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IN-PLACE RETORTING OF OIL SHALE

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This invention relates to the recovery of hydrocarbons from oil shale. More particularly, it relates to a method for the in-place retorting of subterranean oil shale formations and the recovery of the released hydrocarbons.

Vast quantities of hydrocarbons are contained in oil shale formations which are found in several parts of the world and particularly in the Green River Formation of the Piceance Creek Basin of Colorado. In these formations, the oil shale is not a true shale nor does it contain oil in the common usage of that term. The oil shale is a fine-grained, compact sedimentary rock which is generally highly laminated in the horizontal by bedding planes. It is more in the nature of marl-stone. It contains an organic matter, kerogen, which is an amorphous organic solid. Kerogen, particularly, is defined as an organic, high molecular weight mineraloid of indefinite composition. The kerogen is not soluble in conventional solvents but will decompose by pyrolysis upon being heated to temperatures above 500° F. to provide fluid hydrocarbons commonly termed "shale oil." Generally, the decomposition is undertaken at temperatures about 900° F. However, excessive temperatures are usually avoided in the pyrolysis of kerogen to avoid heat consumption by the decomposition of the mineral carbonate constituents in the oil shale. Thus, oil shale must be heated in a process of pyrolysis, which process is usually termed "retorting" in order to obtain the desired recovery of hydrocarbons. For this purpose, it is necessary to either mine the oil shale and then retort it at the earth's surface, or to retort it in-place.

Although some quantities of oil shale are at suitable depths where mining may be carried out, the majority of the great reserves are contained at depths where mining is difficult for various reasons. Thus, under these latter circumstances, the recovery of hydrocarbons from these deposits must be undertaken by some in-place retorting method. The natural characteristics of the oil shale and the formation in which it is contained create grave difficulties in carrying out such in-place retorting methods. Outside of any natural fractures in the formation, the oil shale has essentially no permeability; about the same permeability as found in glazed porcelain. Further, the oil shale has a very low porosity outside of fractures and the like and a coefficient of heat conductivity about that of a fire brick. However, after undergoing pyrolysis with a substantial removal of the kerogen, the oil shale has been found in some instances to have a 40-percent porosity and a permeability to air over 10 millidarcies. Thus, a suitable permeability to carry out in-place retorting methods can be obtained after some initial pyrolysis of the oil shale.

It has been found that in many oil shale formations, natural fractures in paralleling and intersecting relationships are predominantly oriented in the vertical and in the majority in any one plane are found to be spaced apart at less than 12 feet and on the average about 6 feet. These fractures create large sizes of columnar aggregates in the oil shale.

From the foregoing, two major physical obstacles in the oil shale for the carrying out of in-place retorting methods become apparent. First, any original permeability in the oil shale formation must reside in natural fractures. Secondly, the transfer of heat from heating fluids passing through fractures to the interior of any piece of the oil shale is severely restricted in rate by its low coef-

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ficient of heat conductivity and the large aggregate sizes existing between fractures.

It has been proposed to fracture artificially the oil shale for creating additional fractures to expedite in-place retorting. Hydraulic fracturing usually enlarges the existing fractures in the oil shale. Although this means of fracturing provides an increase in permeability to the heating fluid, it does not create new fractures, particularly ones in the horizontal, so that the sizes of the pieces of oil shale are significantly reduced in the vertical. Fracturing by detonating explosive has also been proposed as a means for increasing the permeability of the oil shale. The compression wave (from the explosive detonation) travels to the free face in the oil shale at the first-encountered fracture, crevice, or the like, from which it is reflected placing the traversed piece of oil shale in tension to produce the fragmentation effect. Thus, explosives convert only the immediate adjacent oil shale to a fragmented form over a distance usually not exceeding the spacing of the nearest fracture. It also has been proposed to inject mineral acid into the oil shale for increasing its permeability to the heating fluid by a leaching effect. However, the acid, like the effects of hydraulic fracturing, appears merely to enlarge only the existing openings in the oil shale which have been subjected to weathering. The presence of kerogen appears to hinder conventional acid attack on the carbonate constituents of the oil shale. Thus, in the past, permeability to permit a flow of heating gases could be obtained by conventional methods. However, significant fragmentation of the oil shale to significantly reduced aggregate sizes to expedite the heating of the oil shale for an early and substantial production of hydrocarbons could not be obtained by conventional methods. Thus, the obstacle presented by the low coefficient of heat transfer of the oil shale which basically resides in its large aggregate sizes formed between fractures was not removed by these procedures.

