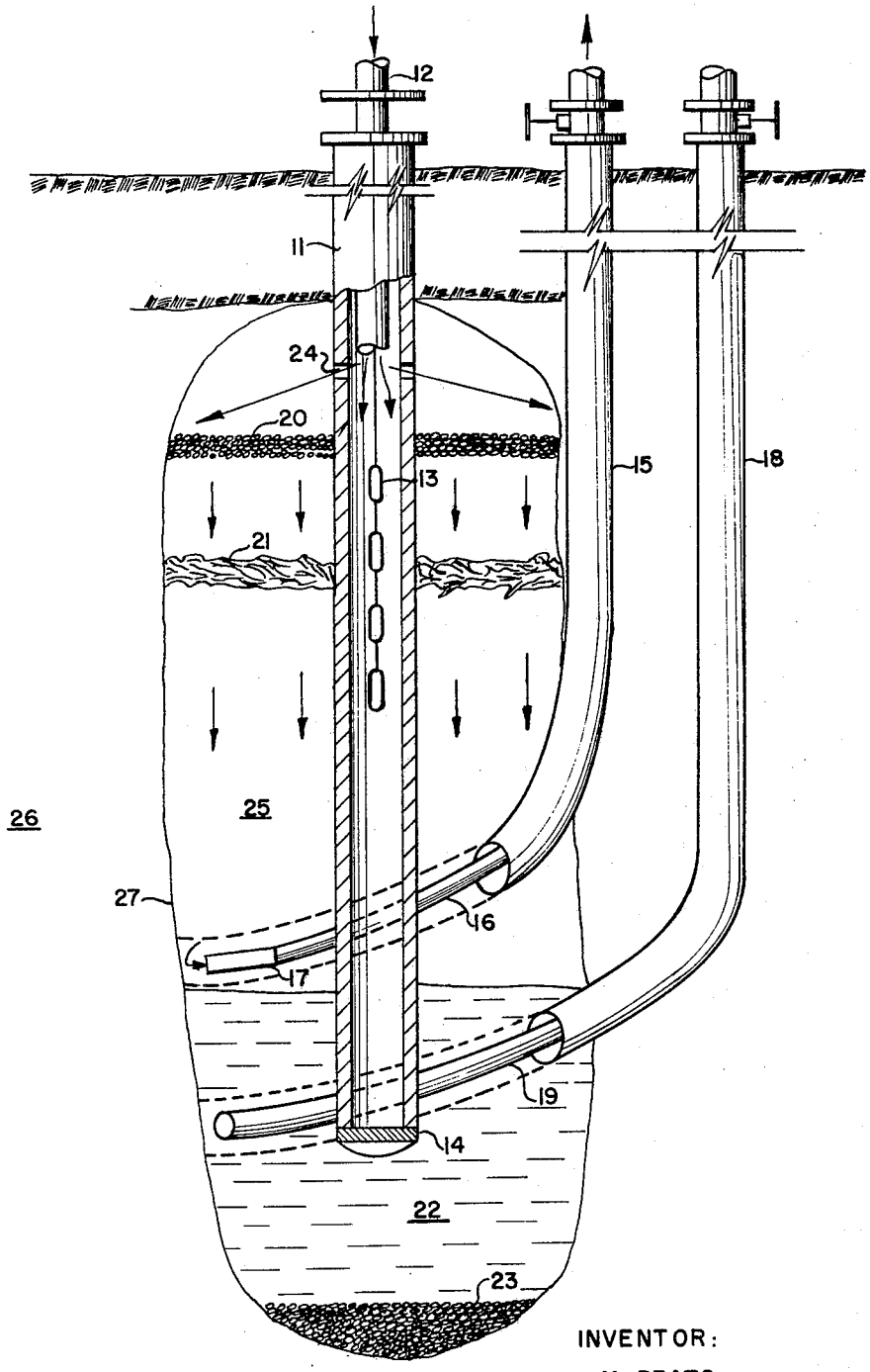
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PROCESS OF RECOVERING OIL AND DAWSONITE FROM OIL SHALE

