



XA04N0928

RADIOACTIVE CONTAMINATION OF OIL PRODUCED FROM
NUCLEAR-BROKEN SHALE

W. D. Arnold
D. J. Crouse

ABSTRACT

The results of small-scale exposure and retorting tests indicate that oil recovered from shale that has been broken with nuclear explosives will be contaminated with tritium. When oil shale was heated in sealed flasks with tritiated water vapor or with tritiated hydrogen, both the shale and the oil subsequently retorted from the shale contained tritium. There was much less contamination of the shale or oil, however, when the shale was exposed to tritiated methane and ethane. Contamination of shale and oil with tritium, as the result of exposure to tritiated water, increased as the exposure temperature, exposure pressure, and the tritium concentration in the water were increased. This contamination also increased as the exposure time was increased up to 25 days, but not significantly thereafter. More than 90% of the tritium was removed from contaminated shale by treating the shale with moist air at elevated temperatures. Only small amounts of the tritium were removed from crude oil by contacting it with solid drying agents or with water. When tritium-contaminated shale oil was distilled, the tritium contents of the recovered fractions were found to be approximately equal.

After being heated with a sample of underground test-shot debris, liquid shale oil became contaminated with radioactive fission products. Most of the radioactivity of the oil was due to finely dispersed solids rather than to dissolved radionuclides. Filtration of the oil removed a major fraction of the radioactive material. When the contaminated oil was distilled, more than 99% of the radionuclides remained in the pot residue.

Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation.

Introduction

Oil shale is a fine-grained sedimentary rock that contains kerogen, a solid hydrocarbon. This organic material is distributed among the inorganic particles, with little or none of it bonded either chemically or physically to the mineral constituents.¹ When kerogen is heated to temperatures above 350°C, it decomposes to gas, water, and a liquid hydrocarbon mixture similar to crude petroleum, leaving a carbonaceous residue. The Colorado oil shales, which are located in Colorado, Utah, and Wyoming, are estimated to contain up to two trillion barrels of oil^{2,3} and represent one of the world's major undeveloped hydrocarbon resources.

The Atomic Energy Commission, in cooperation with several government agencies and commercial organizations, is studying the possibility of breaking deeply buried shale with contained nuclear explosions and subsequently recovering the oil by retorting in place. The shale would be ignited at the top of the nuclear-broken chimney, and combustion would be maintained by introducing air. The hot combustion gases, preceding the burning front, would decompose the kerogen into vaporized shale oil, which would condense in the lower part of the chimney and be pumped to the surface. The carbon residue that remains after the retorting of the oil would provide fuel to the advancing fire front. If successful, this concept would allow the development of the oil shale resources while avoiding the problems associated with mining the shale and with disposal of the spent shale after above-ground retorting. Large-scale operations would be possible with a minimum disturbance of the natural landscape.

Project Bronco is a proposed 50-kiloton experiment to study the feasibility of this concept. The anticipated blast, about 3000 ft below the surface, should break more than a million tons of shale in a chimney 230 ft in diameter and 520 ft high.⁴ In-situ retorting to recover the 660,000 barrels of oil from the broken shale will begin about 15 months after the detonation. This report describes the results of laboratory tests that are being made at the Oak Ridge National Laboratory to study the behavior, in the oil recovery system, of the radioactive contaminants that would be released in the nuclear detonation.

Radionuclides of Concern

The amounts of individual fission products and tritium that are produced in a detonation of a given yield depend on the type of device used. In our initial assessment of the potential problems of radioactive contamination of the shale, we have assumed that most of the energy of the device will be derived from fusion. In this case, when oil recovery is started about 15 months after the detonation, the tritium in the chimney will represent more than 95% of the total radioactivity present. If, however, tritium should prove to be more troublesome than the fission products in this application, it may prove advantageous (as in the case of the natural gas stimulation application) to use a fission device to break the shale.

The shale rubble will be contaminated with certain fission products, principally ^{90}Sr and ^{137}Cs , which have gaseous precursors, and ^{106}Ru and ^{125}Sb , which form volatile compounds. After the cavity formed by the detonation has collapsed, these radionuclides will be deposited on the rubble throughout the chimney and could contaminate the oil as it flows down the chimney. Most of the other long-lived fission products will be trapped in the glassy melt at the bottom of the chimney in a relatively inaccessible form.

Radioactive material will also be formed by neutron activation of the shale immediately surrounding the nuclear device. The principal induced radionuclide present in a shale sample after irradiation in the Oak Ridge Research Reactor was ^{46}Sc . Smaller amounts of ^{54}Mn and ^{59}Fe along with traces of ^{51}Cr , ^{65}Zn , and ^{124}Sb , were also detected in the irradiated shale. Except for the ^{54}Mn and ^{65}Zn , these radionuclides have relatively short half-lives and will decay to only a few percent of their initial concentrations by the time oil recovery is started. In addition, the bulk of these activation products will be captured with most of the fission products in the glassy melt, and therefore, should be in a relatively innocuous form.

Tritium

Assuming that a total of about 25,000 curies of tritium is produced per kiloton of fusion (the approximate mid-point of the 7,000- to 50,000 curies-per-kiloton range specified by Miskel⁴), the detonation will release about $1\mu\text{c}$ of tritium per gram of broken shale in the chimney. Conceivably, the tritium could be present as tritiated water, tritiated hydrogen, or tritiated hydrocarbons. Results of our small-scale equilibration and retorting tests indicate that appreciable contamination of the shale oil will occur from tritiated water or tritiated hydrogen, while contamination from tritiated hydrocarbons should be much less severe (Table I).