The present invention provides a method wherein not only are obtained adequate increases in permeability to permit flows of heating fluid, but also reductions in the aggregate sizes of the oil shale with corresponding increases in surface-to-volume ratios to offset the existing low coefficient of heat transfer. As a result of the present invention, the passage of the heating fluid for carrying out in-place retorting is obtained about smaller-sized oil shale aggregates along with the early production of hydrocarbons after beginning the pyrolysis heating with a greater magnitude of hydrocarbon recovery than heretofore believed possible.

It is an object of the present invention to provide a method of in-place retorting of oil shale formations for the recovery of hydrocarbons, which method does not suffer from the difficulties of the mentioned prior known methods. Another object is to provide a method for increasing the permeability of the oil shale, especially along bedding planes, so that the passage therethrough is facilitated of the heating fluid by which in-place retorting is obtained. Another object is to reduce the aggregating sizes of the oil shale within a subterranean formation whereby a significant increase in their surface-to-volume ratios is obtained. Another object is to reduce the time required to obtain the first production of hydrocarbons after subjecting oil shale to in-place pyrolysis. Another object is to increase significantly the amount of hydrocarbons produced by in-place pyrolysis and to obtain this hydrocarbon recovery in a reduced period of time over known methods.

According to the present invention, hydrocarbons are recovered from an oil shale formation by in situ retorting which employs as one of its steps the injection of a solvent mixture. This solvent mixture provides for open-

ing, "rotting," or otherwise parting the formation along planes of weaknesses, especially the bedding planes, so that therein results a new network of closely spaced-apart paralleling and interconnecting horizontal and vertical fractures. These fractures increase the permeability of the oil shale to heating fluid, such as air, flowing between spaced points in the formation and also reduce the aggregate sizes of the oil shale between fractures with corresponding increases in their surface-to-volume ratios. After such rotting effects are obtained, in situ retorting can be carried out through the passing of a heating fluid through the oil shale subjected to rotting with the recovery from the formation of the resulting hydrocarbons.

More particularly in a preferred embodiment of this invention, as one of its steps, well means by which fluids are passed between the earth's surface and the oil shale formation are provided in fluid communication with existing fractures. Such well means may be formed from the earth's surface into such formation by any procedure. The well means, particularly for input and outlet well means purposes, may be provided by two or more spaced-apart wells for only injection and production purposes, or by a single well having provisions for the introduction of fluid at one horizon and the withdrawal of fluid at another horizon, or by one or more wells which are employed for the injection of fluid for one period and employed at another period for the removal of fluid between the earth's surface and the oil shale formation. Such well means may be of any suitable construction, cased or otherwise equipped, and many well practices obviously can be employed. The arrangement of the well means, or their construction, is not critical in this invention.

As a step of the present invention practiced after suitable well means are obtained, a solvent mixture is introduced through an input well means into the oil shale formation. Generally, the solvent mixture is introduced through the input well means into the formation in a quantity to permeate that portion of the formation desired to be retorted. Thus, it will usually extend between the input and outlet well means. The solvent mixture preferably is introduced in a sufficient quantity so as to extend in fluid continuity between the input and outlet well means whatever their arrangement may be in the oil shale.

