

[54] **METHOD OF PRODUCING
HYDROCARBONS FROM OIL SHALE
FORMATIONS**

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[22] Filed: Apr. 28, 1971

[21] Appl. No.: 138,021

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 835,323, June 23,
1969, abandoned.

[52] U.S. Cl. 166/252, 166/269, 166/271,
166/272, 166/306

[51] Int. Cl. E21b 43/24, E21b 43/26, E21b 43/28

[58] Field of Search 166/252, 254, 266,
166/269, 271, 272, 274, 303, 305, 306; 299/4,
5

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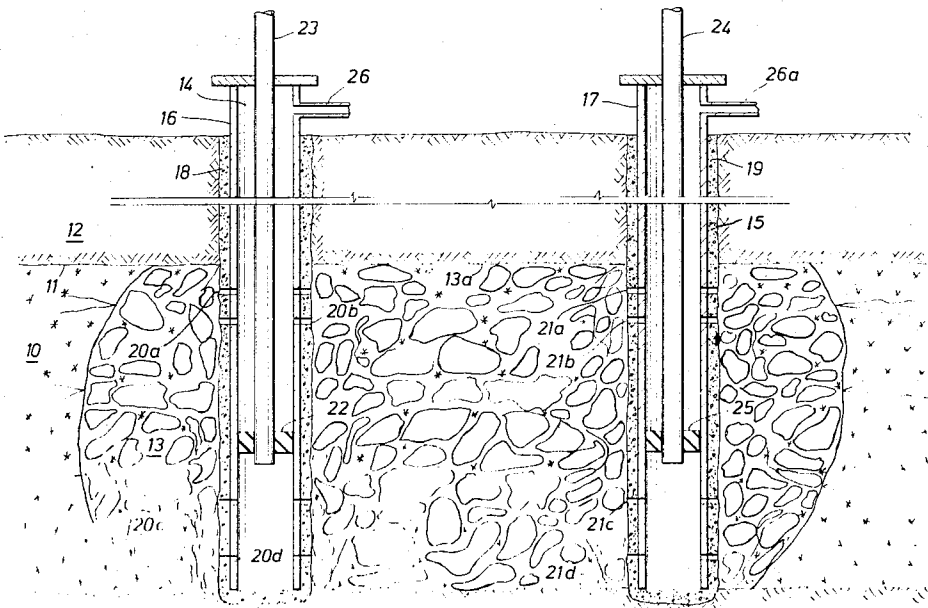
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[57] **ABSTRACT**

A new and improved method of producing hydrocarbons from a subterranean oil shale formation containing heat-sensitive carbonates comprising penetrating said formation with at least one well and forming a cavern therein so that communication is established between the surface and the cavern; circulating a hot fluid preferably in the upper region of the cavern to effect decomposition of the carbonates to carbon dioxide thereby causing pressure build-up resulting in fracturing and/or rubbing and enlarging the cavern upward to a desired dimension; terminating this process by injecting, preferably simultaneously, into the upper region of the cavern a cooling fluid and into the rubblized zone of the oil shale a kerogenpyrolyzing fluid to effect hydrocarbon recovery.

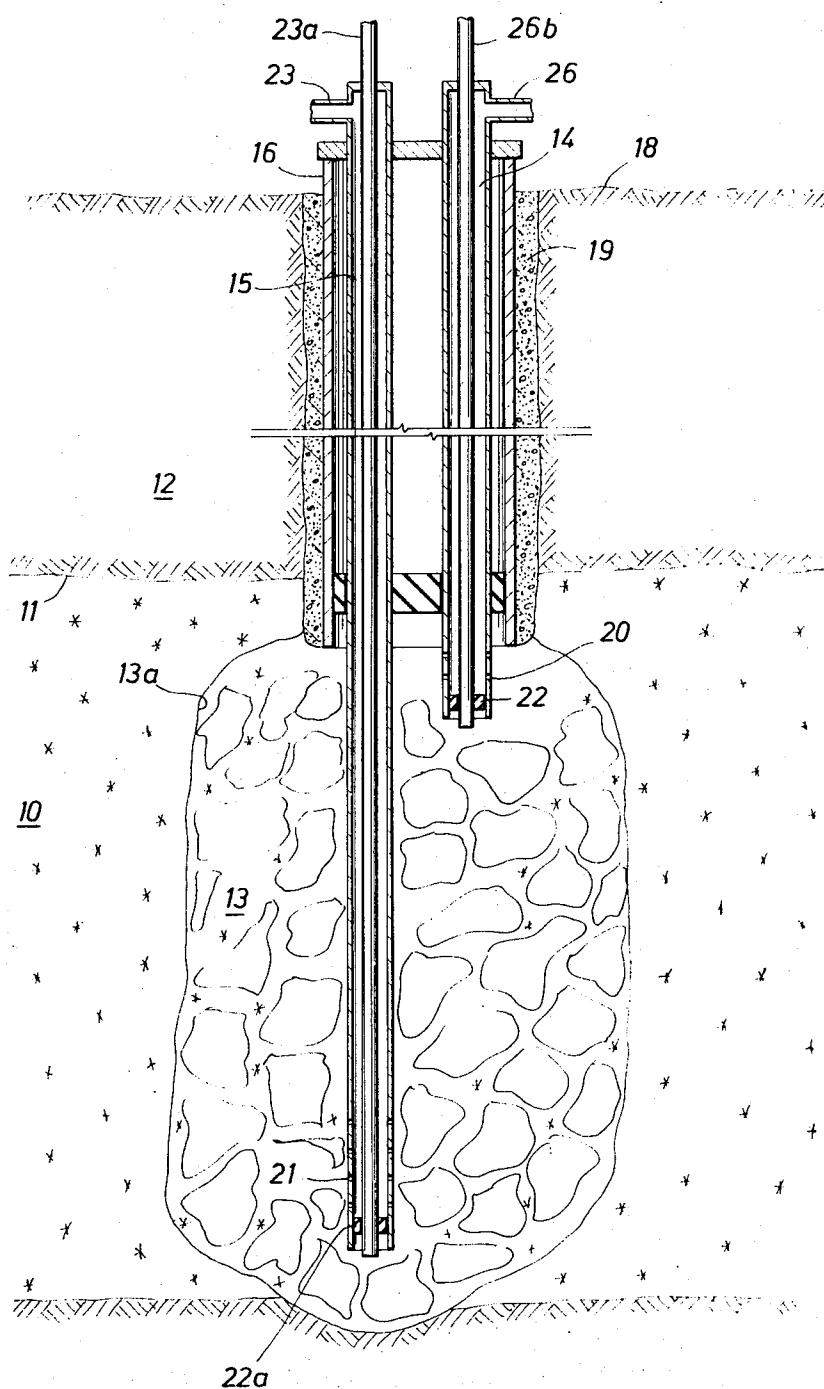
27 Claims, 16 Drawing Figures



PATENTED JUN 26 1973

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SWEET 01 OF 10



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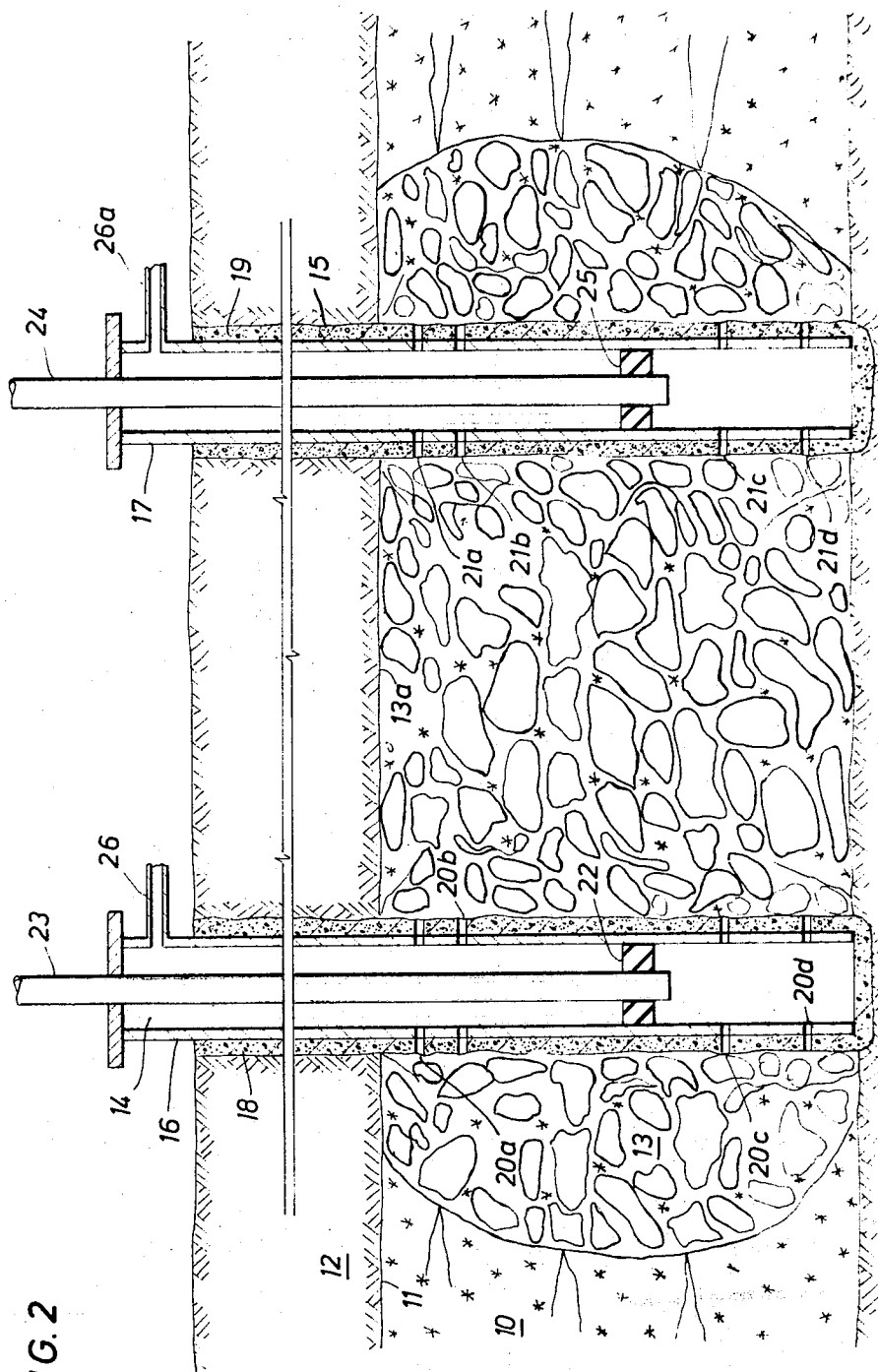


