United States Patent [19]

Beard

[11] **3,759,574**

[45] **Sept. 18, 1973**

[54] **METHOD OF PRODUCING HYDROCARBONS FROM AN OIL SHALE FORMATION**

[75] Inventor: **Thomas N. Beard**, Denver, Colo.

[73] Assignee: **Shell Oil Company**, New York, N.Y.

[22] Filed: **Sept. 24, 1970**

[21] Appl. No.: **75,009**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 770,964, Oct. 28, 1968, abandoned.

[52] **U.S. Cl.** **299/4**, 166/271

[51] **Int. Cl.** **E21b 43/28**

[58] **Field of Search** 166/271, 272, 259, 166/261; 299/4, 5

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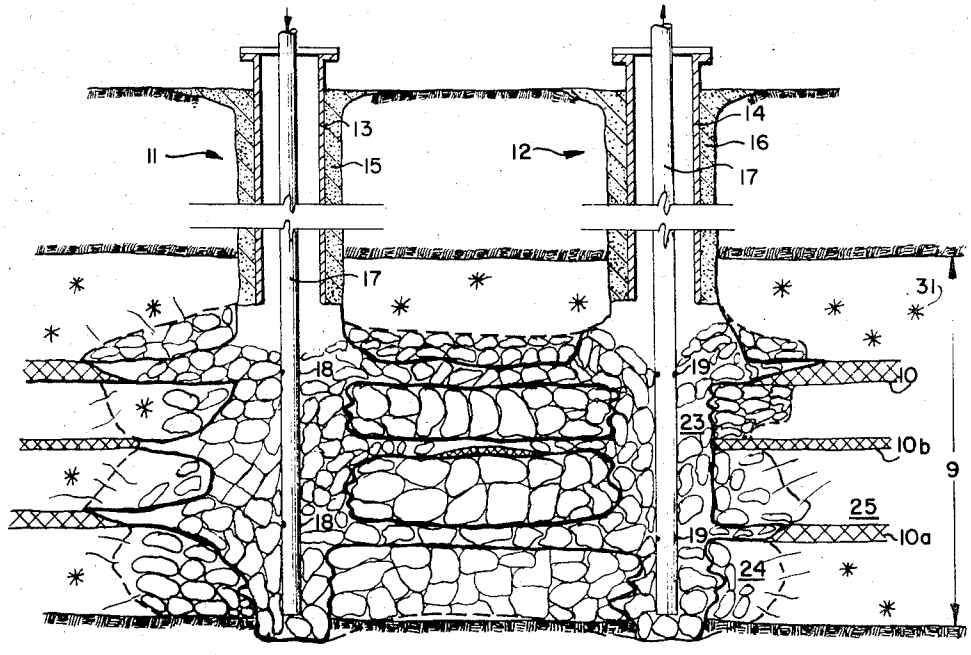
Primary Examiner—Robert L. Wolfe

Attorney—George G. Pritzker and Harold L. Denkler

[57] **ABSTRACT**

A method of producing hydrocarbons and optionally water-soluble minerals from a subterranean oil shale formation containing zone(s) of water-soluble minerals, by penetrating said formation with at least one borehole and leaching or dissolving the water-soluble minerals from the formation with a solvent fluid so as to form a cavern(s) and/or interconnected cavities, followed by fracturization and/or rubblization of the oil shale surrounding the caverns or cavities, and thereafter injecting into fracturized and/or rubblized zones, a pyrolyzing fluid to effect in-situ hydrocarbon recovery therefrom.