The solvent mixture is comprised of a low molecular weight alkyl monocarboxylic acid having not over 5 carbon atoms and a hydrocarbon solvent, both constituents being substantially vaporized at temperatures above 500° F. Various low molecular weight alkyl monocarboxylic acids may be employed. Preferably, it is of great utility to employ acetic acid as the acidic constituent. Other low molecular weight alkyl monocarboxylic acids having not over 5 carbon atoms may be employed if less than optimum results are satisfactory. The selected acid need not be pure. For example, the mixture may contain acetic acid which ranges in concentration from about 25 percent acetic acid with 75 percent water to about 75 percent acetic acid with 25 percent water. Any water from any source may be used. However, the water should not have large amounts of a contaminant reactable with the solvent mixture. However, the exact purity of the selected acid, as with acetic acid and water, contained in the acid constituent of the solvent mixture is not greatly important merely that the reaction time is somewhat varied by the acid's concentration. It is preferred that the water not be present in an amount which creates two phases, unless an emulsion is formed. Any hydrocarbon solvent which is substantially vaporized at temperatures above 500° F. may be employed. Of especial utility are the xylenes. The xylenes may be any of the ortho, meta, and para variants, or any combination thereof. Other hydrocarbon solvents which are substantially vaporized at temperatures above 500° F. may be employed, if desired. For example, benzene, toluene, kerosenes, and the like, may be employed, especially with acetic acid. The amount

of the mentioned acid and hydrocarbon solvent is not critical, but preferably is a 1-to-1 volumetric ratio. However, the mixture may range from about 1-to-10 to about 10-to-1 in volumetric ratios without significantly detracting from the results obtained therewith. Preferably, the solvent mixture is comprised of equal volume amounts of the mentioned acid and hydrocarbon solvent. For example, where the mixture is comprised of xylene and acetic acid, a 1-to-1 volumetric mixture is most satisfactory.

The term comprising the mentioned acid and hydrocarbon solvent used to identify the solvent mixture is intended to mean a fluid consisting essentially of the two groups of basic constituents but not to exclude other ingredients in relatively minor amounts which may have substantially no deleterious effect on the desired results to be obtained whether the fluid is in one or two phases.

As the next step, the solvent mixture is maintained in the oil shale formation for a period of time until such solvent has rotted the formation along planes of weaknesses to result in a new network of paralleling and interconnecting horizontal and vertical fractures. The rotting generally occurs along planes of weakness, especially the bedding planes of the oil shale formation. Thus, many horizontal fractures are created in the oil shale which already may usually have a plurality of vertical fractures in it. As a result, significant increases in fracture numbers, particularly along the bedding planes, are obtained which also significantly reduce the aggregate sizes of the oil shale between fractures. The fractures increase the permeability of the rotted oil shale to fluids flowing between the input and outlet well means with a corresponding increase in the surface-to-volume ratios of the oil shale acted on by the solvent mixture. After the solvent mixture has been in the oil shale for the desired period of time, it is removed from the oil shale formation through an outlet well means. For this purpose, it may be pumped out, or it may be miscibly or immiscibly displaced by passing suitable fluids between input and outlet well means, whichever procedure is desired.

As another step, a heating fluid is introduced through the input well means to flow through the rotted oil shale formation and exiting through the outlet well means. The heating fluid is introduced into the mentioned formation under conditions effecting in situ retorting at temperatures above 500° F. For this purpose, the heating fluid at the surface of the earth, or downhole, may be heated to a suitable temperature so that upon its introduction into the rotted oil shale it can effect in situ retorting of the kerogen into recoverable hydrocarbons. If desired, all or part of the heat for pyrolysis can be obtained by in situ combustion of the oil shale. For this purpose, the heating fluid may be comprised of air or other oxygen-containing fluids at ambient or elevated temperatures, and introduced into the rotted oil shale which is brought to elevated temperatures sufficient to effect ignition such that in situ combustion occurs. Auxiliary fuel may be added to the heating fluid, if desired. Thus, the heating fluid can be used to effect heating by in situ combustion for retorting the oil shale. Inasmuch as the solvent mixture will substantially vaporize at temperatures above 500° F., any of the solvent mixture remaining in the rotted oil shale formation will be vented through the outlet well means along with the heating fluid. The solvent mixture, and other materials, may be recovered from the vented fluids by any suitable means, such as by scrubbers and condensers.

The fluids produced from the outlet well by the in situ retorting can be recovered by suitable apparatus at the earth's surface. From these fluids may be separated the hydrocarbons which were produced by in situ retorting of the rotted oil shale. Where desired, the preceding steps of this invention may be repeated, especially where large aggregate sizes of oil shale are present, or for other reasons.

