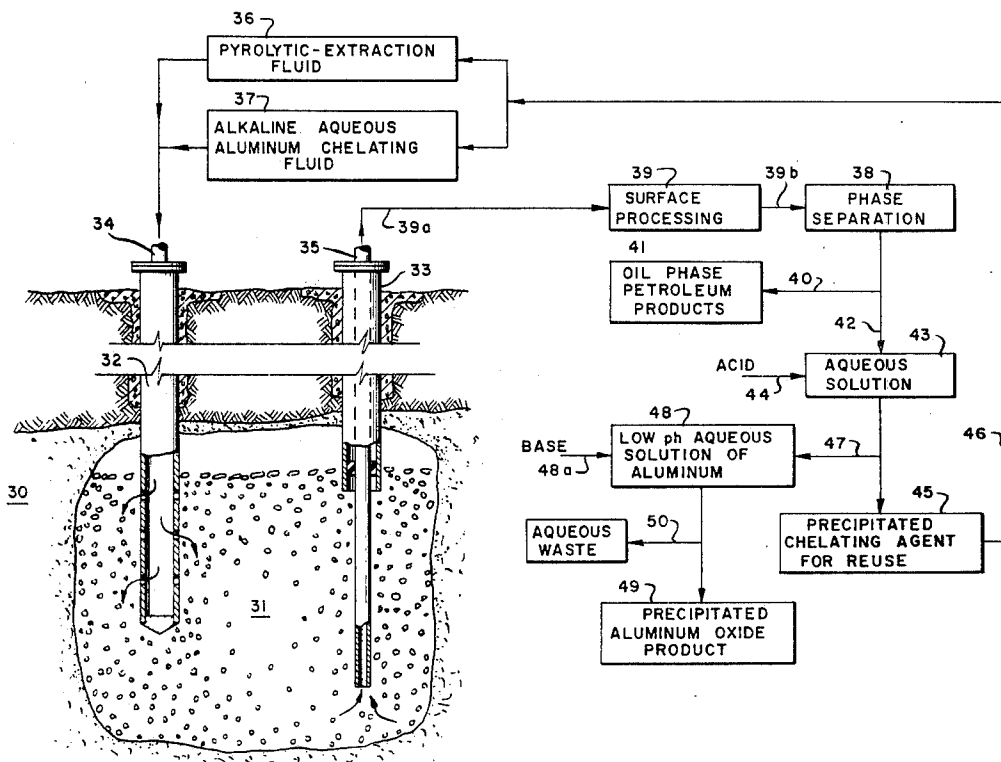


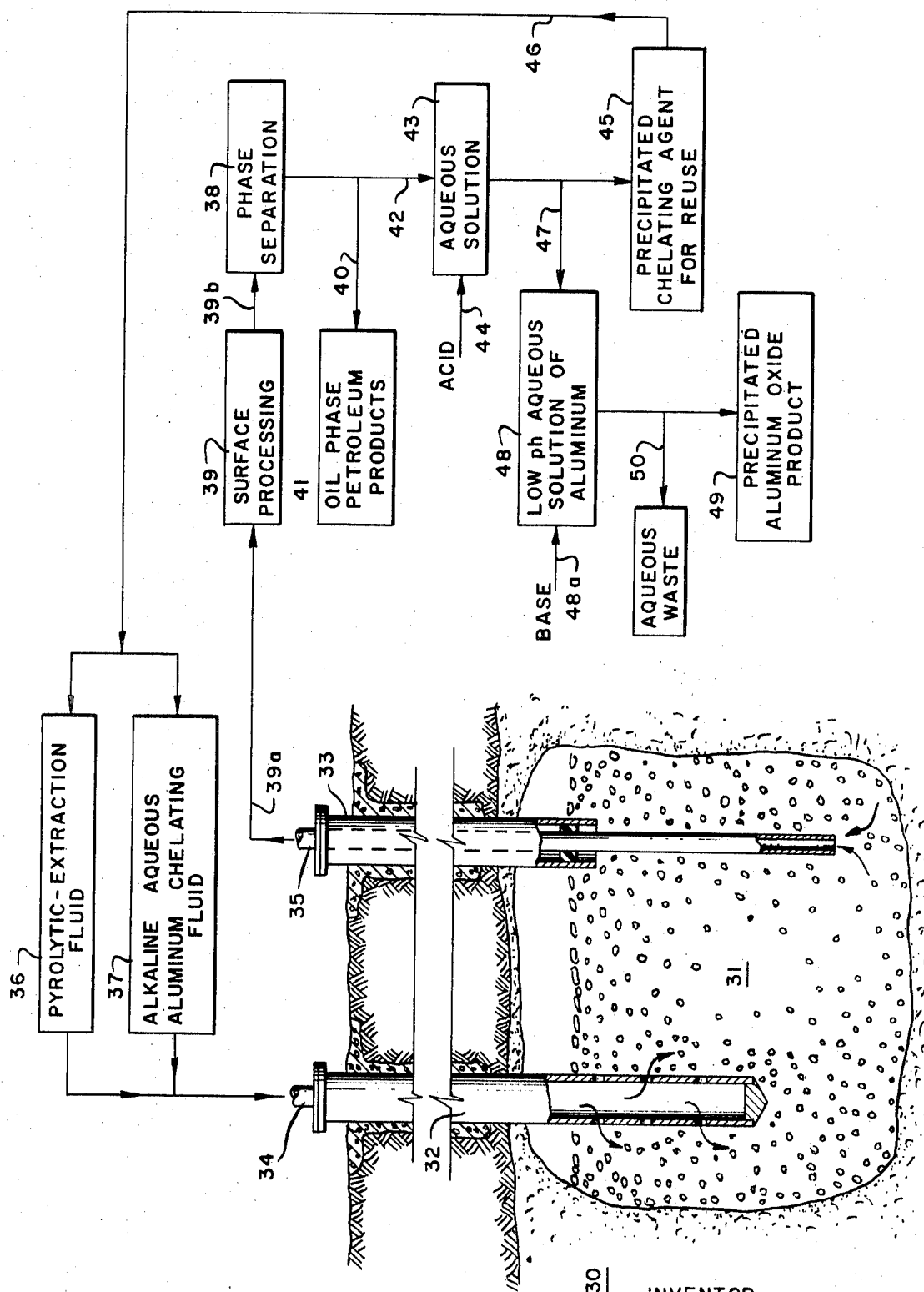
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UNITED STATES PATENTS
3,501,201 3/1970 Closmann et al. 166/259
3,502,372 3/1970 Prats 299/5
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[54] **RECOVERY OF ALUMINUM COMPOUNDS AND OIL FROM OIL SHALE FORMATIONS**
7 Claims, 1 Drawing Fig.
[52] U.S. Cl. **299/4, 166/259**
[51] Int. Cl. **E21b 43/28**
[50] Field of Search. **299/4, 5; 166/259, 271**

ABSTRACT: An improved, new and novel method of recovery of oil and aluminum-containing compounds from subterranean oil shale formations, by treating such formations with alternating slugs of a pyrolytically extractive fluid and an aqueous alkaline fluid containing an acid-insoluble chelating agent and recovering oil and aluminum compounds from said extractive fluids.





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RECOVERY OF ALUMINUM COMPOUNDS AND OIL FROM OIL SHALE FORMATIONS

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention is directed to a new, novel and improved method for recovering shale oil and aluminum-containing compounds from subterranean oil shale formations containing both products by sequential treatment of fracture-permeated zones, such as fractured or rubblized zones and/or fragmented portions of such subterranean formations produced by suitable fracturing and/or solids extracting means, to a controlled pyrolytic extractive process in order to produce organic fluidizable materials such as hydrocarbons and oil and also recovering aqueous soluble minerals such as soluble aluminum-containing compounds, e.g., dawsonite or other soluble minerals capable of forming chelates, when contacted with an aqueous alkaline fluid containing an acid insoluble chelating agent. The recoverable products can be separated from an outflowing fluid by a number of suitable means which will be fully described below.