FIG. 2

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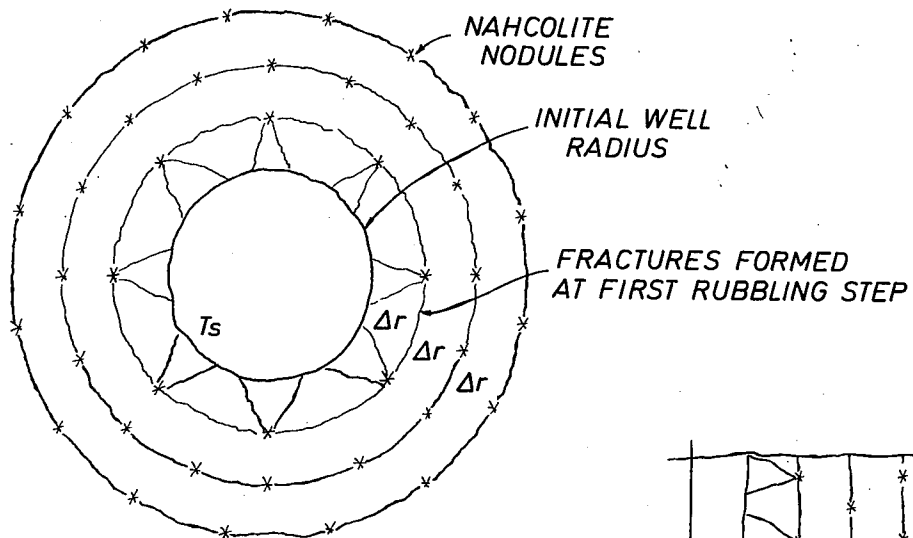


FIG. 3
PLAN VIEW OF CYLINDRICAL
RUBBLING SCHEME

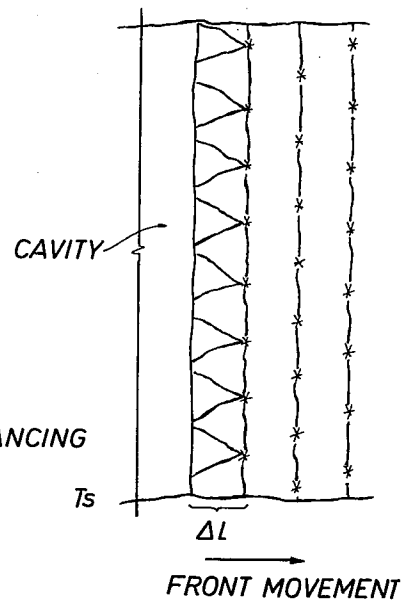


FIG. 3A
LINEAR ADVANCING
RUBBLING
FRONT

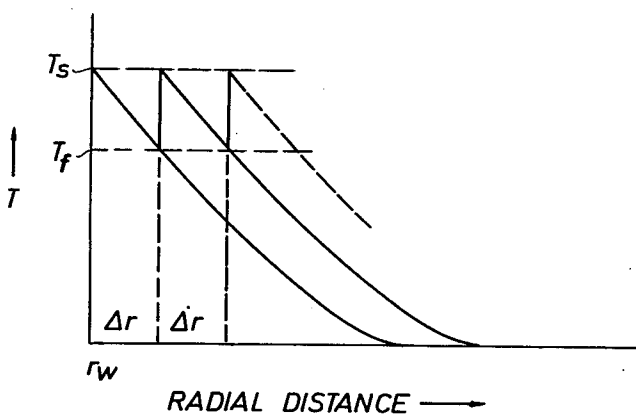


FIG. 4
TEMPERATURE PROFILES
DURING ADVANCE OF THE
RUBBLING FRONT

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FIG. 5 RUBBLING FRONT VELOCITY AS A FUNCTION OF TIME

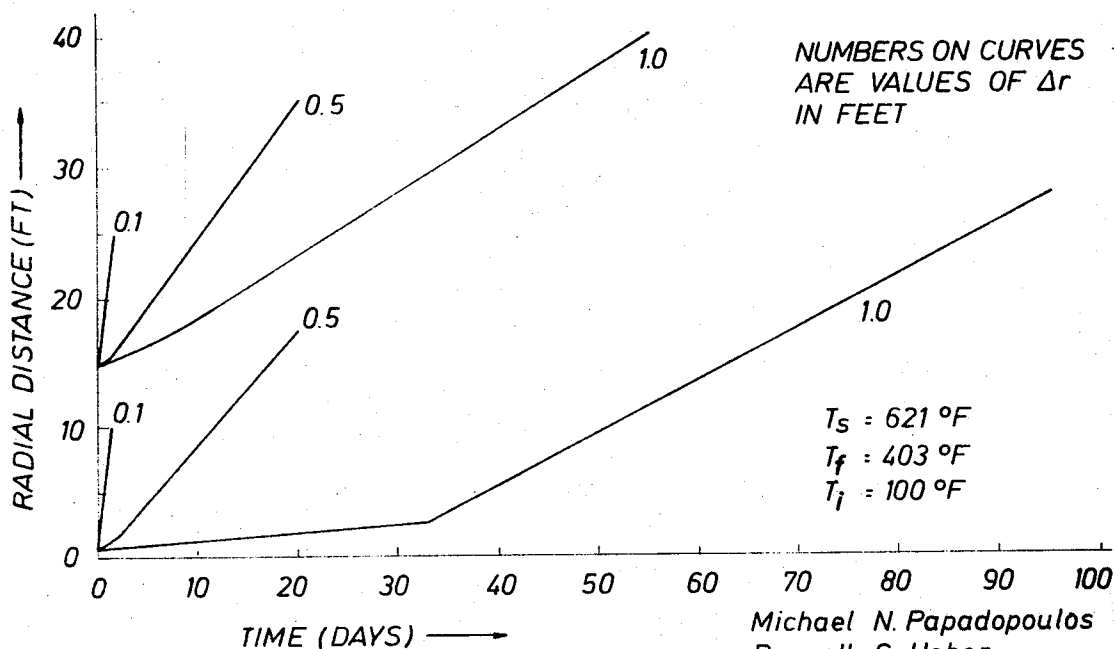
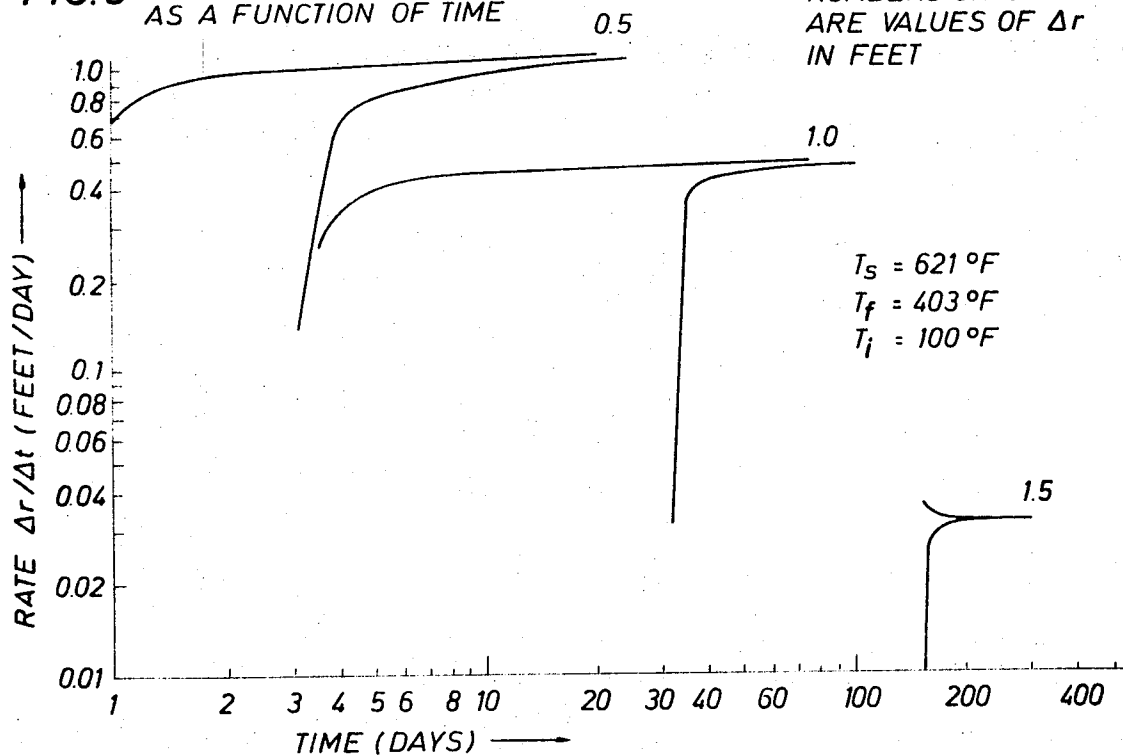


