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MECHANICAL PROPERTIES OF ANNONA CHALK TO 3.8 GPa

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February 5, 1975

MASTER

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Prepared for U. S. Atomic Energy Commission under contract no. W-7405-Eng-48

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MECHANICAL PROPERTIES OF ANNONA CHALK TO 3.8 GPa

ABSTRACT

Pressure-volume (P-V) and uniaxial compression measurements have been made on Annona chalk to provide mechanical properties input for calculations of the response of this oil-bearing rock to a contained high-explosive detonation. During P-V measurements to 3.8 GPa, phase transitions were found at 0.5, 1.4, and 2.4 GPa. A permanent volume decrease of 13.6% was noted after unloading from maximum pressure; this is attributed to pore collapse below 0.3 GPa. Above 0.4 GPa, the P-V loading curve is very similar to that for water-saturated Indiana limestone. The bulk modulus is a very complicated function of pressure and ranges from 1.5 GPa at 0.15 GPa pressure to 75 GPa at 3.8 GPa pressure. In uniaxial compression tests up to 500 MPa confining pressure, the transition from brittle fracture to ductile flow occurred at about 25 MPa confining pressure. Because of work hardening in the calcite and progressive pore collapse with deformation, the shear strength at 3% axial strain increased from 14 to 100 MPa with increasing pressure. The tensile strength under atmospheric pressure varied from 1.4 to 2.0 MPa.

INTRODUCTION

MASTER

We have determined the mechanical properties of Annona chalk to provide input parameters for calculations of the response of this oil-bearing carbonate rock to a contained explosive detonation. The calculations are used to predict peak stresses, particle velocities, and wave velocities which will be compared with field measurements. Other parameters of interest include cavity radius, fracture radius, and permeability changes in the surrounding rock. Results of the laboratory

and field measurements will be incorporated into a joint LLL-industry experiment designed to study the effects of high-explosive fracturing on stimulation of a low-productivity reservoir.

PROCEDURE

Experimental Technique

The axes of the cylindrical samples were approximately parallel to the axis of the original well core. This core was perpendicular to the bedding plane of the formation.

Stresses are referred to an orthogonal coordinate system with σ_1 , σ_2 , σ_3 , as the maximum, intermediate, and least principal stresses, respectively, with compressive stress positive. The corresponding strains are ϵ_1 , ϵ_2 , ϵ_3 , with compression positive. Strain rates during the mechanical properties measurements were about 10^{-4} /s, and all tests were carried out at room temperature.

The pressure-volume (P-V) measurements were made up to 3.8 GPa using tin-jacketed samples, 11.7 mm diameter $\times$ 25.4 mm length. The tin served as a pressure-transmitting medium in a piston-cylinder apparatus. Experimental details are described elsewhere.¹ The volume change was then calculated from the piston displacement together with the equation of state for tin. Gold was used as a reference standard in reducing the data for the chalk to plots of P vs (V/V_0) . The chalk samples were weighed just prior to the experiments to assess weight changes due to loss of fluids and were reweighed after the tests.

The uniaxial deformation behavior was determined from a series of uniaxial compression tests at confining pressures to 0.5 GPa.^{2,3} Samples were 13 mm diameter $\times$ 26 mm length and were jacketed in thin-wall plastic tubing to exclude the confining pressure fluid during deformation.

After a minor correction for the strength of the jacket, the data were converted to differential stress ($\sigma_1 - \sigma_3$) vs ϵ_1 curves. Indirect tension tests (Brazil) were performed on similar sized cylinders under atmospheric pressure.

Starting Material

The samples were prepared from a single core, 65 mm diameter $\times$ 140 mm length taken from TIPCO* Noel D-4 at a depth of 472.7 m. This well is located in the NE quarter of S25, T21N, R15W, Caddo Parish, Louisiana.⁴

A mineralogical study by Borg⁵ shows that the core is partially recrystallized limestone containing mostly calcite but also quartz and clay. The calcite contains 17% fossil fragments and the grain size ranges from less than 1 to 1000 μm , with an average of 100 μm .

RESULTS AND CONCLUSIONS

Weight Changes

The weights of samples prepared for the P-V measurements were monitored while they were in storage. Since they were observed to gain weight in water-saturated air, they were later stored in a dry container to compensate for this increase. These results are given in Fig. 1 for four samples.

Another section of core, from which several samples had already been taken, was heated in a vacuum oven at 75°C for 90 h. A weight loss of

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Fig. 1. Percentage weight change vs time for Annona chalk samples 1, 2, 3, and 4. Final weighings before P-V experiments indicated by arrows.

