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GAS PRESSURE FROM A NUCLEAR EXPLOSION IN OIL SHALE

R. W. Taylor

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GAS PRESSURE FROM A NUCLEAR EXPLOSION IN OIL SHALE

Abstract

In this report we estimate the quantity of gas and the gas pressure resulting from a nuclear explosion in oil shale. These estimates are based on the thermal history of the rock during and after the explosion and the amount of gas that oil shale releases when heated. We estimate that

for oil shale containing less than a few percent of kerogen the gas pressure will be lower than the hydrostatic pressure. A field program to determine the effects of nuclear explosions in rocks that simulate the unique features of oil shale is recommended.

Introduction

The use of nuclear explosives to fracture oil shale has been under consideration for more than 10 years. The idea developed into an in situ oil-recovery scheme called Project Bronco, a joint effort of the U.S. Bureau of Mines and the Lawrence Livermore Laboratory.¹ Recently the idea was reconsidered as Project Utah,² but neither of these projects was carried out.

Because of the recent increase in the value of oil, the recovery of oil from shale is more attractive than ever. Although a large amount of oil shale can be mined by conventional techniques, most of the vast oil shale reserves in the United States are too deep to be recovered in this way. According to a recent study^{3,4} that takes into account advances in the use of nuclear explosives since the time of Project Bronco, the use of nuclear explosives appears to be the least expensive way of recovering oil from deep shale.

What stands in the way of starting a program to find out whether it pays to use nuclear explosions to recover oil from oil shale? The principal technical problem seems to be safety. Before the first nuclear explosion can be detonated in oil shale, we must be certain that the radioactive products of a nuclear explosion will remain underground. After some underground nuclear explosions, escaping gas has brought solid and gaseous radioactive materials to the surface. The greater the amount of gas released by a nuclear explosion, the more likely it is that some will escape to the surface. The amount of gas released is related to the amount of volatile matter in the rock. Oil shale contains organic matter, which releases gas when heated; it also contains water and carbonates. Figure 1 shows how much more gas is released at 1000°C by oil shales than by other rocks.

In this report we estimate the pressure that will result from a nuclear

Fig. 1. When heated to 1000°C, oil shale from the Green River Formation releases more noncondensable (dry) gas than most other kinds of rock. The shaded areas represent the ranges for the various kinds of rock.

explosion in oil shale. The estimate is based on our current understanding of the amount of rock heated by a nuclear explo-

sion and on laboratory determinations of the amount of gas released by heated oil shale.

Containment of Nuclear Explosions

"Containment" is jargon for the technique of keeping underground the gases released from rock by nuclear explosions. Although the bulk of it is not radioactive, this gas can sweep radioactive gases and solid particles to the surface, creating a possible health and safety hazard to workers in the area. Under certain wind conditions, the rapidly released radioactive gas may be swept across international boundaries, thus violating international agreements. In the past, containment failure has occurred in two ways: dynamic venting and seepage.

Dynamic venting is the rapid loss of hot gas, mostly steam, during the first 30 min or so after a nuclear explosion. This kind of venting occurs mostly through a few fissures that may or may not have been present before the explosion.

The scaled depth of burial is perhaps the most important factor in preventing dynamic venting. Experience has shown

that explosions will generally be contained at scaled depths of $>120W^{1/3}$ meters, where W is the yield in kilotons.*

Dynamic venting cannot occur in a dry silicate rock free of carbonates and other volatile materials because all the gas is condensed to a liquid at temperatures of about 3000°C. Cooling to 3000°C is rapid because of the loss of heat by radiation to the surrounding cooler rock.

In an experiment named Salmon, a nuclear explosion was detonated in pure salt. Because of the lack of volatile materials a vacuum was found when the cavity was drilled into.⁵ In contrast, an earlier nuclear explosion in a salt formation that contained beds of wet clay (the Gnome experiment) produced dynamic

*In the International System of Units (SI), the unit for energy is the joule. A 1-kt nuclear explosion corresponds to 4.18×10^{12} J, or 4.18 terajoules (TJ).

venting of steam for about a day after the explosion.⁶

Just how much volatile material a rock can contain before venting occurs is not well known even for an area as well studied as the Nevada Test Site. Presently, the testing of nuclear explosions is not conducted at sites containing more than about 5 wt% CO_2 as carbonates.

Inhomogeneities in rock, such as faults, joints, and bedding planes, can be natural zones of weakness, but close to the explosion they seem to be sealed by shock waves. It is very difficult to quantify the integrity of the rock at the site of an explosion.

Emplacement engineering has been developed to prevent dynamic venting in cases where the volatile-matter content of the rock is below established empirical limits. It has been difficult and expensive to learn to avoid dynamic venting due to failure of stemming and other man-made structures, particularly in the case of shallow low-yield explosions and in the case of explosions emplaced in tunnels. Gas leaks along cables used to be common. They are avoided now by cable blocks, a

series of gasket-like seals. Gas leaks were generally slow leaks of gas called seeps.

Seepage is the slow loss of gas to the atmosphere from the site of a nuclear explosion. The gas is at a temperature below 100°C and is probably composed mostly of CO_2 , H_2 , and O_2 , the most common noncondensable gases found after nuclear explosions in most kinds of rock. A positive gas pressure persists after a nuclear explosion when noncondensable gas is generated. Some kinds of rock formations, particularly the low-density tuff and alluvium at the Nevada Test Site, have large intrinsic permeabilities and porosity. In such cases there are many paths open to the surface through which gas can flow if a gas pressure persists. Large volumes of radioactive gas may displace the air in the rock formations and itself remain below the surface. The air is not detected because it seeps out of the ground over a wide area. When the volume of noncondensable gas exceeds the storage volume--both the intrinsic voids in the rock and the empty void volume--seepage may occur, depending on the permeability of the rock to gas.

Can Containment in Oil Shale Be Predicted?