The shale used in these tests was obtained from the Bureau of Mines shale mine near Rifle, Colorado. This shale assayed at 32 gal of oil and 2.5 gal of water per ton. A sized fraction containing pieces of shale 4.8 to 8.0 mm in diameter was used. Samples of shale weighing 120 g, and tritium (as tritiated compounds) were heated in steel pressure vessels with volumes of about 300 cm³ each. The tritiated water that was added consisted of 1.2 ml of water containing about 120 μc of tritiated water, and the gases that were added consisted of 130 ml of hydrogen, methane, or ethane containing about 100 μc of the corresponding tritiated gas. The vessels were heated under nitrogen pressure for 6 to 7 days at 85°C and 560 psig. At the end of the heating period, the pressure was released and the shale was washed with water and dried with warm (65°C) air. Oil was recovered from a 100-g sample of the dried shale in a small retort composed of two electric furnaces (Fig. 1). The shale sample was held in the lower furnace in a crucible with a perforated bottom. The oil was retorted by increasing the temperature of the shale from 25°C to about 430°C over a period of 5 to 6 hr. A mixture of nitrogen (24 ml/min) and carbon dioxide (24 ml/min) was preheated in the upper furnace and passed through the shale to a condenser at 38°C and a cold trap at 0°C. The gas was routed through a bed of cupric oxide at 700 to 750°C to burn the hydrocarbon gases released by the shale and to convert the hydrogen to water. The water was frozen from the gas stream, which exited from the system through a flowmeter. In a typical run, slightly more than 11 g of oil and 1.2 ml of water were collected in the 38°C receiver; an additional 0.5 ml of water was collected in the 0°C trap. The depleted shale weighed about 85 g.

Factors Affecting Tritium Contamination

A series of equilibration and retorting tests was made to study some of the variables that affect tritium contamination of the shale and oil when the tritium source is tritiated water. The exposure tests were made at atmospheric pressure in 1-liter glass flasks, using 120-g shale samples and 1.2 ml of water containing about 120 μc of tritiated water.

The contamination occurred rapidly (Fig. 2). The tritium concentration of the oil increased from 0.56 $\mu\text{c/g}$ to 0.92 $\mu\text{c/g}$ when the exposure time of the shale to tritiated water vapor at 85°C was increased from 1 day to 29 days. A

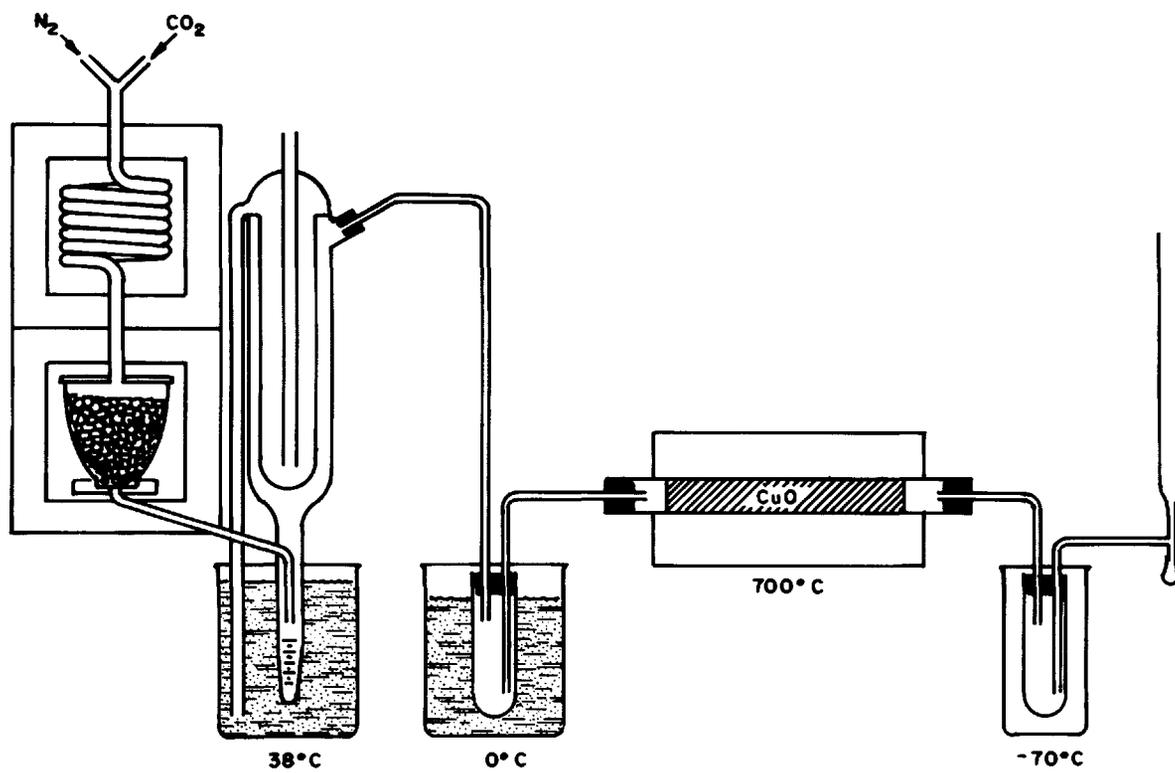


Fig. 1. Bench Scale Retort.