The use of various explosive techniques both nuclear and nonnuclear to fracture, rubblize or break up or fragment underground oil shale formations so as to form a fractured formation or a chimney or a cavern filled with rubble or fragmented oil shale to facilitate shale oil recovery from such fractured, 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 recovery in conjunction with in situ pyrolysis of shale oil recovery, or per se, has not been thought feasible in the past because of the thermally enhanced formation of insoluble oxides and/or silica complexes of aluminum. Such conversions of dawsonite (sodium aluminum basic carbonate) or other soluble aluminum compounds, cause the recovery thereof to become relatively costly and unattractive. Therefore, attempts to recover dawsonite from subterranean oil shale formations has not been attempted except with respect to shallow deposits from which the mineral is mined and processed in surface locations and a valuable source of aluminum and aluminum products has been essentially neglected.

A number of proposals have been made in the art to recover dawsonite from oil shale above ground such as described in U.S. Pat. No. 3,389,975 which is directed to subjecting an oil shale previously retorted above ground to a leaching process using an aqueous solution of sodium carbonate and sodium hydroxide and subsequently precipitating the dawsonite with carbon dioxide in order to recover dawsonite. In copending Ser. No. 769,909, filed Oct. 23, 1968, and now U.S. Pat. No. 3,502,372 in situ recovery of oil and dawsonite from subterranean rubblized oil shale formation is described using a combination of a pyrolysis and solution mining technique involving forming a fracture-permeated zone within a subterranean oil shale formation, prior to such treatment.

The above-ground retorting techniques described above for recovering oil and dawsonite are outside the scope of the present invention, and are undesirable and unsuitable for carrying out the process of the present invention since the process results in the formation of large amounts of insoluble materials which are undesirable and difficult to handle making these operations costly and unattractive. The process described in the copending application is often more effective and less costly than an above-ground retorting technique but tends to cause a formation of some insoluble products and a failure to recover a significant proportion of the soluble aluminum compounds.

Throughout the specification the term "shale oil" refers to one or more of the liquid or gaseous hydrocarbons and/or substituted hydrocarbons resulting from pyrolysis and/or solvent extraction of the kerogen components of an oil shale formation. Similarly, the term "pyrolytically extractive fluid" refers to a hot fluid that initiates or accelerates the pyrolysis of

kerogen and entrains or displaces shale oil. Examples of pyrolytically extractive fluids include the products of an in situ combustion within the oil shale formation; individual or mixed hydrocarbons, such as methane, benzene, etc.; steam or aqueous liquid; mixtures of such fluids with reactive components, such as an acid, a phenol, etc. In a shale oil recovery operation, such fluids are heated so that they have an in situ temperature sufficient to provide a relatively rapid rate of kerogen decomposition, such as a temperature of at least about 500° F.

2. Objects of the Invention

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

It is an object of this invention to recover from subterranean oil shale formations containing aluminum compounds such as dawsonite both the oil and the aluminum compounds by means of pyrolytically extractive fluid and aqueous alkaline fluids containing chelating agents.

It is still another object of this invention to recover oil and dawsonite from subterranean fractured, rubblized or fragmented oil shale formations by circulating through said fractured or rubblized zones alternating slugs of a pyrolytically extractive fluid and an aqueous alkaline fluid containing a chelating agent and recovering oil and dawsonite from the outflowing fluid.

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 a subterranean or underground dawsonite containing oil shale formations by fracturing and/or rubblizing said formation so as to form a permeable zone therein and circulating therethrough alternating slugs of a pyrolytically extractive fluid and an aqueous alkaline fluid containing an effective amount, sufficient to prevent insoluble product formation, of an acid-insoluble chelating agent and thereafter recovering and processing the outflowing fluid so as to effect recovery of the oil-phase from the aqueous-phase and separately processing the oil-phase to recover oil therefrom and aluminum compounds, e.g., dawsonite and the chelating agent, from the water-phase components. In certain instances, depending upon the properties of the oil shale formation being treated and/or the pyrolytically extractive fluid being used, additional portions of aqueous-fluid-solubilized shale oil can be recovered from the water-phase components of the outflowing fluid.