FIG. 6

ADVANCE OF CYLINDRICAL
RUBBLING FRONT WITH TIME

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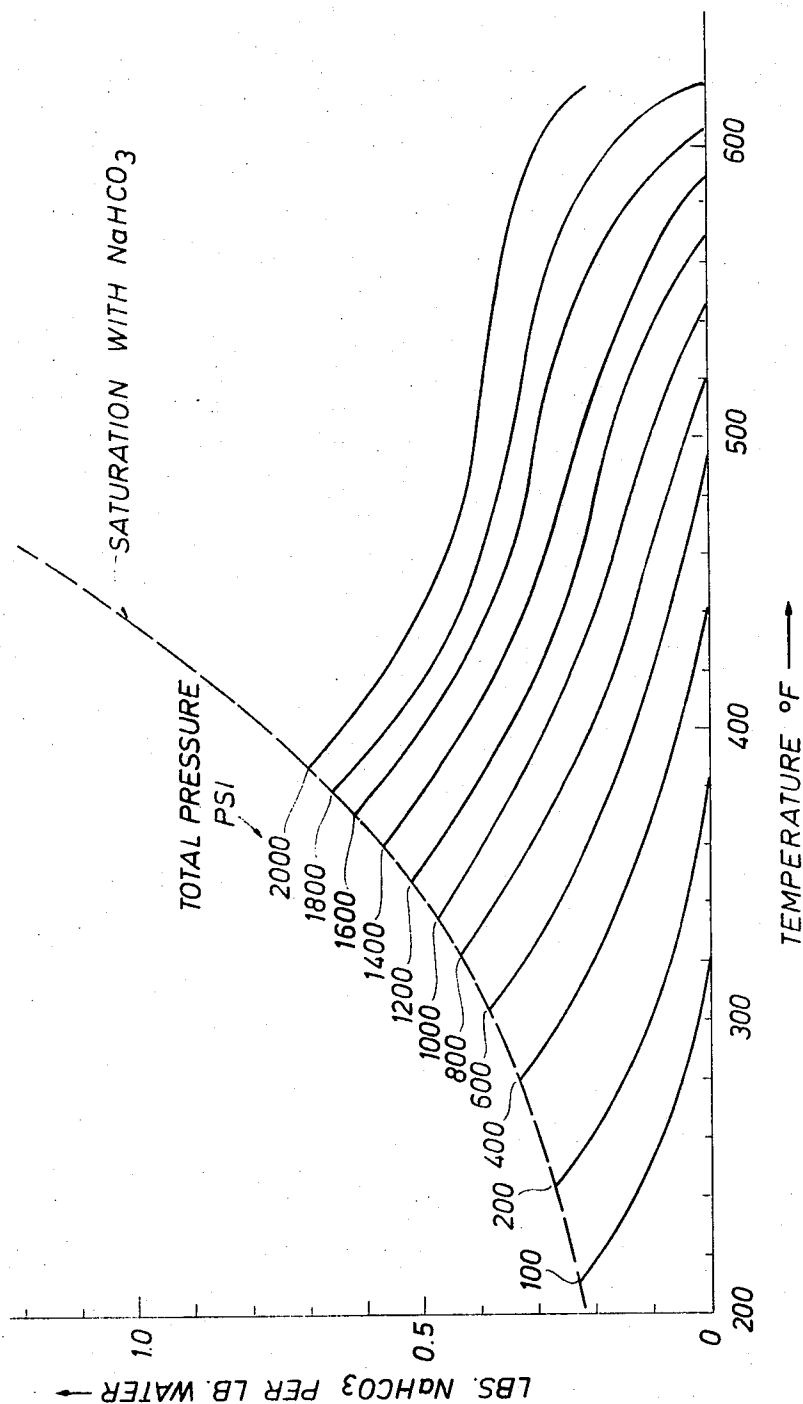
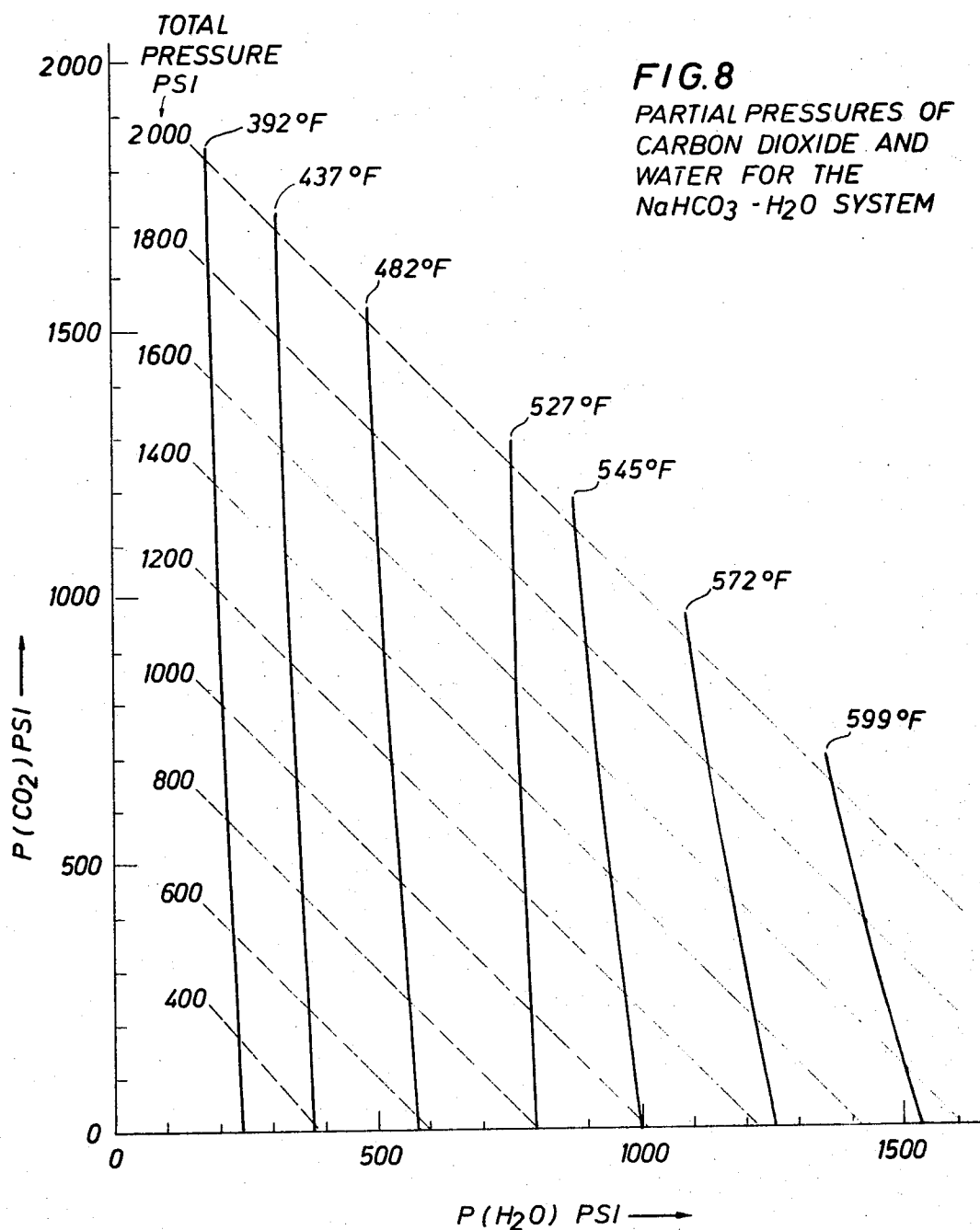


FIG. 7
 NaHCO_3 - H_2O SYSTEM

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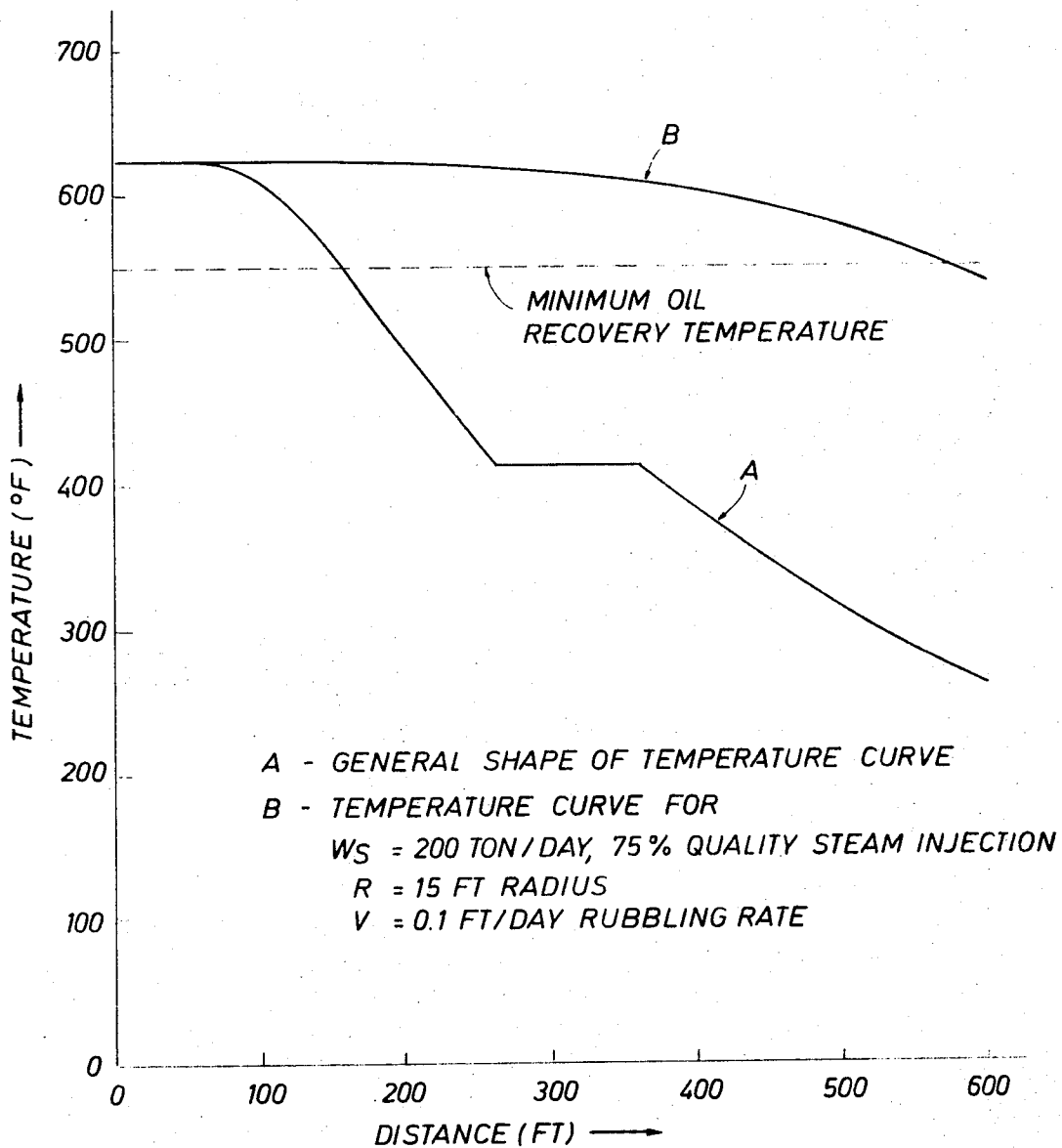


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**FIG. 9**VERTICAL TEMPERATURE
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FIG. 10