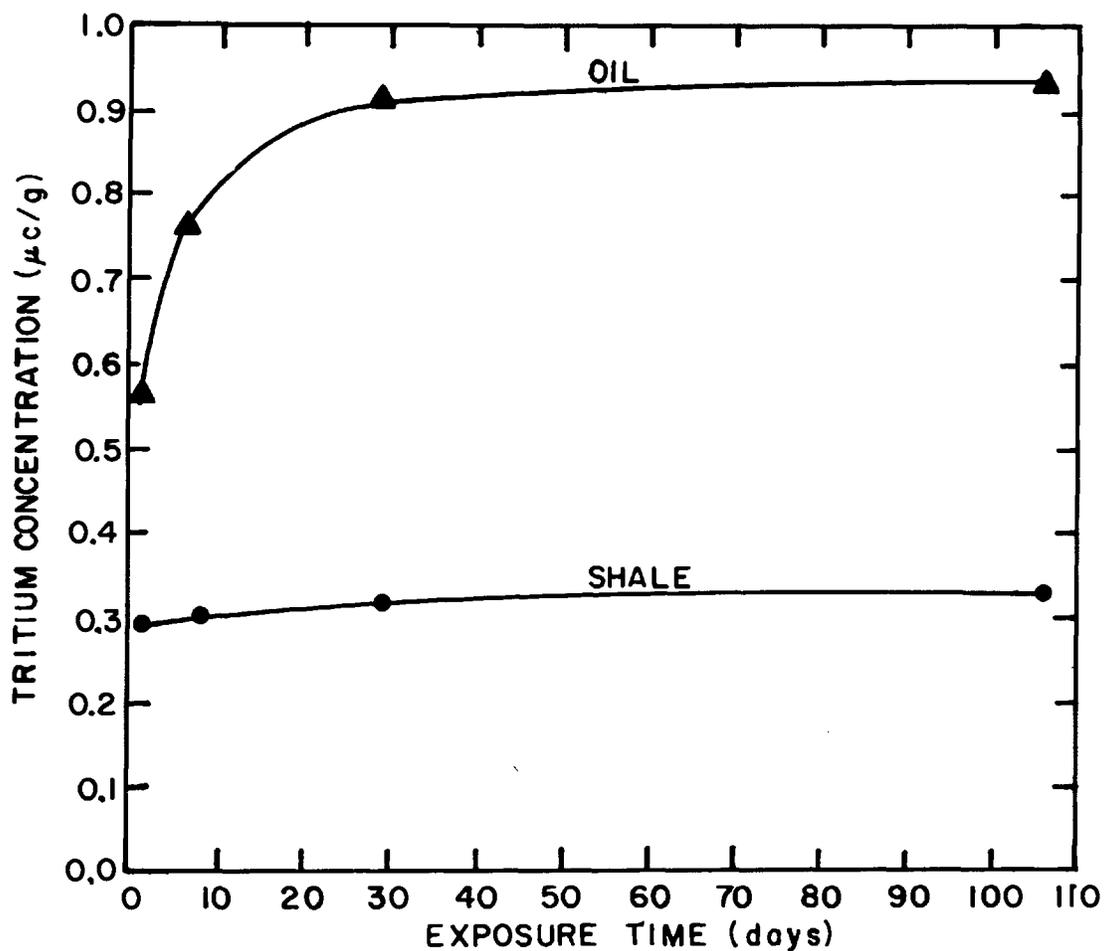


Fig. 2. Effect of Exposure Time on Tritium Contamination of Shale and Oil. Procedure: 120g of shale was heated in a sealed flask at 85°C with 1.2 ml of water containing about 120 μc of tritiated water. After the shale was washed with water and dried with air at 65°C, oil was retorted from a 100-g sample.

Table I. Tritium Contamination of Shale and Oil

Procedure: 120 g of oil shale was heated for 6 to 7 days at 85°C and 560 psig with (a) 1.2 ml of water containing about 120 μc of tritiated water or (b) 130 ml of hydrogen, methane, or ethane containing about 100 μc of the corresponding tritiated gas. After the shale was washed and dried with air at 65°C, oil was retorted from a 100-g sample.

Tritiated Compound Added	Tritium Concentration ($\mu\text{c/g}$)	
	In Dried Shale	In Oil
Water	0.37	0.57
Hydrogen	0.19	0.24
Methane	0.013	0.023
Ethane	0.037	0.024

further increase in exposure time to 106 days increased the tritium concentration of the oil to only 0.93 $\mu\text{c/g}$.

The contamination of the shale and oil was directly proportional to the tritium concentration of the water added to the exposure flask (Fig. 3). The tritium concentration of the water was varied by a factor of 100, resulting in equivalent variations in the tritium concentrations in the shale and in the oil. The exposure time at 85°C was 25 to 29 days.

The tritium contamination of the oil retorted from shale after the shale had been exposed to tritiated water vapor for 25 days increased with increasing temperature in the sealed exposure flask (Fig. 4). The oil contained 0.48 μc of tritium per gram at a flask temperature of 45°C, 0.67 $\mu\text{c/g}$ at 65°C, 0.92 $\mu\text{c/g}$ at 85°C, and 1.0 $\mu\text{c/g}$ at 95°C.

In tests with shale fractions both coarser and finer than the 4.8- to 8.0-mm fraction, the tritium contamination of both the shale and the oil increased as the shale particle size was increased (Table II). The oil from the coarsest shale fraction (8 to 26 mm in diameter) contained almost three times as much tritium as the oil from the finest fraction (1.2 to 2.0 mm in diameter). The surface area and the porosity of the shale samples increased with decreasing particle size, possibly the result of fractures introduced by crushing the shale. Measurements of the pore size distribution indicated that the pores in the 8- to 26-mm shale were small, usually less than 1 micron diameter. The other three samples of shale contained pores or fractures up to 17 microns in diameter. Tritiated water penetrated to the center of a shale cube that measured 28 mm on a side when the cube was heated with tritiated water for 25 days at 85°C. The tritium concentration increased with depth, from 0.46 $\mu\text{c/g}$ in the outer 4-mm layer to 0.22 $\mu\text{c/g}$ in the 5- to 8-mm-deep layer, and to 0.13 $\mu\text{c/g}$ in the center 10-mm cube. The center cube represented 6% of the initial shale weight and contained about 2% of the total tritium in the shale block.

