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Weichman

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[54] **SHALE OIL AND MINERAL RECOVERY PROCESS**

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[21] Appl. No.: **79,823**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 726,950, May 6, 1968, abandoned.

[52] **U.S. Cl.** **423/119,** 201/41, 209/3

[51] **Int. Cl.** **C01f 7/08,** C01f 7/06

[58] **Field of Search** 423/119

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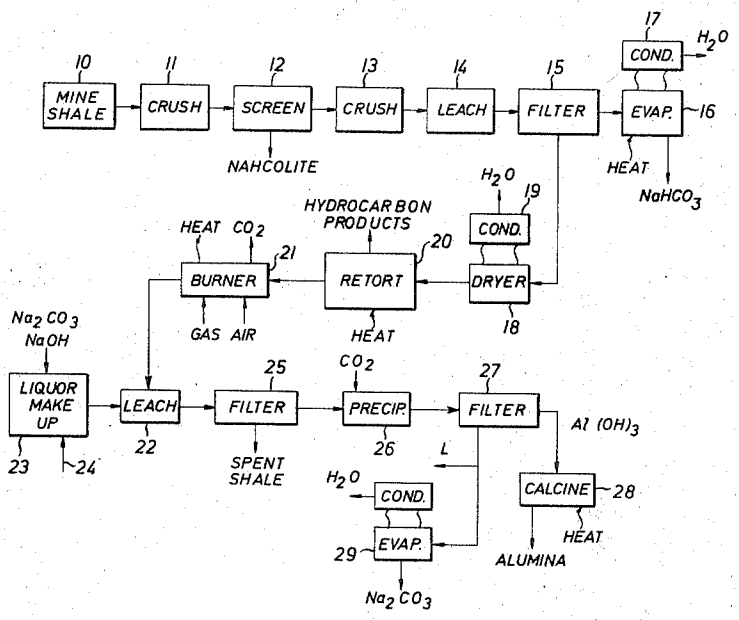
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[57] **ABSTRACT**

Integrated processes are disclosed for recovering hydrocarbon products as well as alumina and sodium carbonate and/or nahcolite from oil shale. The shale is pyrolized or retorted at low temperature to recover hydrocarbon compounds, and the retorted shale is subjected to a weak caustic leach to remove aluminum and sodium compounds. Nahcolite and/or sodium carbonate may be recovered by two disclosed methods, one being by screening crushed shale prior to the retort, and also removing the material from a water leach prior to the retort and from the caustic leach after the retort. The second method includes heating the crushed shale prior to retorting to change the nahcolite into sodium carbonate characterized by a lower bulk density which is separated out to provide a substance useful for scrubbing flue gas.