From field experience we have learned to avoid dynamic venting and seepage by restricting the sites of nuclear explosions to certain families of rocks: granite, basalt, dry tuff, and low-volatile (low-carbonate) alluvium. In order to apply what we have learned to oil shale, certain critical factors must be considered, including the amount of rock heated, the temperature to which it is heated, and the duration of the heating. These things

together constitute the thermal history, which is probably the least known aspect of containment. We must also know the amount and composition of gas released from a rock subjected to a certain thermal history. This is called the "volatile yield of the rock." From these two factors we can estimate the total amount of gas produced.

To estimate the gas pressure, we must know (1) the void volume available underground for the gas, (2) the temperature of

the gas in this void, and (3) the permeability of the surrounding rock. If the gas pressure exceeds the lithostatic pressure for very long, fracture of the rock will probably occur. (This is the basis for using fluid pressure to crack rock in oil and gas production.) A gas pressure higher than the hydrostatic pressure may be safe in one rock but lead to displacement of water and gas release in another.

The oil shale in the Piceance Creek Basin in Colorado is very dense and impermeable at the top of the Parachute Creek Member and at the edges of the basin.⁹ Deeper in the same member, near the center of the basin, is a leached zone that may be very permeable to gas, particularly if it is dewatered (as it must be for retorting).³ At such a site a high gas pressure probably cannot develop. The feasibility of fracturing oil shale by nuclear explosions will probably be tested at the edges of the basin, where the permeability is low enough to prevent chimney flooding. At such sites the permeability may be too low to allow chimney depressurization by subsurface gas flow. In any case, we cannot be sure of the feasibility of fracturing oil shale by nuclear explosions until further well-instrumented containment experiments are conducted at the Nevada Test Site or elsewhere in an impermeable carbonate-rich rock, preferably a marlstone.

We can predict the storage volume available to the gas, at least the explosion-produced void volume, to within about 20%. However, we cannot predict the amount of gas that will be released by a nuclear explosion with nearly the same accuracy, partly because we are not certain

about the amount of rock heated by a nuclear explosion or the quantity of gas released by rocks on heating.

We have been able to measure the amount of gas, mostly CO_2 , released by heat in the case of the three gas-stimulation nuclear experiments Gasbuggy, Rulison, and Rio Blanco. In the case of both Gasbuggy and Rulison, early estimates of the total amounts of CO_2 based on measurements of the concentrations of radioactive gas tracers have subsequently been confirmed by observations of actual gas production.⁷ In the Rio Blanco experiment, the amount of gas released has been calculated from measurements of the concentrations of gas tracers, but the gas production to date has been limited.

The yield of volatile matter from Rio Blanco rocks has been measured by laboratory pyrolysis experiments. By comparing the amount of gas released by laboratory pyrolysis to the amount of pyrolysis-produced gas found after the explosion, we have estimated the amount of rock heated and degraded by the explosion.⁸ These measurements tend to confirm the theoretical model for the thermal history of nuclear explosions presented in Section IV.

Recent attempts to predict and measure the amount of gas released by nuclear explosions at the Nevada Test Site have been disappointing. The rocks are often very heterogeneous, making prediction difficult. Large variations in gas-tracer concentrations have been observed between samples taken from the same hole. Postexplosion gas samples withdrawn from tubes emplaced before the explosions indicate that the radioactive tracer gases are not uniformly mixed with the gas released from the rock by the heat of the explosion.

Thermal History

The heating and melting of rock by nuclear explosions have been reviewed elsewhere.¹⁰ Butkovich¹¹ has calculated the temperature rise as a function of distance for a nuclear explosion of given yield in silicate rock of various densities. His work was based on experimental Hugoniot-type (shock) density-pressure measurements.

A low-density (i.e., porous) silicate rock attenuates the shock of an explosion in a shorter distance than does a high-density (nonporous) rock of the same type. Knowing the melting point of a rock, Butkovich¹¹ calculated the distance out to which rock is melted by the passage of a shock as a function of preshot rock density. Out to this point the rock is heated by the shock to temperatures above the melting point. From the heat capacity of rock, the heat of melting, and other

data, Butkovich calculated the total quantity of heat initially deposited in rocks at the melting point and above as a fraction of the total explosive energy. He concludes that it is this fraction that is available to heat additional rock to the melting point. It is this quantity of heat that we assume to be available to heat oil shale, as shown later. First we must estimate the energy fractionation for oil shale from calculations for silicate rock.

The assumption is made that it is the porosity of a rock, rather than density, that determines the initial disposition of shock-wave energy. Table 1 shows Butkovich's data for a silicate rock with the same melting point as oil shale ($\sim 1200^\circ\text{C}$).^{*} The data were tabulated by

^{*}Jackson¹² found that oil shale from the Piceance Creek Basin started to melt at about 1150°C and was completely melted at 1227°C .

Table 1. Effect of silicate-rock density on the fraction of energy of a 4.18-TJ nuclear explosion deposited by shock in rock at temperatures above the melting point (1200°C).

Density, (g/cm ³)	Porosity ^a (%)	Energy fraction deposited
1.4	50.0	0.71
1.6	42.8	.69
1.8	35.7	.62
2.0	28.5	.55
2.2	21.4	.47
2.4	14.3	.39
2.6	7.1	.30
2.8	0	0.20

^aVolume percent porosity = $100[1 - (\rho/2.8)]$. The crystalline densities of quartz diorite and granite are 2.8 and 2.7, respectively.

Fig. 2. The higher the porosity of a rock, the greater the fraction of the explosive energy of a nuclear explosion that is taken to heat rock to melting temperatures and above. Shown here is the relation for a rock with the melting temperature of oil shale (1200°C).

Butkovich in terms of density and energy fractionation normalized to a 4.18-TJ explosion. The porosity was calculated from the density. Figure 2 is a plot of energy fractionation versus rock porosity.

