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HUGONIOTS OF COLORADO OIL SHALE

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INTRODUCTION

In order to determine the dynamic response of oil shale to the large shock amplitudes experienced in the near-field region surrounding an explosive-filled borehole, we have measured the single-shock Hugoniots of Colorado oil shale as functions of kerogen content and orientation of the shock front to the bedding planes. This report is limited to shock wave behavior above 4 GPa, which is the lower range of in-contact explosive techniques. Behavior in the low-pressure, or far-field, region is presently being investigated using different experimental techniques and in general is considerably more complex.

EXPERIMENTAL

Standard optical techniques,⁽¹⁾ utilizing high-speed streak cameras to record shock-wave arrival times, were used to measure wave velocities (u_s) in the samples. Associated particle velocities (u_p) were determined by the impedance match method, using an aluminum alloy (2024) as the standard. The Rankine-Hugoniot conservation relations,

$$P_H = \rho_o u_s u_p \quad (1)$$

$$V/V_o = (u_s - u_p)/u_s \quad (2)$$

$$E_H = 1/2 P_H (V_0 - V) \quad , \quad (3)$$

which assume thermodynamic and hydrodynamic equilibrium, were then used to obtain the thermodynamic quantities pressure (P), relative compression (V/V_0), and energy (E). Such experiments, of course, cannot define details of the wave profile and dispersive effects, but they do allow determination of the single shock Hugoniot equation of state, $E(P,V)$. The pressure pulses were obtained from explosive plane wave generators 200 - 300 mm in diameter used to detonate carefully machined disks of similar diameter military explosives 100 - 250 mm thick. The explosive was either in contact with the experimental assembly or drove a steel plate impacting the assembly. By using various combinations of explosives, driver thicknesses, and impedance mismatch systems it is possible to achieve pressures in the shale ranging from 4 GPa to nearly 100 GPa, which spans the range of in-contact pressures for most commercial explosives.

We have chosen density as the primary characterization parameter because of the importance of the initial density in shock wave analysis. Furthermore, density can be uniquely correlated with other material properties such as oil yield,⁽²⁾ elastic constants,⁽³⁾ and compressive yield strength.⁽⁴⁾ Large samples of oil shale were provided by the U. S. Energy Research and Development Administration from the Mahogany zone of the Anvil Points mine near Rifle, Colorado. The samples were selectively cut to give as nearly uniform density as possible over the sample volume of 16 x 22 x 6 mm. Oil shale, particularly the richer samples, can be machined to very high tolerances, and samples were typically held flat and parallel to within .005 mm over the 16 x 22 mm faces. Typical samples

are shown in Fig. 1. The samples were divided arbitrarily into six density ranges, including one which was so lean as to be considered pure mineral matrix material, although it was quite porous. Even within these divisions the density of individual samples can vary considerably, and much of the scatter in the data arises from this source. Inclusions of nacholite and other material were sometimes found and can also adversely affect the data.

In order to determine the effect of orientation on wave propagation, shales of average density 2.13 and 2.25 g/cm³ (35 and 25 gal/ton) were investigated with the direction of shock wave propagation both parallel and perpendicular to the bedding planes. The data are shown in Figs. 2-5. No significant differences were found which cannot be accounted for by individual sample density variations. Hence, in this high pressure regime, the shale can be treated as isotropic so far as wave propagation is concerned, at least when samples large compared to the interplane spacing are considered. This does not hold true at lower pressures, and is probably not true for dynamic fracture characteristics either. It is obvious that a simple linear fit in the u_s-u_p plane is not adequate to fit the data over the entire pressure range, particularly for the leaner samples. Such a fit is normal in shock wave work in the absence of phase changes or significant elastic effects. It is certain that phase changes known to exist in constituents of oil shale, such as dolomite⁽⁵⁾ and quartz,⁽¹⁾ play a role in determining the Hugoniot of the mixture. Since we are here primarily concerned with the behavior of oil shale at and below the in-contact pressures of the explosives, we will not consider these high-pressure anomalies, although they are of considerable intrinsic

interest. Figures 6 and 7 show the lower range of oil shale Hugoniot data for each of the six density ranges in the u_s-u_p and $P-\rho$ planes respectively. In this pressure range, a linear u_s-u_p Hugoniot of the form $u_s = C_0 + su_p$ would appear to be sufficient. The solid lines in these figures are not fits of the data, but rather calculations based on a model described below.