25 Claims, 6 Drawing Figures



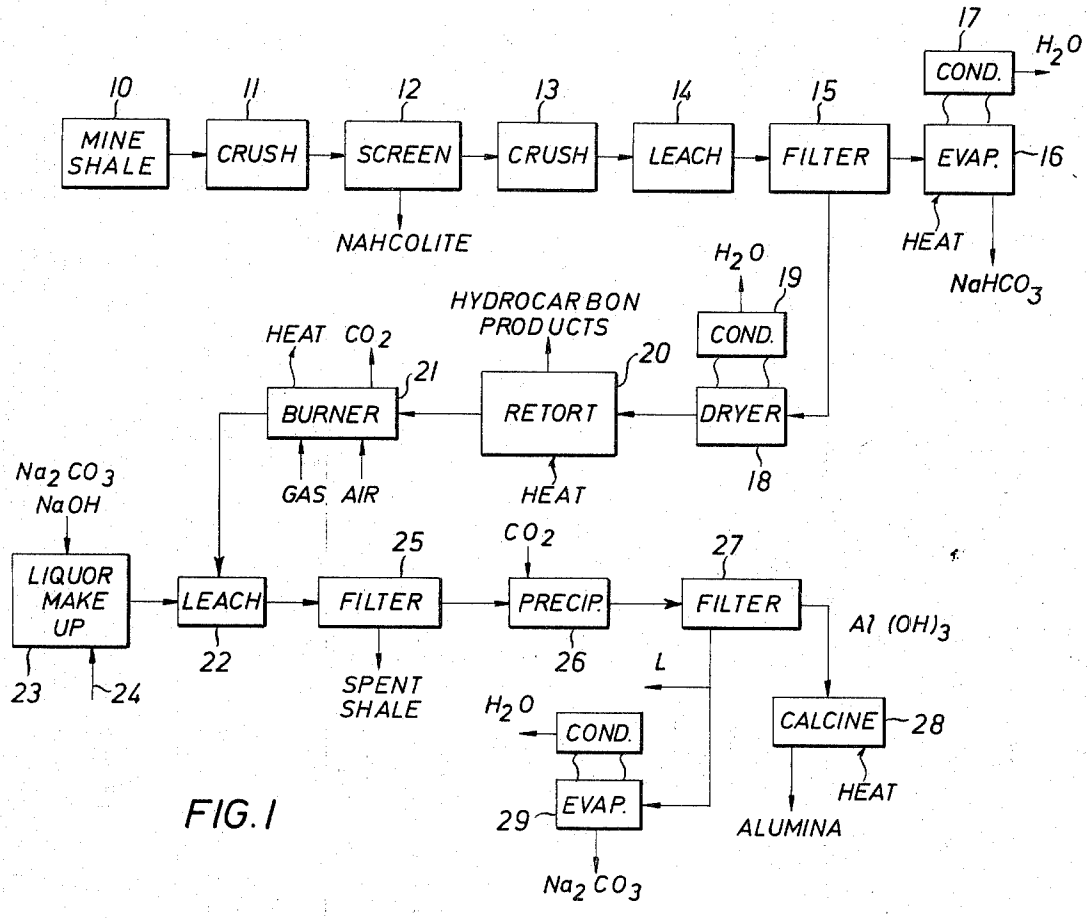


FIG. 1

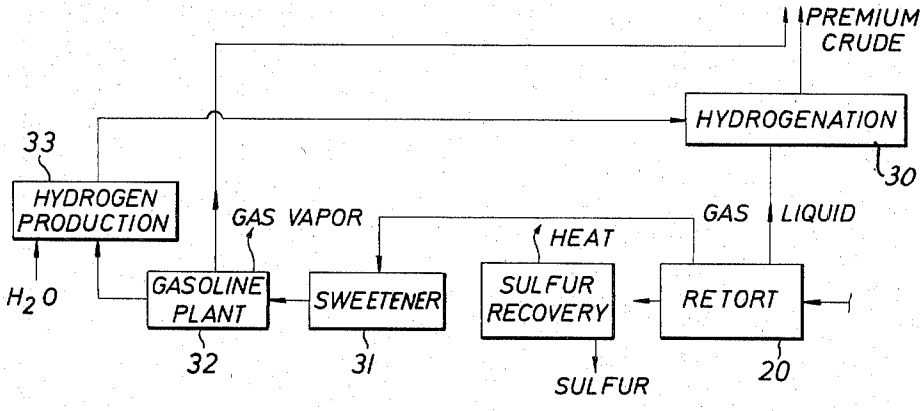


FIG. 2

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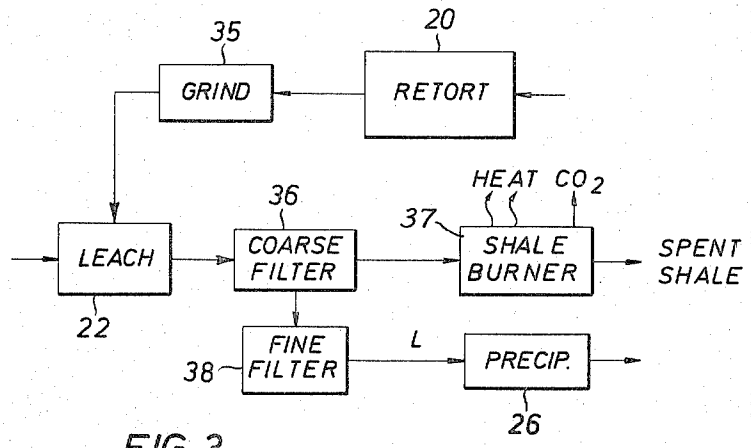