EFFECT OF RADIUS
ON PRODUCTION
RATE

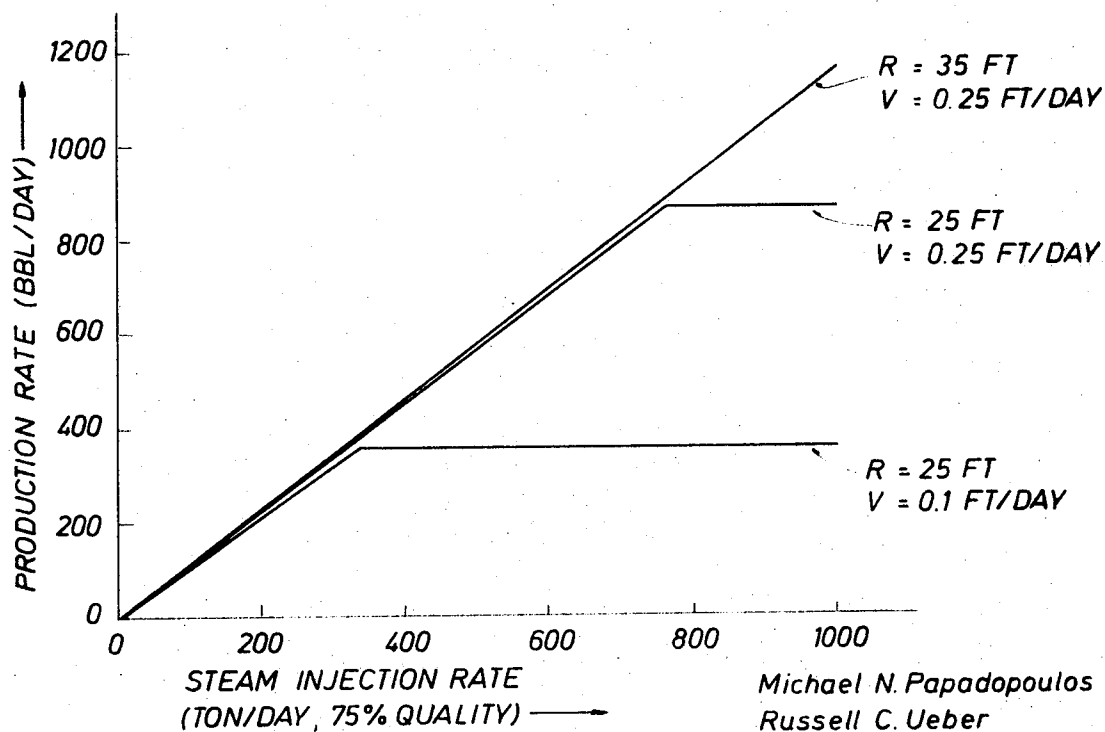
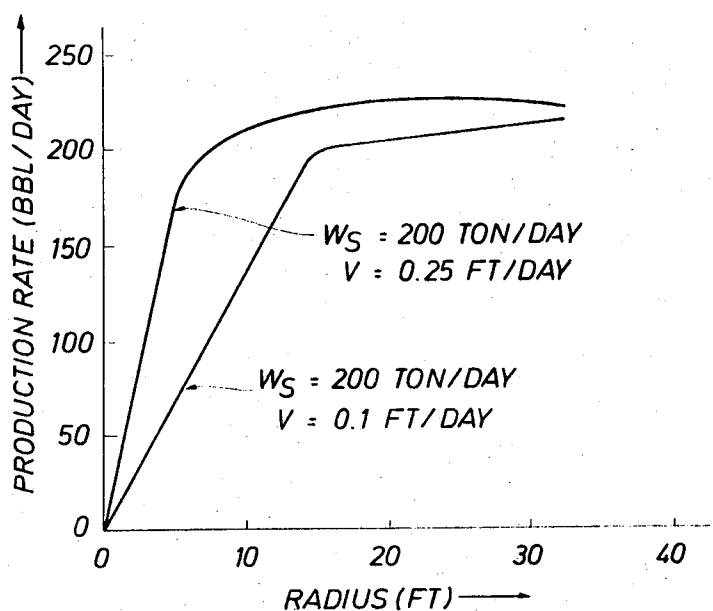


FIG. 11

EFFECT OF STEAM INJECTION RATE
ON OIL PRODUCTION RATE

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FIG. 12

EFFECT OF RADIUS
ON OIL-STEAM RATIO

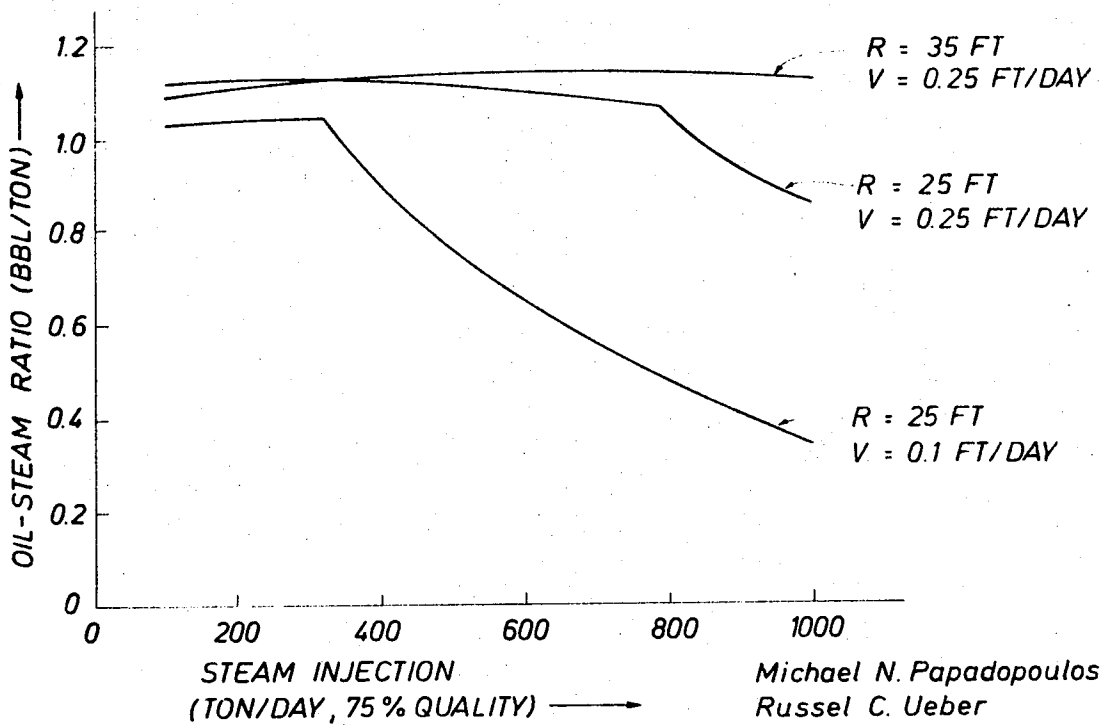
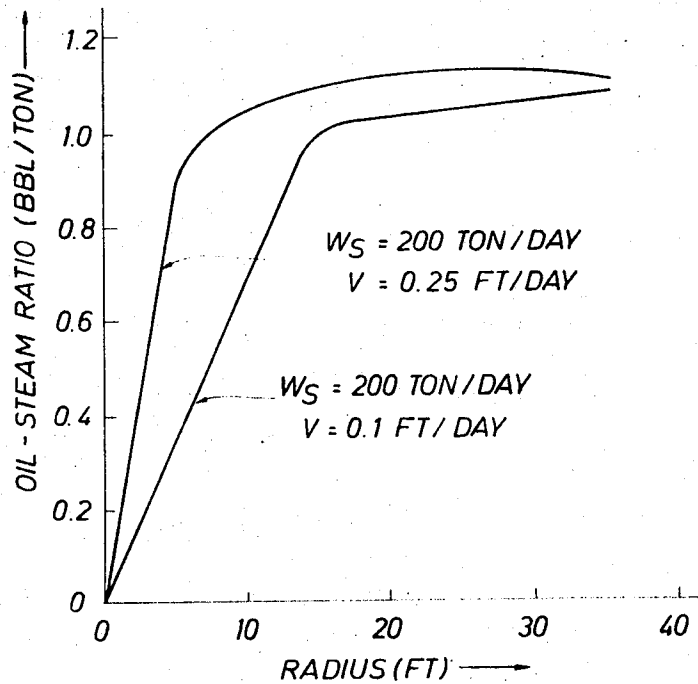


FIG. 13

EFFECT OF STEAM INJECTION RATE
ON OIL-STEAM RATIO

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FIG. 14

EFFECT OF
RADIUS ON
LENGTH OF
RETORT ZONE

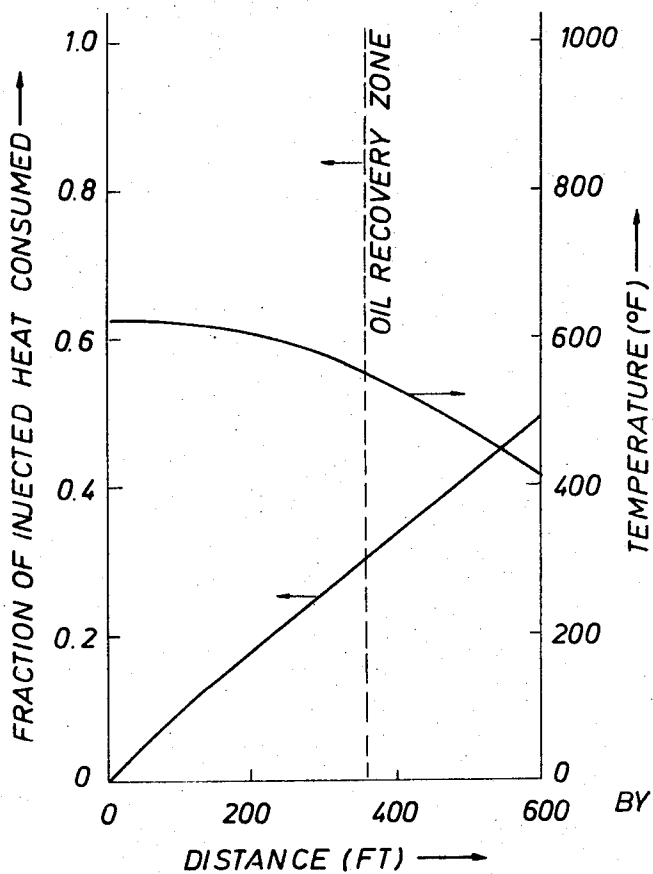
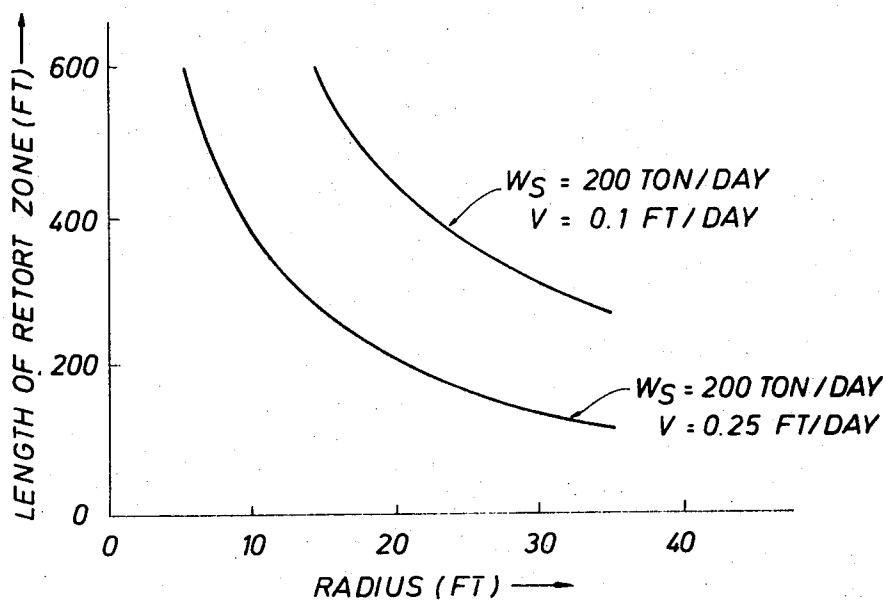


FIG. 15

FRACTION OF
INJECTED HEAT
THAT IS CONSUMED

$W_S = 200 \text{ TON/DAY}$,
75% QUALITY
 $R = 25 \text{ FT}$
 $V = 0.1 \text{ FT/DAY}$

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METHOD OF PRODUCING HYDROCARBONS FROM OIL SHALE FORMATIONS

CROSS-REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of copending application Ser. No. 855,323, filed June 23, 1969 now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to in-situ recovery of hydrocarbons from subterranean or underground oil shale formations containing heat-sensitive carbonates by forming a cavern therein and injecting into the upper region or preferably near the roof of the cavern a hot fluid to effect decomposition of the heat-sensitive carbonates to carbon dioxide thereby causing pressure buildup and fracturing and/or rubblizing of the oil-shale thus enlarging the cavern vertically i.e., in an upward direction to a desired dimension at which point a cooling fluid is injected into this region while a kerogen-propolyzing fluid is injected into the rubbled zone to effect hydrocarbon recovery therefrom.