7.8% was noted. In calculating the composition of the chalk (given in Table 1), we assumed that this weight loss is due to the water and volatile hydrocarbons in the sample. The total hydrocarbons were then calculated from this assumption together with the liquid composition results of Emerson⁴ and the mineralogical results of Borg⁵ (Table 1). The average specific volume $\bar{v}$ is calculated as $0.4381 \text{ m}^3/\text{Mg}$ and is the weighted sum of the specific volumes of the components. It therefore corresponds to a sample with no gas-filled porosity but with an interconnected liquid-filled porosity of 16.9% for the oil and 6.1% for the water.

Table 1. Composition of Annona chalk.

Component	wt%	vol%
Calcite, ^a CaCO_3	82.1	69.1
Quartz, ^{a,b} SiO_2	6.4	5.6
Clay minerals ^{a,c}	2.8	2.3
Oil ^{d,e}	6.0	16.9
Water, ^d H_2O	2.7	6.1
Average specific volume $\bar{v}_{\text{sp}} = 0.4381 \text{ m}^3/\text{Mg}$		
Average gas-filled porosity of samples $\bar{\eta} = 4.4\%$		

^aFrom Ref. 5.

^bAssumed to be α -quartz.

^cAssumed to be illite, with a density like that of illite from Maquoketa shale, Illinois, $\rho = 2.688 \text{ Mg/m}^3$. Ralph E. Grim, Clay Mineralogy, 2d ed. (McGraw-Hill New York, 1968), p. 467.

^dFrom Ref. 4. Liquid composition, 70 vol%; oil, 30 vol% H_2O ; density $\rho = 0.816 \text{ Mg/m}^3$.

^eAssumed to be n-tetradecylcyclopentane, $\text{C}_{19}\text{H}_{38}$, since this is a saturated hydrocarbon with $\rho = 0.816 \text{ Mg/m}^3$ at 25°C , a melting point of 9°C , and a normal boiling point of 327°C . Frederick D. Rossini et al., Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds (Carnegie Press, Pittsburgh, Pa 1953), p. 109.

P-V Measurements

The P vs (V/V_0) curves in Fig. 2 show the results of three experimental runs. The close approach of the loading and unloading curves at 1.5 GPa was observed during each experimental run. For each sample, friction determination runs agree well with the initial run above 1.5 GPa on the loading curve and over the whole pressure range on the unloading curve. Since inflections in the three individual curves occur at corresponding values of P , they are averaged with respect to (V/V_0) . These results are shown in Fig. 3 and summarized in Table 2. As shown in Fig. 3, the permanent volume decrease of the material after unloading is 13.6%. The loading curve indicates phase transitions beginning at about 1.4 and 2.4 GPa; the unloading curve indicates an additional one at about 0.5 GPa. All the transitions are diffuse; this may be caused by porosity changes, by pressure gradients arising from physical inhomogeneity, or by the overlapping of transitions arising from chemical inhomogeneity. Since on a volume basis the system is composed mostly of calcite, oil, and water, it is very inhomogeneous. Known freezing or other phase transition values for calcite, water, and some of the hydrocarbons found in oil are given in Table 3.⁶⁻¹⁰

Above 0.4 GPa the loading curve is quite similar to that for 100% saturated Indiana limestone,¹¹ which is shown in Fig. 3 for comparison. This suggests that in limestones, water content and porosity are most important in determining the shape and position of the curve.

Figure 4 shows that the bulk modulus, K , is a very complicated function of the pressure as would be expected from the P - V curve. The bulk modulus is less than that of 100% saturated Indiana limestone along the loading path and much less along the unloading path.¹¹ The differences are largest at low pressures where gas-filled porosity in the Annona chalk has the largest effect on its mechanical behavior.

Fig. 2. Pressure vs (V/V_0) for Annona chalk showing both loading and unloading paths for three experimental runs.

Fig. 3. Pressure vs (V/V_0) for Annona chalk showing average loading and unloading paths. The loading path for Indiana limestone (100% saturated) is also shown for comparison.

Table 2. Pressure vs (V/V_0) for Annona chalk.