FIG. 3

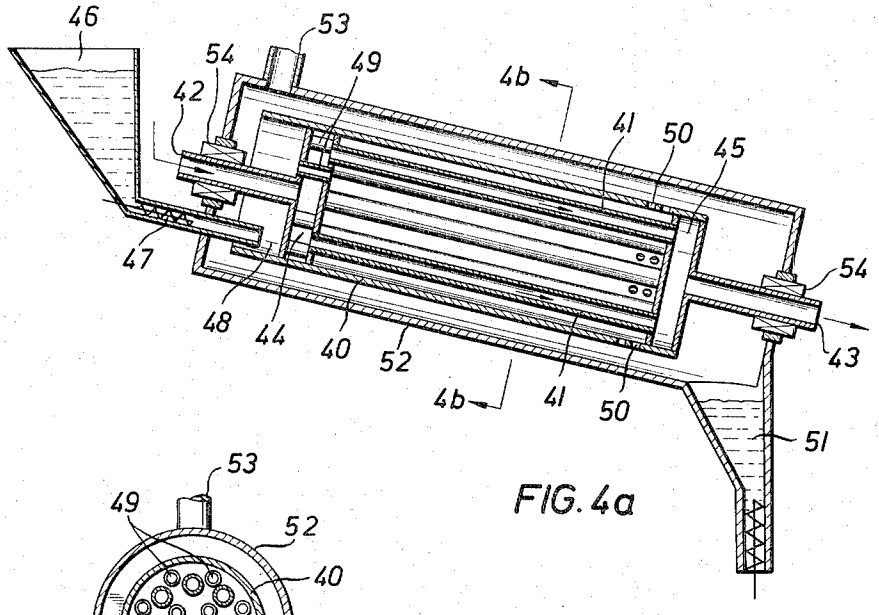


FIG. 4a

FIG. 4b

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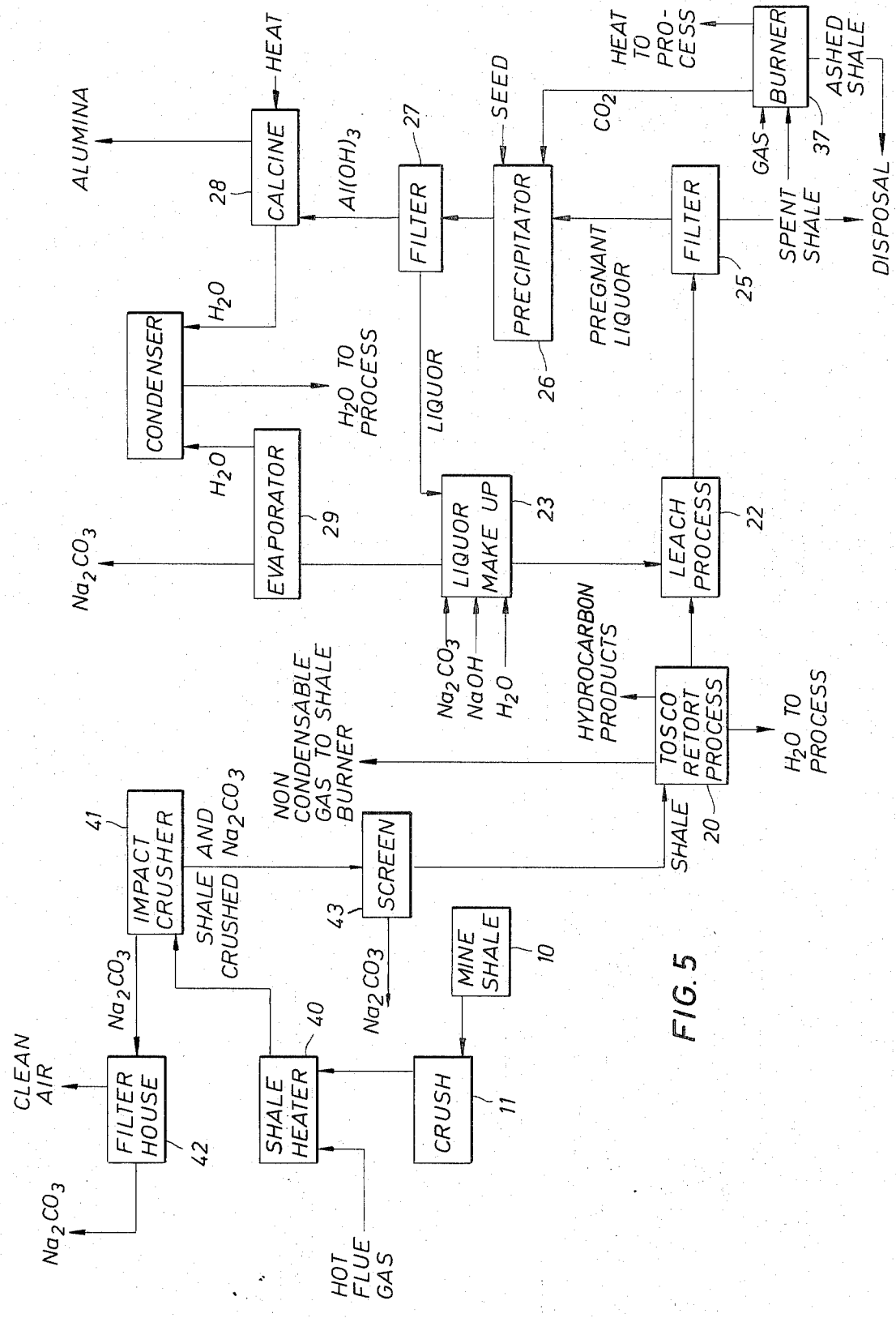

ALUMINA
HEAT
CALCINE
28
$Al(OH)_3$
FILTER
27
SEED
HEAT TO PROCESS
CO_2
BURNER
ASHED SHALE
GAS
37
CONDENSER
H_2O
H_2O TO PROCESS
LIQUOR
PRECIPITATOR
26
PREGNANT LIQUOR
FILTER
25
SPENT SHALE
DISPOSAL
Na_2CO_3
EVAPORATOR
29
LIQUOR MAKE UP
23
LEACH PROCESS
22
Na_2CO_3
NaOH
H_2O
HYDROCARBON PRODUCTS
NON CONDENSABLE GAS TO SHALE BURNER
TOSCO RETORT PROCESS
H_2O TO PROCESS
SHALE
20
41
IMPACT CRUSHER
SHALE AND Na_2CO_3 CRUSHED
SCREEN
43
Na_2CO_3
MINE SHALE
10
CLEAN AIR
Na_2CO_3
FILTER HOUSE
42
SHALE HEATER
40
CRUSH
11
Na_2CO_3
HOT FLUE GAS

FIG. 5

SHALE OIL AND MINERAL RECOVERY PROCESS

CROSS REFERENCE TO RELATED APPLICATION

This is a continuation-in-part of copending application Ser. No. 726,950, filed May 6, 1968 now abandoned.

BACKGROUND OF THE INVENTION

The invention relates to recovery of minerals from the earth, and, more particularly, to processes for recovery of minerals from oil shale deposits.

Large deposits of oil-bearing shale exist which have been almost entirely untouched because of the lack of an economical process for recovery of the oil. The many processes for recovery which have been proposed, either for in situ or for mined shale, have not satisfied the requirements of producing oil at a cost comparable to conventional sources.

It has been found that some oil shale deposits contain substantial quantities of other valuable minerals, so that a possibility of profitable recovery of oil exists if the other minerals can be extracted at the same time for a profitable return. In particular, deposits are found which contain kerogen, or shale oil, along with nahcolite and dawsonite, Nahcolite, $NaHCO_3$, is called natural sodium bicarbonate, and this is useful as is, or easily converted to sodium carbonate, Na_2CO_3, which is known commercially as soda ash. Dawsonite, $NaAl(OH)_2CO_3$, is a source of alumina, Al_2O_3, and also soda ash.

The exisng oil shale retorts and retort processes usually do not operate under conditions which are favorable to recovery of the other minerals, however. In particular, usually high temperatures are used, and the size of retorted shale is too large for extracting the nahcolite and dawsonite by the preferred techniques. In like manner, the classic methods of alumina and soda ash recovery are not compatible with one another, or with oil shale retorting.