22 Claims, 20 Drawing Figures



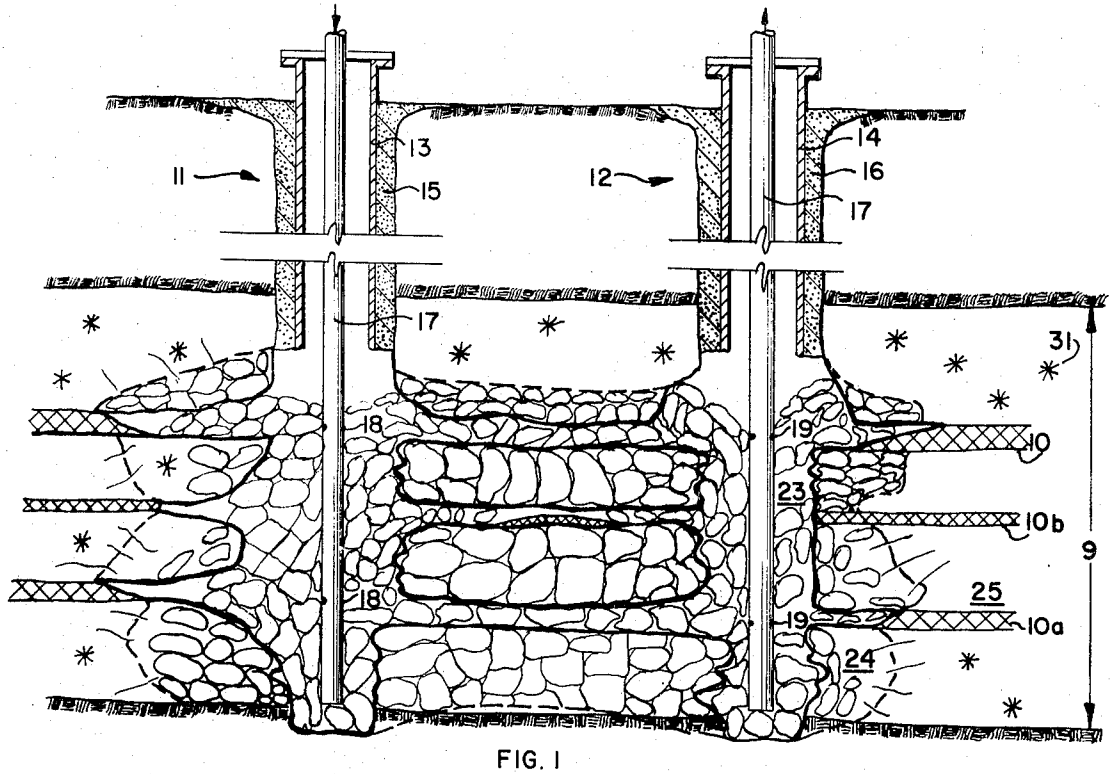


FIG. 1

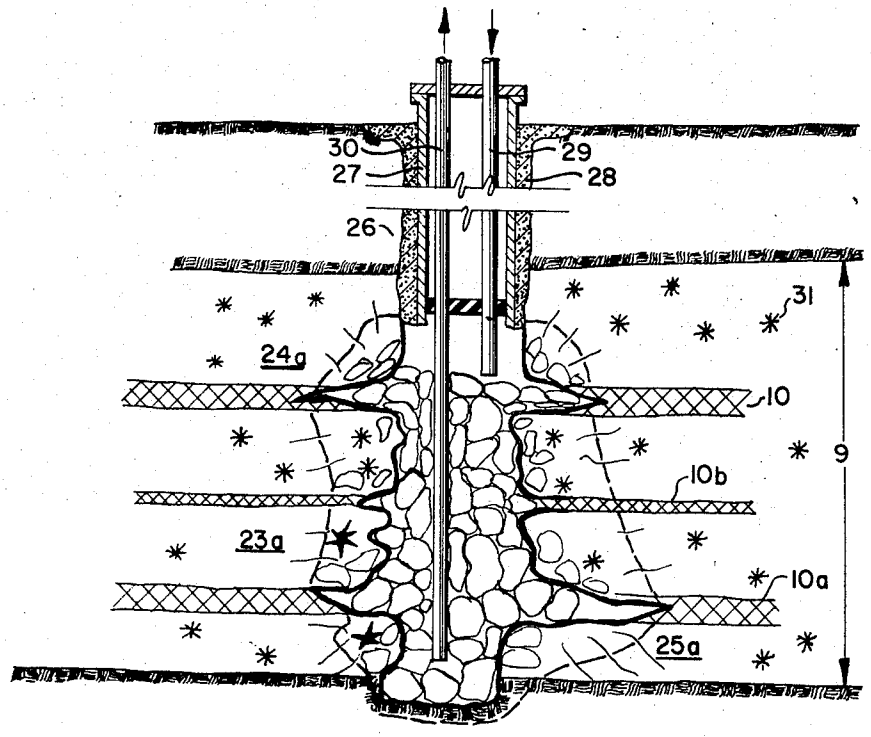


FIG. 2

INVENTOR:
T. N. BEARD
BY: Pierce & Pritzker
HIS AGENT

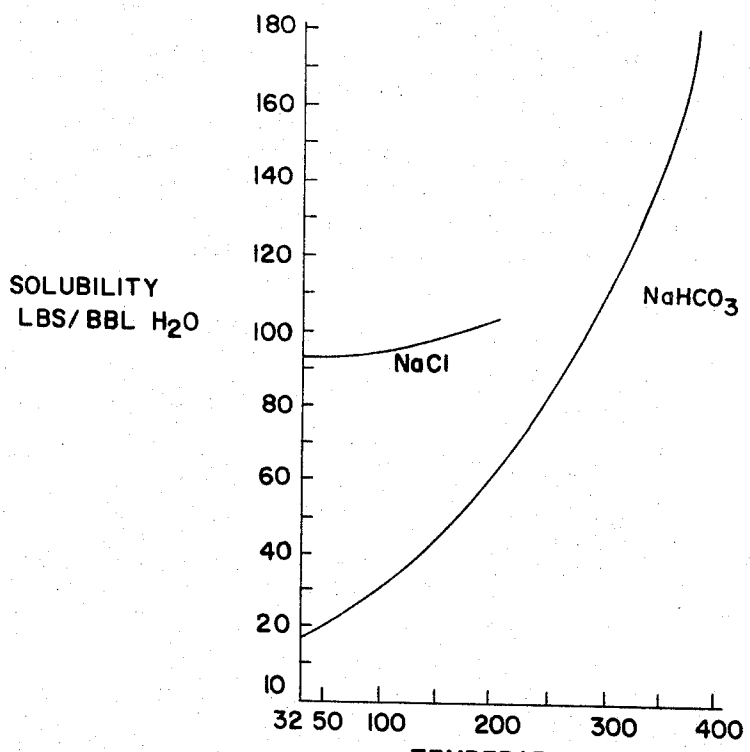


FIG. 3

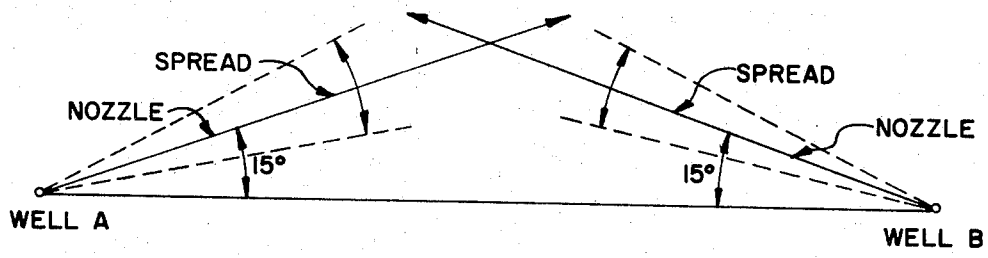


FIG. 4

INVENTOR:
T. N. BEARD
BY: Herman G. Patterson
HIS AGENT

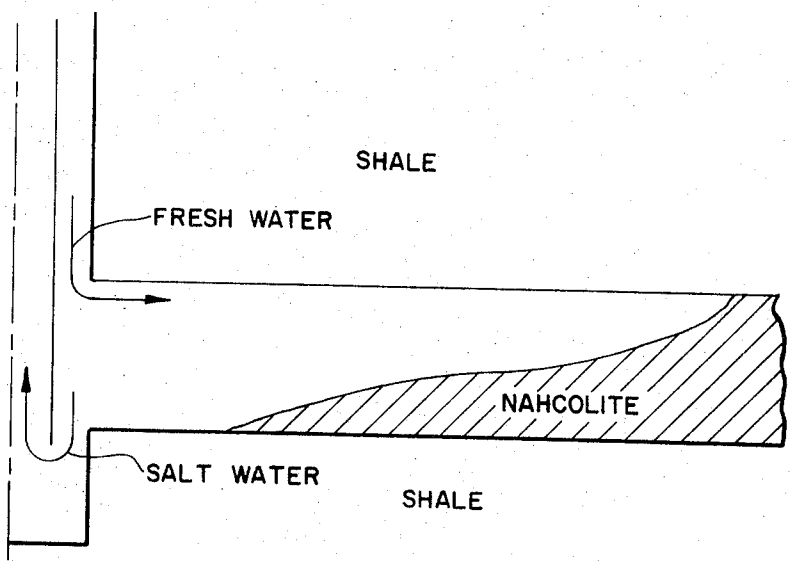


FIG. 5

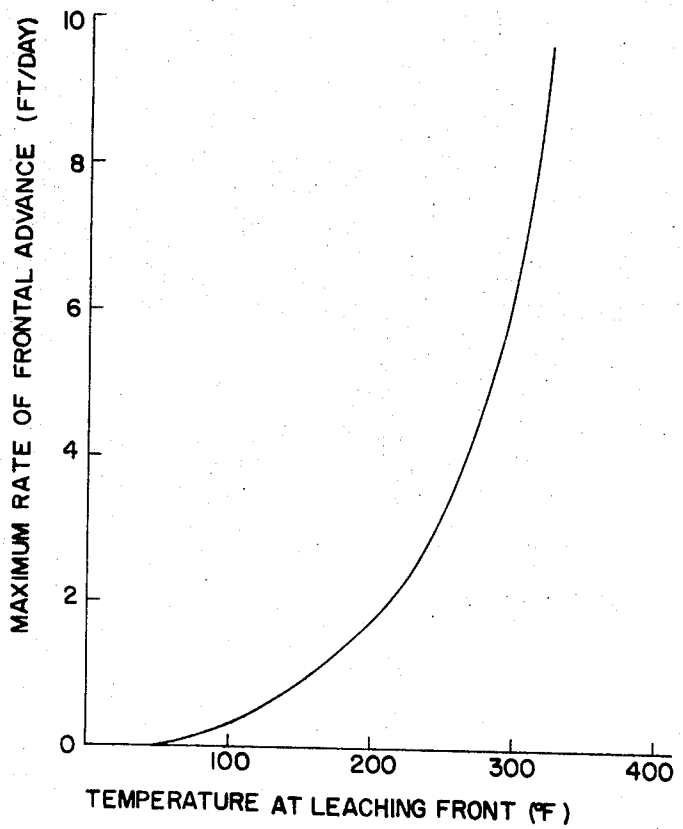


FIG. 6

INVENTOR:
T. N. BEARD
BY: Henry M Pritzker
HIS AGENT

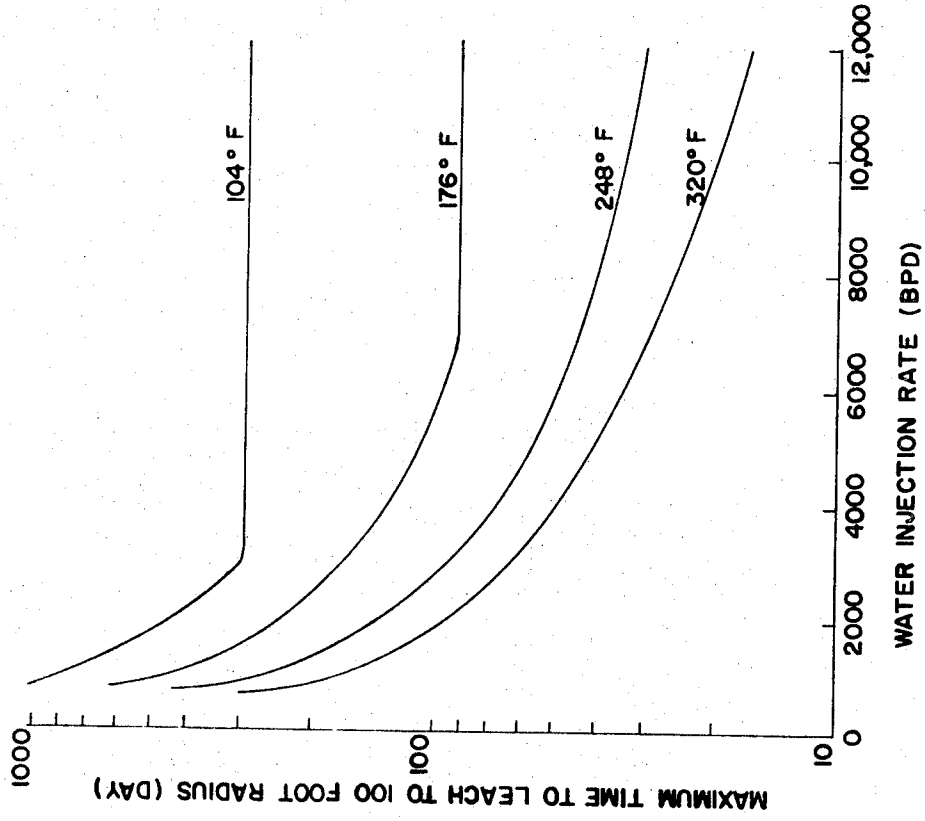


FIG. 8

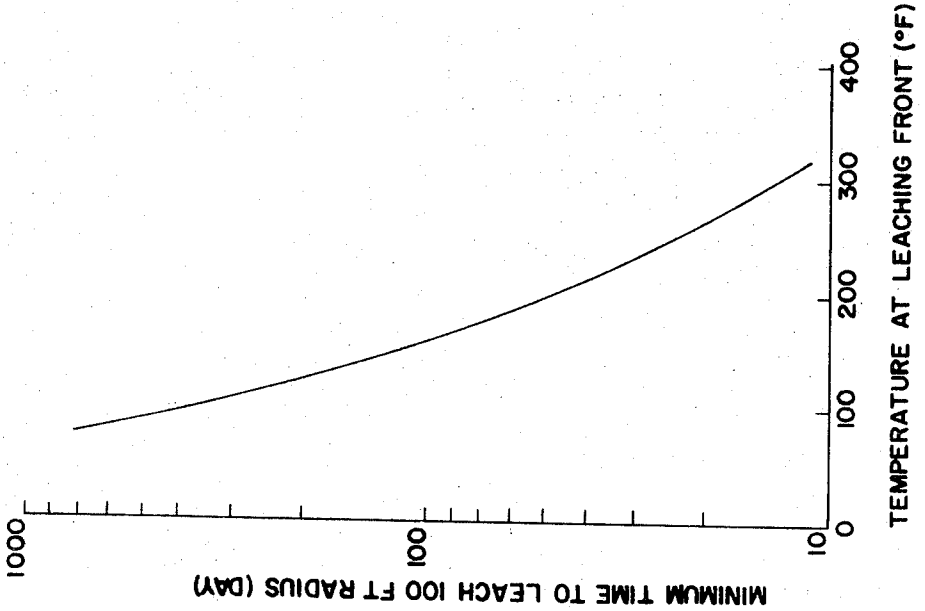
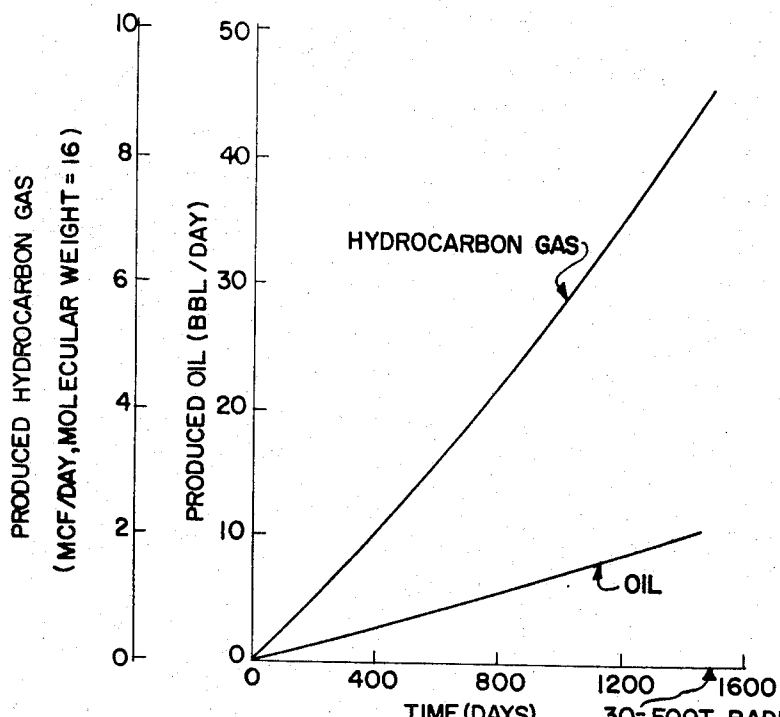