From the foregoing, it will be obvious that the rotted oil shale formation is more permeable to the flow of the heating fluids and that the aggregate sizes of the oil shale between fractures are greatly reduced by created openings with corresponding increases in surface-to-volume ratios. These factors insure a greater degree of retorting of the kerogen from the oil shale into hydrocarbons for any period of time. Thus, it is apparent that the reduction in aggregate sizes of the oil shale reduces in much greater proportion the amount of time required for recovering a certain amount of hydrocarbons by the in situ retorting procedure. Additionally, because the solvent mixture can be recovered during in situ retorting it may be readily recycled to new areas in which the oil shale is desired to be rotted until all activity advantage ceases.

The action of the applicant's solvent mixture in oil shale is not fully understood. It might possibly be that by capillarity this particular solvent mixture is readily drawn into the natural planes of weaknesses existing in the oil shale. Additionally, it may be that the hydrocarbon solvent provides some wetting action for the low molecular weight alkyl monocarboxylic acid by which to attack the carbonate matrix in the oil shale. However, applicant desires not be limited to any particular explanation of the functioning of the solvent. However, it is readily apparent that the solvent mixture of the applicant creates a plurality of fractures by rotting the oil shale along planes of weaknesses.

The steps of introducing the solvent mixture, maintaining it in the oil shale formation and then removing it after the desired rotting effects have been obtained have utility for purposes other than in the described in situ retorting method. For example, it may be desired to stimulate the flow of fluids between a well and the adjacent oil shale formation. For example, increasing the production of hydrocarbons from an existing production well within oil shale is one use of this subcombination. For these purposes, the mentioned steps may be employed to create a new network of fractures by rotting the oil shale about the well so that fluids, especially hydrocarbons can flow more freely between such well and the adjacent formation.

From the foregoing it will be readily apparent that the applicant has provided herein a method well suited for in situ retorting of oil shale formations whereby all of the stated objects and advantages of the present invention are obtained. It will be understood that certain features and subcombinations of steps are of utility and may be employed without reference to other features and subcombinations. This is contemplated by and is within the scope of the claims. Additionally, it is intended that the present disclosure is to be taken as a means of illustration and not in any sense as a limitation of the present invention, and that the only limitations are to be found in the appended claims.

What is claimed is:

1. A method for the in-place retorting of an oil shale formation having natural fractures comprising the steps of:

- (a) forming input and outlet well means for conveying fluids which means extend from the earth's surface into an oil shale formation,
- (b) placing the well means into fluid communication with natural fractures in the oil shale formation,
- (c) introducing through at least one of the well means into the oil shale formation a solvent mixture comprised of a low molecular weight alkyl monocarboxylic acid having not over 5 carbon atoms and a hydrocarbon solvent, said constituents of said solvent mixture being substantially vaporized at temperatures above 500° F. in said oil shale formation, said mixture introduced in sufficient quantity to extend substantially as a continuous fluid between the input and outlet well means,