2. Description of the Prior Art

Large deposits of oil in the form of oil shale are found in various sections of the world such as in various sections of the United States, particularly in Colorado, Utah and surrounding states, Canada, and parts of Europe. Various methods of recovery of oil from oil shale deposits have been proposed. The principle difficulty with known methods is their high cost which renders the recovered oil too expensive to compete with petroleum crudes recovered by conventional methods. The in-situ retorting or conversion of oil shale to hydrocarbons is difficult because of the non-permeable nature of the oil shale and the difficulty of applying heat thereto without extensive mining or drilling operations. Above ground methods of recovering oil from oil shale by mining and removal of the oil by retorting of the shale in above ground furnaces has been also found to be commercially uneconomical.

The art discloses various means or removing hydrocarbons, e.g., of oil from oil shale as described for example in U.S. Pat. Nos. 3,400,762, 3,437,378 or 3,478,825. Various means of increasing permeability of oil shale formations are described in U.S. Pat. Nos. 3,273,649, 3,481,398, and 3,502,372, or copending applications Ser. No. 839,350, filed July 7, 1969; or Ser. No. 770,964, filed Oct. 8, 1968; and Ser. No. 75,009, filed Sept. 24, 1970. 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.

SUMMARY OF THE INVENTION

It is an object of this invention to provide a method for recovering hydrocarbons from oil shale formations containing heat-sensitive carbonate material by forming a cavity within such formations and thermally decomposing these carbonates into carbon dioxide and other decomposition products.

It is a further object of this invention to use the thermal conversion of the heat-sensitive carbonate material present in oil shale formations to fracture and rubble

portions of such impermeable hydrocarbon-bearing formations and displace the fractured and rubblized material into a cavern formed within the formation.

It is a still further object of this invention to use the carbon dioxide and water released as a result of such thermal conversion as a circulatory fluid to enlarge the cavern formed within the formation and aid in recovery of hydrocarbon therefrom.

Still another object of this invention is, after circulating a hot fluid along the roof of the cavern to effect decomposition of the heat-sensitive carbonates to carbon dioxide to cause enlargement of the cavern by vertical migration of the cavern roof to terminate this process by circulating, a cooling fluid along the cavern roof while a kerogen-pyrolyzing fluid is injected to effect hydrocarbon recovery from the rubblized oil shale zone of the formation.

Still another object of this invention is that the cooling fluid and kerogen-pyrolyzing fluid can be injected and circulated through the cavern sequentially on simultaneously.

These and other objects are preferably accomplished by forming a cavern preferably one which is generally horizontally controlled in a subterranean oil shale formation that is impermeable and contains a significant proportion of heat-sensitive carbonate material below its upper boundary region and providing fluid communication between the earth surface and the cavern. Hot fluid is injected and circulated through the cavern in its upper region and should preferably be in contact with the roof thereof at a temperature and pressure so as to cause decomposition of the carbonates into carbon dioxide and water thereby causing a high pressure buildup within portions of the cavern and causing fracturing and rubblizing of the roof of the cavern. As the volume of the hot fluid within the cavern increases, the paths of fluid flow within the cavern are preferably adjusted to keep the hot fluid in contact with the upward migrating roof of the cavern. The hot fluid circulation is continued for a time sufficient to enlarge the cavern by a significant amount. The cavern roof is cooled prior to its migration above a selected depth, such as an upper boundary region of the normally impermeable hydrocarbon-bearing formation, by displacing a cooling fluid into contact therewith. Relatively cool fluid is maintained in contact with the roof of the enlarged cavern while circulating a kerogen-pyrolyzing fluid through the hydrocarbon-bearing material within the cavern to recover hydrocarbons therefrom.

The process of this invention is particularly applicable to various subsurface oil shale formations, such as in the Green River formation in the Colorado area of the United States, which contain water-soluble minerals and/or heat-sensitive carbonate minerals. For example, water-soluble minerals such as halite are commonly encountered along with heat-sensitive carbonate minerals such as nahcolite, dawsonite, trona or the like. The heat-sensitive carbonate minerals are apt to occur within an oil shale in the form of beds, lenses, nodules, loads, veins, or the like, having sizes ranging from microscopic particles to layers that are many feet in thickness and many miles in extent. Dawsonite is particularly apt to occur in the form of microscopic particles in amounts of up to about 10 or 12 percent by weight of the oil shale. The nahcolite can comprise about 5-40 percent by weight of the oil shale.

Oil shale formations which contain such water-soluble and/or heat-sensitive minerals are often encountered in geological structures such as sedimentary basins. A normally impermeable portion of an oil shale that contains heat-sensitive carbonate mineral is apt to be vertically extensive over a significant distance, such as one or more hundreds of feet, and to be located below a water-permeated zone in which some or all of the water-soluble mineral has been dissolved by the action of natural waters.

The present process provides a means for enlarging a permeable zone within a normally impermeable oil shale by circulating a hot fluid such as hot water, steam, mixtures thereof or non-aqueous fluids to effect decomposition of the carbonates present therein to carbon dioxide at a temperature between about 300° F and about 1,500° F, preferably between 350° F and 650° F. The invention also provides a means for terminating the enlargement of the permeable zone at a selected depth and avoiding the danger of extending fractures to surface of subsurface locations that would create a danger or disadvantage by means of cooling fluids. It further provides a procedure that generates significant amounts of carbon dioxide as a circulating fluid which also has a significant stripping action on the hydrocarbon materials released from the heated oil shale by a kerogen pyrolyzing fluid which may be an aqueous or non-aqueous pyrolyzing fluid or by use of hydrocarbon extracting materials such as phenols etc. Oil shale begins to release hydrocarbons at significant rates at temperatures above about 400° F and preferably 550° F to 750° F. In the presence of carbon dioxide, the hydrocarbons released from the oil shale by a pyrolyzing fluid such as steam tend to be entrained and transported in the form of vapors. This provides both an economy in the recovery of hydrocarbon products and their upgrading. The carbon dioxide and water that are generated in-situ can be used as a part of the hot fluid that is circulated along the cavern roof to cause vertical expansion of the cavern within a subterranean oil shale. This results in a significant increase in the amount of shale oil recovered.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a vertical sectional view partly diagrammatic of an embodiment of the invention showing a formation penetrated by a single well, and

FIG. 2 shows a similar diagram of a formation penetrated by more than one well.

FIG. 3 is a diagrammatic view of an idealized cylindrical rubbling scheme in a oil shale formation containing nahcolite nodules uniformly distributed around a well in concentric patterns spaced from one another in the radial direction by a distance Δr .

FIG. 3A is a diagrammatic plan view of an idealized linear rubbling scheme in an oil shale formation containing nahcolite nodules uniformly distributed along planes spaced from one another by a distance Δl in the direction of front movement.

FIG. 4 shows the temperature profile during advance of the rubbling front for the cylindrical rubbling scheme of FIG. 3, assuming that when the nahcolite decomposition temperature, T_d , is reached at a nahcolite nodule, fracturing occurs, oil shale rubble falls into the central cavern and the newly exposed surface is instantly raised to steam temperature, T_s .

FIG. 5 is a graphical representation of rubbling front velocity as a function of time for the cylindrical rubbling scheme of FIG. 3 for two initial well radii — 0.5 and 15 feet and for various values of nodule spacing, Δr .

FIG. 6 is a graphical representation of the advance of the cylindrical rubbling front in FIG. 3 for initial well bore radii of 0.5 and 15 ft., and for various values of nodule spacing, Δr .

FIG. 7 is a plot of nahcolite (NaHCO_3) concentration as a function of temperature and pressure for a nahcolite-water system.

FIG. 8 is a graph of partial pressures of carbon dioxide and water for the nahcolite-water system as a function of total pressure and temperature.

FIG. 9 is a graphical representation of the vertical temperature distribution in a well along the face of a 600-ft. thick oil shale zone treated according to the method of this invention.

FIG. 10 is a graph of production rate versus well radius for two exemplary in-situ oil shale production processes.

FIG. 11 is a graph of oil production versus steam injection rate for exemplary in-situ oil shale recovery processes.

FIG. 12, is a graph of oil-steam ratio versus cavity radius for exemplary in-situ oil shale recovery processes.

FIG. 13 is a graph of oil-steam ratio versus steam injection rate for exemplary in-situ oil shale recovery process.

FIG. 14 shows the length of the zone in which oil shale is retorted as a function of cavity radius for two exemplary in-situ oil shale recovery processes.

FIG. 15 shows the fraction of heat consumed and the temperature as a function of distance from the top of a 600 ft.-thick oil shale zone treated according to the method of this invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

In accordance with the present invention, known geological investigative procedures and techniques are available and may be used for locating heat-sensitive carbonate mineral containing oil shale formations. For example, suitable investigative procedures are described in copending applications Ser. Nos. 770,964 and 75,009. A total concentration of heat-sensitive carbonate, which may, include nahcolite, dawsonite, trona or the like and their mixtures which should occur within the oil shale under consideration to be exploited in the manner described can range from at least about 5 percent to above 40 percent by weight of the oil shale. Such amounts of carbonates in an oil shale formation can induce an upward migration of the roof of a cavern and also aid in hydrocarbon recovery by the process of this invention. Although the techniques of our invention will be described hereinbelow with respect to oil shale formations, such techniques are obviously applicable to any normally impermeable hydrocarbon-bearing earth formation containing a significant proportion of heat-sensitive carbonate material.

