation of state for CaCO_3 . The LEEOS and TIGER codes' calculational results are those reported by Pasternak, Lee, and Miller,¹⁶ and are furnished by them for this work. Figure 4 shows the radiation corrected gas equation of state for H_2O . Both of these figures also include their grain density Hugoniot and show representative release paths from different shocked states from their Hugoniots.

FIG. 3. Radiation corrected gas equation of state for CaCO_3 .

FIG. 4. Radiation corrected gas equation of state for H_2O .

Release paths from the selected pressures on respective Hugoniot are calculated for each component. Figures 5a and 5b show Hugoniot and release paths calculated for a pure silicate rock with grain densities 2.3 and 2.8 g/cm³, respectively. Figure 5c is for grain density CaCO₃, and Fig. 5d is for H₂O (see Table 3 for a legend of Figs. 5 to 10).

TABLE 3. A legend for Figs. 5 to 10 showing calculated release paths off the Hugoniot (the uppermost line curve is numbered 1 in all figures).

Line No.	Hugoniot pressure from which the release curves were calculated		
	Rock content		
	Silicate (SiO ₂) (MPa)	Carbonate (CaCO ₃) (MPa)	Water (H ₂ O) (MPa)
1	1.0×10^9	1.0×10^9	1.0×10^9
2	3.0×10^8	3.0×10^8	3.0×10^8
3	1.0×10^8	1.0×10^8	1.0×10^8
4	3.0×10^7	3.0×10^7	3.0×10^7
5	1.0×10^7	1.0×10^7	1.0×10^7
6	3.0×10^6	3.0×10^6	3.0×10^6
7	1.0×10^6	1.0×10^6	1.0×10^6
8	5.0×10^5	5.0×10^5	5.0×10^5
9	3.0×10^5	3.0×10^5	3.0×10^5
10	2.0×10^5	2.0×10^5	2.0×10^5
11	P _v	1.0×10^5	1.0×10^5
12	--	7.0×10^4	7.0×10^4
13	--	5.0×10^4	5.0×10^4
14	--	3.0×10^4	3.0×10^4
15	--	--	2.0×10^4
16	--	--	1.0×10^4

FIG. 5. A comparison of Hugoniot and release paths for pure silicate rock, carbonate, and water.

FIG. 6. A comparison of Hugoniot and release paths for pure silicate rock and rock containing 10, 20, and 30% water.

FIG. 7. A comparison of Hugoniot and release paths for pure silicate rock and rock containing 10, 20, and 30% water in a pressure-compression space.

FIG. 8. Hugoniots and release paths for composite rocks.

FIG. 9. Hugoniot and release paths for composite rocks in pressure-compression space.

FIG. 10. Release paths for dry, porous silicate rock (SiO_2).

Calculating the unloading from a given shock pressure on the composite Hugoniot for a multicomponent rock is a rather complex procedure. Taken individually, each component has its own Hugoniot. If sufficient PAV work is done on a component, phase changes occur. Solids are transformed into a liquid or a gas. Composite release paths then can be made up of various combinations of solids, liquids, or gases, where one component can expand as a solid and another as a gas. When a solid-to-liquid phase change occurs, the expansion that follows is not too different than that of the solid phase, with the volume change being affected primarily by the thermal heating. This relatively small difference is ignored in the model. Following a phase change where the end product is a gas, however, the volume change or expansion can be very large.

The mixing scheme assumes that each component of the composite material (silicate, carbonate, and water) behaves independently of the others in both the loading and the unloading process while in continuous pressure equilibrium. This assumption is based on an analysis of the timing of the phenomenology of a buried nuclear explosion. When considering this timing, one realizes that it is not completely an equilibrium process. All of the energy of the device is released in less than a microsecond.

Calculations have shown that the rock vaporization stage occurs in about $70 W^{1/3}$ microseconds, where W is the energy yield in kilotons (4.186 TJ). During this time, an element of composite rock close to the explosion center will have acquired enough PAV energy to be vaporized. Typically, the energy released is distributed to the surrounding material within a few tenths of a second.¹⁷ During this time, the shock vaporized material has expanded to its maximum volume, and the rarefaction from the free surface has returned to a point near the expanded cavity.