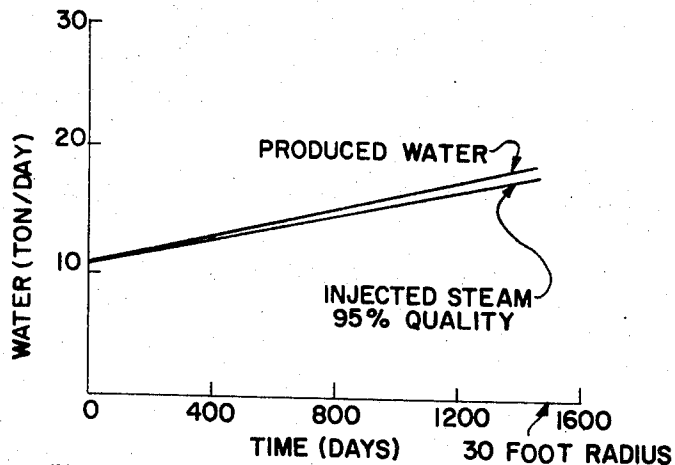
FIG. 7

INVENTOR:
T. N. BEARD
BY: Herman G. Pritzker
HIS AGENT



OIL AND HYDROCARBON GAS PRODUCTION RATES FOR RUBBLING RATE OF 0.02 FT/DAY.

FIG. 9



INJECTED STEAM AND PRODUCED WATER FOR RUBBLING RATE OF 0.02 FT/DAY

FIG. 10

INVENTOR:
T. N. BEARD
BY: Herne M Pritzker
HIS AGENT

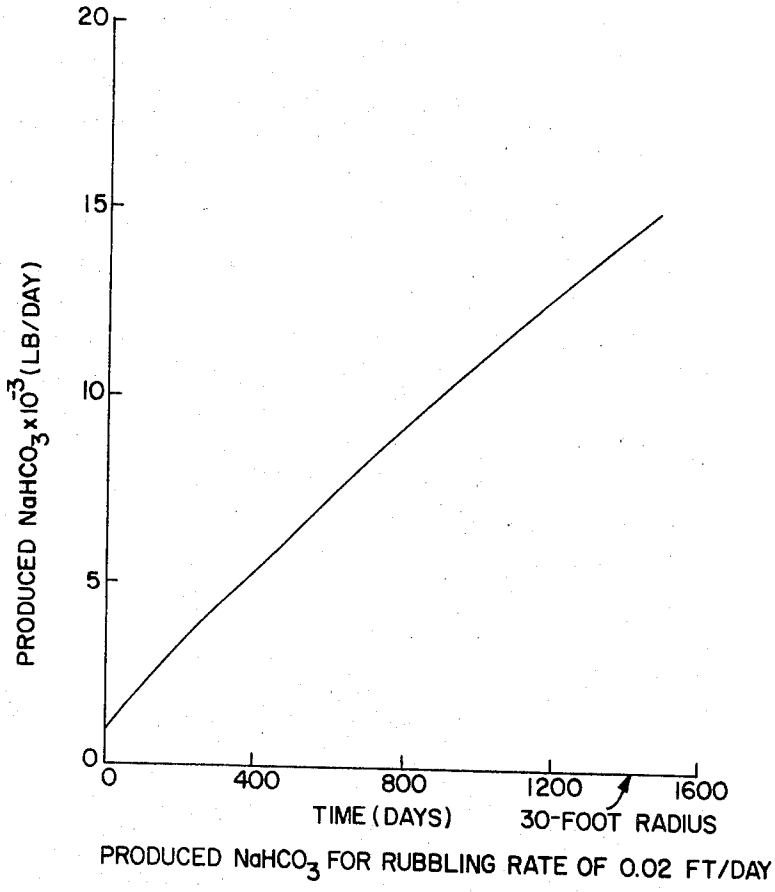
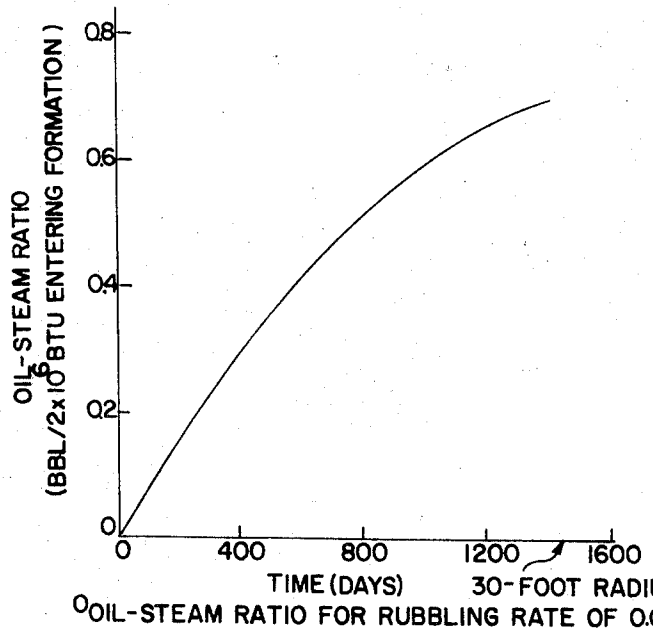