Although oil shale is a very porous rock, most of its pores are filled with kerogen. (The bulk density of oil shale decreases from 2.4 to 1.8 as the amount of kerogen increases from a few percent to 34 wt%.) We know that kerogen is less compressible than air, but more compressible than void-free (solid) rock. The shock heating of a rock in which some fraction of the pores is filled with water (or kerogen) has not yet been calculated.

For a rough approximation, a kerogen-filled pore in the inorganic matrix of oil shale is assumed to have the same heating effect on shock compression as a pore of half the volume filled with gas. Because the density of kerogen is approximately

1.0 g/cm^3 and the density of the inorganic part of oil shale is about 2.6 g/cm^3 , an oil shale containing 5 wt% kerogen contains about 12 vol% kerogen. The effect of the kerogen-filled pores on shock heating in this example is assumed to be the same as that of a porosity of 6 vol%, 1.7 times the weight percent of kerogen.

The gas-filled-pore volume of the oil shale from the Mahogany Zone of the Piceance Creek Basin in Colorado is about 3%, according to laboratory saturation¹³ and compression¹⁴ measurements. Since the saturation method measures only interconnected pores, the results tend to be minimum values. The saturation method applied to 11 samples gave an interconnected-porosity range from 0.2 to 12%, with an average of 2.9%. The compression method consisted of measuring the net volume change of oil shale as a result of static compression to 4 GPa (40 kbar) followed by release to 0.1 MPa. The average volume decrease corresponded to a loss of porosity of 2.6% (the range for five samples was 0.6 to 4.4% porosity).

These laboratory determinations of porosity should probably be considered to be maximum values because the oil-shale samples may have partly dried out during handling before the measurements were made. They may not represent the porosity of oil shale *in situ*, particularly that of oil shale below the water table.

The percent porosity of oil shale that is effective in increasing the localized shock heating, called the effective porosity P_e , is probably in the range

$$P_e = 1.2 (\text{wt\% kerogen}) + (2 \pm 1). \quad (1)$$

In order to estimate the amount of energy available for heating, gas release, and melting of the rock, it is necessary to know the hydrogen content of the shale. (We also, of course, must know the hydrogen content because of the volatility of the kerogen.) Early in this work it became clear that, the richer the oil shale, the more volatile material it contained and the more likely that containment could be a problem. In the section "Sites for a Nuclear Explosion in the Piceance Creek Basin" we discuss the composition of oil shale at some sites that seem suitable for a nuclear explosion. At this point it must be noted that there are many such sites (i.e., sites containing 5 wt% kerogen and less). The effective porosity of an oil shale containing 5 wt% kerogen is, by Eq. (1),

to 0.1. According to Fig. 2, the fraction of the energy of a nuclear explosion available for degassing and melting a shale with P_0 in this range is 0.3 ± 0.05 . For a nuclear explosion of yield M , in an oil shale containing 5 wt% kerogen, the quantity of heat available to heat shale,

$$Q = (0.3 \pm 0.05) M. \quad (2)$$

In order to estimate the total amount of gas released by a nuclear explosion, we must estimate the amounts of rock heated to various temperatures. In doing this we assume that the only heat available to raise the temperature of the rock is Q . The amount of oil shale that can be heated to some temperature T by this quantity of heat depends on the heat capacity of the oil shale, the ambient temperature, and all the various heats of transitions (e.g., melting and decomposition) that oil shale undergoes when heated.

The calculation is carried out in a way that to a certain extent simulates the events following an underground nuclear explosion. First the mass of oil shale that can be melted by Q is calculated. We know from experimental observations that when oil shale is melted it loses all of the CO_2 from carbonates. In this case we must take into account not only the heat necessary for fusion (ΔH_f) but also the heat that will be consumed by the decomposition of carbonates (ΔH_d). The zone in which melting occurs is called zone 1.

One is inclined to think of these zones as certain volumes of rock having a certain general shape (e.g., spherical shells). However, because we are uncertain about chimney formation, rubble size, and the like, it is best to consider the zones as simply a certain amount of rock in a certain temperature interval. The total mass of oil shale that can be melted (M_1) by a quantity of heat Q is formulated as follows:

$$M_1 = \frac{Q}{\int_{T_a}^{T_m} C_p dT + F_1 K \Delta H_f + \Delta H_d} \quad (3)$$

where

M_1 = mass of oil shale in zone 1, the mass that can be heated to 1200°C and melted by Q .

T_a = ambient temperature, 30°C .

T_m = melting temperature, 1200°C .

C_p = heat capacity, assumed to be constant, $\approx 1.04 \text{ J/g}^\circ\text{C}$ ($0.25 \text{ cal/g}^\circ\text{C}$).

F_1 = fraction of the total carbonate CO_2 in the oil shale in zone 1 released at the temperature of zone 1 (F_1 is a parameter determined by experiment, as discussed under "Release of Gas from Heated Oil Shale"). At the melting temperature of oil shale, $F_1 = 1$. It decreases to 0 at about 300°C .

K = weight fraction of CO_2 in the oil shale. It will be shown that an average value for oil shale is 0.15.

ΔH_r = heat required to release CO_2 from the carbonates in oil shale.

According to our x-ray diffraction measurements, the principal reaction in oil shale that liberates CO_2 on long-term heating is the reaction between dolomite and quartz to form diopside¹³:

The heat required for reaction (4) is

$$\Delta H_{r-4} = 1.77 \text{ kJ/g } \text{CO}_2 \text{ (423 cal/g } \text{CO}_2\text{)}.$$

The exact reaction depends on the mineral composition of the shale. A shale containing only calcite will release CO_2 by the reaction¹³

The heat required for reaction (5) is

$$\Delta H_{r-5} = 2.00 \text{ kJ/g } \text{CO}_2 \text{ (447 cal/g } \text{CO}_2\text{)}$$

ΔH_f = heat of fusion of oil shale, about 334 J/g (80 cal/g of oil shale).