SUMMARY OF THE INVENTION

It is therefore a primary feature of the present invention to recover economically shale oil along with other minerals such as alumina and soda ash or nahcolite. Another feature is to provide a compatible process for recovering hydrocarbon products along with alumina and soda ash from oil shale or the like, particularly a self-contained process which may be performed at remote locations without significant supply of materials other than the shale and water. Also, it is a feature to provide mineral recovery techniques compatible with oil shale retorting but useful separately.

In accordance with one feature of the invention, mined oil shale containing nahcolite and dawsonite is crushed to a small size and fed into a preheater where controlled heating decomposes the nahcolite from sodium bicarbonate to sodium carbonate. The sodium carbonate is then separated out and the oil shale and dawsonite are retorted at a low controlled temperature to recover hydrocarbon products. The pyrolized shale from the retort is then subjected to a weak caustic leach of controlled composition to recover aluminum and sodium carbonate. Aluminum is precipitated out of the leach liquor in the form of aluminum hydroxide which is calcined to provide alumina. The excess leach liquor is evaporated to recover Na_2CO_3.

By another feature of the invention, mined oil shale is first crushed and nahcolite is separated out as fines, this being possible because of the brittle nature of this mineral compared to the host shale. The shale is then leached to remove more of the nahcolite. The dried shale is retorted at a low, controlled temperature as above to recover hydrocarbon products, then the spent shale from the retort is subject to a weak caustic leach of controlled composition to recover aluminum and sodium carbonate as before. Aluminum hydroxide is precipitated out of the leach liquor and calcined to provide alumina, while the excess leach liquor is evaporated to provide Na_2CO_3. The spent shale is burned, either before the caustic leach or after, to provide heat for the system and CO_2 for the precipitate tank and, when burned before, to increase the recovery of the aluminum component. If before, the temperature of burning of the spent shale, if prior to the caustic leach, must be controlled to avoid reducing solubility of the desired products in the leach.

In accordance with another aspect of this invention which also may have application other than in the other processes described herein, a process is provided for the separation of nahcolite from the oil shale by reducing it to sodium carbonate. By this process, nahcolite in oil shale is decomposed to sodium carbonate of lower bulk density and greater brittleness than oil shale, without significantly pyrolizing the oil shale or breaking down any other minerals which would cause a chemical reaction. The exact temperature of the heating depends on the amount of fines and residence time. The sodium carbonate is separated from the oil shale by reducing the particle size of the sodium carbonate and screening the reduced size particles from the oil shale. The particle size reduction of the sodium carbonate can be accomplished by one method in an impact crusher.

In the operation of an impact crusher, the sodium carbonate, being very brittle, will disintegrate whereas the oil shale will not. In the method using the impact crusher employing a gas stream, the sodium carbonate particles laden in the gas are separated out in a filter such as a conventional filter house or dry cyclone.

BRIEF DESCRIPTION OF THE DRAWINGS

Specific embodiments of the invention will now be described with reference to the accompanying drawings which are briefly described as follows:

FIG. 1 is a flow chart of one embodiment of a mineral and shale oil recovery process according to the invention;

FIG. 2 is a flow chart of one arrangement for treating hydrocarbon output from the retort in the process of FIG. 1;

FIG. 3 is a flow chart of a portion of the process of FIG. 1 with a modification of treatment of the spent shale from the retort;

FIG. 4*a* is a schematic elevational view in section of an oil shale retort which may be used in the process of the invention;

FIG. 4*b* is a sectional view of the apparatus of FIG. 4*a*, taken along the line 4*b*—4*b*; and

FIG. 5 is a flow chart similar to that of FIG. 1, for a preferred embodiment of the invention.

DETAILED DESCRIPTION OF SPECIFIC EMBODIMENTS

FIG. 1

With reference now to FIG. 1 of the drawing, one embodiment of a process according to the invention will be described with reference to a flow chart, it being understood that the apparatus used for the various steps of the process is of conventional form and need not be described in detail.

The feed material for the process is oil shale of the type discussed above, i.e., containing kerogen along with nahcolite and dawsonite. The shale is mined by appropriate means, this mining step 10 being, for example, by the room-and-pillar method, from either a surface entry along the dip of the bed to be mined, or by vertical shaft down to the selected bed. In the room-and-pillar method, as much as 75 percent of the rock is removed and 25 percent or more remains as pillars for support. A face of up to 100 feet may be mined by this method. The mined shale is in the form of large chunks, up to perhaps several feet in size, and is transported by conveyor or hopper to crushing apparatus 11 which provides the first crushing step.

A feature of this embodiment, although not needed in the preferred embodiment of FIG. 5, is the use of a multiple stage crushing sequence for initial recovery of a large part of the nahcolite in the shale by mechanical separation. The nahcolite, because of its extreme brittleness compared to the more resilient oil shale, will break up in the crushing apparatus 11, primarily into fines. The crushing apparatus 11 and 13 reduces the shale in a series of crushing steps to a maximum of 1 inch, preferably less than ½ inch, chunks.

The shale is passed through screening apparatus 13 which screens out the fines, i.e., everything of about minus 35 mesh. FIG. 1 shows the screening step 12 to be between crushing steps 11 and 13; however, the screening step may follow two sequential crushing steps. The impure nahcolite screened out after the crushing stages will contain perhaps 20 percent oil shale, but the screened fines will be comprised mostly of nahcolite. This material may be either sold as is for the purpose of air pollution control, i.e., cleaning flue gas, or other uses. Alternatively, the screened fines may be transported to a water leach for recovery of pure sodium bicarbonate. In the latter case, the remaining oil shale could be returned to the retort. In any event, this screening process which removes the fines will remove from about 75 percent to about 90 percent of the nahcolite from the shale, the remainder passing on through the second crushing operation and being recovered in a water leach by evaporating the water, and a small part may continue through to the retort to aid in controlling the final leach as will be described.