ANALYSIS

An analytic equation of state depending only on the density would obviously be of value for predicting the Hugoniot of oil shale of arbitrary kerogen content. In view of the nature of oil shale as mineral particles uniformly mixed with polymerized hydrocarbons, this material should behave much like a composite of unbonded dissimilar materials in its high pressure shock response. It has been shown that, for materials which have no chemical interaction between the constituents, it is possible to predict the Hugoniot of the mixture from the known equations of state of the components.⁽⁶⁾ The approach used is to interpolate pressure-volume Hugoniots at constant pressure on the basis of the volume occupied by the two components. Small thermal corrections are necessary because the components are heated differently upon shocking. This correction is most easily accomplished by performing the mixing calculation at a temperature of absolute zero and using the Mie-Grüneisen theory, with an effective Grüneisen parameter γ of the mixture, to account for shock thermal expansions. The resulting relation $E(P,V)$ for the mixture is then given by

$$E = E_H + (P - P_H)/\rho\gamma \quad (4)$$

with

$$\frac{1}{\rho_Y} = \sum m_i \left(\frac{1}{\rho_i \gamma_i} \right) \quad (5)$$

where the m_i 's are the mass fractions of the components. When combined with Eq. (3), the Hugoniot of the mixture is determined.

For oil shale, one component can conveniently be considered kerogen and the other considered as the remaining rock or mineral matrix, consisting of dolomite and other carbonates, feldspars, illites, quartz, and a number of minor constituents. Unfortunately, the Hugoniot of neither component is known. To define the Hugoniots of these materials, it is sufficient to specify the initial densities and the slopes and intercepts of a linear fit in the u_s - u_p plane. The densities of both components are known from x-ray work⁽³⁾ and are given in Table I. Also,

TABLE I. Hugoniot Parameters for the Constituents of Oil Shale

Material	ρ_0 (g/cm ³)	C_0 (km/s)	s	γ	C_p (erg/g-deg.K)
Rock Matrix	2.65	4.3	1.25	1.5	1×10^7
Ker gen	1.05	2.6	1.5	1.0	5×10^7

since the bulk moduli of both the rock and kerogen have been estimated by extrapolating the elastic constants determined by ultrasonic measurements to the pure end members, the Hugoniot zero-pressure intercepts of both components can be estimated quite accurately. The Hugoniot of the matrix can be determined from the data on lean, porous samples shown in Fig. 6.

Since this material can itself be considered as a particularly simple mixture of minerals and air, one need only assume a Grüneisen parameter γ and slope s in order to calculate the desired bulk density Hugoniot by a reversal of the mixing calculation described earlier. This has been done on the basis of known thermodynamic parameters for the components of the matrix and the relation

$$\gamma = \frac{3\alpha C_0^2}{C_p} \quad (6)$$

where α is thermal expansion, C_0 the bulk sound speed, and C_p the specific heat at constant pressure. The assumption $\gamma p = \text{constant}$, known to be valid for a large number of materials,⁽¹⁾ has also been used. The calculation has been restricted to the region below 20 GPa in order to avoid the complication of the dolomite phase change, which is rate dependent and ill-defined. The parameters which best fit the data are given in Table I.

Although in principle the same 'unmixing' calculation could then be used to determine the Hugoniot of the kerogen component by using the rock Hugoniot and that of any intermediate mixture, we could not achieve sufficient accuracy with this calculation and a different approach was taken. Extensive work at Los Alamos on the equations of state of polymers⁽⁷⁾ has shown that the zero pressure bulk modulus measured ultrasonically is generally not representative of the compressibility at only slightly higher pressures, a consequence of the van der Waals' nature of the interchain bonds. The calculated intercept for kerogen of 1.9 km/s is quite similar to that determined for other polymers at zero pressure, while a more typical experimental Hugoniot intercept lies in the range of 2.5 - 2.6 km/s. We have therefore chosen a slope and intercept for kerogen to agree with that of bulk polystyrene, a polymer with the same initial density and zero