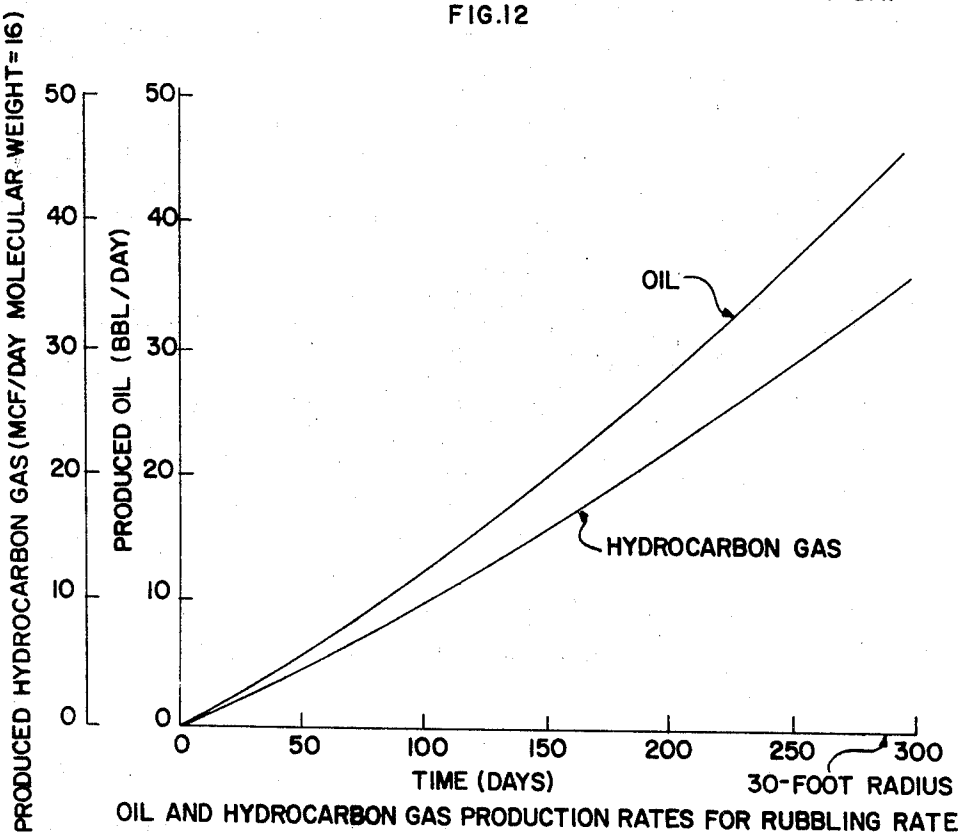
FIG. 11

INVENTOR:
T. N. BEARD
BY Pennie M Pritzker
HIS AGENT



OIL-STEAM RATIO FOR RUBBLING RATE OF 0.02 FT/DAY

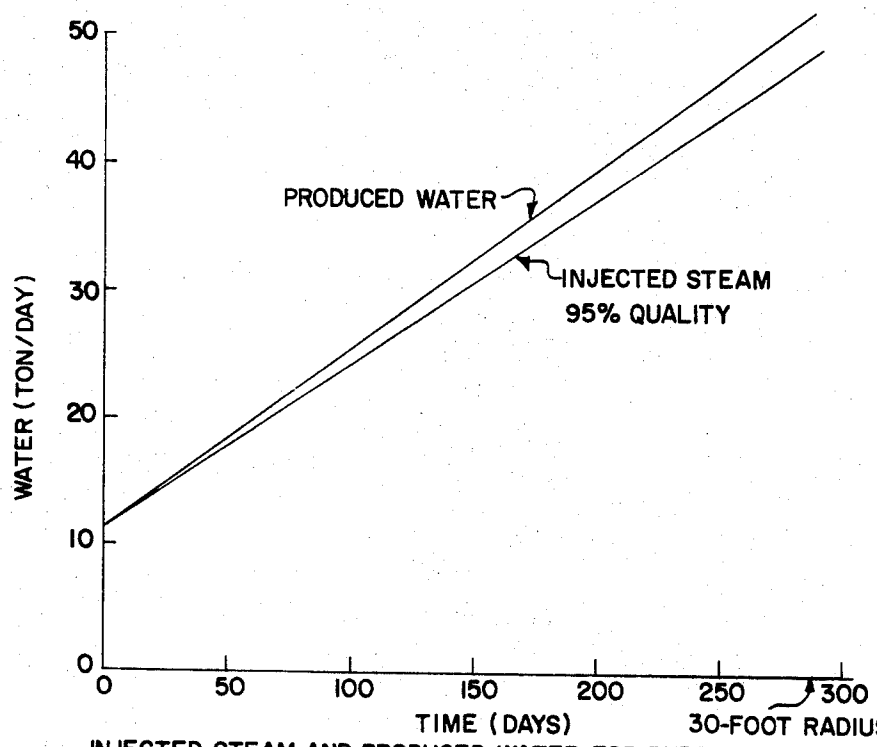
FIG. 12



OIL AND HYDROCARBON GAS PRODUCTION RATES FOR RUBBLING RATE OF 0.1 FT/DAY

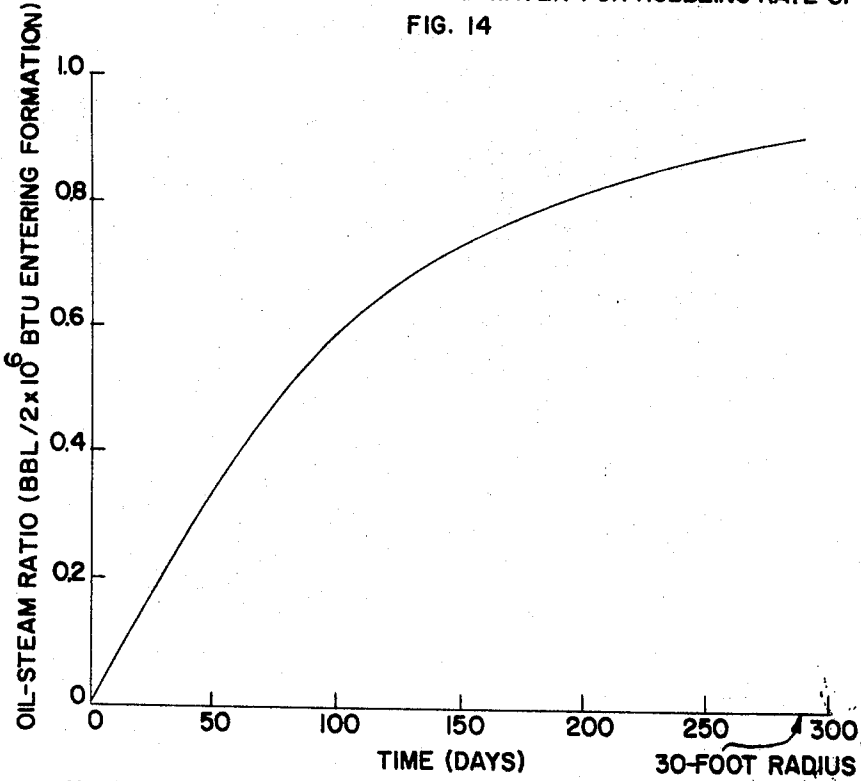
FIG. 13

INVENTOR:
T. N. BEARD
BY: Herne & Pritchett
HIS AGENT



INJECTED STEAM AND PRODUCED WATER FOR RUBBLING RATE OF 0.1 FT/DAY

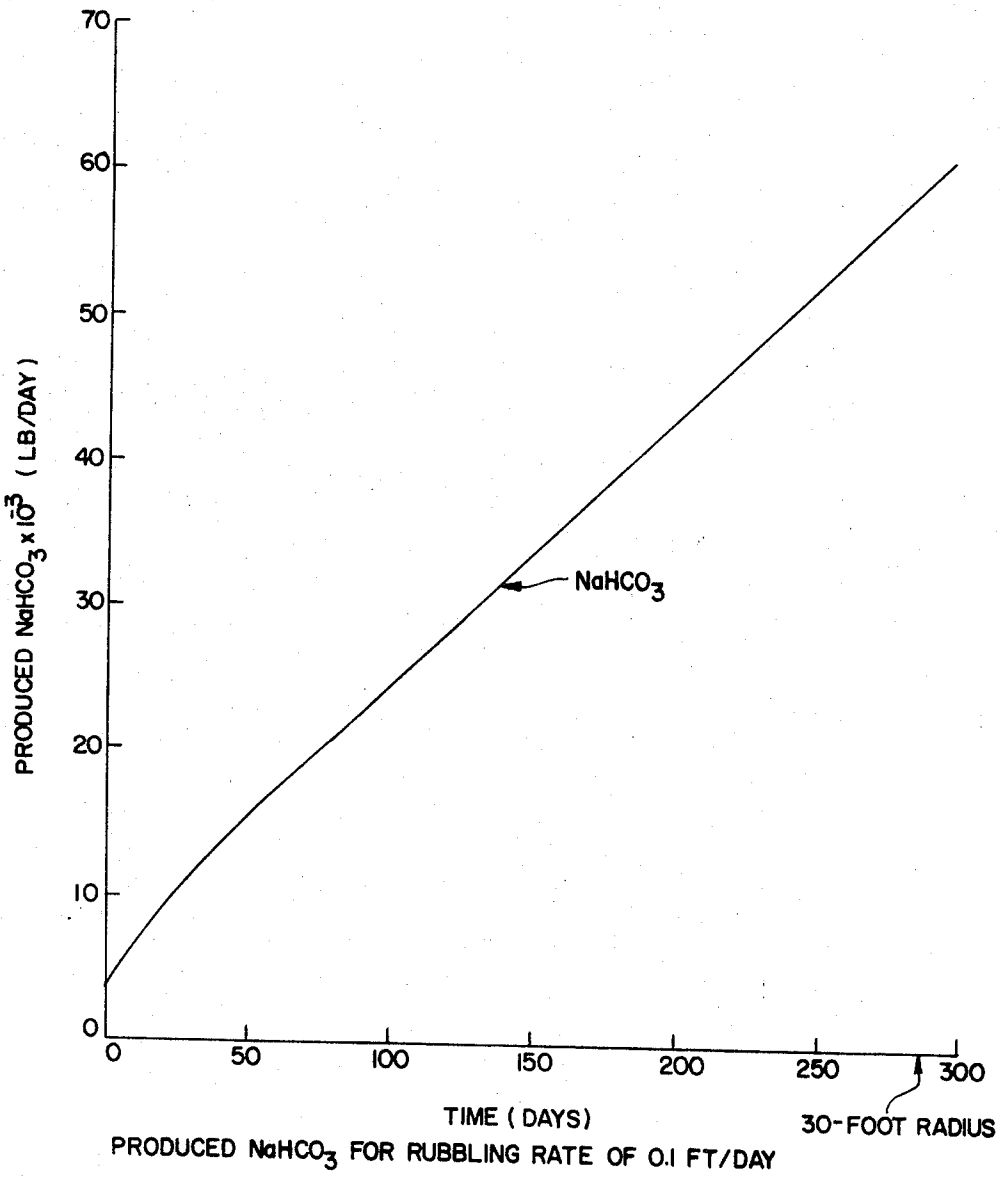
FIG. 14



OIL-STEAM RATIO FOR RUBBLING RATE OF 0.1 FT/DAY

FIG. 16

INVENTOR:
T. N. BEARD
BY: Henne & Pritzker
HIS AGENT

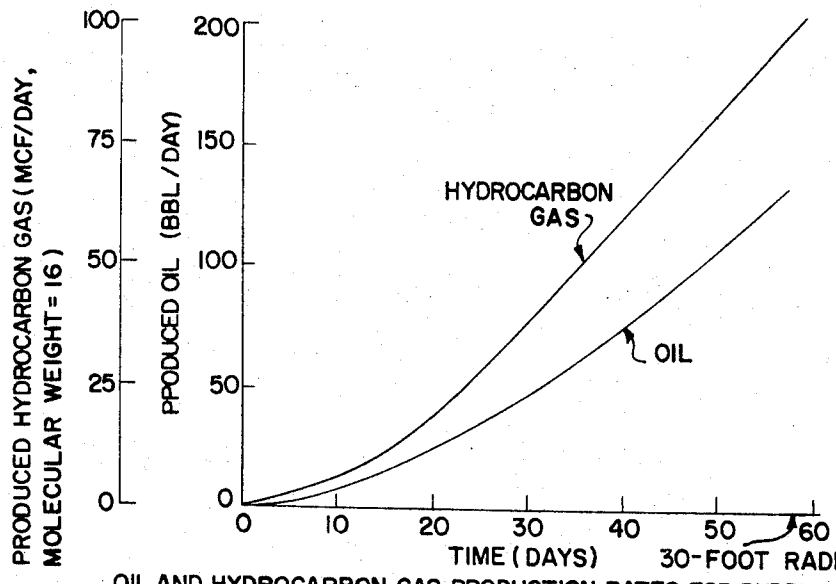


PRODUCED $NaHCO_3$ FOR RUBBLING RATE OF 0.1 FT/DAY

FIG. 15

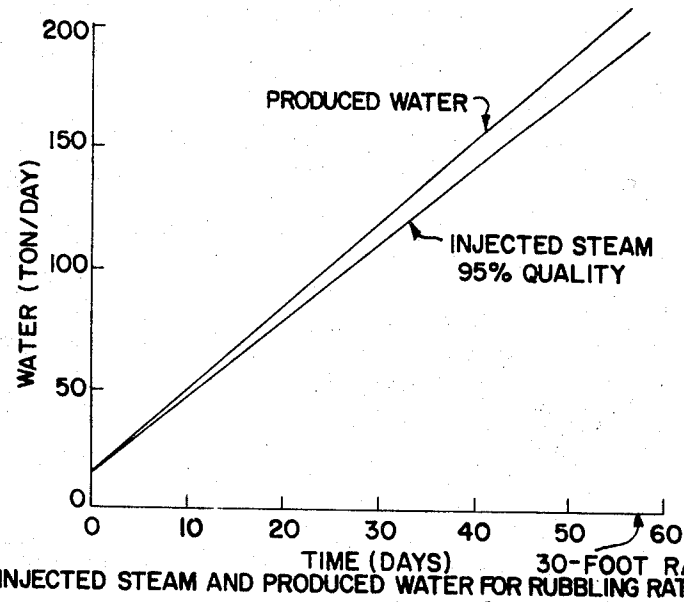
INVENTOR:
T. N. BEARD
BY Maurice M Pinsker
HIS AGENT

FIG. 17

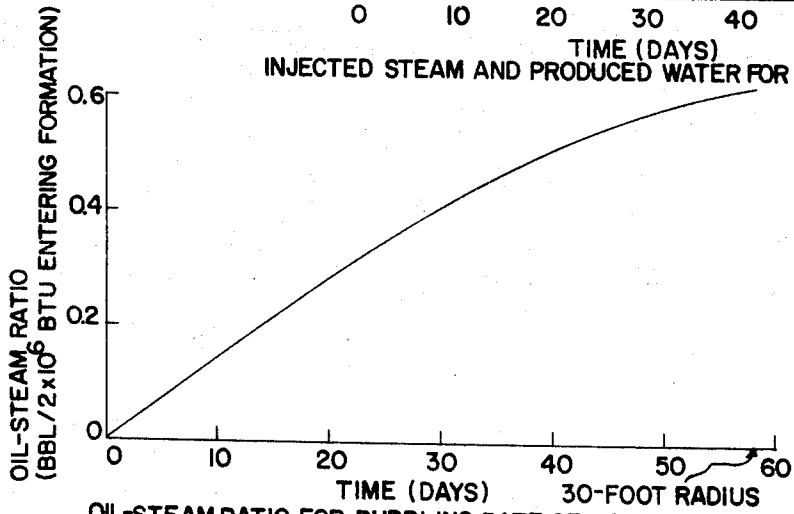


OIL AND HYDROCARBON GAS PRODUCTION RATES FOR RUBBLING RATE OF 0.5 FT/DAY

FIG. 18



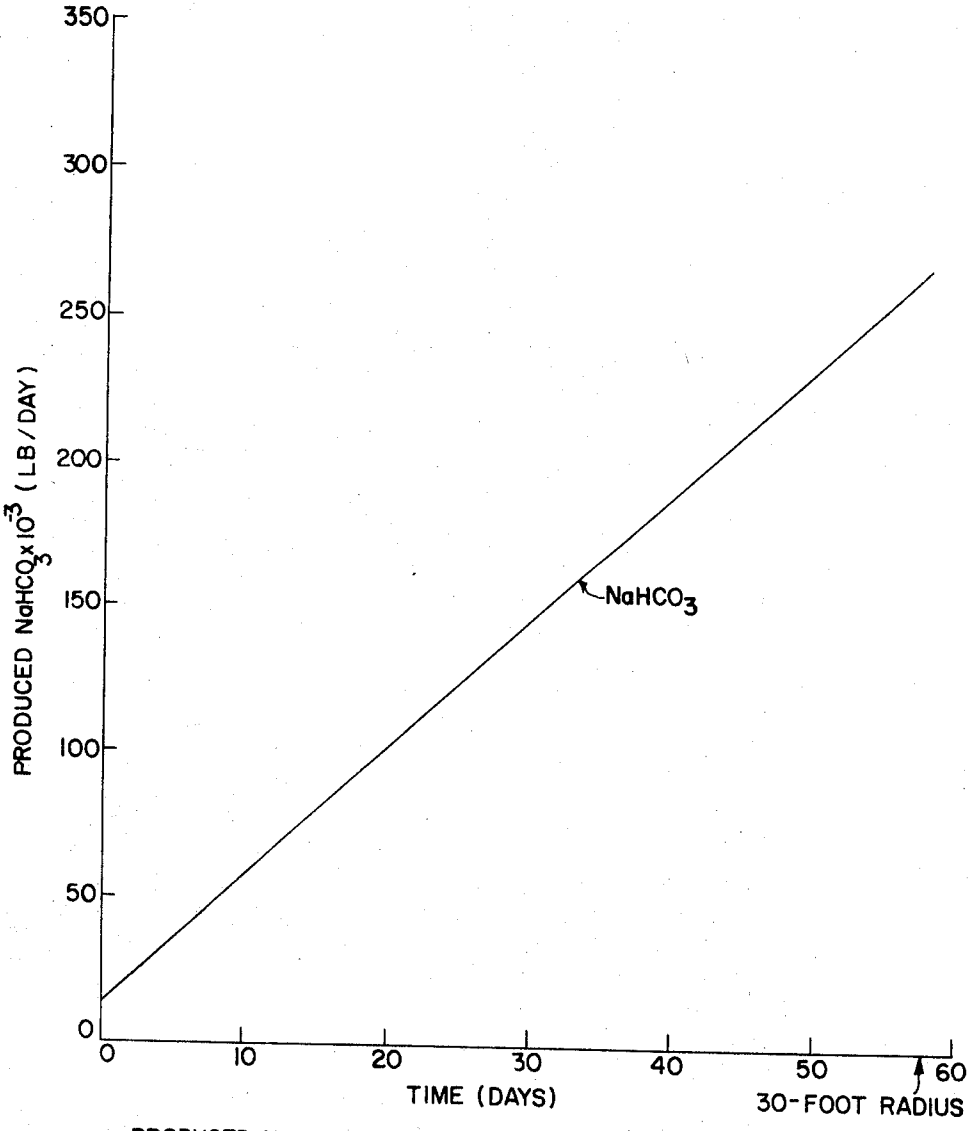
INJECTED STEAM AND PRODUCED WATER FOR RUBBLING RATE OF 0.5 FT/DAY



OIL-STEAM RATIO FOR RUBBLING RATE OF 0.5 FT/DAY

FIG. 20

INVENTOR:
T. N. BEARD
BY
HIS AGENT



PRODUCED $NaHCO_3$ FOR RUBBLING RATE OF 0.5 FT/DAY

FIG. 19

INVENTOR:
T. N. BEARD
BY George G. Pritzker
HIS AGENT

METHOD OF PRODUCING HYDROCARBONS FROM AN OIL SHALE FORMATION

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of copending application Ser. No. 770,964, filed Oct. 28, 1968 and now abandoned. Copending application Ser. No. 75,061 and Ser. No. 75,067 filed Sept. 24, 1970 also are continuations -in-part of the application and claim subject matter similar to that claimed herein.