The crushing apparatus 11 and 13 reduces the shale to about pea size, this size being preferable for the following leach, and as feed for the retort.

The shale after being crushed to pea size or less, is then transported to leach tanks 14 which contain water at a temperature of less than about 70°F. but greater than about 40°F. This leach is for the purpose of removing the remaining nahcolite. The temperature here is maintained fairly low so that alumina is not dissolved out at this point where it would be lost to the process. Lower temperatures, however, require longer to provide the needed leaching, so a temperature in the noted range is preferred.

Two desirable features are provided at this leach step due to the fact that all of the remaining nahcolite need not be removed. First, the leach can be accomplished in a relatively short period of time, on the order of 15 minutes or less, and, secondly, about one-quarter of the remaining nahcolite may be left in the shale to generate a portion of a subsequent sodium carbonate leach liquor. The exact percentages of nahcolite that are removed by screening, and the time which the shale remains in the water leach tanks 14, will depend upon the character and composition of the shale at a particular location. The object is to remove all of the nahcolite, or an amount of nahcolite so that the sodium carbonate concentration in the subsequent leach liquor will not exceed the limits as will be discussed.

The contents of the leach tank 14 including the shale and liquor are transported to a filter 15 which functions to separate liquid from solid. Usually the filter 15 would be in the form of a filter press designed to handle large volumes of material. The water or leach liquor is piped to an evaporator 16 to which heat is applied as derived from the later burning step as will be described. Heat may also be generated by conventional fuel burning. Water vapors driven off in the evaporator 16 are recovered in a condenser 17 to provide feed water for the leach tank 14, or for use in other parts of the process. The rate of crystalization in the evaporator is selected to produce a quite pure quality of sodium bicarbonate from the leach liquor. Thus, one of the outputs of the process is pure sodium bicarbonate from the evaporator 16. The pea sized oil shale, separated from the leach liquor in the filter 15, is conveyed to a dryer 18 where the shale is dried and preheated in preparation for entry into the retort. Heat for the dryer may also be obtained from the subsequent shale burning step. Water vapors from the dryer are collected in a condenser 19, from which the recovered water is used as a supply for the leach tanks or other parts of the process.

The dried and pre-heated crushed shale is not fed into an oil shale retort 20 for recovery of hydrocarbon products. Although many different types of oil shale retorts have been proposed in the past, it is important that the retort used here have certain characteristics. Generally, liquid and gaseous hydrocarbons are separated from the shale by heat in retorts of this type. It is important in the performance of the process of the invention, however, that heat not be applied in an uncontrolled manner, and that the temperature not exceed certain maximums. To this end, combustion type retorts are not suitable for the purposes herein described, because of the excess temperatures involved and the lack of control of heat, i.e., occurrence of hot spots in the combustion zone of such retorts. Accordingly, it has been found advantageous to use a retort of the type described below, or in the alternative to employ a retort generally of the type which has become known in the industry as the "TOSCO Retort." One example of this retort is referred to in U.S. Pat. No. 3,025,223, issued Mar. 13, 1962 to O.E.A. Aspergren, et al, and assigned to The Oil Shale Corporation.

In the TOSCO type retort the oil shale is heated by mixing with preheated ceramic balls, the balls being heated from the combustion products resulting from burning the spent shale or conventional heating proc-

esses and upon heating the shale the oil is driven off as a vapor and/or liquid. The liquid is usually of low gravity and high pour point, and needs to be hydrogenated to render it a high gravity, low pour point crude. Treatment of the hydrocarbon products will be discussed in more detail below.

Control of temperature in the retort is an important feature of the invention, because heating of sodium carbonate above about 600°C. tends to reduce or destroy its solubility. In addition, the solubility of dawsonite begins to decrease upon heating above 600°C., and at 900°C. the dawsonite is rendered insoluble in all but a very concentrated acid or base solution. So, a temperature high enough to recover effectively a good portion of the hydrocarbons is selected, but low enough to avoid detriment to the solubility of sodium carbonate and dawsonite. Preferably this temperature is about 475°C., although temperatures up to about 550° to 600°C. may be used if recovery of hydrocarbons is emphasized or other factors are involved. This temperature may be as low as about 450°C.

The spent shale coming out of the retort is in the form of a powder which contains a small amount of coke which is combustible. The percentage of coke will vary with the quality of the shale, but in one location is found to be about 4 percent. This spent shale is conveyed to a burner **21**, which may be a conventional furnace of the conveyor feed type or other known device, where the coke in the spent shale will burn to supply heat to the remainder of the process in the places noted. The temperature within the burner **21** is regulated by controlling the rate of feed-in of shale, by controlling the blowers which feed-in air to the furnace, and/or by controlled application of volatile gas fed into the burner. This gas, principally methane, is derived from the retort or from the treatment of the hydrocarbon output from the retort. The by-products provided by the burner include carbon dioxide, which is separated from sulfur dioxide, hydrogen and particulate matter by scrubbers to produce a CO_2 source for the alumina recovery stage as will be described below.

The temperature in the burner **21** is maintainedd below a certain maximum due to several critical factors. For example, the solubility of the dawsonite must not be destroyed, as mentioned above, while similar considerations apply to gibbsite. In addition, the mineral analcite is found in varying amounts in the oil shale of the areas of major deposits. Analcite is a sodium aluminum silicate, $NaAlSi_2O_6\ 2H_2O$, a zeolite which is also extremely soluble for a silicate. It will dissolve in a basic solution of only slightly higher pH than dawsonite, and when it dissolves silica is released into the solution. Silica is a major contaminant in alumina and rapidly decreases the value of the product. Analcite becomes less soluble as heat is applied, so a higher temperature in the burner is preferred for this purpose.