In calculating the amount of oil shale heated to other (lower) temperatures, the assumption is made that additional oil shale is added to the melted rock by collapse, "blowoff," and the like, in such a way that the temperature is kept nearly uniform. This assumption will not hold if large blocks of oil shale fall into the hot region, as they will not be heated uniformly except after a long time. For this reason the amount of rock that is heated to some temperature calculated by the method outlined here might be considered a maximum.

The mass of oil shale heated to temperatures below the melting point is calculated in 100°C temperature zones. In zone 2, which extends from 1050 to 1150°C , the average temperature $\bar{T}_2$ is 1100°C . The mass of oil shale in zone 2 is

$$M_2 = \frac{Q_1 - M_{1,\text{CO}_2} \Delta H_r}{\int_{T_a}^{\bar{T}_2} C_p dT + F_2 K \Delta H_r} \quad (6)$$

Here the term $M_{1,\text{CO}_2} \Delta H_r$ is the amount of energy lost due to the decomposition of CO_2 in the preceding zone (M_{1,CO_2} is the mass of CO_2 lost in zone 1), F_2 is the fraction of the total carbonate CO_2 in the oil shale in zone 2 released at the temperature of zone 2, and the other terms are as defined in Eq. (3). The term ΔH_f does not appear in any zone after zone 1 because no additional oil shale is melted.

For any zone i except zone 1

$$M_i = \frac{Q_{i-1} - M_{i-1,\text{CO}_2} \Delta H_r}{\int_{T_a}^{\bar{T}_i} C_p dT + F_i K \Delta H_r} \quad (7)$$

On the basis of economic considerations, it appears that an acceptable explosive yield³ for oil recovery in the Piceance Creek Basin is roughly 418 TJ. For such an explosion, Q, by Eq. (2), is equal to 125 TJ. Table 2 shows the amount of oil shale, containing 15 wt% CO₂ and 5 wt% kerogen, that can be heated to various temperatures by a 418-TJ explosion. It also shows the energy lost by the release of CO₂ as well as the amount of CO₂ released per zone, as explained in the next section. Figure 3 is a bar graph of the mass of oil shale heated to various temperatures.

Fig. 3. Amount of oil shale heated to various temperatures by a 418-TJ nuclear explosion. Ambient temperature is assumed to be 30°C, and the shale contains 15 wt% CO₂ and 5 wt% kerogen.

Table 2. Amount of oil shale, containing 5 wt% kerogen and 15 wt% CO₂ as carbonates, heated to various temperatures by a 418-TJ nuclear explosion and the amount of CO₂ released.

Zone	Temperature range (°C)	Mass of shale in zone, M _i (10 ⁹ Gg)	M _i - M _{i-1} (10 ⁹ Gg)	F _i ^a	Incremental CO ₂ released ^b (10 ⁹ Gg)	Energy lost by CO ₂ release (TJ)	Energy available in each zone (TJ)
1	1150-1250	69.0	69.0	1.0	10.4	18.3	125.4
2	1050-1150	77.7	8.7	1.0	1.30	2.31	107.1
3	950-1050	82.2	4.5	1.0	0.680	1.20	104.8
4	850-950	87.8	5.6	1.0	0.84	1.49	103.6
5	750-850	96.0	8.2	0.99	1.22	2.13	102.1
6	650-750	108.0	12.0	0.86	1.55	2.75	99.9
7	550-650	138.4	30.4	0.41	1.87	3.31	97.1
8	450-550	183.9	45.5	0.08	0.55	0.97	93.8
9	350-450	241.2	57.3	0	0	0	92.8
10	250-350	330.5	89.3	0	0	0	92.8

^aFraction of the total (carbonate) CO₂ in the oil shale in zone 1 released at the temperatures of zone 1 (Fig. 5).

^bThe total amount of CO₂ released (the sum of this column) is 18.4 × 10⁹ g, or 418 × 10⁶ moles.

Release of Gas from Heated Oil Shale

In the preceding section an estimate was made of the amount of shale heated to various temperatures by a nuclear explosion. This section deals with the amount of gas released by oil shale when it is heated.

Oil shale contains three components that yield volatiles: water, kerogen, and carbonates. When oil shale is heated, gas is released at temperatures from 100 to 1200°C. Up to about 250°C, the principal gas released is steam. From 250 to 530°C, kerogen is converted to hydrocarbon gas and char. Most of this hydrocarbon gas will condense to oil if it is cooled. The remaining gas is H_2 , CH_4 , other light hydrocarbons, CO_2 , and CO. At temperatures above about 530°C, carbonates decompose, releasing CO_2 . The equilibrium CO_2 pressures that can be generated by the thermal decomposition of carbonates in oil shale are shown as a function of temperature and carbonate mineralogy in Fig. 4. At temperatures above 800°C, CH_4 and other hydrocarbons decompose to solid carbon (char) and hydrogen. Also above about 800°C, carbon may be gasified by reactions with CO_2 or H_2O .

A series of experiments and calculations have been made to determine the amount of gas that is liberated from oil shale by these various processes. This work is presented in a complementary report.¹⁵ Samples of rich and lean oil shale were heated in closed vessels at various temperatures and pressures for various times, and the amount and composition of gas released were measured. The decompositions of kerogen and carbonates

Fig. 4. Equilibrium CO_2 pressure for the thermal decomposition of calcite ($CaCO_3$), dolomite [$CaMg(CO_3)_2$], and mixtures of calcite, quartz (SiO_2), and wollastonite ($CaSiO_3$). Pressures that can be generated by the thermal decomposition of the mixture of dolomite and silicates in oil shale probably are between the curves for dolomite and wollastonite.

were more or less independent of each other. In other words, the fraction of the total carbonates decomposed after a certain amount of time at some temperature is about the same for rich or lean oil shale. The same is true for kerogen decomposition. The results are shown in Figs. 5 and 6.