Referring to the drawing, FIGS. 1 and 2 show a subterranean oil shale formation 10 having an upper boundary 11 the depth of which is known or has been determined as discussed hereinabove. Earth formation 12 overlies oil shale formation 10 which includes heat-sensitive carbonate material therein.

A cavern 13 is formed within oil shale formation 10 penetrated by one well (FIG. 1) or more than one well (FIG. 2). The cavern 13 can comprise substantially any type of cavernous fluid flow path that contains a significant amount of solid-free space and has a generally horizontal roof, such as roof 13a. Cavern 13 may be formed by substantially any means, and can be initiated by solution mining a strategically located layer of water-soluble material in a lower portion of the normally impermeable heat-sensitive carbonate mineral-containing oil shale formation 10. Suitable solution mining processes are disclosed in copending applications Ser. Nos. 770,964 and 75,009 and U.S. Pat. Nos. 3,500,913 and 3,501,201. Measurements of geological properties that provide information on the depth and thickness of such an oil shale formation 10 are preferably utilized to arrange a pattern of well boreholes that are spaced and equipped for circulating fluid through the areally extensive cavern 13 having a roof span 13a that can exceed 50 feet or more. Where the oil shale formation 10 is not more than a few hundred feet thick and underlies a water producing formation, the wells are preferably arranged so that the roof span 13a does not exceed the overburden-supporting capability of the oil shale formation 10. Where desirable, that overburden-supporting capability of the oil shale formation 10 may be supplemented by maintaining a relatively high pressure on the fluid being circulated through the cavern 13 as will be discussed further hereinbelow. In forming the initial cavern 13, hydraulic or explosive fracturing, acidizing, or solution or mechanical mining techniques may be utilized, singly or in combination. Where fracturing is employed and the oil shale is located below a water-bearing zone, the fracturing should be controlled to avoid the extension of fractures between the cavern and the water-bearing zone.

Referring specifically to FIG. 2, a pair of well boreholes 14 and 15 are preferably extended into communication with cavern 13 and preferably cased, as at casings 16 and 17, respectively, with the casing 16 and 17 cemented therein, as at cemented intervals 18 and 19 respectively, above and below the interval to be exploited or, if desired, cemented to the bottom of the well. Suitable techniques and equipment are available to those skilled in the art and selected intervals may be chosen near the top and bottom of the vertical interval to be exploited as illustrated in FIG. 2. Casing 16 is perforated at perforations 20a through 20d, extending along the vertical interval of formation 10 with perforations 20a and 20b disposed at substantially the top and perforations 20c and 20d disposed at substantially the bottom of oil shale formation 10. In like manner, casing 17 is perforated at perforations 21a through 21d, with the perforations 21a and 21b disposed substantially at the top of oil shale formation 10 and perforations 21c and 21d disposed at substantially the bottom of oil shale formation 10. The casings are preferably perforated in stages, from the bottom portions upward, as the roof of the cavern is migrated up through the interval to be exploited. The casings may be provided with means such as slip-joint means for accommodating changes in length due to thermal expansion and/or contraction and/or subsidence of surrounding earth formations.

Hot fluid such as steam, is then circulated through the cavern in contact with the roof 13a as shown in

FIG. 2 via tube 26. The circulating fluid is preferably injected and produced through flow conducting and controlling equipment, such as tubing strings and/or packers, adapted to control the pattern of flow within the cavern 13 while the cavern 13 is being enlarged. Thus, well borehole 14 is preferably provided with a tubing string 23. Well borehole 15 is preferably provided with a tubing string 24 packed off from casing 17, by packing means 25 which also packs off perforators 21a and 21b from perforations 21c and 21d. In like manner, packing means 22 packs off tubing string 23 from casing 16 and perforations 20a and 20b from perforations 20c and 20d. An annulus outlet 26 is disposed at the top of casing 16 for introducing hot fluids into the annulus between tubing string 23 and casing 16 above packing means 22 and out perforations 20a and 20b. Also if desired, hot fluids may be injected down tubing string 23, past packing means 22 and out perforations 20c and 20d.

An annulus outlet 26a is in like manner, disposed at the top of casing 17 for removing hot fluids entering perforations 21a and 21b. Hot fluids entering perforations 21c and 21d are removed by tubing string 24. The hottest and least dense gaseous or liquid phase portion of the fluid may advantageously be injected and produced at points above the packers 22 and 25 at a relatively high rate of flow while a somewhat cooler and relatively denser portion is injected and produced or left substantially static within the cavern 13 at points below the packers 22 and 25 in order to enhance the efficiency of the heat-induced enlargement of the cavern 13. The fluid injected and produced above the packers 22 and 25 may advantageously be steam or a mixture of steam or steam and aqueous liquid while that injected and produced below the packers 22 and 25 can be also steam or mixtures of steam and hot water or hot solvents but preferably hot aqueous liquids. Alternatively, downhole heating means may be used to heat the injected fluids as is well known in the art.

The tubing string as shown in FIGS. 1 and 2 should be well insulated to prevent heat losses. This aids in subsequent hydrocarbon recovery.

As the roof is migrated upward due to circulation of a hot fluid along the cavern roof causing decomposition of the bicarbonates and/or carbonates to carbon dioxide and rubble of the oil shale, the flow paths within the cavern 13 are adjusted to keep the hot fluid flowing along the roof 13a. For example, the points at which the hottest portions of the fluid are injected and produced may be raised, incrementally or continuously, so that both are kept near the level of the cavern roof 13a. Alternatively, the point of hot fluid injection may be moved up while the point of production is kept constant with the hotter fluid being held against the roof 13a by its tendency to rise above the cooler and denser fluid within the cavern 13. The hot fluid may be injected via 26 and/or 23 into, and produced via 26a and/or 24 from, cavern 13 at one or a plurality of points along the vertical interval of the cavern 13, but at least one point of hot fluid injection should be moved upward as required to keep it near the level of the roof 13a of the cavern 13. Where the injected hot fluid is steam or contains steam or steam and carbon dioxide the production rate is preferably adjusted so that the produced fluid contains a significant proportion of vapor. As mentioned hereinabove, entrained hydrocar-

bons may advantageously be recovered from such vapors.

In general, the hot fluid which is circulated to enlarge the cavern and decompose the bicarbonates and/or carbonates therein to carbon dioxide can include aqueous and/or non-aqueous fluids such as hot water, steam mixtures, of steam and hot water, mixtures of steam and CO₂, etc. The temperature of the circulating hot fluid, during its residence within the cavern 13, can range from at least about 250° F at which the rate of conversion of the heat-sensitive carbonate mineral to carbon dioxide and water is significant, with a temperature of from about 300° F to about 1,500° F preferred. The carbon dioxide outflowing from well borehole 15 can be pressurized, heated and recycled. The fluid circulation may advantageously include the circulation of a solvent under supercritical conditions, which conditions provide enhanced rates of oil recovery as disclosed in U.S. Pat. No. 3,474,863 wherein a process is disclosed for producing shale oil from a permeable fragmented zone within a subterranean oil shale formation by circulating a volatile normally liquid oil solvent therethrough under supercritical conditions of temperature and pressure. Particularly during the cavern-enlarging stage of the present process, the use of a solvent under supercritical conditions is advantageous in increasing the rate of shale oil recovery that accompanies the enlargement of a permeable zone within the oil shale.

The volume of fluid within the cavern 13 is increased and the flow paths are adjusted as required to maintain contact between hot fluid and the roof 13a of cavern 13 as the cavern 13 is enlarged by an upward migration of the roof 13a. The use of a fluid containing a hot aqueous liquid phase can provide oil shale exfoliation benefits during this phase of our invention, as disclosed in U.S. Pat. No. 3,537,528 wherein a process is set forth by producing shale oil from a subterranean oil shale formation by controlled in-situ combustion in a cavern that contains a mass of fracture-permeated oil shale and is located within an oil shale formation. When a fracture-permeated oil shale is preheated with hot aqueous liquid, the pieces of oil shale undergo an exfoliation which causes a reduction in their particles size and improves the distribution of permeabilities and surface area-to-volume ratios. In the present process, such an exfoliation of the oil shale may be effected within the cavern prior to the initiation of underground combustion by, for example, circulating steam along the cavern roof 13a while circulating hot aqueous liquid through the lower portions of the cavern 13.

In making measurements of geological properties, as discussed hereinabove, such measurements preferably include measurements of the proportion of heat-sensitive carbonate minerals that are contained within the oil shale interval 10 from which oil is to be recovered. Where this proportion tends to be low relative to the proportion of water-soluble minerals such as halite, the hot fluid which is being displaced during the expansion of the cavern 13 is preferably an aqueous fluid such as steam and/or hot water that forms or contains a significant proportion of a liquid phase during its residence within the cavern 13. In such a situation, this both increases the rate at which an additional void space is created by the dissolving of solid material and improves the distribution of permeability throughout the mass of oil shale that is displaced into the cavern

13, by means of the exfoliation effect discussed above. Where the heat-sensitive carbonate mineral content is relatively high, the fluid may advantageously comprise a gas such as steam, air, natural gas, carbon dioxide, or the like; an oil solvent such as benzene, phenol, or the like; or a mixture of such gases with each other or with a liquid. The use of such gaseous fluids tends to reduce the cost of the cavern expansion operation due to the utilization of a low-cost fluid and/or a concurrent recovery of oil during the cavern expansion. The rate of such oil recovery may be enhanced by the use of supercritical conditions with respect to a solvent as discussed above.

The upward migration of the roof 13a of the cavern 13 is stopped when desirable by displacing a relatively cool fluid such as methane, hydrogen, CO₂, etc. and mixtures thereof down well borehole 14 via 26 and/or 26a and maintaining it in contact with the cavern roof 13a before the roof 13a has migrated above a selected depth, such as the upper boundary region 11. The cooling fluid may be injected through 26 while kerogen-pyrolyzing fluid such as steam is injected down tubing string 23. In this manner, a downhole gravity segregation may be made of the fluids flowing out of well borehole 15 into separate liquid and gas streams having outflow rates which are separately controlled in order to maintain a layer of gas along the roof 13a of the cavern 13. The hydrocarbons and other products can be recovered by tubing 24 or via casing outlet 26a when the latter is not used to inject cooling fluid.