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to the recovery of hydrocarbons and optionally water-soluble minerals from underground oil shale formations containing water-soluble mineral deposits. More particularly, it relates to hydrocarbon recovery by in-situ thermal fluid extraction of oil shale within a fracturized and/or rubblized portion of a subterranean oil shale formation in and around a cavern and/or interconnected cavities formed by leaching or dissolving, e.g., solution mining of the water-soluble minerals therefrom.

2. Description of the Prior Art

Large deposits of oil in the form of oil shale are found in various sections of the United States, particularly in Colorado and surrounding states and Canada. Various method of recovery of oil from these shale deposits have been proposed and the principal difficulty with these methods is their high cost which renders the recovered oil too expensive to compete with petroleum crudes recovered by more conventional methods. Mining the oil shale and removing the oil therefrom by above-ground retorting in furnaces presents a disposal and pollution problem and also such processes are also generally commercially uneconomical. In-situ retorting to convert the oil shale to recover the oil contained therein is made difficult because of the non-permeable nature of the oil shale. The art discloses various means of improving oil recovery of oil from oil shale such as described in U.S. Pat. Nos. 3,400,762 or 3,437,378, or 3,478,825 and particularly various means of increasing permeability of oil shale formations as described in U.S. Pat. Nos. 3,273,649 or 3,481,398 or 3,502,372, or copending application Ser. No. 839,350, filed July 7, 1969. Although these references are directed to an advancement of the art, the basic technique for recovering oil from oil shale still requires rubblization techniques such as by means of explosive devices, e.g., nuclear energy which is expensive, difficult to control and presents a radioactive contamination problem, all of which are very undesirable.