The thermal decomposition of the carbonates in Green River oil shale is shown in Fig. 5. Curve A is for oil shale heated in its own decomposition products

Fig. 5. The fraction of carbonates in oil shale decomposed after heating for ~1000 hours. The broken curve represents steam-enhanced low-temperature decomposition.

for ~1000 hours. Curve B is an estimate of the low-temperature enhancement of carbonate decomposition by steam at high pressures.¹⁵ Such conditions are possible in the case of limited or delayed chimney collapse.

Figure 6 is an estimate of the amount of noncondensable (dry) gas that may be produced from the kerogen in Green River oil shale, depending on the environment in which it is heated. For example, if oil shale is heated to 1200°C and kept at that temperature, most of the kerogen will form oil (if there is a cool place for it to condense) and char; the amount of gas released is shown by curve A-B. If oil shale is heated to 1200°C and there is no place for oil to condense, the hydrocarbon gas will be completely pyrolyzed to char and hydrogen (curve A-C). It is also probable that the char will react with CO₂ from the decomposition of carbonates to form CO (curve A-D). If an abundant sup-

Fig. 6. Amount of noncondensable gas released by kerogen as a function of temperature. Curve A-B is for the case where the kerogen produces char and oil. The oil collects in the cool part of the chimney, and the char avoids further chemical reaction. Curve A-C represents the case where the kerogen is pyrolyzed to H₂ and char at high temperatures, and thus no oil escapes. Curve A-D represents the reaction of char with CO₂ to form CO at high temperatures. Curve A-E is for the case where char reacts with steam to form H₂ and CO.

ply of steam is present, char may react with it to form H₂ and CO (curve A-E).

These possibilities are formulated in Table 3.

Each curve in Fig. 6 is a model for various conditions that may prevail in the chimney after a nuclear explosion. It is possible that steam will contact hot char. Curve A-E is used in conjunction with the thermal history (see "Thermal History") to estimate the maximum amount of gas that can be generated by kerogen in oil shale heated to any given temperature.

Table 3. Gas generation by the pyrolysis and reactions of kerogen.

Model ^a	Formulation ^b	Net production of noncondensable gas, T ≈ 1200°C (moles per kg of kerogen)
A-B	$\text{CH}_{1.6} \rightarrow \text{oil} + \text{C} + \text{H}_2 + \text{CH}_4 + \text{C}_2\text{H}_6 + \dots$	14
A-C	$\text{CH}_{1.6} \rightarrow \text{C} + (1.6/2)\text{H}_2$	58
A-D	$\text{CH}_{1.6} + \text{CO}_2 \rightarrow 2\text{CO} + (1.6/2)\text{H}_2$	132
A-E	$\text{CH}_{1.6} + \text{H}_2\text{O} \rightarrow \text{CO} + (3.6/2)\text{H}_2$	205

^aSee Fig. 6.^bHere $\text{CH}_{1.6}$ is used as an approximation for the composition of kerogen and C represents char.

Sites for a Nuclear Explosion in the Piceance Creek Basin

The best available sites for the application of nuclear explosions to the economic recovery of oil from shale seem to be directly below the rich beds of shale deep in the Parachute Creek Member of the Green River Formation. Collapse of the void blasted by the explosive will create a vertical cylinder of rubble in which retorting can be carried out.³ In order to evaluate the containment of the explosion-produced gases, we need to know the content of components that yield volatiles.

Table 4 and Fig. 7 show the relation between the carbonate and the organic matter content of shale samples collected deep in the basin and from surface outcrops that probably represent lean zones within the formation. For comparison, the compositions of a suite of samples from the Anvil Points Mine and a sample of shale from the Mahogany Zone of upper Piceance Creek are also given. The CO_2 content was

measured by the evolution of CO_2 gas when

The amount of organic matter in the shale is much more variable than the CO_2 content. Thick zones containing less than 10 wt% organic matter are common deep in the basin, and locations containing less than 5 wt% organic matter have been found immediately below rich shale; an example is a horizon 46 m thick along upper Piceance Creek at the eastern side of the basin (see Fig. 7).

The water content of fresh oil shale is probably in the range 1 to 3 wt% regardless of the kerogen content.¹⁵⁻¹⁷ The amount of water reported in chemical analyses depends on the temperature to which oil shale is heated during the analysis.¹⁵⁻¹⁷

It appears that we can be assured of sites for nuclear explosions with about 5 wt% organic matter; the carbonate CO_2 content will be near 15 wt%, and the water content will be about 2 wt%.

Table 4. Carbonate and organic matter content of oil-shale samples collected near the base of the Parachute Creek Member of the Green River Formation, the Anvil Points Mine, and the Mahogany Zone of the Piceance Creek Basin, Colorado.^a

Location	Depth (m)	CO ₂ (wt%)	Organic matter ^b (wt%)
Rio Blanco E-01 (composite samples)	640.1 to 670.6 670.6 to 701.0 701.0 to 731.5 731.5 to 762.0 762.0 to 792.5 792.5 to 823.0 823.0 to 853.5	9.49 11.04 12.26 11.85 10.43 15.55 14.64	11.5 10.0 8.8 3.6 1.2 1.9 1.9
Bronco (composite samples)	561.4 to 793.4 854.5 to 868.7 908.3 to 929.7 955.6 to 955.9	16.1 11.8 9.93 15.1	18.0 17.1 6.9 5.1
Lean zone L-5, lower Piceance Creek	Surface out- crops (15 m thick)	12.25	2.9
Garden Gulch Formation, lower Piceance Creek	Surface out- crops (15 m thick)	11.3	8.7
Upper Piceance Creek, lean zone	Surface out- crops (46 m thick)	13.6	1.2
Anvil Points Mine	Mahogany Zone	22.0 13.8 11.6 22.0 17.9 13.5	7.1 25.8 29.4 15.9 14.2 24.0
Mahogany Zone, upper Piceance Creek	Surface	14.1	18.7

^aAll analyses were performed at LLL.