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PROCESS OF RECOVERING OIL AND DAWSONITE FROM OIL SHALE

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ABSTRACT OF THE DISCLOSURE

A method of shale oil and dawsonite recovery from dawsonite-containing oil shale formations utilizing sequentially an in situ pyrolysis technique for shale oil recovery and solution mining for dawsonite recovery. The pyrolysis is controlled to prevent conversion of the dawsonite to insoluble oxides.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to a new, novel and improved method for recovering both shale oil and dawsonite from subterranean oil shale formations containing both products by sequential treatment of fracture-permeated zones, such as rubblized caverns and/or fragmented portions of such formations produced by suitable fracturing and/or solids-extracting means, to a controlled in situ pyrolysis, in order to pyrolize the organic components into fluid or fluidizable and recoverable oil products and thereafter injecting into the oil depleted area containing therein dawsonite an aqueous liquid capable of dissolving the dawsonite and recovering the dissolved dawsonite from the recovered liquid by any suitable means.

The use of various explosive techniques both nuclear and non-nuclear to rubblize or break-up or fragment underground oil shale formations so as to form a chimney or cavern filled with rubble or fragmented oil shale to facilitate shale oil recovery from such fragmented or rubblized areas by in situ pyrolysis is well known in the art. Although some oil shale formations under discussion are known to also contain dawsonite and/or other soluble aluminum compounds, their recovrey in conjunction with in situ pyrolysis of shale oil recovery, or per se, has not been thought feasible in the past because of the temperature conditions encountered which generally result in the fromation of insoluble oxides or aluminum making dawsonite (sodium aluminum carbonate) or other soluble aluminum compound recovery impossible or very costly and unattractive. Therefore, attempts to recover dawsonite from oil shale formations have not been attempted and a valuable source of aluminum and aluminum products has been essentially neglected.

OBJECTS OF THE INVENTION

It is an object of the invention to recover soluble aluminum compounds from underground oil shale formations.

It is another object of this invention to sequentially recover shale oil and dawsonite from underground oil shale formations.

It is still another object of this invention to sequentially recover shale oil and dawsonite from underground rubblized or fragmented oil shale formations using in situ combustion or pyrolysis techniques and solution mining techniques for recovering oil and soluble aluminum compounds, respectively, from dawsonite-containing oil shale formations.

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

SUMMARY OF THE INVENTION

The present invention is directed to recovery of shale oil and soluble aluminum compounds such as dawsonite from underground dawsonite-containing oil shale formations by sequential treatment of such formations to effect pyrolysis of the organic matter, preferably by in situ combustion thereby recovering oil therefrom and subsequently subjecting the formation to solution mining to recover the dawsonite by means of aqueous solutions capable of dissolving the dawsonite and effecting above ground the separation of the dawsonite from the solution by any suitable means known to the art.

To effect and facilitate this recovery process of both oil and soluble aluminum compounds such as dawsonite, the formation containing these materials should be fragmented or rubblized, for example, by means well known in the art, prior to treating or injecting sequentially into the resulting fracture-permeated zone of the formation a kerogen-pyrolyzing fluid and an aqueous solution capable of dissolving therein the soluble aluminum compounds such as dawsonite.

In order to accomplish the recovery of both the oil and dawsonite from dawsonite-containing oil shale formations most efficiently, it has been found that it is essential to control the pyrolyzing fluid temperature and/or composition within specified limits so as to effect desired oil recovery while preventing the decomposition of the dawsonite or other soluble aluminum compounds into an insoluble oxide. To accomplish this the fracture-permeated zone of the oil shale formation is treated under controlled conditions by:

(1) Flowing into the recovery zone hot oil-shale pyrolyzing fluid having a pH of less than about 8 and a temperature above the formation temperature (and preferably above about 500° F.) through portions of a fracture-permeated oil shale that contains an aqueous fluid soluble aluminum compound, such as dawsonite, so that organic components of pyrolyzed oil shale are entrained and displaced by the oil-shale-pyrolyzed fluid;

(2) Flowing aqueous liquid into contact with oil shale from which organic components have been removed by said oil-shale-pyrolyzing fluid, so that aluminum-containing mineral components, such as dawsonite, are dissolved in the aqueous liquid; and

(3) Recovering oil and aluminum from fluids produced from the said fluid-contacted oil shale.