OBJECTS OF THE INVENTION

It is an object of this invention to provide an improved method for recovering hydrocarbons from a water-soluble mineral containing oil shale formation by leaching or dissolving the water-soluble minerals such as by solution mining so as to form a cavern and/or interconnected cavities within the oil shale formation.

It is a further object of the invention to effect rubblization and/or fracturization of the water-soluble mineral leached oil shale formation surrounding the cavern and/or cavities so as to form a permeable zone thereby enhancing in-situ thermal fluid extraction (pyrolysis) of hydrocarbons therefrom.

Still another object of this invention is to effect in-situ pyrolysis to produce hydrocarbons from oil shale subjected to leaching, rubblization and/or fracturization as indicated in the previous two paragraphs, and subsequently recovering the hydrocarbons by suitable means.

Still another object of the present invention is to recover water-soluble minerals from a rich water-soluble mineral containing oil shale formation(s) that may be removed during the leaching and/or solution mining, rubblization and/or fracturization, and/or pyrolysis processes.

Still another object of the present invention is to sequentially and/or simultaneously recover water-soluble minerals and hydrocarbons from rich water-soluble mineral containing oil shale formations that may be removed during the leaching and/or solution mining, rubblization and/or fracturization and/or pyrolysis processes.

Other objects of the invention will be apparent from the following description.

SUMMARY OF THE INVENTION

The present invention is directed to recovery of hydrocarbons and optionally water-soluble minerals from water-soluble mineral containing oil shale formations by the following steps: (1) subjecting a rich water-soluble mineral zone(s) of an oil shale formation to a leaching, dissolving or solution mining process so as to dissolve and preferably remove the water-soluble minerals, thereby creating porosity to allow for thermal expansion of the oil shale and establish communication through the treated zone(s), (2) effecting in said leached zone(s) rubblization and/or fracturization so as to form zone(s) of rubblized and/or fractured oil shale with large surface area for more efficient heat treatment by in-situ thermal fluid extraction (pyrolysis), and (3) injecting into the rubblized and/or fracturized oil shale zone(s) a pyrolyzing fluid to effect hydrocarbon recovery.

The water-soluble mineral(s) and hydrocarbons may be recovered sequentially or simultaneously and if the latter, the two products can be separated by suitable means such as settling or solvent extraction above ground. The oil shale formation may contain more than one zone of rich water-soluble minerals which zones may be separated by impermeable oil shale layers of several feet to several hundred feet and each of these water-soluble mineral layers or zones can be leached or dissolved or solution mined in accordance with the process of the present invention. Also, the water-soluble mineral zones may contain the same or different minerals such as carbonates, bicarbonates, halites or mixtures thereof.

By water-soluble minerals present in the oil shale is meant to include water-soluble silicates, halides, carbonates, and/or bicarbonates salts, such as alkali metal chloride, carbonate, bicarbonate and silicate, e.g., halite, trona, nahcolite and the like.

The first or initial step should be so designed to create a cavern or interconnecting cavities in the water-soluble mineral bed(s) or zone(s) by dissolving, leaching or solution mining techniques through at least one borehole penetrating said formation. Leaching can be effected by cold or hot aqueous solutions either at atmospheric or elevated pressures. When hot solutions are used such as hot water or acidified hot water and/or

steam, more rapid dissolution is effected of certain water-soluble minerals such as nahcolite, trona, halite to produce void spaces in the oil shale formation thereby providing and enhancing well communication, space for thermal expansion of the shale, and greater surface for contact with subsequent pyrolyzing fluid. Water can be cold or hot or steam or any other aqueous fluids can be used such as steam and/or water containing acids, e.g., HCl, or HCl + HF, surfactants, sequestering agents, etc. If the initial cavities are not in communication, fracturing may be necessary.

If necessary, fracturing the formation either before or after leaching by conventional means such as hydrofracturing, explosive means, nuclear means, etc., may be desirable. The leaching solutions can contain chemical agents to enhance dissolution of the minerals. Under certain leaching conditions decomposition of certain water-soluble minerals, e.g., bicarbonates, into solublizing materials may take place of such minerals as dawsonite and silicates which might be present in the formation, thereby increasing the porosity of the formation. For example, when nahcolite is dissolved with water, the pH of the dissolution fluid is increased and thereby aids in the dissolution of silicates, etc.

Leaching or solution mining of the water-soluble minerals such as halite or nahcolite can be accomplished by a suitable solution mining technique such as described in U.S. Pat. Nos. 2,618,475; 3,387,888; 3,393,013; 3,402,966; 3,236,564; 3,510,167 or Canadian Pat. Nos. 832,828 or 832,276 or as described in copending application Ser. No. 2,765 filed Jan. 17, 1970. Spalling and rubbling can be accomplished by the method described in U.S. Pat. No. 3,478,825 or by other means such as by hydraulic, explosive, nuclear and/or electrical means. Preferably rubblization is accomplished by hot fluid circulation through the cavern causing the walls to spall and fracture. In-situ thermal recovery of oil can be effected by a pyrolyzing fluid such as steam and/or hot water or solvent extraction means.

The circulation of a pyrolyzing fluid not only effects oil recovery but also effects thermal rubbling and/or fracturization. Also, if the pyrolyzing fluid such as steam is used to extract and recover oil, more minerals may be dissolved perpetuating the process.

By the term "pyrolyzing fluid" is meant a liquid or gas which by means of thermal, chemical and/or solvent action, interacts with the kerogen components of an oil shale to produce and entrain hydrocarbon such as steam, Such a fluid can be hot fluids such as hot water of steam, or mixtures of hot water and strea, hot hydrocarbons and/or mixtures of such fluids with chemicals such as acids, e.g., HCl and/or organic solvents, benzene, toluene, cumene, phenol, etc. The kerogen pyrolyzing fluid can be heated by surface or borehole-located heating devices. The kerogen-pyrolyzing fluid can advantageously comprise or contain a solvent for the soluble mineral, such as steam condensate or a hot aqueous solution of organic and/or inorganic acid, having a temperature such as at least one hundred degrees Fahrenheit, such as from about 450° F to above about 1,500° F and preferably from about 550° F to 1,000° F. Where the kerogen-pyrolyzing fluid contains or forms aqueous components, its circulation through the treated oil shale formation can enlarge the cavern, by solution mining the soluble minerals, while shale oil is being produced. Also, simultaneously or sequentially pyrolyzing and oil extracting fluids can be used such as steam followed by a solvent such as phenol or benzene.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a vertical sectional view, partly diagrammatic, of an embodiment of the invention showing a formation penetration by more than one well.

FIG. 2 is a sectional view of an embodiment of the invention, the formation being penetrated by a single well.

FIG. 3 is a graphical illustration showing the solubility of sodium chloride (NaCl) and sodium bicarbonate ($NaHCO_3$) in water as a function of temperature.

FIG. 4 is a schematic illustration of a method for providing communication between a pair of well boreholes in accordance with the techniques of this invention.

FIG. 5 is a schematic illustration partially in vertical section illustrating the mechanism of single-well salt leaching.

FIG. 6 is a graphical representation of maximum rate of nahcolite leaching as a function of leaching fluid temperature.

FIG. 7 is a graphical representation of minimum time required to leach a nahcolite cavity of 100-foot radius as a function of leaching fluid temperature.

FIG. 8 is a graphical representation showing estimated maximum time to leach a nahcolite cavity of 100-foot radius as a function of leaching fluid injection rate and temperature.

FIGS. 9–12 show graphical representations of various process parameters as a function of time in an example application of the process of this invention where the rubbling rate is 0.02 feet per day.

FIGS. 13–16 show graphical representations of various process parameters as a function of time in an example application of the process of this invention where the rubbling rate is 0.1 feet per day.

FIGS. 17–20 show graphical representations of various process parameters as a function of time for an example application of the process of this invention where the rubbling rate is 0.5 feet per day.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Referring to FIG. 1 of the drawing, a plurality of well boreholes are shown penetrating into a subterranean oil shale formation **9** which contain rich zones of water-soluble minerals **10**, **10***a* and **10***b*. An injection well borehole **11** is shown extending into oil shale formation **9** and rich soluble mineral zone(s) **10** or multizones such as **10***a* and **10***b* that are located within the oil shale formation **9** and are also encountered by well borehole **12**. Well boreholes **11** and **12** are illustrated as having casings **13** and **14**, respectively, cemented in place in their respective boreholes by suitable sealants **15** through **16**, respectively. Although only a single injection well borehole **11** and a single production well borehole **12** have been illustrated, obviously various combinations of one or more injection and production wells may be provided by one skilled in the art.

In carrying out the method of this invention, the location of zones rich in substantially water-soluble minerals is determined in a conventional manner.

Fluid communication between well boreholes **11** and **12** (FIG. **1**) and the zones rich in water-soluble minerals therebetween may be established by solution mining a cavern or cavities **23**, through the soluble mineral

zones. Communication can be enhanced by means of conventional hydraulic, electric, and/or explosive fracturing techniques, all well known in the art. Where, for example, subterranean stresses in and around soluble mineral zones **10, 10***a* and **10***b* are conducive to the formation of horizontal fractures, the fluid communication between well boreholes **11** and **12** and the soluble mineral can be established by a conventional hydraulic fracturing technique. Referring to FIG. **1**, after fluid communication has been established between a pair of wells, aqueous leaching or solution mining liquid is injected through tubing **17** down well borehole **11**, out through perforations **18** opposite any or all of the soluble beds through the bed **10, 10***a* and/or **10**b up borehole **12** through tubing via perforation **19** creating a leached cavern **23.** The aqueous liquid may comprise water and/or steam or aqueous solutions of acid or acid-forming materials and is circulated at pressures either above or below the over-burden pressure. The circulating aqueous liquid dissolves the water-soluble minerals and mineral by-products thereof are recovered from the fluid flowing out of well borehole **12,** for example, by conventional evaporation and/or precipitation procedures.