Loading path		Unloading path	
(V/V_0)	Pressure, GPa	(V/V_0)	Pressure, GPa
0.9969	0.01	0.8652	0.01
.9844	0.05	.8631	0.05
.9595	0.10	.8608	0.10
.9274	0.15	.8584	0.15
.8988	0.20	.8561	0.20
.8665	0.30	.8504	0.30
.8542	0.40	.8437	0.40
.8479	0.50	.8388	0.50
.8433	0.60	.8354	0.60
.8396	0.70	.8324	0.70
.8364	0.80	.8294	0.80
.8334	0.90	.8266	0.90
.8306	1.00	.8238	1.00
.8277	1.10	.8209	1.10
.8243	1.20		
.8198	1.30	.8182	1.20
.8145	1.40	.8157	1.30
.8105	1.50	.8123	1.40
.8065	1.60	.8086	1.50
		.8051	1.60
.8033	1.70	.8009	1.70
.8002	1.80	.7959	1.80
.7975	1.90	.7893	1.90
.7948	2.00	.7820	2.00
.7921	2.10	.7772	2.10
.7883	2.20	.7729	2.20
.7832	2.30	.7682	2.30
.7772	2.40	0.7648	2.40
.7708	2.50		
.7649	2.60		
.7605	2.70		
.7575	2.80		
.7556	2.90		
.7540	3.00		
.7523	3.10		
.7508	3.20		
.7494	3.30		
.7480	3.40		
.7469	3.50		
.7457	3.60		
.7444	3.70		
0.7434	3.80		

An estimate of the liquid-filled interconnected porosity can be made from the specific volume of the samples after the P-V runs since most of the gas-filled interconnected porosity is removed during the runs. From the average specific volume of $0.4574 \text{ m}^3/\text{Mg}$ before the runs, the total specific volume loss of $0.0622 \text{ m}^3/\text{Mg}$, and the specific volume loss

Table 3. Phase transitions for calcite, water, and hydrocarbons at 25°C.

Pressure, GPa	Reaction	ΔV , %	Reference
<u>Inorganic components</u>			
0.6	$6\text{H}_2\text{O} + \text{CaCO}_3 \rightarrow \text{CaCO}_3 \cdot 6\text{H}_2\text{O}$	20.0	7, 8
0.98	$\text{H}_2\text{O}(\ell) \rightleftharpoons \text{Ice VI}$	7.0	9
1.43	$\text{Calcite I} \rightleftharpoons \text{Calcite II}$	1.3	10
1.74	$\text{Calcite II} \rightleftharpoons \text{Calcite III}$	3.5	10
2.23	$\text{Ice VI} \rightleftharpoons \text{Ice VII}$	5.7	9
<u>Organic components</u>			
<u>Normal straight chain hydrocarbons</u>			
0.04	$n\text{-Hexadecane } (\ell) \rightleftharpoons (\text{s})$	10.9	11
0.17	$n\text{-Dodecane } (\ell) \rightleftharpoons (\text{s})$	10.3	11
0.30	$n\text{-Decane } (\ell) \rightleftharpoons (\text{s})$	7.3	11
0.54	$n\text{-Octane } (\ell) \rightleftharpoons (\text{s})$	6.1	11
1.12	$n\text{-Heptane } (\ell) \rightleftharpoons (\text{s})$	4.3	11
<u>Other hydrocarbons</u>			
0.03	$p\text{-Xylene } (\ell) \rightleftharpoons (\text{s})$	16.4	11
0.03	$\text{Cyclohexane } (\ell) \rightleftharpoons (\text{s})$	4.2	11
0.07	$\text{Benzene } (\ell) \rightleftharpoons (\text{s})$	9.6	11
0.23	$o\text{-Xylene } (\ell) \rightleftharpoons (\text{s})$	7.1	11
0.30	$\text{Tetrahydronaphthalene } (\ell) \rightleftharpoons (\text{s})$	6.2	11
0.31	$\text{Styrene } (\ell) \rightleftharpoons (\text{s})$	4.9	11
0.34	$\text{Mesitylene } (\ell) \rightleftharpoons (\text{s})$	3.4	11
0.74	$\text{Cyclohexane I} \rightleftharpoons \text{Cyclohexane II}$	4.1	11

of $0.0055 \text{ m}^3/\text{Mg}^{-1}$ due to the slight loss of liquid during the runs, the final specific volume is calculated as $0.4002 \text{ m}^3/\text{Mg}$. This corresponds to a liquid-filled interconnected porosity of 2.5 vol% for water plus 8.8 vol% for oil, and a liquid concentration of 2.9 wt%.

Fig. 4. Bulk modulus vs pressure for Annona chalk showing average loading and unloading moduli, based on Fig. 2.

Up to one-third of the difference between these results and the corresponding ones in Table 1 may be due to errors in the determination of the total specific volume loss during the P-V runs. The rest may be due to variations in liquid concentration either in the original core or in sections of it that were treated differently during storage and sample preparation. The specific volume for all the samples used in the experimental work of this paper is between $0.4442 \text{ m}^3/\text{Mg}$ and $0.4762 \text{ m}^3/\text{Mg}$ and would correspond to a liquid concentration of 8.6 to 12.8 wt% if there were no gas-filled porosity. This is further evidence for the lack of homogeneity of the samples and presumably also of the original core as it was received in the laboratory.