Subterranean oil shale formations that contain water-soluble aluminum compounds can be located by various known exploration techniques. Fracture-permeated zones can be formed within such formations by detonating one or more nuclear or nonnuclear explosive devices within the borehole of one or more wells, by mining portions of the oil shale to leave tunnels which can be collapsed to form a fracture-permeated zone, or by various combinations of hydraulic fracturing, solution mining, acidizing, and the like techniques. Fluids can be circulated through such fracture-permeated zones by opening the borehole of at least one well into fluid communication with at least two separated regions within the zone, inflowing fluid by pumping it into at least one well conduit in fluid communication with one region within the zone and outflowing fluid by pumping it from at least one well conduit in fluid communication with another region within the zone. If desired, the fluid circulation can be accomplished through a single well that communicates with a single region within a fracture-permeated zone, by inflowing fluid against the back pressure created by the injection of the fluid and outflowing the fluid by reducing the pressure within the well and allowing the fluid to return in response to the pressure within the subterranean region.

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 nonalkaline combustion products, hot hydrocarbons such as benzene, volatile compounds of oil shale, steam or hot aqueous nonalkaline fluids, phenolic materials, mixtures of hydrocarbons with phenols, polyacids or the like, etc.

The chelating agents useful as additives in the aqueous alkaline fluid of this invention can include any organic chelating agent capable of chelating with the aluminum or other prevalent metallic compounds present in the oil shale and forming soluble compounds in the aqueous solution and include nitrogen-containing carboxylic acids and amine or metallic salts thereof such as amino-, imino-, nitrilo-, carboxylic acids and salts thereof such as described in U.S. Pats. No. 2,631,978; No. 2,959,547; No. 3,256,196 and No. 3,409,551 and include amino carboxylic acids, e.g., ethylene diamine tetracetic acid and salts thereof, methyl iminodiacetic acid, nitroacetic acid, phenyl iminodiacetic acid of which preferred are the amine and alkali metal (sodium) salts of ethylene diamine tetracetic acid, e.g., di-, tri- and tetrasodium ethylene diamine tetracetic (Na_{21} , Na_{31} , or Na_4EDTA) and mixtures thereof.

In the present invention, the presence of the chelating agent in the aqueous alkaline solutions inhibits and/or alleviates the effects of the conversion of aqueous-fluid soluble aluminum compounds, such as dawsonite, to substantially insoluble aluminum compounds, such as analcite. Particularly in oil shale formations at relatively shallow depths, both forms of aluminum compounds may be present in the natural formation. When a hot aqueous alkaline solution is being circulated through a fracture-permeated zone of an oil shale formation that contains a soluble aluminum compound, a conversion to an insoluble compound such as analcite may occur during the contact between the hot alkaline solution and the oil shale. When the hot alkaline solution contains a chelating agent, the aluminum is held in solution in the form of an aluminum-chelating-agent complex and the formation of insoluble aluminum silicate compounds is inhibited. The formation of insoluble aluminum silicate compounds is also retarded by the presence of calcium ions in such hot alkaline solutions, since the calcium ions tend to combine with the silicate to form insoluble calcium silicate compounds to such an extent that the aluminum remains in solution. Particularly, in respect to chelating agents, such as an aminopolycarboxylic acid chelating agent, aluminum is held more tightly than is calcium in complexes with the chelating agent; and, thus, the beneficial effects of the presence of calcium ions and chelating agent in a hot alkaline solution are at least supplementary. Hot alkaline solutions containing both the chelating agent and calcium ions tend to inhibit the conversion of soluble aluminum compounds to insoluble aluminum silicate compounds and also enhance the rate at which naturally occurring insoluble aluminum silicate compounds, such as analcite, are digested and converted to dissolved, soluble aluminum-chelating-agent complexes and precipitated, insoluble calcium silicate compounds.