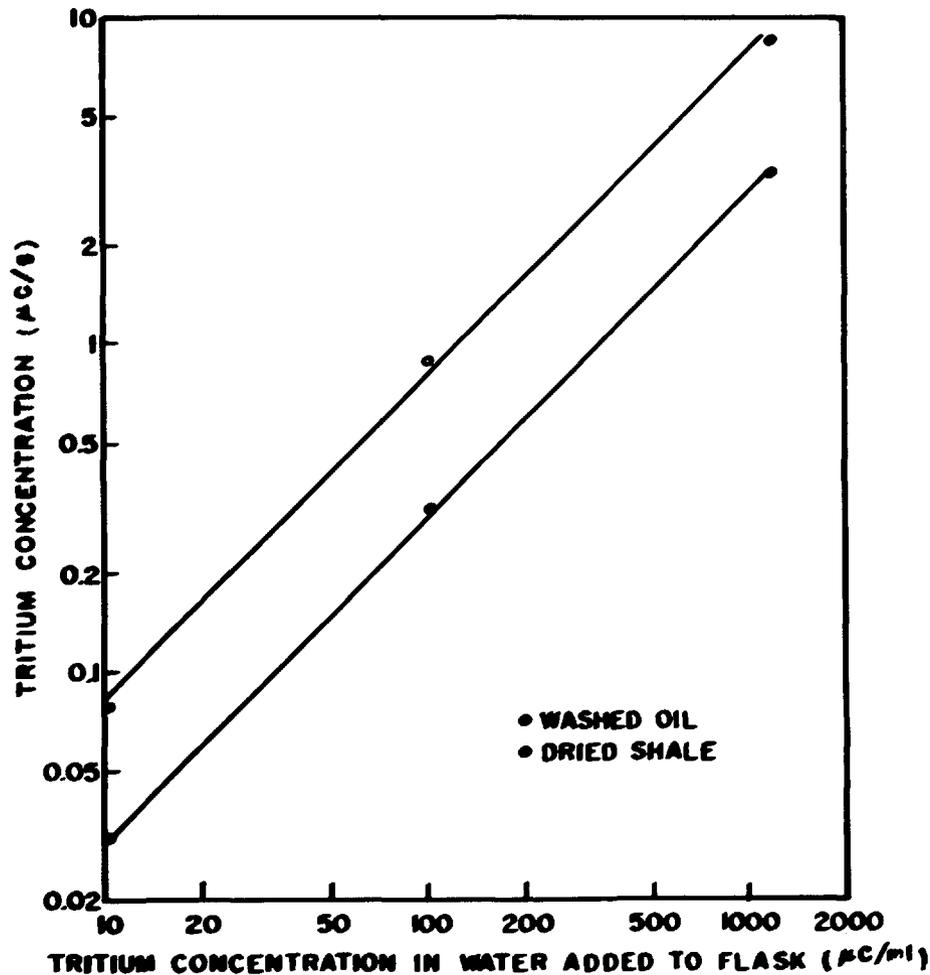


Fig. 3. Effect of Tritium Concentration in Water Added to Reaction Flask on Tritium Contamination of Shale and Oil. Procedure: 120g of shale and 1.2 ml of water, containing the indicated concentration of tritiated water, were heated in a sealed flask at 85°C for 25 to 29 days. After the shale was washed with water and dried with air at 65°C, oil was retorted from a 100-g sample.

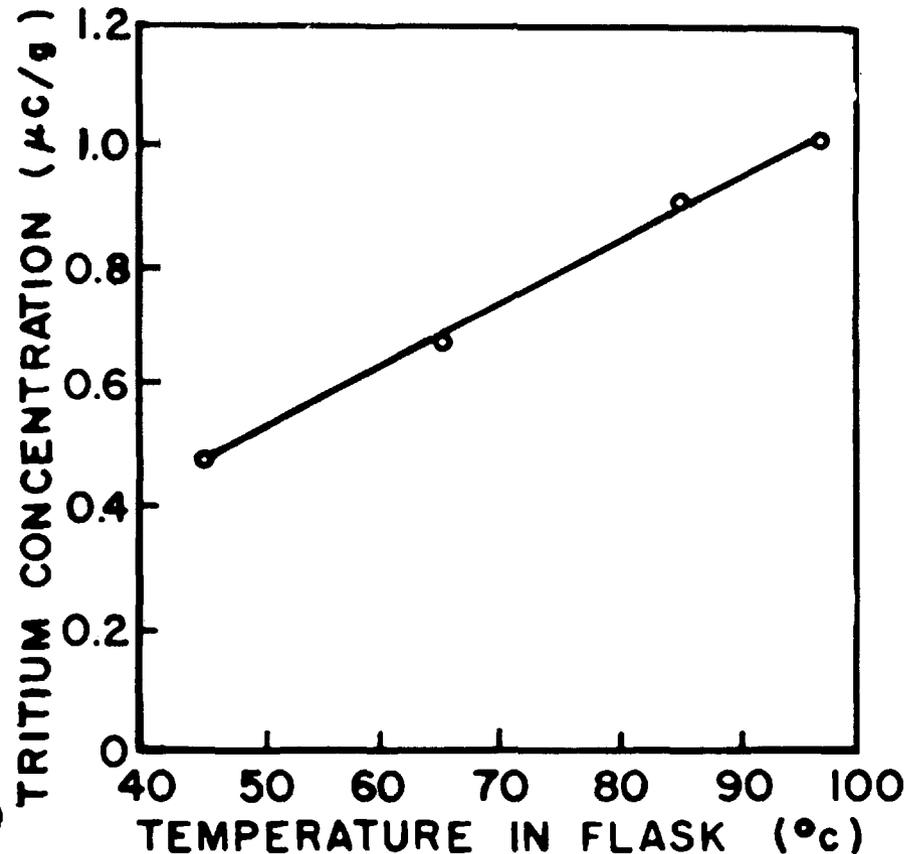


Fig. 4. Effect of Reaction Temperature on Tritium Contamination of Oil. Procedure: 120g of shale and 1.2 ml of water containing 120 µC of tritiated water were heated in a sealed flask for 25 days at the indicated temperatures. After the shale was washed with water and dried with air at 65°C, oil was retorted from a 100-g sample.