The oil-shale-pyrolyzing fluid can comprise the combustion products of substantially any type of in situ combustion in which the combustion-supporting fluid is sufficiently free of alkaline material to form non-alkaline combustion products, hot hydrocarbons such as benzene, volatile compounds of oil shale, steam or hot aqueous non-alkaline fluids, phenolic materials, mixtures of hydrocarbons with phenols, polyacids or the like, etc.

BRIEF DESCRIPTION OF THE DRAWING

The figure schematically drawn shows a rubblized or fragmented or fractured chimney formed area of an underground oil shale formation that contains inorganic soluble aluminum compounds, such as dawsonite, penetrated by wells through which, sequentially, (a) pyrolyzing fluids are injected to effect recovery of organic components such as oil and (b) aqueous liquids or solutions are injected to effect dissolution of the inorganic materials, such as dawsonite, and recovering both products from one or more production wells.

DESCRIPTION OF THE PREFERRED EMBODIMENT

As shown in the drawing a dawsonite-containing oil shale **26** has been rubbelizing, fragmented or fractured to form a nuclear detonation cavern or chimney **27** which

contains fragmented oil shale and which has been conditioned by gravel packing **20** to normalize permeability so as to effect efficient pyrolysis when injecting a pyrolysis fluid through tubing string **12** in well **11** which is within the chimney **27**. Well **11** contains perforations **24** in addition to tubing string **12** which has been suspended therein, temperature-sensing devices **13** and packing **14**. The pyrolyzing fluid injected via tubing string **12** enters the formation via perforations **24** and penetrates through the gravel pack **20**, to establish a combustion front or zone **21**. As the combustion front **21** proceeds downward under controlled conditions a pyrolyzing zone **25** is established from which oil can be recovered via well **15** which contains a tubing string **16** and pump **17**. At a desired time combustion and oil recovery are stopped and an aqueous liquid is injected into the formation **22** via well **15** and/or **18** in an amount sufficient to form a liquid filled zone **22** so as to dissolve dawsonite and recover it as a solution via tubing string **19** and/or **16**. Solidified impermeable material is shown by numeral **23**. The process of establishing a combustion zone by injection of a pyrolysis fluid and subsequently injecting an aqueous liquid to dissolve dawsonite and recovering both products is repeated in cycles until the area is worked over and depleted of these materials.

In order to obtain a relatively rapid rate of operation the combustion zone or front **21** should be within a temperature range of about 800° F. to about 1000° F. and the pyrolyzing zone **25** should be between about 600° F. and about 950° F. Also, the aqueous liquid used to dissolve the inorganic mineral, namely dawsonite, can be an alkaline solution preferably having a pH of at least about 10.

The widely varying permeabilities of the fragmented and fractured oil shale that is formed, for example, within a nuclear detonation chimney, can be normalized by forming a permeability-normalizing layer **20** by forming a gravel pack across the top of the fragmented oil shale as described in my copending patent application Ser. No. 768,666, filed Oct. 16, 1968 or by any other suitable means. Thus, to produce shale oil from a subterranean oil shale by means of in situ combustion the zone from which the oil is to be recovered may be treated by exploding a relatively high energy explosive device within the oil shale formation thereby forming a fragmented zone having the configuration as shown in the figure with a void space at the top of the zone which is filled with a layer of granular material for permeability adjustment. The combustion front is initiated by injecting via tubing string **12** a pyrolyzable fluid such as air, oxygen or a mixture of oxygen-containing gas and an aqueous liquid near the upper end of the granular filled fragmented zone so as to advance a combustion front down the zone and as it advances downward producing oil shale pyrolysis products. Preferably, the oil shale is pyrolyzed by injecting a mixture of air and water above a permeability-normalizing layer in order to advance a combustion front down through the chimney.