DESCRIPTION OF THE DRAWINGS

The FIGURE is an illustration of a preferred embodiment of this invention wherein 30 is the oil shale formation of which zone 31 is fractured and fragmented and from which oil and dawsonite is to be recovered. The formation is penetrated by an injection well 32 and a production well 33 each of which have tubing strings 34 and 35, respectively, in which through tubing string 34 is alternatively injected a pyrolytic extracting fluid from 36 and an alkaline aqueous alkaline fluid containing a chelating agent from vessel 37. The injection via tubing string 34 of fluids 36 and 37 is alternatively carried out as required to effect oil pyrolysis and dawsonite solubilization to be recovered as outflowing fluids via well 33 through tubing

string 35. At the surface the outflowing fluid from 35 is processed for separation by flowing into separator 38 via lines 39a and 39b between which is a surface processing unit 39 and the oil phase is separated in 38 and directed via line 40 to vessel 41. The aqueous phase is directed to through line 42 into vessel 43 where it is acidified in line 44 and the chelating agent precipitated in vessel 45 separated and returned to vessel 37 via line 46. The pH adjusted aqueous solution of dawsonite is directed via line 47 into vessel 48 where the solution is treated with a base and on precipitation the precipitated aluminum oxide product is recovered in vessel 49 and the aqueous waste discarded via line 50.

SPECIFIC EMBODIMENT OF THE INVENTION

In a preferred process for conducting the present invention the pyrolytically extractive fluid is formed in situ by initiating an underground combustion within the fracture-permeated zone in the oil shale formation and injecting a combustion-supporting fluid to produce a pyrolytically extractive fluid resulting from the products of combustion. The combustion-supporting fluid may contain components, such as an aqueous liquid, to control the temperature and heat-transport properties of the combustion, foam to control the sweep efficiency of fluids moving through interstices within the fracture-permeated zone, fuel to supplement that available in the exposed oil shale surfaces, etc.

In the preferred process, a slug of an aqueous alkaline solution containing a chelating agent is preferably injected prior to the initiation of the underground combustion such as an amino-carboxylic acid, e.g., ethylene diamine tetra acetic acid (EDTA) and salts thereof (e.g., Na_4EDTA) via vessel 37 is shown in the FIGURE. The inflowing aqueous solution is heated, preferably by means of surface-located or borehole-located heating device, so that it preheats the oil shale to a temperature approaching the ignition temperature of the oil shale. Such a process of preheating an oil shale for an in situ combustion is described in greater detail in the copending patent application of J. A. Herce et al. Ser. No. 767,174, filed Oct. 14, 1968 and is directed to a process for 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. The oil shale fragments are preheated with an aqueous liquid to cause a reduction in their particle size and improve the distribution of permeabilities and surface area-to-volume ratios within the cavern prior to the initiation of underground combustion.

Such an aqueous-fluid preheating is particularly advantageous in that it induces the exfoliation of portions of the fracture-permeated oil shale into small pieces and thus improves both the distribution of effective permeabilities within the interstices between the pieces of oil shale and the ratio of surface area of the oil shale pieces to the volume of the oil shale pieces.

In general, in the present process, each slug of aqueous alkaline solution containing a chelating agent, e.g., Na_4EDTA , should have a volume at least exceeding the solid-free void space of both the fracture-permeated zone within the oil shale formation and the inflow and outflow conduits. If desired, the outflowing portions of a relatively small size slug can be reheated and recycled through the fracture-permeated zone. Where the fracture-permeated portion of the oil shale has not been preheated, the inflowing portions of the chelating-agent solution are preferably heated, continuously or incrementally, to increasingly higher temperatures which are significantly greater than the normal temperature of the oil shale formation. The pressure of the inflowing chelating-agent solution is preferably increased, by maintaining a back pressure on outflowing portions, if necessary, to the extent/required to maintain substantially all of the solution in the liquid phase. When the chelating-agent solution is being injected prior to the initiation of an underground combustion, the injecting and heating are preferably conducted so that, at least near the point of