^bOil yield is generally expressed as gallons per ton, which is approximately equal to 1.52 times the organic content in weight percent.¹⁶

Fig. 7. Volatile content of selected oil-shale samples from the Green River Formation. The weight percent of CO₂ is measured by the release of CO₂ by acid. The variation in the organic content is greater than the variation in CO₂ content. Sites deep in the basin containing less than 5 wt% organic material are common.

Amount of Noncondensable Gas Released from Typical Lean Oil Shale by a Nuclear Explosion

The production of CO₂ from oil shale has already been estimated in Table 1. The estimate was based on the amount of shale heated to various temperatures (Table 2 and Fig. 3) and the experimental factor F, which is the fraction of the total amount of CO₂ released as a function of temperature (Fig. 5). The total amount of CO₂ released by a 418-TJ nuclear explosion from an oil shale containing 15 wt% CO₂ is estimated to be 18.4×10^9 g (418×10^6 moles).

This estimate is based on curve A in Fig. 5. If the steam pressure is high, CO₂ is released at lower temperatures than without steam, as shown by curve B. The total amount of CO₂ released in the pres-

ence of steam is 22×10^9 g, 16% more than the amount released without steam. Figure 8 shows the total amount of CO₂ released from each temperature zone, including the increment caused by steam.

The production of gas from kerogen pyrolysis and reactions can also be estimated in a similar way. The amount of noncondensable gas released per kilogram of kerogen is given in Fig. 6. The various curves represent various models, as explained under "Release of Gas from Heated Oil Shale." Curve A-E may be the appropriate curve for lean oil shale. It represents the maximum amount of noncondensable gas that can be generated from

Fig. 8. Amount of CO_2 released from an oil shale containing 15 wt% CO_2 by a 418-TJ nuclear explosion. The steam-enhanced release of CO_2 at low temperatures is indicated. No CO_2 is released by rocks heated to temperatures below $\sim 200^\circ\text{C}$.

kerogen. It takes into account the reaction of kerogen with steam at high temperatures to form H_2 and CO . The total amount of noncondensable gas generated from kerogen is estimated in Table 5. As before, a 418-TJ explosion is considered, and the first four columns in Tables 5 and 2 are the same. For convenience, an oil shale containing 1 wt% kerogen is assumed. The total amount of gas is 189×10^6 moles.

In the case of lean shale, the amount of gas evolved from kerogen is probably proportional to the kerogen content. Typical oil shale contains about 15 wt% CO_2 , and 418×10^6 moles of CO_2 are released by a 418-TJ explosion. Kerogen can contribute more gas than the carbonates when the kerogen content is in excess of 2.2 wt% (approximately 3.4 gal/ton as determined by Fischer assay, a standard distillation).

Table 5. Amount of oil shale heated to various temperatures by a 418-TJ nuclear explosion and amount of noncondensable gas released from kerogen in an oil shale containing 1 wt% kerogen.

Zone	Temperature range ($^\circ\text{C}$)	M_i (10^9 Gg)	$M_i - M_{i-1}$ (10^9 Gg)	Gas evolved per kilogram of kerogen ^a (moles)	Incremental increase in gas in zone (10^6 moles)
1	1150-1250	69.0	69.0	195	134
2	1050-1150	77.7	8.7	170	15
3	950-1050	82.2	4.5	120	5.4
4	850- 950	87.8	5.6	78	4.4
5	750- 850	96.0	8.2	50	4.1
6	650- 750	108.0	12.0	35	4.2
7	550- 650	138.4	30.4	25	7.6
8	450- 550	183.9	45.5	14	6.4
9	350- 450	241.2	57.3	10	5.7
10	250- 350	330.5	89.3	-	<u>1.8</u>

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^aFrom curve A-E in Fig. 6.

Chimney Size and Temperature

The pressure produced by the gas in the void volume created by a nuclear explosion depends on the temperature of the gas and the gas composition (gas compressibility). For the first few days, the temperature of the gas will depend mostly on the amount of rubble that is formed and the fraction of the heat of the explosion that is transported to the rubble by the gas. At present we are not sure how much rubble will be formed by a nuclear explosion in oil shale. Estimates can be made on the basis of available experience in other kinds of rock, as correlated by Butkovich and Lewis.¹⁸ They have obtained an empirical relation that suggests that the larger the void volume created by an explosion, the lower will be the bulking factor and the more rubble will form until the rubble column, the chimney, is bulked full. The relation is

$$B = 4.62R_c^{-0.927} \quad (8)$$

where B is the volume fraction of voids in the rubble column (bulking factor) and R_c is the cavity radius in meters. A 418-TN nuclear explosion at a depth of 400 m is expected to create a spherical void about 50 m in radius.¹⁸ From Eq. (8), the bulking factor for the rubble created by the collapse of such a spherical void is 0.123. The bulking factors estimated in this way are average values; gradients within a chimney may occur.

There have been several nuclear explosions that produced cavities about 50 m radius. Bulking factors of 0.07 to 0.18 were calculated from measurements of chimney

height and the volume of subsidence craters in cases where the chimney reached the surface. The only available data suggesting chimney bulking factors lower than 0.18 are from subsidence-crater-forming explosions in tuff and rhyolite. In these cases the bulking factor is calculated by subtracting the volume of the subsidence crater from the cavity volume and assuming that the difference is distributed in the chimney. (Chimneys are assumed to grow until they bulk full.) The intrinsic porosity of most tuffs and some rhyolites is greater than 20%. When large explosion-produced cavities in such rock collapse, some of the intrinsic porosity may be lost and the density of the rock may increase. This may either increase the chimney height or increase the volume of the subsidence crater. In such cases the calculated bulking factors may be correctly applied to a compressible or friable rock, but a model based on such kinds of rock cannot be extended to less compressible types of rock.