Since the core depth was 437 m, corresponding to a lithostatic pressure of 0.010 GPa and a formation pressure (fluid) of about 0.004 GPa, it was probably fully saturated with liquid. Release of this pressure after the coring operation would cause expansion of gases originally in solution in the liquid phase in situ, with consequent loss of pore liquids in unknown amounts. Sampling problems of this sort exist for most rocks but are worst for those with liquid- and gas-filled porosity at high pressure.

If the Annona formation is saturated or nearly saturated with liquid, the P-V results of this investigation should be used with caution since liquid-saturated Annona chalk should behave similarly to the saturated Indiana limestone sample for which the P-V loading curve is given in Fig. 3. Such a difference in P-V behavior may substantially affect the predictions from calculational codes which use it as input.

Uniaxial Stress Measurements

Failure in all Brazil tests was characterized by tensile fracture only on a single plane oriented normal to σ_3 . However, in the compression tests, two distinct types of failure behavior were noted. At confining

pressures (σ_3) less than 25 MPa, loading was terminated when the chalk failed by through-going tensile and/or shear fractures at axial strains of less than 2%. In these samples, the tensile planes were normal to σ_3 and the shear planes were oriented at about 30° to σ_1 . Cohesion of the tested samples from all Brazil tests and of samples in compression at pressures less than 25 MPa was either lost or poor at best. Behavior in these cases is termed brittle. In tests conducted at confining pressures of 25 to 500 MPa, all samples could be deformed to at least 15% by either well distributed microfracturing or plastic flow in the calcite with no loss in cohesion.¹²⁻¹⁴ This behavior is termed ductile. For purposes of correlation of strengths from each test, we arbitrarily placed the transition region from brittle fracture to ductile flow at 3 to 5% permanent axial strain (ϵ_1).

The failure strengths from each of the compression tests are shown in Fig. 5 along with the inferred failure envelopes for 3 and 5% ϵ_1 in the ductile region. At low pressures, both surfaces became identical in the brittle regime.

The data summarized in Table 4 and illustrated in Fig. 5 show considerable scatter at 100 and 400 MPa. More tests were not possible because of lack of material. Both envelopes appear to be parallel with a monotonic decrease in slope with increasing σ_3 . The increase in shear strength with strain in the ductile region may be due to either work hardening in the calcite or the progressive decrease in porosity with deformation. Both mechanisms are well documented in the rock mechanics literature^{3,12-14} and both probably contribute to the observed behavior.

The Annona chalk from the 472.7-m depth is somewhat more ductile and slightly weaker than other porous limestones.^{11,15} The variable grain size, which indicates only partial recrystallization,⁴ coupled with the poor cementation, is probably at least partially responsible for these properties. The measured tensile strength (Table 4) of 1.4 - 2.0 MPa is low compared to that of other limestones.^{11,16}

Fig. 5. Shear stress [$\tau = (\sigma_1 - \sigma_3)/2$] vs confining pressure for Annona chalk calculated at 3 and 5% ϵ_1 . Brittle-ductile transition indicated by arrows.

Table 4. Summary of uniaxial stress tests. Annona chalk, compression normal to bedding.

Test type	σ_1 3% ϵ_1	σ_1 5% ϵ_1	σ_2	σ_3	τ^a 3% ϵ_1	τ 5% ϵ_1	Behavior
Brazil	4.2 ^b	b	0.1	-1.4	2.8 ^b	—	Brittle
Brazil	6.0 ^b	b	0.1	-2.0	4.0 ^b	—	Brittle
Uniaxial	27.5 ^b	b	0.1	0.1	13.8 ^b	—	Brittle
Compression	27.0 ^b	b	0.1	0.1	13.5 ^b	—	Brittle
Compression	58 ^b	b	10	10	23.8 ^b	—	Brittle
Compression	91	93	25	25	33	34.0	Ductile
Compression	135	147	50	50	42.7	48.5	Ductile
Compression	202	230	100	100	51.0	65.0	Ductile
Compression	170	170	100	100	35.0	35.0	Ductile
Compression	324	332	200	200	62.0	66.0	Ductile
Compression	434	441	300	300	67.0	71.0	Ductile
Compression	602	628	400	400	101.0	114.0	Ductile
Compression	498	496	400	400	48.9	47.9	Ductile
Compression	639	631	500	500	69.7	65.6	Ductile

^a

$$\tau = \frac{\sigma_1 - \sigma_3}{2}$$

^b Test terminated at 5% > ϵ_1 > 3%.

ACKNOWLEDGMENTS

We thank H. R. Washington and E. M. Lilley for preparation of samples and other assistance in the experimental work. This paper benefited greatly from reviews by A. Abey, B. Bonner, M. Costantino, A. Duba, and R. Schock.

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