Table II. Effect of Shale Particle Size on Tritium Contamination of Shale and Retorted Oil

Procedure: 120-g samples of Green River oil shale were heated at 85°C for 25 days in sealed 1-liter flasks with 1.20 ml of water containing about 120 µc of tritiated water. Oil was retorted from 100 g of the washed and dried shale samples.

Range of Shale Particle Sizes (mm)	Surface Area (m ² /g)	Porosity (%)	Tritium In Shale (µc/g)	Tritium In Retorted Oil (µc/g)
1.2-2.0	0.165	4.7	0.14	0.52
2.0-4.8	0.127	3.2	0.17	0.51
4.8-8.0	0.092	1.7	0.32	0.92
8.0-26	0.004	0.5	0.36	1.42

Increasing the pressure during exposure of oil shale to tritiated water vapor increased the tritium contamination of the shale and the oil (Fig. 5). The tritium concentration of the oil recovered from shale after being exposed to tritiated water vapor for 25 days measured from 0.48 µc/g to 0.73 µc/g when the exposure pressure at 85°C was increased from 50 psig to 860 psig. Increasing the exposure time at 85°C and 560 psig increased the tritium contamination of the oil, but the increases were smaller than those measured at atmospheric pressure. The oil retorted from a shale sample that had been exposed for 1 day contained 0.47 µc of tritium per gram. The contamination was 20% and 35% higher for shale exposed 6 days and 26 days, respectively.

In one test, the oil recovered on retorting a sample of tritium-contaminated shale was collected in increments. The tritium concentration was essentially the same in the three oil fractions:

<u>Oil Fraction</u>	<u>Retort Temperature Range (°C)</u>	<u>Oil Volume (ml)</u>	<u>Tritium In Oil (µc/ml)</u>
1	226 - 363	4.1	0.49
2	363 - 383	4.2	0.52
3	383 - 426	4.9	0.52

Removal of Tritium from Shale

Although the mechanism by which tritium is held in contaminated shale is not known at this time, it appears likely that it is present as tritiated water and that tritiation of the shale hydrocarbons occurs during retorting. We have been able to remove most of the tritium from contaminated shale by contacting it with a gas phase containing water vapor for prolonged periods. About 95% of the tritium was removed from a sample of contaminated shale ($0.3 \mu\text{c/g}$) by treating it for 15 days at a temperature of 200°C with a gas stream that had been saturated with water at 38°C (Fig. 6). About 40% of the tritium was removed from the shale in the 4-hr period required to heat the shale from room temperature to 200°C , whereas a total of 70% was removed in the first day of treatment at 200°C . The oil that was retorted from the shale after 15 days of treatment contained $0.12 \mu\text{c}$ of tritium per gram, which is equivalent to slightly more than 1% of the tritium that was added to the reaction flask at the beginning of the test. Originally, the shale was contaminated with tritium by heating it at 85°C for 25 days with tritiated water. In the tritium removal test, a 100-g sample of the contaminated shale was heated at 200°C in the retort, and the gas stream (24 ml/min of N_2 plus 24 ml/min of CO_2) was saturated with water at 38°C and passed through the shale. In a similar test with a shale sample that had been exposed to tritiated water vapor for 108 days, about 90% of the tritium was removed from the shale in 15 days of treatment at 200°C , and the oil that was retorted from the shale after the treatment contained $0.20 \mu\text{c}$ of tritium per gram.

The removal of tritium from contaminated shale by intermittent treatment with moist air at lower temperatures was less efficient. In these tests, the contaminated shale ($0.3 \mu\text{c/g}$) was treated with preheated water-saturated air for 2 hr each day at the rate of 20 ml/min . The shale was held at temperature between the treatments. Slightly more than 80% of the tritium was removed from the shale in 6 treatments at 95°C , and about 50% was removed in 8 treatments at 85°C . In other tests, more than 80% of the tritium was removed from contaminated shale in two 1-week submersions in hot water (95°C) and about 50% was removed by heating a shale sample for 24 hr at 110°C under reduced pressure (1 mm Hg) while passing air through the shale.

The removal of tritium from a shale cube that measured 28 mm on a side was somewhat less efficient than removal from the 4.8- to 8.0-mm shale used in the tests described above. The shale cube, contaminated with tritium by exposure to tritiated water vapor for 25 days at 85°C , was heated for 10 days in a sealed flask at 95°C . For 2 hr each day, air saturated with water at 85°C was passed through the flask at the rate of 20 ml/min . This treatment removed only 20% of the tritium from the shale and forced a portion of the remaining tritium deeper into the cube. The outer 4-mm layer contained $0.39 \mu\text{c}$ of tritium per gram, the 5- to 8-mm-deep layer contained $0.48 \mu\text{c/g}$, and the center 10-mm cube contained $0.43 \mu\text{c/g}$.

These tests indicate that a significant fraction of the tritium could probably be removed from the shale by passing moist air through the chimney prior to retorting. Appreciable removal may also occur as a natural result of the retorting operation since the shale over most of the length of the chimney will be exposed to a flow of hot moist gases for a prolonged period prior to attainment of the retorting temperature. Some provision for removing the tritiated water from the effluent gases would probably be needed before the gases are recycled to the chimney. The efficiency of tritium removal may be limited by deep penetration into large shale chunks since the removal of tritium from this material will be much less efficient than from smaller shale pieces.