In the process disclosed hereinabove, an areally extensive cavernous permeable zone (i.e., cavern 13) is expanded by causing its roof 13a to migrate upward within heat-sensitive carbonate mineral-containing oil shale formation 10. The roof migration is effected or enhanced by converting the carbonate mineral to carbon dioxide and water. This effect is enhanced by the areal extent of roof 13a, which causes the roof 13a to sag and be placed in tension. As gases are released from the carbonate material surrounded by the impermeable oil shale material that forms the roof 13a the gases provide localized internal pressures within the roof material. Since the roof material is in tension the internal pressures cause it to spill into the cavern 13. The carbon dioxide and water may be used to supply, or supplement, hot fluid that is circulated through the cavern to cause the migration of the cavern roof 13a and/or to recover oil. The roof migration is terminated before it has moved beyond a selected depth, such as the upper boundary region of the normally impermeable formation, by displacing a relatively cool fluid, into contact with the roof 13a of the cavern 13. Further upward migration of the roof is prevented by maintaining relatively cool fluid in contact with the cavern roof 13a while pyrolyzing the fracture-permeated oil shale within the cavern 13 and recovering petroleum materials released by its pyrolysis.

The combination of steps provides a vertically extensive column of fracture-permeated hydrocarbon-bearing material, such as oil shale rubble, without the necessity of using nuclear or chemical explosives or multiple hydraulic fracturing procedures. It provides a way of extending such a column from near the bottom of a vertically-extensive, normally impermeable hydrocarbon-bearing formation to near the upper boundary of that formation without the danger of opening a fluid flow path into a source of relatively cool subterranean

water. If such a flow path were to be opened, it would be difficult or impossible to keep the water from interfering with the oil recovery operation. The present process also provides an economical means for generating fluids which may be used for heating and expanding a subterranean cavern and/or recovering oil from oil-bearing material that is contained within such a cavern. Such fluids are needed in increasing amounts as the volume of the cavern is increased. Hydrocarbons may be recovered from the outflowing portions of the kerogen-pyrolyzing fluid as illustrated in FIG. 2 via tube 24 and as is well known in the art.

FIG. 1 illustrates a single well system which can be used to recover hydrocarbons by the process of the present invention similar to that described above relative to FIG. 2 which shows a formation penetrated by a pair of wells. Thus, in FIG. 1, a hot circulating fluid can be injected via 26 and/or 26b along the roof 13a of cavern 13 to effect carbonate and/or bicarbonate decomposition to CO₂ and effect enlarging the cavern 13 and rubblization of the oil shale. A cooling fluid is then injected via 26 and a kerogen pyrolyzing fluid is injected via 26b and also via 23 and hydrocarbons are produced via tubing string 23a. The recovery of hydrocarbons via 23 is optional.

In all cases the well's tubing strings should be well insulated to prevent heat losses and aid in recovery of the hydrocarbons as well as aqueous fluids which may contain materials capable of plugging the tubing string. By proper insulation and maintaining the temperature in the tubing string and annuluses in the wells through which fluids are injected, circulated and are recovered (above 250° F, preferably above 450° F) plugging by precipitation of foreign materials can be prevented.

ILLUSTRATION OF AN EMBODIMENT OF THE INVENTION

Rubbling Phase

Using a single well system as shown in FIG. 1, rubbling of an oil shale formation containing nahcolite may be induced by decomposition of the nahcolite nodules and generation of CO₂ gas pressure, the rubbling rate being estimated on the following assumptions:

1. that the nahcolite nodules are distributed uniformly in the radial direction from the well as shown in FIGS. 3 and 3a;
2. that heat, e.g., steam of constant temperature and pressure is applied to the formation's face;
3. that heat of decomposition of nahcolite can be neglected in determining temperature rise;
4. that when the nahcolite decomposition temperature is reached and CO₂ formed, fracturing occurs and the oil shale rubble formed falls into the cavern; and
5. That as newly exposed surfaces occur, they are exposed to the heating, decomposition, fracturing and rubbling process as outlined above. Thus, a newly exposed surface is instantly raised to steam temperature, when steam is used, and heating proceeds from this surface as illustrated by FIG. 4. The rubbling velocity for this process can be plotted as a function of time as shown in FIG. 5. FIG. 6 is a plot of the radial distance to the rubbling front as a function of time. In FIG. 5, it can be noted that for greatly different well radii, 0.5 feet and 15 feet, the rubbling front eventually approaches the same limiting value.

Using photographs of a core for the distribution of nahcolite nodules, the rubbling rate of oil shale based on the decomposition of the nahcolite nodules within the shale can be estimated based on the time required to heat the rock from one fracture generating nodule to the next using the formula:

$$t = \frac{X^2}{4\alpha \left[\text{erf}^{-1} \left(\frac{T_f - T_s}{T_i - T_s} \right) \right]^2}$$

where:

t = time

x = distance between fracturing planes, L

α = thermal diffusivity, L²/t

erf^{-1} = inverse error function

T_s = exposed surface of the shale maintained at temperature T_s

T_i = initial shale temperature

T_f = temperature required at nodule for fracturing

Photographs of a core from Rio Blanco County, Colorado, were used to estimate the rubbling rate of the oil shale due to the decomposition of nahcolite nodules. The distances between nodules and the size of nodules were measured. The rubbling rate was then calculated for several intervals as a function of the pressure and temperature within the nodules required for fracturing. The rubbling rates are listed in Table 1 for the assumed conditions of $T_s = 550^\circ\text{F}$, $T_i = 100^\circ\text{F}$, $\alpha = 0.48\text{ ft}^2/\text{day}$, and equilibrium between the nahcolite and the pressure of carbon dioxide and water. The calculation considered all nahcolite nodules greater than 0.5 inch in diameter, all concentrations of smaller nodules, and any nahcolite stringers.

In the Table 1, it is seen that the rubbling rate varies considerably between the various sections and decreases for increasing fracturing pressure. In some sections, the rubbling rate may be controlled by the decomposition of the nahcolite nodules, while in other sections a different mechanism may control the rubbling rate.

TABLE 1

RUBBLING RATE OF OIL SHALE DUE TO THE DECOMPOSITION OF NAHCOLITE NODULES

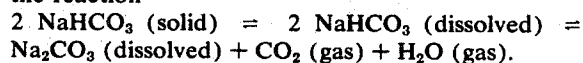
Section (Depth in ft)	Fracturing Temperature and Pressure			
	239.8°F 150 psia	316.4°F 500 psia	368.8°F 1000 psia	402.5°F 1500 psia
2262.2-2214.9	1.940	0.938	0.528	0.338
2262.2-2214.9	4.074	1.970	1.109	0.710
2214.9-2164.8	0.930	0.450	0.253	0.162
2214.9-2164.8	1.236	0.597	0.336	0.215
2164.8-2112.0	0.051	0.025	0.014	0.009
2164.8-2112.0	0.053	0.025	0.014	0.009
2112.0-2067.3	0.217	0.105	0.059	0.038
2112.0-2067.2	0.271	0.131	0.074	0.047
2262.2-2067.3	0.147	0.071	0.040	0.026
2262.2-2067.3	0.160	0.077	0.043	0.028

The first value in the table considers the distance between the centers of the nodules to be the distance between the fracturing planes. The second value in the table considers the distance between the edges of adjacent nodules to be the distance between fracturing planes.

Nahcolite Decomposition Phase

When a hot fluid such as hot water at a given temperature and pressure contact oil shale containing nahcolite, NaHCO₃ will dissolve until the sum of the CO₂ and H₂O vapor pressures equals the imposed total pressure.

FIG. 7 is a plot of such NaHCO_3 concentrations (as lb NaHCO_3 per lb water) for a pressure and temperature range of interest in the nahcolite solution and/or decomposition step of the in-situ oil shale recovery process. If more nahcolite is present then can be dissolved, the additional NaHCO_3 will decompose, according to the reaction



Thus Na_2CO_3 may be formed in the liquid phase and a gas phase forms. The composition of the first portion of gas which is formed may be read from FIG. 8 by interpolating between the temperature and total pressure lines and reading p_{CO_2} and $p_{\text{H}_2\text{O}}$ from the axes.

Thus when hot water at a total pressure of 1,600 psi and at 500° F contacts nahcolite, from FIG. 7 it can be predicted that the NaHCO_3 concentration will build up to about 0.285 lb/lb of water before a gas phase is formed and from FIG. 8, in the initial gas phase $p_{\text{H}_2\text{O}}$ is found to be 630 psi and p_{CO_2} to be 970 psi.

If the aqueous phase is kept in contact with nahcolite, more NaHCO_3 will dissolve, some of which will decompose to form Na_2CO_3 in solution and evolve additional gas. Eventually saturation with respect to Na_2CO_3 will exist.

Continuing with the example, for a total pressure of 1,600 psi at 500° F, the total sodium in solution for the Na_2CO_3 (sat'd)- NaHCO_3 - H_2O system is equivalent to 0.960 lbs of NaHCO_3 per lb water. Since 0.375 lb of NaHCO_3 per lb water was used to form the Na_2CO_3 , the actual NaHCO_3 in solution is 0.585 lb NaHCO_3 per lb water, or much greater than the NaHCO_3 content of the NaHCO_3 - H_2O system at the same temperature and pressure. Finally, $p_{\text{H}_2\text{O}} = 530$ psi and $p_{\text{CO}_2} = 1,070$ psi for the equilibrated ternary system, which reflects only a moderate change in composition of the gas phase.

When the above system stays in contact with nahcolite, and additional volume for gas is formed, more NaHCO_3 is dissolved, all of it going to form CO_2 and H_2O (most of which would go to the gas phase) and more Na_2CO_3 (all of which would precipitate). If the total pressure is increased at the existing temperature, no NaHCO_3 would dissolve, and some of the gaseous CO_2 and Na_2CO_3 solid might combine to form NaHCO_3 , tending to push the system to saturation with respect to both NaHCO_3 and Na_2CO_3 . It should be mentioned that, while the evolution of gaseous CO_2 from a supersaturated solution is fast, the dissolving of gaseous CO_2 in an undersaturated aqueous solution is much slower.

Oil Production Phase

Under the following conditions oil may be recovered from a single well from a nahcolite containing oil shale formation in accordance with the procedures for the present invention.

1. Basic data

- steam injection at 625° F, 75 percent quality;
- initial temperature of shale is 100° F;
- shale contains 30 percent by weight nahcolite;
- shale contains 5 percent by weight dawsonite;
- shale richness is 25 gal/ton (gross)
- minimum kerogen decomposition temperature is 550° F;
- 90 percent of Fischer Assay was recovered as oil; and
- interval considered was 600 feet high.

On the graphs,

WS = injection rate of 75 percent quality steam, ton/day;

R = cavity radius, ft; and

V = radial rubbing rate, ft/day.

2. Temperature distribution in well (FIG. 9). Curve A in FIG. 9 shows the general shape of the temperature distribution in the well. There are several distinct regions along the curve. Initially the curve is flat due to the condensation of steam; the temperature then falls using the heat in the flowing fluid. The second flat portion in the curve occurs due to the heat releasing reaction of Na_2CO_3 going to NaHCO_3 . The temperature then falls to that of the virgin shale.