Fluid communication can also be established in one borehole between at least two spaced portions of the well borehole and the water-soluble minerals (as for example, in FIG. **2** communication is through the tubing string the ends of which are open to the water-soluble minerals and some distance apart.) Thus a single well may be utilized by a dual zone completion arrangement as shown in FIG. **2** such that fluids can be injected at one point of the well and produced from another point of the same well. In FIG. **2,** the wellbore is **26,** the casing is **27,** the sealant is **28,** within the casing are the injection tubing string **29** and production tubing string **30,** the borehole **26** penetrates oil shale formation **9** with mineral zone(s) **10** or or multizones **10***a* and **10***b*.

Fracturing pressures are generated within the oil shale formation **9** while lower pressures are maintained within the cavern **23** which is formed within oil shale formation **9** by the removal of the water-soluble minerals. These pressures are preferably generated by merely circulating hot fluid through cavern **23.** As the walls of the cavern(s) **23** (**23***a* FIG. **2**) are heated kerogen is pyrolyzed within the cavern walls and the pressures of the pyrolysis products increase until portions of the walls are spalled into the cavern **23** creating a rubblized zone **24** (**24***a* FIG. **2**) and surrounding fracture area **25** (**25***a* FIG. **2**).

Alternatively, fracturization and/or rubblization can be accomplished by conventional means such as hydraulic, explosive means and the like. To provide additional void space, if necessary, further leaching can be conducted.

Finally, a kerogen-pyrolyzing fluid such as steam is circulated from well borehole **11** (FIG. **1**) through the rubblized zone **24** and fractured zone **25** of oil shale formation **9** and out of well borehole **12.** Hydrocarbon materials are then recovered from the heated fluid circulating out of well borehole **12** by means well known in the art. Removal of hydrocarbons from the oil shale provides additional void space enlarging the original rubblized zone, perpetrating the process. Similar techniques can be applied to single wells as shown in FIG. **2.**

Conventional equipment and techniques, such as heating means, pumping means, separators and heat exchangers may be used for pressurizing, heating, injecting, producing and separating components of the heated fluid circulating through the oil shale formation **9.** The production of the fluid may be aided by downhole pumping means, not shown, or restricted to the extent necessary to maintain the selected pressure within the oil shale formation **9.**

The fluid circulated through rubblized zone **24** and fractured zone **25** (FIG. **1**) to recover oil shale from oil shale formation **9** may comprise any heated gas, liquid or steam. Oil shale reactive properties may also be imparted to the circulating fluid as discussed hereinabove.

Where the oil formation contains a zone rich in substantially water-soluble minerals in which zone the soluble minerals occur in the form of adjacent but discrete nodules or lenses **31,** or the like, the present process is applied as described above. In this situation, the caverns comprise a network of relatively small cavities that are interconnected by fractures.

EXAMPLES

Leaching Phase

A. In a continuous oil shale formation containing a nahcolite bed, a pair of wells are completed into a nahocolite layer at 2,100 feet with a downhole well separation of 70 feet. Solution mining of the nahcolite ($NaHCO_3$) by injection of hot water therein provides both communication between the wells and the void space necessary to effect fragmentation and subsequent in-situ thermal treatment of the formation to recover oil.

In such a situation a bulk density (p) was found to be a 2.2 gm/cc and the permeability (K) was found to be 0.065 millidarcy for the nahcolite layer at about 2,055 feet. Experimentally, samples of this nahcolite were found to be completely dissolved in hot water, leaving 6 percent by weight insolubles.

Minimum volumes of water required to establish a channel 1 foot wide, three feet high and 70 feet long (between two wells about 50 feet apart, for example) which contains 13.4 tons of nahcolite may be determined from the solubility of sodium carbonate and bicarbonate in water.

As can be seen in FIG. **3** the solubility of pure $NaHCO_3$ in water at formation temperature (90° F) is about 30 lbs/bbl. Thus, a minimum of 700 bbls of water is required to establish communication between wells. On the other hand, a cylindrical cavity of the same height but 50 feet in radius contains 1,620 tons of nahcolite, and requires at least 10^5 bbls of water at formation temperature.

Water requirements may be reduced by a factor of five if the water is heated to 400° F ($\Delta T = 310°$ F). Heating the water also has the added advantage that it results in a higher dissolution rate. Thus heating the water results in a shorter operating life, and requires the handling of relative small volumes of water. On the other hand, it requires the use of heaters with their attendant requirements of water quality and fuel supply. Also, the water disposal lines may become plugged with precipitate as the temperature of the line drops at the surface.

If the water is injected at formation temperature, a slight reduction in temperature takes place. The heat of solution of sodium bicarbonate is 4 kcal/mole, which

results in as much as a 10° F drop in the solution temperature. Because the solution is not saturated, the observed temperature drops are in fact much smaller and thus may be discounted.

The addition of acids, such as 15 percent HCl to mining solutions is beneficial since it generally may be expected to result in a reduction in operating time, because of the high rate of reaction between the acid (HCl) and nahcolite. For example, injection of an acid solution into the wellbore will speed up the rate at which the cavity is made.

Communication may be established between the two wells by means of mechanical nozzles having controllable orientation through which the solvent is introduced. As illustrated schematically in FIG. 4, where the uncertainty in orientation of the nozzles is ± 10°, the nozzles may be directed from both wells A and B, with the orientation of the nozzles ranging from 0° to 15° from their centerlines. This procedure insures eventual communication between the wells and reduces the time to obtain communication.

The degree of saturation of the effluent liquid is closely related to the mean residence time of the fluid in the subsurface, the circulation pattern of the fluid, and the rate at which the nahcolite goes in solution. The solution efficiency may be increased by increasing the residence time, that is, by increasing the operating time. Where sufficient water capacity is available and the operating time is to be kept low, it would appear that low solution efficiencies may be tolerated, especially if it is not intended to heat the water. On the other hand, the mining effect may be greatly enhanced if fragments resulting from jetting are removed as solids.

After solution mining to form the cavern, the formation is fractured in the vicinity of the cavern and oil is recovered therefrom by means of in-situ oil recovery means as is well known in the art.

B. Results for a single well leaching to a 100-foot radius was determined experimentally for a nahcolite layer oil shale. The leaching rate results show that leaching rates are a function of temperature.

FIG. 5 shows the mechanism of single well salt leaching. Fresh water enters at the top of the formation and flows along the top of the cavity. Once it reaches the salt layer it dissolves the salt, becoming denser. The denser fluid then flows to the bottom of the cavity along the edge of the salt. There are two important parameters which control the rate of frontal advance of the cavity, natural convection and diffusion in the vertical direction. The slowing of the frontal advance is caused by diffusion in the vertical direction from the salt solution to the incoming fresh water. As the concentration of salt in the water reaching the leading edge of the cavity increases, the rate of frontal advance slows proportionally.

An experiment was scaled for 2,000 bpd at room temperature in a 6-foot layer of NaCl. This corresponds to scaling nahcolite leaching in the same size layer at 8,300 bpd and 300° F. It was found that the rate of frontal advance was constant out to the scaled test radius of 100 feet. The concentration of salt in the produced solution increased from 12 percent of saturation to 85 percent of saturation during the course of the experiment.

Using the results of the experiment, estimates were made of the maximum leaching rate of the subject nahcolite layer as a function of the temperature of the fluid at the leading edge of the cavity. Since a perfectly circular pattern was not obtained in the experiment, the minimum leaching rate was used in the estimates. It was also assumed that there were 20 percent insolubles in the nahcolite and that their only effect was in reducing the available surface area for leaching. FIG. 6 shows the rate of leaching as a function of the temperature of the fluid at the leading edge. FIG. 7 shows the minimum time required to leach a 100-foot radius as a function of temperature. It appears that a flow rate of 2,000 bpd should be practical for a 6-foot layer.

The test showed that the production well was producing saturated solution when the frontal advance rate decreased and the maximum time required to leach a 100-foot radius can be calculated from a material balance and the solubility of nahcolite in water. FIG. 7 shows this minimum leaching time as a function of leaching time and flow rate. In making the calculations for FIG. 7, the constraint that the rate of advance could not exceed the maximum values given in FIG. 6 was used.

FIG. 8 shows the effect of temperature on water injection rates leaching a cavity with a radius of 100 feet.

It should be noted that the temperature at the leading edge of the advancing front will not be the same as the injected temperature due to heat losses to the shale. The temperature drop will be roughly proportional to the temperature difference between the injected fluid and the initial shale temperature and will increase as the front advances.

Rubblization Phase

Following the leaching phase rubbling using hot water and steam on the oil shale was performed. This consisted of cementing a large rectangular block of oil shale into a stainless steel container such that the lower 3-½ inches of the block was unconfined and was contacted with hot water or steam. A spring-loaded plate positioned below the block allowed for the detection of any falls occurring during the experiment. Thermocouples placed in the steam chamber and into the shale block monitored the temperature at these points. Pressures surrounding the shale were maintained at 900 to 1,000 psi with nitrogen gas.

Three tests (A_1, B_1 and C_1) were run under essentially the same conditions. The first, A_1, utilized a lean shale block (8 gal/ton); the lower face of the block was contacted with 500° F steam for a 6-day period. At the conclusion of the test, the shale container was opened and the block examined, and it was only evidented that the steam induced considerable cracking and rubbling. No oil was recovered during or after the experiment.