Underground mining operations have been carried out in rhyolite and tuff at the Nevada Test Site and in oil shale in the Piceance Creek Basin. Tunnels in tuff and rhyolite, even a few meters wide, must be supported, whereas oil shale is mined by a room-and-pillar technique in which the rooms are 18 m across. An unsupported span of 36.5 m was reached in oil shale in the experimental mine at Anvil Points before collapse was observed, and even then the collapse served only to give the test room an arched ceiling.¹⁹ Hence extensive spontaneous collapse of the cavity produced by a nuclear explosion in oil shale cannot be

Fig. 9. The relation between chimney height, expressed in terms of cavity radii, and chimney temperature for three fractions of the explosive energy transmitted to the chimney by high-pressure gas. Explosive yield 418 TJ, cavity radius (R_c) 50 m.

assured. We do not know how much rubble will be produced by a nuclear explosion in oil shale.

The more rubble produced, the more rapidly will the gas be cooled, decreasing the likelihood of high pressures. On the other hand, the taller the chimney, the closer to the surface the gas pressure can act, so that even relatively low pressures may cause trouble. In subsequent parts of this report we consider the effects of chimney height on gas pressure and containment. Chimney height is expressed in terms of cavity radius measured from the location of the explosive.

Figure 9 shows the temperature rise of the chimney as a function of chimney height, for various fractions of the explosive energy distributed throughout the chimney as heat. Estimates of the fraction of the explosive energy ending up as heat in the rubble in the chimney range from 0.25 to 0.5. These estimates are based on the observed temperature of the gas produced from the Gasbuggy chimney and esti-

mates of chimney size.²⁰ As the chimney height increases, the temperature rise decreases as a particular fraction of the explosive energy is deposited in the chimney as heat. This is shown in Fig. 9. For example, if the ambient temperature is 30°C and half the explosive energy becomes heat in a chimney $3R_c$ high, the chimney temperature will be 285°C (255°C above ambient temperature). If one-fourth of the explosive energy is in the chimney, the temperature will be 160°C. For a fixed amount of gas in the chimney, the difference in pressure between these two cases will be proportional to the ratio of the absolute temperatures:

$$\frac{285 + 273}{160 + 273} = 1.3.$$

For a chimney height of $4R_c$, this ratio decreases to 1.2; at $5R_c$, it is 1.1. Thus the precise energy fractionation is important only for a chimney height of

less than about $4R_c$. A chimney height of less than $4R_c$ is probably unlikely. In the pressure estimations presented in the

next section, one-fourth of the explosive energy is assumed to be in the chimney as heat.

Gas Pressure

The pressure of gas resulting from a nuclear explosion in oil shale can be estimated by means of the equation

$$P = ZnRT/V, \quad (9)$$

where Z is the compressibility factor for the gas. It is approximately equal to unity for H_2 , CH_4 , and CO over the range of temperatures and pressures of interest. The compressibility factor for CO_2 is shown in Fig. 10.²¹ At $50^\circ C$, for example, $Z = 0.82$ for CO_2 at a pressure of 4 MPa. The other terms in Eq. (9) are defined as follows: n is the moles of CO_2 (Table 2) plus moles of gas from kerogen (Table 5); T is the gas temperature in kelvins, given as a function of R_c in Fig. 9, assuming 25% of the energy of the explosion heats the chimney (add $30^\circ C$ for ambient temperature); R is the gas constant ($82 \text{ cm}^3\text{-atm/mole-K}$); and V is the volume in the chimney, assumed to be equal to the cavity volume:

$$\begin{aligned} \frac{4}{3}\pi R^3 &= \frac{4}{3}\pi (50 \text{ m})^3 \\ &= 5.23 \times 10^5 \text{ m}^3 \\ &= 5.23 \times 10^{11} \text{ cm}^3. \end{aligned}$$

It is convenient to consider the CO_2 partial pressure in the chimney independently of the other gases for a compressibility factor can be applied to CO_2

Fig. 10. The compressibility of CO_2 as a function of temperature and pressure. When the partial pressure of CO_2 in the gas in the chimney is greater than about 4 MPa and the chimney temperature is less than about $100^\circ C$, the chimney pressure will be less than the pressure calculated by the ideal-gas law.

independently of the other gases in the chimney.

As an example, the CO_2 partial pressure in a large chimney is calculated. This represents a low gas temperature and a compressibility factor as different from unity as is probable. If $R_c = 10$, the chimney temperature will be $55^\circ C$ (328 K). The amount of CO_2 (n_{CO_2}) is about 416×10^6 moles. Assuming $Z = 1$:

$$\begin{aligned} P_{CO_2} &\approx (Zn_{CO_2}T)/V \\ &\approx 1.57 \times 10^{-10} \text{ nT,} \end{aligned}$$

$$\begin{aligned}
 & \approx (1.57 \times 10^{-10})(418 \times 10^6)(328) \\
 & = 21.5 \text{ atm} \\
 & = 2.15 \text{ MPa.} \quad (10)
 \end{aligned}$$

According to Fig. 10, the compressibility factor for CO_2 at a CO_2 partial pressure of 2.15 MPa and a temperature of 55°C is about 0.91. This value is used to improve the estimate of the CO_2 partial pressure:

$$\begin{aligned}
 P_{\text{CO}_2} &= 2.15(0.91) \\
 &= 1.96 \text{ MPa.}
 \end{aligned}$$

Fig. 11. Partial pressure of CO_2 in the chimney estimated for the case of a 418-TJ explosion in oil shale containing 15 wt% CO_2 . Cavity radius 50 m. Kerogen-pyrolysis gas not included. One-fourth of the explosive energy is assumed to heat the rubble in the chimney.

Figure 11 shows the partial pressure of CO_2 in the chimney calculated in this way.