It is important that the ratio of water to air and the flow rate and pressure of the oxygen-containing mixture be controlled to avoid overheating portions of oil shale that contain water soluble mineral components, such as dawsonite, before they are contacted with an alkaline aqueous liquid. When such minerals are overheated they tend to be converted to insoluble oxides. The dawsonite-containing portions of oil shale can be heated in contact with liquid, with liquid having a pH below about 7 at substantially any oil shale pyrolysis so that most of the organic components are removed and the dawsonite is exposed to contact with an aqueous liquid in which it is soluble.

Various types of procedures and equipment are available for monitoring the location of the combustion front and the temperatures being generated. As shown in the figure, a borehole **11** is extended through the fragmented oil shale, plugged at a lower level **14**, perforated at an upper level **24**, and used to inject a combustion-supporting fluid or a tubing string **12** into the chimney and to convey measuring elements, such as temperature-sensing devices **13**, into the zones of interest. Alternatively, the temperatures being generated can be controlled by other procedures, such as subjecting samples of the oil shale to various combustion conditions and using the conditions that are productive of the selected temperatures and rates of combustion front advance, etc.

When a zone of dawsonite-containing oil shale has been contacted by hot fluid for a time sufficient to remove a substantial portion of the organic material, the injection of such a fluid is temporarily interrupted and aqueous liquid is flowed into contact with the pyrolyzed oil shale. One way of doing this, which is shown in the figure, utilizes a series of wells **15** and **18** drilled so that substantially horizontal portions of wells traverse the chimney at different depths. In using such wells, the lower portions of the cavern can be kept filled with a relatively dense and low-cost liquid such as water as shown by **22**. During the advancing of the combustion front, the boreholes extending into the lower regions can be closed and fluids inclusive of combustion products, petroleum, and aqueous solutions of minerals can be produced, preferably with the aid of a pump, from one or more upper wells that traverse the chimney below the location of the combustion front.

When a dawsonite-containing zone has been pyrolyzed, the combustion-supporting fluid injection is interrupted and aqueous liquid is injected into the pyrolyzed oil shale. This fluid can be injected through either the production well **15** or through the injection well **18**, during an interruption of the injection of combustion-supporting fluids. During the aqueous liquid injection, combustion-supporting fluids can be produced from the permeable zone to the extent desirable to prevent the overpressuring of the cavern. The aqueous liquid which is injected to dissolve minerals is preferably an alkaline solution having a pH of at least about 10 and includes sodium hydroxide, calcium oxide solutions, lime solutions etc. The resulting aqueous liquid solution of minerals (dawsonite) is produced from the production well and the injection of combustion fluid is reinitiated.

A preferred feature of the present invention resides in the discovery that the addition of saturated calcium hydroxide solution to a sodium hydroxide solution greatly increased the effectiveness of aqueous alkaline solutions for extracting aluminum from dawsonite bearing oil shales.

An equimolar solution of saturated calcium hydroxide and sodium hydroxide has been found will extract approximately 600% more dawsonite aluminum than a solution of sodium hydroxide of the same alkalinity. It has been found that the aluminum concentrations of effluent alkaline solutions are initially quite high when sodium hydroxide solution is flowed through crushed oil shale but fell off rapidly with increased flow and time. Conversely, the aluminum concentration of the calcium hydroxide-sodium hydroxide solution is quite small initially but continually increases with time. The pH of these effluent solutions varied in the same manner as the aluminum concentration of the effluent; i.e., low aluminum concentration—low pH. Since the idealized chemical reaction is between the dawsonite and hydroxide ion, a process which maintains a high pH is more efficient.

Also, important in the recovery of dawsonite aluminum is the need for preheating the raw shale. Experiments have shown that without preheating aluminum extraction by aqueous alkaline solutions is virtually impossible. Furthermore, the amount of preheating is significant. Aluminum recovery from an oil shale preheated for 5 days was four times greater than that from the same shale preheated for 2 days.