pressure compressibility as kerogen. With this assumption, and reasonable choices for the Grüneisen parameter and specific heat of kerogen, we have performed the mixing calculation indicated earlier. Appropriate parameters for both components are shown in Table I, and calculated results below 200 kb are shown in Figs. 6 and 7 in the u_s-u_p and $P-V/V_0$ planes respectively. Here, the solid lines are theoretical predictions for the Hugoniot centered at the average density of each data set. The results are quite adequate to describe analytically the dynamic equation of state of oil shale of arbitrary kerogen content in this pressure range.

CONCLUSIONS

Using standard experimental shock wave techniques, we have obtained Hugoniot of Anvil Point oil shale as functions of richness and orientation in the pressure regime encountered in the near-field region of an explosion. The shock response was found to be sensitive to kerogen content but independent of bedding orientation relative to the direction of shock propagation. A two-component model combining the inferred dynamic parameters for the end members (kerogen and mineral matrix) is adequate to predict the Hugoniot of oil shale of any arbitrary composition. Hence, the Hugoniot, as for other material properties, can be ultimately uniquely related to the oil yield. Preliminary dynamic results from samples obtained from other sites in Colorado and Wyoming indicate that this is generally true within the accuracy required for predictive explosive rock breakage calculations.

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CAPTIONS

Fig. 1. Representative samples of oil shale used in this study. The figure shows different views of four samples used in the equation of state studies. At the top are relatively rich shales with a correspondingly small inter-plane spacing. The bottom pictures show samples with lower organic content and higher density; the lamellae are ordinarily spaced farther apart in this case. The samples on the right were cut such that the direction of shock propagation is perpendicular to the bedding planes, with the shock wave propagating upward.. Those on the left were oriented such that the shock wave runs parallel to the bedding planes, with the shock wave propagating normal to the plane of the picture. Inclusions such as that in the sample on the lower right are not unusual, and can account for some of the scatter in the data.

Fig. 2. $u_s - u_p$ Hugoniot data for oil shale of average density 2.13 g/cm^3 . Both orientations are shown, and it is obvious that there is but little effect of orientation on shock velocity.

Fig. 3. $p-p$ Hugoniot data for oil shale of average density 2.13 g/cm^3 . These data have been transformed from Fig. 2 by use of the Rankine-Hugoniot conservation relations.

Fig. 4. $u_s - u_p$ Hugoniot data for oil shale of average density 2.26 g/cm^3 . Again, both orientations are shown, and the differences between the two are well within the experimental scatter. A linear fit to these data lies slightly higher than that of Fig. 2, which is reasonable for a multicomponent material such as oil shale.

Fig. 5. $P-p$ Hugoniot data for oil shale of average density 2.26 g/cm^3 . These data are the Hugoniot transforms of the velocity data shown in Fig. 4.

CAPTIONS (cont)

Fig. 6. $u_s - u_p$ Hugoniot data for oil shale of varying density and for pressures below 20 GPa. The solid lines are theoretical calculations of the Hugoniots centered at the average density of each data set according to the model presented in the text. Although there is considerable scatter in the data because of variations in density even within each grouping, it is felt that the theoretical representation is quite adequate for design and specification of the stress field in the near-borehole region. The high-density data shown with the solid circles (●) lie quite low in this plane because of the high porosity (11%) of the samples. These data allowed extraction of the effective rock Hugoniot used for one end member in the calculation.

Fig. 7. $P - V/V_0$ Hugoniot data for oil shale below 20 GPa. Both the data and the theoretical calculations were transformed from Fig. 6 by use of the Rankine-Hugoniot equations. The calculations represent the data quite well in this plane, which does not necessarily follow from Fig. 6 unless the thermal contribution to the pressure is known accurately. It is felt that the highest set of data points indicate the beginning of the dolomite phase transformation.

10 mm

Figure 1

Figure 2

Figure 3

Figure 4

Figure 6

Figure 7