inflow into the fracture-permeated zone of oil shale, the oil shale is heated to a temperature of at least several hundred degrees F. for a period of at least several days, with temperature of at least about 400° F and times of at least one week being preferred. In general, the alternations of slugs of chelating-agent solution and pyrolytically extractive fluid are preferably repeated by interrupting the circulation of the pyrolytically extractive fluid (e.g., by maintaining an underground combustion), initiating circulation of chelating-agent solution, interrupting the circulation of chelating-agent solution, reinitiating the circulation of pyrolytically extractive fluid, etc. Where the regional tectonics and/or the well assembly equipment make it undesirable to inflow an aqueous fluid at a pressure sufficient to keep it substantially liquid at the temperatures created by a pyrolytic extraction, e.g., those created by an underground combustion, the inflowing of the chelating-agent solution is preferably preceded by the inflowing of a slug of water that is softened to an extent preventing scaling at the temperature existing within the fracture-permeated zone. The time and volume of such a water circulation are preferably adjusted to lower the temperature, at least near the point of inflow into the oil shale, to a temperature at which inflowing portions of a chelating-agent solution can be kept substantially liquid under pressures which are desirable for employment.

ILLUSTRATED EMBODIMENT OF THE PRESENT INVENTION

After a rubblized or fractured subterranean oil shale formation has been subjected to a dry in situ combustion, an aqueous solution containing an alkaline agent such as NaOH or Na₂CO₃ and a chelating agent such as an alkali metal salt of ethylene diamine tetra acetic acid, e.g., Na₄EDTA (the sodium salt of ethylenediaminetetraacetic acid) is injected through a well into the partly cooled recovery zone of the shale formation at a temperature of from about 200° to about 225° C, with the aluminum remaining soluble as a mixture of Al-EDTA and aluminate ion AlO₂⁻. The solution returning from a production well to the surface containing some EDTA is in the form of metal complexes (Al-EDTA¹, Ca-EDTA¹², or Mg-EDTA¹², expected from leaching spent oil shale), since the metal-EDTA form is more stable at higher temperatures than the free EDTA. The produced solution is cooled in a heat exchange scheme to less than 100° C. to recover the EDTA as precipitated H₄ EDTA by acidifying the produced solution with an acid such as hydrochloric acid or sulfuric acid to a pH of about 1.6. The solid H₄ EDTA is separated from the solution by either filtration or decantation, the solution is then al-

kalized by NaHCO₃ or NaCO₃, or a mixture of both, so that a pH of 6.5 to 7.5 the Al(OH)₃·xH₂O when filtered off may contain enough impurities to warrant its solution in acid, and a second alkalization with Na₂CO₃ to obtain high purity Al(OH)₃·xH₂O. Finally, the Al(OH)₃·xH₂O is again filtered off, and calcined to Al₂O₃. Such Al₂O₃ can then be sent to conventional electrolytic plants for production of aluminum metal.

The separated H₃EDTA is dissolved in a NaOH solution, which can be blended with fresh natural brine, to form an aqueous phase suitable to be sent to the injection wells.

I claim:

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

- a. creating a fractured or rubblized or fragmented oil shale formation or cavity;
- b. flowing into the formation or a cavity pyrolytically extractive fluid;
- c. flowing into the formation or cavity an aqueous liquid containing a chelating agent in an amount sufficient to dissolve soluble aluminum compounds;
- d. outflowing the liquids produced by steps (a) and (b);
- e. separating the aqueous phase from the oil phase and,
- f. recovering an aluminum compound from the aqueous phase.

2. The method of claim 1 wherein the in situ combustion for oil recovery and aqueous liquid dissolution of the dawsonite is sequentially repeated and the aqueous liquid is an aqueous alkaline liquid containing a sodium salt of a alkylene polyamine polycarboxylic acid.

3. The method of claim 1 wherein the aluminum compound is recovered from dissolved dawsonite.

4. The method of claim 3 wherein the oil shale is pyrolyzed by injecting therein an in situ combustible material at an elevated temperature sufficient to effect oil extraction and the chelating agent in the aqueous fluid is an alkali metal salt of an amino carboxylic acid.

5. The method of claim 4 wherein the aqueous alkaline liquid is an aqueous alkaline solution containing tetra sodium ethylene diamine tetracetate.

6. The method of claim 4 wherein the fluid is recovered by combustion treatment is shale oil and the aqueous liquid containing a chelating agent used to dissolve the dawsonite is an aqueous alkaline liquid containing an acid insoluble chelating agent.

7. The method of claim 6 wherein the combustion mixture is maintained as a foamed mixture of air and water.