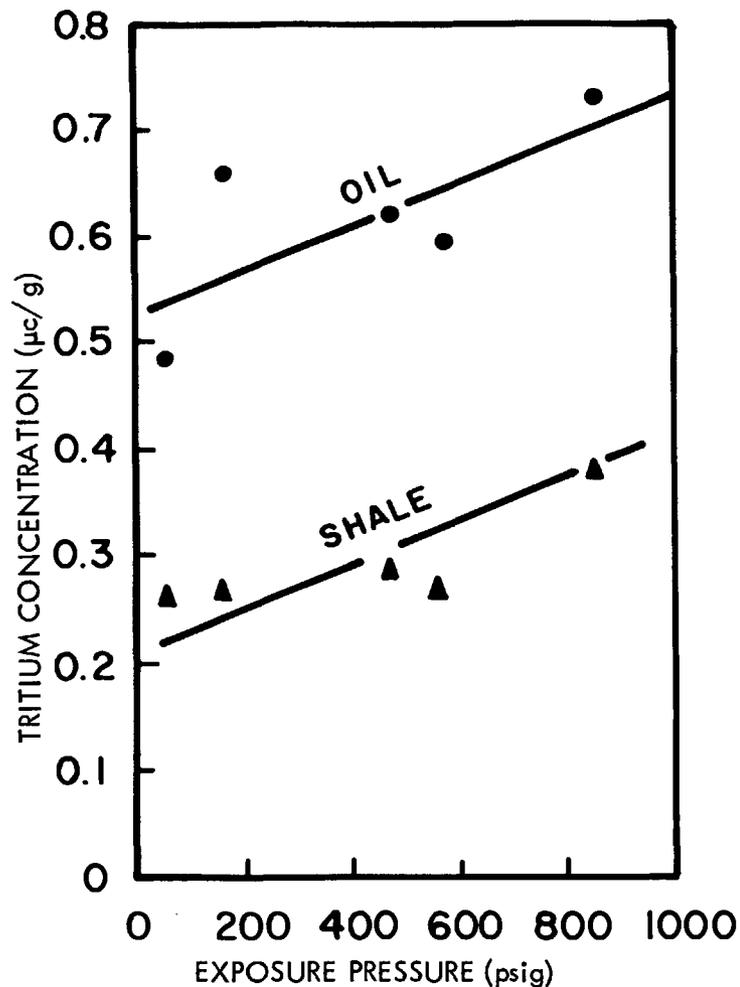


Fig. 5. Effect of Exposure Pressure on Tritium Contamination of Shale and Oil. Procedure: 120g of shale and 1.2 ml of water containing about 120 μc of tritiated water were heated for 25 days at 85°C and at the indicated pressures. After the shale was washed with water and dried with air at 65°C, oil was re-ported from a 100-g sample.

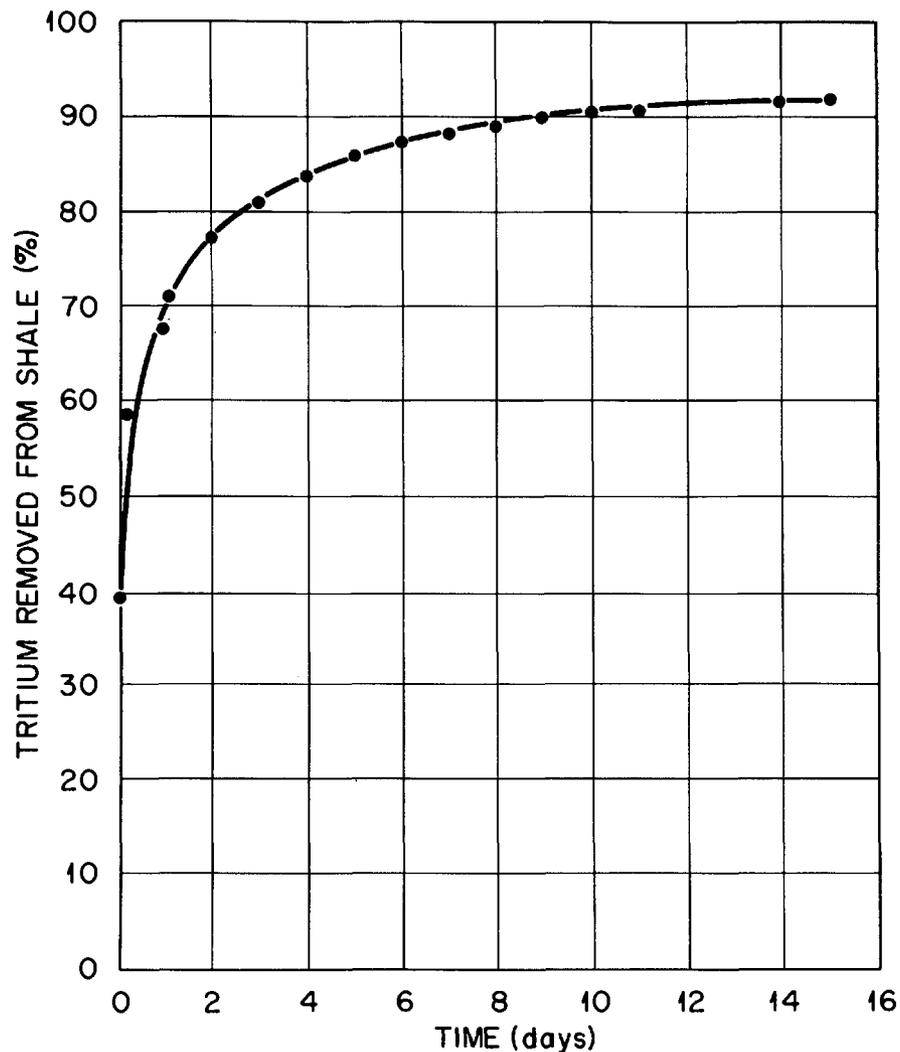


Fig. 6. Removal of Tritium from Shale at 200°C. Procedure: 100 g of tritiated shale (0.3 $\mu\text{c}/\text{g}$) was heated at 200°C in a gas stream that had been saturated with water at 38°C.