Heat applied to dawsonite alters its solubility in a manner as now will be explained. At 370°C. dawsonite loses weight and changes to another compound which is more soluble than dawsonite, then at 600°C. this compound begins to lose its solubility for two reasons. First, it loses some solubility because of a little understood structural change, and secondly it loses solubility because the sodium present appears to form a type of insoluble glass which surrounds some of the soluble aluminum, thus retarding solubility. Then, at 730°C., the compound undergoes additional weight loss and becomes a material resembling sodium aluminate; however, this material differs from sodium aluminate in that when dissolved in water it has a pH of 9 whereas sodium aluminate has a pH of 11. This compound is soluble in a light base solution. Heating above 730°C. decreases the solubility until at 900°C. it is totally insoluble for all practical purposes. Not all of the dawsonite converts to this soluble compound. There is a continuous loss of recoverable alumina from the dawsonite upon heating at temperatures above 600° C.

Accordingly, the presence of both dawsonite and analcite in the oil shale requires that an optimum heat be selected for the burner **21** to render soluble the maximum amount of dawsonite and the minimum amount of analcite. Preferably, this temperature is about 475°C., although temperatures up to perhaps 550° to 600°C. might be used, but in any event the absolute maximum is 900°C., while the lower temperature will be above 370°C.

Higher temperatures can be used if sodium carbonate is not attempted to be recovered from the dawsonite. The optimun temperature varies according to the relative concentrations of the various minerals in the feed stock, the particular value being selected to minimize the amount of silica in the subsequent leaching solution.

As will be explained below, rather than burn the spent shale at this stage in the process, the shale from the retort may be otherwise processed such as by grinding before leaching, then the shale burned to supply heat later. Also, the burning or grinding step is not always necessary. In the process of FIG. **1**, after the shale is burned in the furnace **21**, it is dumped into a leach tank **22**, which contains a leach liquor of sodium carbonate in water. The concentration of sodium carbonate is kept below about 0.5 normal. The upper limit of sodium carbonate concentration might be as high as about one N., although at such values it becomes almost impossible to change the pH of leach liquor to the desired value.

Also in a leach liquor exceeding 0.5 normal, the concentration of sodium ions relative to the aluminum ions obtained from the dawsonite and other minerals is too high, so as to favor the subsequent precipitation of dawsonite rather than aluminum hydroxide. This point is illustrated in reference to the following test data:

TABLE 1

Amenability Test Results at 20 Percent Pulp Density Retorted Shale from Fischer Assay

Determinations	Test No	Al_2O_3 Extr. %	Silica in the precipitate (ppm)	Al/Si	pH*	Na_2/Al
Water**	262	24.6	—	—	10.1	1
0.5 n Na_2Co_3	283	94.5	31	162	11.9	4.95

TABLE 1—Continued

Amenability Test Results at 20 Percent Pulp Density Retorted Shale from Fischer Assay

Determinations	Test No	Al_2O_3 Extr. %	Silica in the precipitate (ppm)	Al/Si	pH*	Na_t/Al
0.5 n Na_2CO_3 10 ml NaOH***	280	101.0	89	56	12.2	5.8
2.0 n Na_2CO_3	275	82.0	29	152	11.5	12.0
2.0 n Na_2CO_3 10 ml NaOH	272	96.5	146	32	12.2	18

*pH after 3 minute leaching
**500 ml water or Na_2CO_3
***10.0 n NaOH

Table 1 shows in tabular form test data conducted on spent shale from the Fischer Assay retorts at 20 percent pulp density, an industry standard. The column for "Al_2O_3 Extr." refers to the percentage of Al extracted compared to the theoretical maximum using the strongest of conventional techniques. The column for Na_t/Al is the molar ratio of Na in all forms to Al in the leach liquor.

So, the leaching solution is preferably maintained at a concentration of sodium carbonate of no greater than about 0.5 or 0.4 N., i.e., no more than about 53 grams per liter Na_2CO_3. The sodium carbonate tends to act as a buffer to maintain the pH at about 11.9. However, it may be preferable that the pH of the leach liquor be slightly higher than this, up to about 12.2, so this is one of the reasons that a light sodium carbonate solution is used. A small amount of sodium hydroxide is added to bring the pH up to the desired value. A pH of as high as 12.2 would be used if little or no analcite were present in the shale, but if substantial analcite is found then the pH should not exceed about 11.9. the pH should not decrese below about 11 as it would not then function as a caustic leach. The presence of analcite causes the pH and Normal solution control to be somewhat critical; if there is no analcite in the shale then the permissible range for these factors is greatly increased. An acceptable range for the sodium carbonate solution is perhaps about 0.1 to 0.5 N., since below about 0.1 the solution is not strong enough to dissolve dawsonite in a reasonable period of time. The time for allowing the spent shale to remain in the leach tank **22** is about 15 minutes. The temperature in the leach tank is not critical, it being permitted to heat or cool depending upon the feed water input and the temperature of the spent shale from the burner. Higher temperatures will of course decrease the time necessary for the spent shale to remain in the tank.