The pressure of kerogen-derived gas in the chimney can be estimated in a similar way. However, since this gas is not as compressible as CO_2 , the compressibility factor can be ignored. According to Table 5, a 418-TJ nuclear explosion will release 189×10^6 moles of gas from oil shale containing 1 wt% kerogen. The pressure produced by this gas will depend on the chimney height and the kerogen content, as shown in Fig. 12. (The chimney is assumed to be heated by 25% of the explosive energy.)

Fig. 12. Pressure of noncondensable gas released by pyrolysis and reactions of kerogen in oil shale as a function of chimney height (chimney temperature) and kerogen content (indicated by the percentages on the curves). One-fourth of the explosive energy is assumed to be in the chimney. Char is assumed to react with steam at temperatures above about 1000°C .

Containment

The gas pressure resulting from a nuclear explosion in oil shale can be estimated. How is this pressure related to containment? Most of the studies on containment have been concerned with short-term dynamic effects. We have not had experience with a sustained gas pressure because our work was conducted under conditions where (1) little noncondensable gas was generated (see Fig. 1) or (2) the gas that was generated, mostly from carbonates in permeable rocks, escaped from the chimney and was retained underground by air displacement.

We need to know what sustained fluid pressure can be tolerated at depth without cracking rock. It is common practice to use fluid pressure at depth to crack rock to aid in the recovery of oil and gas. Fluid pressures in the range of 1.2 to 1.5 times the lithostatic pressure are used to initiate fracture, and then fluid pressures below the lithostatic pressure (0.6 times the lithostatic pressure) are sustained to extend the fracturing.

A reasonable way to begin evaluating the containment of a nuclear explosion is to compare the estimated gas pressure to the lithostatic and hydrostatic pressures at the top of the chimney, for that is the point nearest the surface where the pressure is applied. Figure 13 shows the depth to the top of the chimney for a 418-TJ explosion at 823 m based on a cavity radius of 50 m. Figure 14 shows the lithostatic and hydrostatic pressures as a function of chimney height expressed in terms of cavity radii. Figure 15 contains the same information and, in addition, shows the gas

Fig. 13. Depth to the top of the chimney for a 418-TJ explosion at 823 m, assuming a cavity radius of 50 m.

Fig. 14. Lithostatic and hydrostatic pressures at the top of a chimney as a function of chimney height. Based on a 50-m cavity radius resulting from a 418-TJ explosion at a depth of 823 m.

Fig. 15. Total gas pressure for a 418-TJ nuclear explosion in an oil shale containing 15 wt% CO_2 as a function of chimney height and kerogen content (indicated by the percentages on the curves).

pressure resulting from a 418-TJ nuclear explosion in oil shales containing 15 wt% CO_2 and 2, 4, and 6 wt% kerogen. This figure shows that the gas pressure for the case of 2 wt% kerogen more or less follows the hydrostatic pressure, independently of

the chimney height over the range of $2R_c$ to $10R_c$. The pressure at the top of the chimney approaches the lithostatic pressure only in the case of both high chimneys ($>10R_c$) and kerogen concentrations in excess of 6 wt%.

Conclusions and Recommendations

Nuclear explosions deep in the Piceance Creek Basin will generate a long-term gas pressure lower than the hydrostatic pressure if the kerogen content of the shale near the site of the explosion is less than 2 wt%. In this context, "near" means close enough to be heated by the explosion. About 330×10^9 g of oil shale can be heated to 300°C and above by a 418-TJ explosion, as shown in Table 2. The volatile-matter content of oil shale, particularly the kerogen content, within about 30 m of the location of the explosive is of importance to containment. It is the oil shale within this distance that may be

heated to about 300°C and above and may produce gas.

One of the most important, and least certain, assumptions made in this work is the high-temperature pyrolysis of kerogen to hydrogen and the reaction of the remaining char with steam. Some, perhaps a large fraction, of the kerogen may form hydrocarbon vapors, which can condense in the cooler parts of the chimney. Even the kerogen in oil shale heated to 1200°C may escape complete pyrolysis to hydrogen and char, depending on the rate at which it is heated. We also cannot be certain that sufficient steam will be available to react

with char. This is particularly true as the kerogen content increases. One cannot assume that a nuclear explosion in oil shale containing 10 wt% kerogen will produce twice as much gas as an explosion in shale containing 5 wt% kerogen.

The assumption has been made that no gas leaks out of the chimney. Some gas leakage is probable, particularly in the leached zones in the basin. The maximum gas pressure that can be sustained will depend on the relative rates of gas loss and gas generation. In subsequent work on containment in oil shale, specific sites should be considered and the gas permeability measured in order to take gas leakage into account.

We can make some estimates of the rate of gas generation. From 50 to 70% of the total amount of noncondensable gas comes from rock that is melted ($T > 1200^{\circ}\text{C}$). The release of gas from melted rock is rapid, but we do not know for how long a time after a nuclear explosion additional rock is being melted. We need to learn more about the length of time rocks are heated to various temperatures by a nuclear explo-

sion. Actual temperature measurements and modeling of the heat flow in the vicinity of nuclear explosions are needed, particularly in the case of explosions with yields in excess of 200 TJ in relatively dry rock.

Some insight into the thermal history of nuclear explosions has come from the analysis of gas samples collected at various places and times after nuclear explosions. The amount and composition of the gas observed after explosions have been compared to the amount and composition of gases released by heating samples of the same rock in the laboratory. This approach has been particularly useful in the recent Rio Blanco experiment.⁸

A containment experiment designed to simulate the unusual features of a nuclear explosion in oil shale is essential. Such an experiment would be carried out in a gas-generating but impermeable rock. The experiment would be instrumented to measure pressure, temperature, and to sample gases as a function of time. The rock should be a fine-grained mixture of silicates and carbonates (e.g., marlstone) to simulate the irreversible gas release by carbonates in oil shale.

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