Different conditions may expand or compress the general temperature curve. Curve B in FIG. 9 is an example of how the general temperature curve may be expanded for different operating conditions. For the conditions of curve B, oil recovery is obtained from almost the entire 600-foot interval.

3. Production rate of oil.

FIG. 10 shows the effect of radius on the production rate of oil. Initially the production rate increases linearly with radius until the production well temperature falls below the kerogen decomposition temperature. Then the production rate is essentially constant. The high rubbing rate results in a slightly higher maximum production rate due to the heat loss term.

If the heat loss term was not considered, the injected steam would have the capacity to heat a fixed volume of shale to the decomposition temperature of kerogen. If the production well temperature was above the decomposition temperature, all the steam would not be used effectively. If the production well temperature was below the decomposition temperature, a fixed production rate would occur for all rubbing rates and contacted vertical intervals. This production rate would be proportional to the steam injection rate.

Heat loss is considered to occur out of the top, bottom and the sides of the cavity. If the heat loss out the side of the cavity is dominant, a shorter retorting zone will yield a slightly higher production rate. If the heat loss out of the top of the cavity is dominant, a longer retorting zone will have a slightly higher production rate. This is the reason for the curvature in the production rate from 15 feet to 35 feet at the higher rubbing rate in FIG. 10.

FIG. 11 shows the effect of steam injection rate on the oil production. For the 35-foot radius curve the production well temperature is always below the decomposition temperature of kerogen. For this case the production rate is essentially proportional to the injection rate. For the other two cases on the figure the production rate is proportional to the injection rate until the production well temperature rises above the decomposition temperature; then it is constant.

4. Oil-steam ratio.

FIG. 12 shows the effect of radius on the oil-steam ratio and FIG. 13 shows the effect of injection rate on the oil-steam ratio. These figures correspond to the production rate shown on FIGS. 10 and 11. Therefore, the same general comments hold for these. Once the production well temperature falls below the decomposition temperature, the oil-steam ratio is essentially constant at 1.1 bbl/ton.

The oil-steam ratio can be increased above this value, however, by increasing the length of the retorting zone with time. In the calculations presented the freshly rub-

bled shale is at the initial formation temperature. If the length of the retort zone can be increased with time, advantage will be taken of the preheating that occurred earlier in the lower zones of the well. This will result in an increased oil-steam ratio.

5. Length of retorting zone.

Even though a relatively high oil-steam ratio may be obtained, the length of the retorting zone may be small compared to the total shale interval contacted. FIG. 14 shows the effect of radius on the length of the retorting zone. If the retorting zone is short, much of the producible oil in place will not be recovered.

6. Heat efficiency

The fraction of heat consumed in the oil recovery zone is low and is generally low over the entire contacted interval, even for relatively cool production temperatures. FIG. 15 shows the fraction of heat that is consumed and the temperature as a function of distance down the well. In the oil recovery zone only 30 percent of the injected heat has been consumed. At the production well with a production temperature of 415° F, less than 50 percent of the injected heat has been used.

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.

We claim:

1. A method of producing hydrocarbons from a subterranean oil shale formation containing heat sensitive carbonate material comprising the steps of:

measuring the geological properties of subterranean formations to identify the depth of at least an upper boundary region of a vertically extensive hydrocarbon bearing formation that is normally impermeable and contains a significant proportion of heat-sensitive carbonate material;

forming a generally horizontally-extensive cavern in the formation below said upper boundary region;

opening fluid communication between a surface location and said cavern;

circulating hot fluid from said surface location through said fluid communication and into contact with the roof of said cavern at a temperature sufficient to release carbon dioxide from said carbonate material and back to said location;

increasing the volume of said fluid within said cavern to maintain said circulating hot fluid in contact with the roof of the cavern for a time sufficient to enlarge the cavern by migration of the roof;

displacing relatively cool fluid into contact with the roof of the cavern before the roof has migrated above said upper boundary region, with said relatively cool fluid having a temperature at which the rate of said upward migration of the roof of the cavern is insignificant; and

circulating a kerogen-pyrolyzing fluid through the cavern, and recovering hydrocarbon therefrom.

2. The method of claim 1 including the step of maintaining said relatively cool fluid in contact with the cavern roof while circulating kerogen-pyrolyzing fluid through hydrocarbon-bearing material within the cavern.

3. The method of claim 2 including the step of recovering hydrocarbons from outflowing portions of said kerogen-pyrolyzing fluid.

4. The method of claim 1 wherein the step of forming a cavern includes the step of forming said cavern by solution mining water-soluble material from a lower portion within said hydrocarbon-bearing formation.

5. The method of claim 1 wherein the step of forming a cavern includes the step of forming an areally extensive cavern having a roof span exceeding about 50 feet but not exceeding the overburden-supporting capability of the formation.

6. The method of claim 5 including the step of maintaining a relatively high pressure on said kerogen-pyrolyzing fluid circulating within said cavern.

7. The method of claim 1 wherein the step of circulating a hot fluid through the cavern into contact with the roof of said cavern includes the step of circulating a fluid at a temperature of at least about 250° F.

8. The method of claim 7 wherein the step of circulating a hot fluid through the cavern in contact with the roof of said cavern includes the step of circulating a fluid containing a hot aqueous liquid phase.

9. The method of claim 8 wherein the step of circulating a hot fluid containing a hot aqueous liquid phase includes the step of circulating an aqueous fluid containing a significant proportion of steam.

10. The method of claim 1 wherein the step of circulating a hot fluid through the cavern in contact with the roof of said cavern includes the step of circulating a volatile, normally liquid oil solvent therethrough under supercritical conditions of temperature and pressure.

11. A method of producing hydrocarbons from a subterranean hydrocarbon-bearing earth formation that is normally impermeable and contains a significant proportion of heat sensitive carbonate material, comprising the steps of:

forming a generally horizontally-extensive cavern in the formation below the upper boundary region of said formation;

opening fluid communication between a surface location and said cavern;

circulating hot fluid from said surface location through said fluid communication and into contact with the roof of said cavern at a temperature sufficient to fracture at least portions of the roof of said cavern by releasing carbon dioxide from said carbonate material, and back to a surface location; and

increasing the volume of fluid within the cavern and changing the flow paths of fluid within the cavern to maintain hot fluid in contact with the roof of the cavern for a time sufficient to enlarge the cavern by an upward migration of the roof of the cavern.

12. The method of claim 11 including the step of displacing relatively cool fluid into contact with the roof of said cavern before the roof has migrated above said upper boundary region, at a temperature sufficiently low to cool said roof.

13. The method of claim 11 wherein the formation is an oil shale formation containing zones of heat-sensitive carbonate material and the hydrocarbon produced is an oil.

14. The method of claim 13 wherein the heat-sensitive carbonate is nahcolite.

15. The method of claim 11 wherein the formation is an oil shale containing nahcolite and the hot fluid is selected from the group consisting of steam, hot water and mixtures thereof.

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16. A method of producing oil from a subterranean oil shale formation containing heat-sensitive carbonate material comprising the steps of:

measuring the geological properties of subterranean formations to identify the depth of at least an upper boundary region of a vertically extensive oil-bearing formation that is normally impermeable and contains a significant proportion of heat-sensitive carbonate material;

forming a generally horizontally-extensive cavern in the formation below said upper boundary region; opening fluid communication between a surface location and said cavern;

circulating hot fluid from said surface location through said fluid communication and into contact with the roof of said cavern at a temperature sufficient to release carbon dioxide from said carbonate material and back to said surface location;

increasing the volume of said fluid within said cavern to maintain said circulating hot fluid in contact with the roof of the cavern for a time sufficient to enlarge the cavern by an upward migration of the roof of the cavern;

displacing relatively cool fluid into contact with the roof of the cavern before the roof has migrated above said upper boundary region, with said relatively cool fluid having a temperature at which the rate of said upward migration of the roof of the cavern is insignificant;

circulating a kerogen-pyrolyzing fluid through the cavern; and recovering oil therefrom.

17. The method of claim 16 wherein the heat-sensitive carbonate material is nahcolite; the circulating hot fluid is selected from the group consisting of steam, hot water and mixtures thereof, and the kerogen-pyrolyzing fluid is steam.

18. The method of claim 17 wherein at least a portion of the steam is replaced with an organic solvent.

19. The method of claim 18 wherein the solvent is selected from the group consisting of benzene and phenol.

20. A method of producing oil from a subterranean oil shale formation containing heat-sensitive carbonate material comprising the steps of:

penetrating at least one well bore into said formation; injecting an aqueous leaching fluid into said carbonate material containing oil shale to leach a portion of the carbonate material and form a cavern; fracturing and rubblizing the partially leached cavern;

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circulating a hot fluid onto the roof of said fractured rubblized cavern at a temperature sufficient to release CO₂ from the carbonate material;

displacing cool fluid into contact with the roof of the cavern;

circulating a kerogen-pyrolyzing fluid through the cavern; and

recovering oil therefrom.

21. The method of claim 20 wherein the carbonate material is nahcolite; the hot fluid is selected from the group consisting of steam, hot water and mixtures thereof; the cool fluid is water and the pyrolyzing fluid is steam.

22. A method of producing hydrocarbons from a subterranean hydrocarbon bearing earth formation containing heat-sensitive carbonate materials comprising the steps of:

a. penetrating the formation containing the heat-sensitive carbonates with at least one well;

b. forming a cavern in formation (a) and establishing communication via the well between the cavern and the surface.

c. contacting the roof of the cavern with a hot fluid at a temperature sufficient to decompose the heat-sensitive carbonates to carbon dioxide and water for a time interval sufficient to effect rubblizing of the oil shale and enlargement of the cavern;

d. terminating contacting the cavern roof with a hot fluid as in (c) and contacting the cavern roof with a cool fluid to terminate carbonate decomposition and rubblizing;

e. injecting a kerogen-pyrolyzing fluid through the cavern; and

f. recovering hydrocarbons therefrom.

23. The method of claim 22 wherein the hot fluid effecting decomposition of the heat-sensitive carbonates to CO₂ and H₂O is steam and the kerogen-pyrolyzing fluid is steam.

24. The method of claim 22 wherein the hot fluid effecting decomposition of the heat-sensitive carbonates to CO₂ and the H₂O is a mixture of steam and hot water and the kerogen-pyrolyzing fluid is steam.

25. The method of claim 23 wherein the heat-sensitive carbonate is nahcolite.

26. The method of claim 24 wherein the heat-sensitive carbonate is nahcolite.

27. The method of claim 22 wherein the formation is penetrated by at least a pair of wells.

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