Removal of Tritium from Shale Oil

Tritium is not easily removed from contaminated oil. Tests showed that prolonged refluxing of tritiated oil with water removed only a few percent, while none was removed by equilibrating the oil with solid drying agents.

Failure to remove more of the tritium from the oil under these conditions indicates that the tritium is probably present in the oil as part of the hydrocarbon structure rather than as tightly bound water. Further evidence lending credence to this hypothesis was obtained by distilling a tritiated oil sample. Each of the oil fractions, the residuum, and the small amount of recovered water were found to have about the same tritium content; the tritium concentration in these fractions was also about the same as that in the original crude oil (Table III). Further fractionation, by gas-liquid chromatography, of the naphtha showed that it contained at least 20 components. Tritium could not be detected in the minor peaks, but was definitely present in the three major peak groups.

Fission Products

Most of the fission products from the nuclear detonation will be trapped in the fused rock (puddle glass) that accumulates at the bottom of the chimney. However, the crushed shale will be contaminated to some extent with fission products that have gaseous precursors (e.g., ^{90}Sr and ^{137}Cs) and those that form volatile compounds (e.g., ^{106}Ru and ^{125}Sb). These fission products will be deposited on the surfaces of the broken shale and could contaminate the oil as it flows down the chimney. The potential contamination of oil with fission products was studied by heating crude shale oil samples with underground test-shot debris and measuring the radioactivity of the oil. Tests were made both with aged debris (several years old) and with debris only a few months old.

The aged debris consisted of chimney rubble and puddle glass from the bottom of the chimney. At $68,000 \text{ counts min}^{-1} \text{ g}^{-1}$, the gross gamma activity of the puddle glass was an order of magnitude greater than that of the rubble (Table IV). The dominant radionuclides were ^{144}Ce , ^{90}Sr , and ^{60}Co in the glass and ^{137}Cs , ^{90}Sr , and ^{106}Ru in the rubble. Barely measurable oil contamination occurred when 10-ml samples of shale oil were heated under reflux with 10-g samples of the debris fractions. After 4 hr at an oil temperature of 220°C , the gamma activity of the oil samples was only about 130 counts/min (40% of background count):

<u>Debris Fraction</u>	<u>Total Activity of Oil (counts/min)</u>
Rubble	129
Glass	138

The major radionuclides in the newer debris sample, a mixture of rubble and puddle glass, were ^{95}Zr - ^{95}Nb , ^{103}Ru , and ^{141}Ce , which are all relatively short-lived isotopes. This debris was much more radioactive than the older sample; the gross gamma activity was about $3.5 \times 10^7 \text{ counts min}^{-1} \text{ g}^{-1}$. Longer-lived radionuclides, such as ^{106}Ru , ^{137}Cs , and ^{144}Ce that would be of greater importance at the time of oil recovery were not detected in the initial radiometric analysis due to interference from the short-lived radionuclides; however, they were detected in a later analysis of the debris. Shale

Table III. Distillation of Tritiated Shale Oil

Procedure: 100 ml of tritiated shale oil (prepared by contacting Green River oil shale with water vapor containing tritiated water for 25 days at 85°C in a sealed flask and retorting; to increase the volume of oil for the distribution test, the oil was diluted with uncontaminated shale oil to give oil with 0.056 μc of tritium per ml).

Fraction	Temp. Range (°C)	Pressure	Distillate Volume (ml)	Tritium Concentration ($\mu\text{c}/\text{ml}$)
Naphtha	To 200	Atmospheric	10	0.051
Light oil	To 225	40 mm Hg	26	0.037
Heavy oil	225-300	40 mm Hg	29	0.047
Residuum		40 mm Hg	33	0.055
Water ^a			1	0.048

^aWater taken from cold trap. None of the oil fractions contained any visible water.

oil that had been heated in contact with the debris became contaminated with the fission products present in the debris (Table V). The gross gamma activity of a 25-ml oil sample that had been heated for 4 hr with 5.2 g of the debris under reflux conditions at 220°C was found to be about 1×10^5 counts $\text{min}^{-1} \text{ml}^{-1}$. Releaching the debris with two additional portions of fresh oil yielded oil that was contaminated to the same level as the first oil sample. The activity of the oil obtained from two final leaches, each with 50 ml of fresh oil, was 5×10^4 counts $\text{min}^{-1} \text{ml}^{-1}$. Based on the measurements of the gross gamma activity, the combined oil samples contained 7.5% of the radioactive material initially present in the debris. Most of the radioactivity of the oil was due to ^{95}Zr - ^{95}Nb and ^{103}Ru . The combined oil samples contained about 2% of the ^{95}Zr - ^{95}Nb and 5% of the ^{103}Ru along with 2% of the ^{141}Ce and 1% of the ^{140}Ba - ^{140}La initially present in the debris. As was true for the debris sample, the longer-lived radionuclides were not detected in the contaminated oil samples.