- (d) maintaining the solvent mixture in the oil shale formation for a period of time until said solvent mixture has rotted the formation along planes of weakness, including bedding planes, resulting in a network of paralleling and interconnecting horizontal and vertical fractures therein to increase the degree of permeability to gases flowing between wells and to reduce the aggregate sizes of the oil shale between fractures with an increase in the surface-to-volume ratios of the oil shale subsequently exposed to a heating fluid,
 - (e) after said period of time, removing the solvent mixture from the oil shale formation through at least one of the well means,
 - (f) passing a heating fluid through the input well means to flow through the rotted oil shale formation and exiting through the outlet well means, said heating fluid introduced into the mentioned formation under conditions effecting in-place retorting at temperatures above 500° F. to drive hydrocarbons from the oil shale formation, and
 - (g) removing the fluids driven from the oil shale by retorting from the outlet well means for recovery of hydrocarbons.
2. The method of claim 1 wherein the solvent mixture consists essentially of acetic acid and xylenes.
3. The method of claim 1 wherein the solvent mixture consists essentially of acetic acid and xylenes, and the heating fluid introduced into the oil shale formation is air with such formation adjacent the well means employed for introducing the heating fluid being heated to ignition temperatures whereby in situ combustion of the oil shale formation is obtained to effect in situ retorting.
4. The method of claim 1 wherein the steps (c) through (g) are repeated whenever the hydrocarbon recovery decreases to a reduced level with the re-use of the recovered solvent mixture from the retorted gases.
5. In a method for the in-place retorting of an oil shale formation having natural fractures wherein a heating fluid is passed, under conditions effecting in-place retorting at temperatures above 500° F., from an input well means to an outlet well means through the fractures in the oil shale formation for driving out hydrocarbons therefrom, practicing prior to introduction of the heating fluid the steps comprising:
- (a) introducing through at least one of the well means into the oil shale formation a solvent mixture comprised of a low molecular weight alkyl monocarboxylic acid having not over 5 carbon atoms and a hydrocarbon solvent, said constituents of said solvent mixture being substantially vaporized at temperatures above 500° F. in said oil shale formation, said mixture introduced in sufficient quantity to extend substantially in fluid continuity between the input and outlet well means,
 - (b) maintaining the solvent mixture in the oil shale formation for a period of time until said solvent mixture has rotted the formation along planes of weakness, including bedding planes, resulting in a network of paralleling and interconnecting horizontal and vertical fractures therein to increase the degree of permeability to gases flowing between the well means and to reduce the aggregate sizes of the oil shale between fractures with an increase in the surface-to-volume ratios of the oil shale subsequently exposed to a heating fluid, and
 - (c) after said period of time, removing the solvent mixture from the oil shale formation through at least one of the well means.
6. The method of claim 5 wherein the solvent mixture consists essentially of acetic acid and xylenes.
7. The method of claim 5 wherein the solvent mixture consists essentially of acetic acid and xylenes, and the heating fluid introduced into the oil shale formation is

air with such formation adjacent the well employed for introducing the heating fluid being heated to ignition temperatures whereby in situ combustion of the oil shale formation is obtained to effect in situ retorting.

8. The method of claim 5 wherein the steps (a) through (c) are repeated whenever the hydrocarbon recovery decreases to a reduced level with the re-use of the recovered solvent mixture from the retorted gases.

9. As a subcombination, the steps of:

(a) introducing through a well means into an oil shale formation a solvent mixture comprised of a low molecular weight alkyl monocarboxylic acid having not over 5 carbon atoms and a hydrocarbon solvent, said constituents of said solvent mixture being substantially vaporized at temperatures above 500° F. in said oil shale formation, said mixture introduced in sufficient quantity to extend substantially in fluid continuity through the portion of the formation to be treated from said well means,

(b) maintaining the solvent mixture in the oil shale formation for a period of time until said solvent mixture has rotted the formation along planes of weakness, including bedding planes, resulting in a network of paralleling and interconnecting horizontal and vertical fractures therein to increase the degree of permeability to gases flowing between the treated formation and well means in fluid communication therewith and to reduce the aggregate sizes of the oil shale between fractures with an increase in the surface-to-volume ratios of the oil shale exposed to a subsequently introduced fluid, and

(c) after said period of time, removing the solvent mixture from the oil shale formation through a well means in fluid communication therewith.

10. As a subcombination, the steps of:

(a) introducing through a first well means in fluid communication with an oil shale formation a solvent

mixture comprised of a low molecular weight alkyl monocarboxylic acid having not over 5 carbon atoms and a hydrocarbon solvent, said constituents of said solvent mixture being substantially vaporized at temperatures above 500° F. in said oil shale formation, said mixture introduced in sufficient quantity to extend substantially in fluid continuity through the formation between the first well means and a second well means in fluid communication with said formation at a location spaced from said first well means,

(b) maintaining the solvent mixture in the oil shale formation for a period of time until said solvent mixture has rotted the formation along planes of weakness, including bedding planes, resulting in a network of paralleling and interconnecting horizontal and vertical fractures therein to increase the degree of permeability to gases flowing between the input and outlet well means and to reduce the aggregate sizes of the oil shale between fractures with an increase in the surface-to-volume ratios of the oil shale exposed to a subsequently introduced fluid, and

(c) after said period of time, removing the solvent mixture from the oil shale formation through one of the well means.

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