A separate tank **23** is shown in FIG. **1** for the purpose of makeup of the leach liquor. The original start-up would comprise water and sodium carbonate, which may be provided by decomposing nahcolite from the output of the screen **12.** A controlled amount of sodium hydroxide is also added to establish the pH level, this sodium hydroxide also being obtained from the raw material of screened nahcolite or other source. The amount of sodium carbonate placed in the make-up solution takes into account the amount of nahcolite which will have remained in the oil shale as it progressed through the leach tank **14,** the retort **20** and the burner. As discussed above, about 5 percent or less of the original amount of nahcolite may remain in the spent shale which is dumped into the leach tank **22.** Thus, the makeup liquor should not contain an amount of sodium carbonate which would cause the solution in the leach tank to exceed the desired maximum. Another factor to consider here is the percentage of calcium carbonate in the original shale. Calcium carbonate will react with sodium carbonate in the leach liquor to release hydroxide ions and increase the pH of the solution. So, the composition of the makeup liquor will also be dependent upon the calcium carbonate concentration in the shale.

The reason for the upper limit of the pH of the leach liquor is that the shale usually contains feldspar, which is a finely crystalline material which will break down to silica in a basic solution if the pH is too high. On the other hand, a pH of 11 or preferably above is needed to dissolve significant amounts of alumina.

After the initial start-up, the leach liquor makeup is re-cycled, concentrated liquor from the output of the subsequent filters, being applied at an input **24** indicated in FIG. **1.**

After the spent shale has remained in the leach tanks **22** an appropriate time, the material is conveyed to a filter press **25** which functions to separate the spent shale from the leach liquor. The spent shale is conveyed to a disposal area, it being noted that this spent material is clean and non-contaminating so that it may be used as fill for a dam or the like. The spent shale may be burned at this point to provide heat and CO_2 for the process. Also, the spent shale from the filter **25** may be returned to the mine to fill the excavated area, so that it may be possible to remove the pillars. The spent shale and waste water may be transported through a pipeline in a manner similar to coal slurry to the disposal area.

The leach liquor which is filtered off from the spent shale at the filter **25** is conveyed into a precipitate tank **26** for recovery of aluminum hydroxide. Precipitation of aluminum hydroxide from the leach liquor is dependent on the molar ratio of sodium to aluminum in the leach liquor. At ratios of greater than 6 moles of sodium to one mole of aluminum, the dominant precipitate may be dawsonite. At molar ratios of less than 6 moles of sodium to one of aluminum the dominant precipitate is aluminum hydroxide.

The precipitate tank **26** may contain a large rotary agitator from which carbon dioxide is bubbled into the liquor. This is conventional apparatus which need not be described in detail. The rate of agitation and the flow of carbon dioxide is controlled in known manner to precipitate out the optimum quality of crystals of aluminum hydroxide, the size of the crystals being important. If precipitation is too fast a gelatinous substance results which is hard to remove by filtration. Precipitation and desirable crystallization may also be effected by seeding the pregnant liquor with any number of materials all of which are known in the present art.

Following the precipitate tank **26,** the liquid is conveyed to a filter **27** which serves to separate the leach

liquor from the aluminum hydroxide. The precipitate is conveyed to a calcining stage **28** where heat is applied to drive off water and leave alumina which is the desired product. Calcining of aluminum hydroxide to produce alumina is of course conventional and need not be described in detail.

The remaining leach liquor from the filter **27** is used in part as the input **24** to the makeup tank **23,** while the excess leach liquor is applied to an evaporator **29** where the excess sodium carbonate is separated out to produce the other product, Na_2CO_3. Water vapor from the evaporator will be condensed and piped back into the water supply for the leach tanks.

The products produced by the process which has been described are (1) nahcolite of commercial grade resuling from the screening **12,** this being impure but a marketable product, (2) sodium bicarbonate recovered from the leach **14** at the evaporator **16** of pure grade, (3) hydrocarbon products recovered from the retort **20,** (4) alumina recovered from the calcined precipitate obtained in the tank **26,** and (5) pure sodium carbonate from the excess liquor at the evaporator **29.**

The technique used to recover alumina according to the invention should be noted to be quite distinct from the so-called Bayer process which uses a very strong caustic leach. In the Bayer process, contamination with silica is not avoided. A sodium hydroxide solution of perhaps 10 – 15 N. is used, wherein the pH is at the upper theoretical limit.

It will be noted that this process as described above is essentially self-sufficient in that heat is obtained from the burner for use in the retort and the various evaporators, while water from the condensers provides the water supply, and CO_2 from the burner is used in the precipitator. Also, volatile waste gas from the hydrocarbon treatment of the output of the retort may be used in the burner and/or to supply additional heat. Self-sufficiency is quite important due to the remote inaccessible locations of most deposits of oil shale, there being no convenient supplies of water, fuel, electric power, etc. The process is also characterized by a substantial absence of contaminated wastes.

FIG. 2

Turning now to FIG. **2** of the drawing, details of the treatment of hydrocarbon products obtained from the retort **20** will be described. The liquid output from the retort **20** is hydrogenated by conventional means **30** to produce a premium crude feedstock for refining. The volatile gas from the retort may be applied to a gas sweetener **31,** the output of which is applied to a gasoline plant complex **32.** The lean gas from the plant may be used in making hydrogen from water at a hydrogen production unit **33.** The hydrogen output is used to hydrogenate the shale oil, which is one of the steps in rendering it a premium feedstock. Stabilizer overhead vapor from the gas plant is used in the shale burner. Stabilized gasoline from the plant **32** is one of the premium outputs. As noted in FIG. **2,** sulfur may be recovered from the gas exiting from the retort. Conventional methods and apparatus would be used for sulfur recovery.