Butkovich¹⁸ has shown that pressure differences of the order of 10^4 MPa can exist immediately behind a shock front in different types of rock and behind a shock wave of the same velocity in water. Similarly, large differences in temperature and particle velocity would be calculated between the rock components and water. In addition, it was shown that the large pressure differences between the rock matrix and water will equilibrate in time for a shock wave to propagate from a region of higher pressure to one of lower pressure. This will occur during a period of time from a fraction of a

microsecond to a few microseconds, depending primarily upon how the water inclusions are distributed in the matrix.¹⁸ Since the time is small compared with a cavity expansion time of 0.1 to 0.3 seconds, it seems reasonable to assume pressure equilibrium between all the components of the composite. However, it cannot be demonstrated that temperature equilibrium will be attained in a time which is short compared with full cavity growth time. Estimator for temperature equilibrium, run from a few to many seconds depending upon the heat transfer mechanism used.

When release paths from composite Hugoniot are required, release paths from selected pressures on the Hugoniot for each component are calculated and the component release paths are combined using

$$V = (1 - Z)CV_S + CV_C + ZV_W \quad (9)$$

The total volume change upon release is

$$\Delta V = \Delta V_S + \Delta V_C + \Delta V_W \quad (10)$$

where ΔV_S , ΔV_C , and ΔV_W are the volume changes of the three components. Each release path from a given pressure on the composite Hugoniot is calculated using Eq. (9). That is, taking the P-V release paths for each component from the same Hugoniot pressure, the specific volumes for each component are added according to their weight fractions at the same P for each point along the paths.

Figures 6a and 6b show the Hugoniot and release paths for 2.5 g/cm³ grain density silicate rock and for water, respectively. Figures 6c, 6d, and 6e show composite Hugoniot and release paths for silicate rock containing, respectively, 10, 20, and 30% by weight water. Figures 7a-e show the same results in pressure-compression space.

Figures 8a, 8b, and 8c show the calculated Hugoniot and release paths for a composite rock containing 10% by weight CaCO₃ and 0, 10, and 20% by weight water, respectively. Figures 9a, 9b, and 9c show the same results plotted in pressure-compression space.

Figures 10 and 11 show the effect of air-filled porosity on the release paths. Figures 10a-d show the release paths for dry, porous silicate rock with 0, 10, 20, and 30% air-filled porosity, respectively. Note how the compression accounts for the permanent loss of air-filled porosity.

Figure 11 gives the effect on the release paths of air-filled porosity with CaCO_3 , with Figs. 11a, 11b, and 11c indicating 0, 10, and 20% air-filled porosity, respectively. Note here a similar permanent loss of air-filled porosity. Figures 12a, 12b, and 12c show the same results plotted in pressure-compression space.

FIG. 11. Release paths for pure CaCO_3 .

FIG. 12. Release paths for pure CaCO_3 in pressure-compression space.

SUMMARY

The LLNL nuclear explosion phenomenology codes (such as SOC and TENSOR) require constitutive relations of pressure, density, and energy for the rock surrounding the explosion. Equation of state inputs for gaseous, liquid, and solid phases are required. Then these are used to calculate the loading and release paths for each point in the rock affected by the explosion. With pure substances such as silicate, carbonate, or water, equations of state can be derived from measurements and theoretical considerations for all of the three phases. However, many rocks contain arbitrary mixtures of these substances. Most rocks contain porosity, either partially or fully saturated with water, and some rocks contain carbonates. The almost infinite variety of mixtures of different weight fractions of the three components makes it impractical to make the measurements which are necessary to define the Hugoniot equation of state and unacceptable to calculate the equilibrium gas equation of state for every possible combination. It is much more likely that only simple measurements on a rock sample will be made to determine its bulk density, grain density, water content, and carbonate content.

A technique developed to construct the P-V Hugoniot equation of state for porous and non-porous silicate rock that is fully or partially saturated with water has been extended to include the carbonate component. The Hugoniot defines the PVE shock states in SOC and TENSOR calculations. If sufficient energy is added to a component of the rock to cause it to vaporize or decompose, release paths from these points are calculated with a gas equation of state. Since the different components require different amounts of energy to vaporize or decompose, each component of the composite rock can be different with any mixture of gases, liquids, and solids, depending upon the peak shock pressure experienced.

With the timing of the explosion phenomenology in mind, the mixing scheme used assumed that the components of the composite rock behave independently of each other while in constant pressure equilibrium in both loading and release, regardless of phase.

Other aspects of the model include the radiation correction to the equilibrium gas equation of state for silicate (SiO_2), carbonate (CaCO_3), and water (H_2O) and account for the additional energy required to remove porosity that might be present in the silicate and carbonate components of the composite rock.

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