Much of the radioactive contamination of the oil was due to the entrainment of finely dispersed solids rather than to dissolved radionuclides. When the oil from the leaching tests was diluted with crude shale oil and subsequently distilled, more than 99% of the radioactive material remained in the pot residue (Table VI). The heavy oil fraction contained only about 0.3% of the radioactive material initially present in the crude oil, and the amounts detected in the naphtha and light oil fractions were barely detectable. When 3-g samples of the crude oil and residuum from the distillation were treated at 60°C with 4 successive 5-ml portions of hexane, the insoluble residue accounted for 35 to 40% of the gross gamma activity but only 0.2% and 0.5%, respectively, of the initial sample weights. Filtration of the hexane solutions through a Millipore filter containing stacked papers of 8- μ , 0.8- μ , and 0.1- μ pore size removed an additional 45% of the radioactive material (0.9% and 2.5% of initial sample weight, respectively). Most of the solids that

Table IV. Radiochemical Analysis of Underground
Test-Shot Debris

Radionuclide	Concentration (dis min ⁻¹ g ⁻¹)		
	Sample A ^a		Sample B ^b
	Rubble	Glass	
⁶⁰ Co	0.081 x 10 ³	3.0 x 10 ⁴	c
⁸⁹ Sr	c	c	0.28 x 10 ⁷
⁹⁰ Sr	0.86 x 10 ³	3.9 x 10 ⁴	c
⁹⁵ Zr- ⁹⁵ Nb	c	c	9.3 x 10 ⁷
¹⁰³ Ru	c	c	1.9 x 10 ⁷
¹⁰⁶ Ru	0.39 x 10 ³	0.65 x 10 ⁴	0.7 x 10 ⁷ (ref. e)
¹³⁷ Cs	21.0 x 10 ³	1.3 x 10 ⁴	0.04 x 10 ⁷ (ref. e)
¹⁴⁰ Ba- ¹⁴⁰ La	c	c	0.28 x 10 ⁷
¹⁴¹ Ce	c	c	1.4 x 10 ⁷
¹⁴⁴ Ce	0.094 x 10 ³	5.2 x 10 ⁴	0.5 x 10 ⁷ (ref. e)
Gross gamma ^d	6.8 x 10 ³	6.8 x 10 ⁴	3.5 x 10 ⁷

^aSeveral years old.

^bSeveral months old.

^cNot detected.

^dGross gamma activity is given in counts min⁻¹ g⁻¹.

^eNot detected in initial analysis; measured after short-lived radionuclides had decayed; concentration calculated to date of initial analysis.

were filtered out of the hexane solutions were found on the 8-μ paper. The dried solids were gray-black in color and flocculent.

Discussion

Our investigation thus far indicates that oil recovered from nuclear-broken shale is more likely to be contaminated with tritium than with fission products if a fusion device is used. The extent of the tritium contamination of the shale and oil will depend on the form in which the tritium exists in the chimney. Appreciable contamination will occur from tritiated water or tritiated hydrogen, but much less is expected from tritiated hydrocarbons. Tritium contamination will possibly be reduced by the removal of a significant fraction of the tritiated compounds from the shale by the front of hot moist gases that precedes the retorting front down the chimney. This will be limited to some extent, however, by the relatively inefficient removal of the tritiated compounds that penetrate deeply into large chunks of shale. The removal of tritium from the retorted oil does not appear practical at this point since it evidently is present in the oil as part of the hydrocarbon structure.

Table V. Results Obtained by Leaching Test-Shot
Debris with Shale Oil

Procedure: 5.2 g of test-shot debris (see Table IV for analysis) was heated successively with three 25-ml portions and two 50-ml portions of shale oil at 220°C under reflux conditions. The contact time for each leach was 4 hr. The oil was centrifuged before analysis.

Radionuclide	Radioactivity of Combined Oil Samples	
	dis min ⁻¹ ml ⁻¹	% of Initial
⁹⁵ Zr- ⁹⁵ Nb	5.6 x 10 ⁴	2.0
¹⁰³ Ru	2.9 x 10 ⁴	5.2
¹⁴¹ Ce	8.6 x 10 ³	2.1
¹⁴⁰ Ba- ¹⁴⁰ La	8.7 x 10 ²	1.0
Gross gamma ^a	7.8 x 10 ⁴	7.5

^aGross gamma activity is measured in counts min⁻¹ ml⁻¹.

The amount of tritium in the chimney could be drastically reduced by using an all-fission device to break the shale. This would increase the relative importance of the fission products with respect to radioactive contamination of the oil product. Although fission product behavior has not been studied as extensively as tritium behavior, our test results indicate that the fission products will not significantly contaminate the overhead distillate fractions, which are the most valuable shale oil products. Subsequent use and processing of the residuum to recover by-products, however, could be complicated by the presence of fission products.

Acknowledgment

We are indebted to W. B. Howerton, D. R. Shaw, and D. E. Spangler for technical assistance in these studies. J. W. Landry designed the retort and made some of the initial retorting runs. Measurements of the physical properties of the shale samples and many of the radiochemical analyses were made in the ORNL Analytical Chemistry Division.

Table VI. Distillation of Contaminated Shale Oil

Procedure: 100 ml of oil contaminated with fission products was distilled. The gross gamma activity of the crude oil was 3930 counts min⁻¹ ml⁻¹.

Fraction	Temp Range (°C)	Pressure	Volume (ml)	Gross Gamma Activity	
				counts min ⁻¹ ml ⁻¹	% of Total
Naphtha	To 200	Atmospheric	7	10	< 0.05
Light oil	To 225	40 mm Hg	25	< 10	< 0.05
Heavy oil	225 to 300	40 mm Hg	34	30	0.3
Residuum			35	11,640	99.7
Water ^a			0.6	190	< 0.05

^aRecovered from cold trap.

References

1. P. R. Tiscot and W. I. R. Murphy, Physical Structure of Green River Oil Shale from Colorado, USBM-R1-6184 (1963).
2. Mineral Facts and Problems, U. S. Bureau of Mines Bulletin 585 (1960).
3. D. C. Duncan and V. E. Swanson, Organic-Rich Shale of the United States and World Land Areas, U. S. Department of the Interior GSC 523 (1965).
4. J. A. Miskel, Characteristics of Radioactivity Produced by Nuclear Explosives, Third Plowshare Symposium, TID-7695 (April 1964).
5. Project Bronco, PNE-1400 (Oct. 13, 1967).