In no instance should the heated shale be contacted with an aqueous phase at temperatures above 175° C. (350° F.). Above this temperature, an insoluble aluminum silicate, analcite, is rapidly formed and recovery of the aluminum is not possible.

Generally, the in-situ combustion can be reinitiated when the oxygen injection is resumed and the combustion-supporting fluid contacts the hot oil shale. The combustion can be reinitiated by known procedures and the combustion front advanced through the permeable zone from which the soluble minerals have been extracted so as to produce additional shale oil from this region, and to preheat a region further downstream as well, from which the desired minerals can then be extracted as described above. The steps of the process are repeated in sequence until both the oil and the soluble minerals are essentially completely recovered.

When the location of the combustion front has approached the borehole of an upper production well, that well can be shut-in. When one or more upper wells is shut-in, the combustion-drive and solution-mining operations are conducted through one or more lower wells.

The well patterns, oil-shale-pyrolyzing procedures, and solution-mining procedures can be varied widely. For example, in place of, or in addition to, using the permeabilty-normalizing barrier, a relatively uniform advance of the combustion front can be obtained by the process as described in copending patent application Ser. No. 689,181, filed Dec. 8, 1967, now Patent No. 3,448,807, and comprises advancing the combustion front by injecting a foamed mixture of air and water. One or more plural completion wells can be used for the injection and production wells. The oil shale can be pyrolyzed by injecting gas heated to oil-shale pyrolyzing temperatures at a surface location or a location other than the chimney, etc. Thus, the combustion front can be controlled at a temperature high enough to permit oxidation of the residual hydrocarbons within the formation at a relative high rate without generating excessive temperatures by injecting a quantity of water into the formation through the injection well cocurrently with the injection of the combustion-supporting gas. A surface-active foaming material is mixed with the gas and water so as to move the gas and water through the formation in the form of a foam. The foam keeps the water mixed with the gas and thus, even in reservoirs where segregation occurs due to the oil becoming thermally mobilized and settling below the incoming combustion-supporting gas upstream of the combustion front, keeps the combustion from attaining the high temperature of "dry" combustion that would be attained if the water and gas were not converted into foam.

The foregoing description of the invention is merely intended to be explanatory thereof. Various changes in the details of the described method may be made within the scope of the appended claims without departing from the spirit of the invention.

I claim as my invention:

1. In a method of producing shale oil and soluble aluminum compounds from subterranean soluble aluminum-containing oil shale formation comprising the steps of:

creating a rubblized or fragmented oil shale in said formation cavity;

flowing into the top of the rubblized cavity a combustion-supporting fluid, establishing a combustion front, and directing the flow of the established combustion front in a downward direction while controlled temperature conditions in said cavity to effect recovery of hydrocarbons and said oil-shale-pyrolyzing fluid without danaging the chemical standard composition of the soluble aluminum compound;

flowing an aqueous liquid into the pyrolyzed area from which the pyrolyzed fluid has been removed, in an mount sufficient to dissolve the soluble aluminum compound; and

recovering the soluble aluminum compounds from the liquid.

2. The method of claim 1 wherein the aluminum compound is dawsonite.

3. The method of claim 2 wherein the fluid recovered by the combustion treatment is shale oil and the aqueous liquid used to dissolve the drawsonite is an aqueous alkaline liquid having a pH of at least about 10.

4. The method of claim 3 wherein the oil shale is pyrolyzed by injecting therein a mixture of air and water and maintaining the pyrolyzing zone between 600° F. and 950° F.

5. The method of claim 4 wherein the combustion mixure is maintained as a foamed mixture of air and water.

6. The method of claim 3 wherein the aqueous alkaline liquid is an aqueous solution containing a mixture of alkali metal and alkaline earth metal hydroxides.

7. The method of claim 6 wherein the hydroxides are sodium and calcium hydroxides, respectively.

8. The method of claim 2 wherein the si-situ combustion for oil recovery and aqueous liquid dissolution of the dawsonite is sequentially repeated.

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