The second test, B_1, was essentially a repeat of A_1, using a richer shale (27 gal/ton) and a different heating medium, hot water instead of steam. The water temperature was held constant for a 1- or 2-day period and then raised in 50° F increments. The water temperature was raised and held constant at 300° F for 16 hours. Several large cracks (¼ inch to ½ inch wide) were developed even at these mild temperatures. After a day's delay, the test was restarted and a major fall occurred (water temperature = 350° F). Smaller falls of 5 to 10 pounds occurred at 25 hours. The test was terminated after 312 hours; the maximum temperature, 520° F, maintained for the last 51 hours. No oil was detected in the effluent water stream, but the outlet lines were

found to be coated with a tarry residue readily soluble in benzene.

The results of B_1 indicated that rubbling took place even at mild temperatures (350° F).

Test C_1 was run under conditions similar to B_1 and the specific conditions are shown in Table 1.

Table 1

C_1 — TEST CONDITIONS

Water Temp. (°F)	Time at Temp. (hours)	Shale Temp. (°F)	Pressure (psi)
300	48	185	975
350	48	210	1000
400	48	245	1000
450	48	275	1000
x			

x temperature was then reduced in 50° increments. Total test time = 312 hours (13 days)

Upon examining the shale at the termination of the test, it was apparent that a large slab (54 lb) had almost entirely separated from the main body of the shale block. The major fractures formed did not continue through the entire slab. There was good correlation between the position of the vertical cracks (perpendicular to the bedding plane) and the positions of distortions occurring in the bedding. Fractures also occurred at sites where there was marked variation in the mineral content. These variations were in the form of streaks of crystalline material.

Heating the shale four days at 520° F resulted in greatly increased fracturing over that resulting from heating to 450° F. After heating at 450° F, many cracks had formed, but none completely cleaved the slab. After heating to 520° F, a number of these cracks had been considerably widened and had propogated through the entire extent of the slab. The strain, measured for the slab, had increased to 0.057 and average slab thickness increased from 4 to 4-½ inches. No oil was produced with the effluent water.

Peculiar to test C_1 was the correlation between the positions of bedding plane distortions and the occurrence of vertical cracks upon heating. The previous sample B_1 was very evenly bedded and did not show this behavior.

In summary, the amount of fragmenting and fracturing of oil shale increased with increasing richness of the oil shale sample. There was a significant increase in fracturing at T - 520° F over that produced below 450° F in unconfined shale samples. Good correlation exists between the positions of vertical (perpendicular to the bedding) cracks and the positions of distortions in the bedding plane.

Recovery Phase

Calculations were made to estimate the performance of a shale oil recovery project in accordance with the method of this invention wherein steam is used as the pyrolyzing fluid to effect hydrocarbon recovery as well as recovery of other products as shown in FIGS. 9–20.

The basic data used for the calculations were:

a. steam injection at 625° F, 95 percent quality,

b. 10 tons of steam condensed coming down injection pipe,

c. initial temperature of shale is 100° F,

d. shale contains 39 percent by weight nahcolite,

e. shale richness was 24.2 gal/ton (gross),

f. interval considered was 100 feet high,

g. initial cavity diameter was 22 inches,

h. 20 percent by weight of the produced hydrocarbon flowed in the gas phase, and

j. production well temperature was 450° to 500° F.

FIGS. 9–20 show the produced oil and hydrocarbon gas, the injected steam and the produced water; the produced $NaHCO_3$; and the oil-steam ratio. FIGS. 9–12 are for a rubbling rate of 0.02 ft/day, FIGS. 13–16 are for a rubbling rate of 0.1 ft/day, and FIGS. 17–20 are for a rubbling rate of 0.5 ft/day.

It is understood that various changes in the detailed described to explain the invention can be made by persons skilled in the art within the scope of the invention as expressed in the appended claims. I claim as my invention:

1. A method of producing hydrocarbons from a subterranean oil shale formation containing zones of water-soluble minerals comprising the steps of:
   a. extending at least one well borehole into the water-soluble mineral containing zone of the oil shale formation;
   b. removing water-soluble minerals by leaching, dissolving or solution mining with a non-acidic fluid, thereby creating porosity in said zone of the formation;
   c. effecting rubblization and fracturization of oil shale adjacent leached zone (b);
   d. injecting into said rubblized, fracturized oil shale a pyrolyzing fluid; and
   e. recovering hydrocarbons from said rubblized fracturized oil shale.

2. The method of claim 1 wherein the leaching solution (b) is hot water, and the pyrolyzing fluid is steam.

3. A method of producing oil from a subterranean oil shale formation containing a zone of water-soluble minerals comprising the steps of:
   creating a cavity in the oil shale formation by circulating aqueous a non-acidic solution-mining fluid into the water-soluble mineral zone through a first well, and out of the water-soluble mineral zone through a second well;
   recovering the water-soluble mineral from aqueous fluid circulating out of the second well;
   fracturing and rubbling the oil shale formation surrounding the cavity;
   flowing a kerogen-pyrolyzing fluid into the fractured and rubblized formation; and
   recovering oil from the pyrolyzed treated fracturized and rubblized formation.

4. A method for producing oil from a subterranean oil shale formation having at least one zone which contains water soluble minerals comprising the steps of:
   extending at least one well borehole into said formation and into said zone;
   establishing fluid communication between said well borehole and said zone at at least two spaced locations within said well;
   circulating aqueous liquid from one of said spaced locations to another in contact with said zone to dissolve water-soluble minerals and leave a fluid-filled cavern within the oil shale formation while
   maintaining fluid pressures within said cavern below overburden pressure within other regions in said oil shale formation;
   generating fluid pressures within said oil shale formation sufficient to create fractures and displace solid oil shale material toward and into said cavern;

flowing a kerogen-pyrolyzing fluid from one of said locations to another through the fractures and cavern within the oil shale formation;

outflowing kerogen-pyrolyzing fluid from said well; and

recovering shale oil from outflowing portions of said kerogen-pyrolyzing fluid.

5. A method for producing oil from a subterranean oil shale formation having at least one zone which contains water soluble minerals, comprising the steps of:

extending at least one well borehole into said formation and into said zone;

establishing fluid communication between at least one well borehole and said zone at at least two spaced locations within said well;

circulating aqueous liquid from one of said spaced locations to another in contact with said zone to dissolve water-soluble minerals and leave a fluid-filled cavern within the oil shale formation while

generating fluid pressure within said oil shale formation sufficient to create fractures and displace solid oil shale material toward and into said cavern;

flowing a kerogen-pyrolyzing fluid from one of said locations, to another through the fractures and cavern within the oil shale formation;

outflowing kerogen-pyrolyzing fluid from said well; and

recovering shale oil from outflowing portions of said kerogen-pyrolyzing fluid.

6. The method of claim **5** including the step of establishing fluid communication between said borehole locations through said zone water-soluble mineral by hydraulically fracturing at least a portion of said oil shale formation containing said zone.

7. A method of claim **5** including the step of establishing fluid communication between said borehole locations through said zone water-soluble mineral by explosively fracturing at least a portion of said oil shale formation containing said zone.

8. The method of claim **5** including the step of establishing fluid communication between said borehole locations through said zone water-soluble mineral by electrically fracturing at least the portion of said oil shale formation communicating with said well boreholes.

9. The method of claim **5** wherein the step of circulating aqueous fluid includes the step of imparting acidic properties to said aqueous fluid and circulating said fluid liquid at pressures above the overburden pressure.

10. The method of claim **5** wherein the step of circulating aqueous liquid includes the step of imparting acidic properties to said aqueous fluid and ciculating said aqueous fluid at pressures below the overburden pressure.

11. The method of claim **5** wherein the step of generating fluid pressures sufficient to create fractures is carried out by the step of circulating fluid through said cavern at a temperature sufficient to pyrolyze the kerogen within the oil shale adjacent to the walls forming said cavern and to spall-off portions of said walls into said cavern.

12. The method of claim **5** wherein the step of generating fluid pressures sufficient to create fractures is carried out by the step of pumping fluid explosives into said cavern; and

detonating said explosives so as to produce an initial pulse of high pressure within the cavern followed by a pressure that becomes lower than that within the adjacent oil shale formation thereby displacing said solid material towards said cavern.

13. The method of claim **1** including the step of establishing fluid communication between at least a pair of well boreholes within said mineral containing zone, said communication being accomplished by jetting aqueous liquid from each of said well boreholes to a point intermediate said boreholes.

14. A method of producing oil from a subterranean oil shale formation containing rich water-soluble mineral zones comprising the steps of:

a. subjecting the formation to leaching of the water-soluble minerals by injecting into the formation a non-acidic leaching solution to leach out the minerals and thereby effecting a zone of communicating cavities in the formation;

b. injecting a kerogen-pyrolyzing fluid into cavities zone (a) of the formation so as to effect spalling and rubblization of the oil shale;

c. continuing injection of the kerogen-pyrolyzing fluid to effect oil extraction; and

d. recovering the oil.

15. The method of claim **14** wherein the solvent is an aqueous liquid and the kerogen-pyrolyzing fluid is steam.

16. The method of claim **14** wherein the water-soluble mineral is water-soluble carbonate, the water-soluble leaching solution is hot water and the kerogen-pyrolyzing fluid is steam.

17. The method of claim **15** wherein the water-soluble mineral is nahcolite.

18. The method of claim **5** wherein the water-soluble minerals are recovered from the formation prior to injection of the kerogen-pyrolyzing fluid.

19. The method of claim **3** wherein the dissolved water-soluble mineral by-products are recovered prior to flowing kerogen-pyrolyzing fluid into the formation.

20. The method of claim **5** wherein the aqueous liquid is hot water and the kerogen-pyrolyzing fluid is steam.

21. The method of claim **20** wherein the water-soluble mineral is water-soluble carbonate.

22. The method of claim **20** wherein the water-soluble mineral is nahcolite.

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