FIG. 3

Referring now to FIG. **3,** an embodiment of the process of the invention is illustrated wherein the spent shale from the retort **20** is first ground and dumped into the leach liquor, prior to burning. Control of the temperature in the shale burning step is thus unnecessary. Temperature control is needed to aovid destroying the solubility of sodium, and even aluminum, but if burning is avoided before the leach then there need be no temperature concern in the subsequent burning step. The purpose for burning the spent shale is to supply heat and CO_2 to the system. However, the burning step does provide an additional function between the retort and the leach, this being to remove residual carbon or coke which appears to retard the recovery of alumina. It appears as if the residual carbon coats the alumina in the oil shale and protects it from coming into contact with the leach solution. So, rather than burn to remove the carbon, the spent shale is conveyed to a grinder **35** in FIG. **3** which functions to grind or tumble the spent shale to break apart the protected particles of aluminum-bearing rock, so that contact with the leach solution will be effective. Slight abrasion of these particles will crack the carbon coating, enabling the leach to dissolve the alumina. Following grinding, the spent shale is conveyed to a leach tank **22** just as before. The slurry from the leach tank is filtered in two stages. First a coarse filter **36** removes the spent shale, which is fed to a burner **37** where heat control is unnecessary. Indeed, the hotter the better, for the shale is burned here only to supply heat to the system and to recover CO_2 from the flue gas. CO_2 is separated out in scrubbers as mentioned above. It is possible also to recover sulfur from the flue gas, and this will be done if sulfur is present.

The leach liquor is run from the first filter **36** to a fine filter **38** to remove very fine particulate matter and any silica gel that may be in the leach. This two step filtering process results in a clean liquor from which relatively pure sodium carbonate and aluminum hydroxide can be recovered. The liquor from the fine filter **38** is run into a precipitate tank **26** just as in the prior embodiment, and the remainder of the process is exactly the same as described above. Aluminum hydroxide is precipitated out by seeding or by reducing the pH by bubbling carbon dioxide through the liquor, then the aluminum hydroxide is calcined to produce alumina. The sodium carbonate-rich leach liquor is piped to the leach makeup tank where the excess is run off and evaporated for soda ash.

The process according to FIG. **3** has certain advantages over the process of FIG. **1,** depending upon the composition of the shale. In most shale, dawsonite is the prime mineral supplier of aluminum compounds; however, another mineral is present which also supplies aluminum, this mineral containing aluminum hydroxide and in fact being present as two minerals. These minerals are gibbsite and nordstrundite, both of which have the same general formula and character. Dawsonite supplies about 80 percent of the available aluminum, while gibbsite and nordstrundite supply about 20 percent. The solubility of dawsonite as a function of the temperature to which it had been heated was discussed above. The solubilities of gibbsite and nordstrundite are different. These latter minerals are more soluble than dawsonite up to temperatures of 350°C., at which point gibbsite and nordstrundite hydrate and begin to become less soluble, while at 550°C. solubility is lost entirely, whereas dawsonite increases in solubility at this point. Therefore, by not burning the shale prior the leach, a part of the aluminum from gibbsite and nord-

strundite can be recovered since the hottest temperature to which it will have been subjected is about 475°C. in the retort. Considering all of the minerals which heat affects in this process, it appears that 475°C. it about an optimum temperature for the retort. Dawsonite becomes more soluble starting at 370°C., while gibbsite and nordstrundite begin to lose solubility at 350°C. but do not lose solubility entirely until about 550°C. Analcite begins to lose solubility at about 300°C. Ideally, the basic solution should dissolve most of the available dawsonite, dissolve some of the gibbsite and nordstrundite, and none of the analciate.

If the analcite content is high in the shale, it would be preferred to use the burning process of FIG. 1 to tie up the analcite. On the other hand, it may be preferred in some instances to leave out the burning or grinding prior to the leach, than then using a less caustic leach, no sodium hydroxide at all added, depnding upon the desired products and the composition of the shale.

FIGS. 4*a* and 4*b*

Referring to FIGS. 4*a* and 4*b*, an oil shale retort is shown which may be used in the process of the invention. This retort is of the non-combustion type, and does not require the separate heating of ceramic balls as in the retort discussed above. The retort includes a rotating cylinder **40** in which particulate oil shale is tumbled for a time sufficient for recovery of hydrocarbons. Running the length of the cylinder are a plurality of conduits **41** or pipes through which is passed hot gas which enters at an input **42** and exits at an output **43.** The hot gas is distributed to all of the conduits **41** by a manifold **44** at one end of the cylinder, and collected at a manifold **45** at the lower end. The hot gas heats the walls of the pipes or conduits **41,** not directly contacting the particulate shale, and this provides the heat for retorting. The hot gas may be a combustion product from the subsequent burning of the spent shale, or may use methane from the hydrocarbon products. Finely ground shale is introduced into a hopper **46,** from which it is fed into the upper end of the rotating cylinder by an auger **47.** From the receiving end **48** of the cylinder, the shale passes through conduits **49** in the manifold **44,** then tumbles along the length of the cylinder at a rate dependent upon the slope of the cylinder and the rate of rotation. The shale exits through holes **50** in the lower end of the cylinder **40,** then falls into a hopper **51** and is augered out. The entire apparatus is enclosed within an outer cylinder **52,** so pressure can be maintained within the retort. Hydrocarbon vapors exit through an outlet **53,** from whence the vapor may pass to a condenser for separation. The vapor escapes from the interior of the cylinder **40** through the conduits **49** and through the holes **50.** Rotation of the cylinder **40** within the cylinder **52** is permitted by bearings **54,** while the means for rotating the cylinder is not shown.

FIG. 5

Another aspect of the invention now to be described with reference to FIG. **5,** relates to a process for the separation of nahcolite from mined oil shale in the form of sodium carbonate. Nahcolite is a basic sodium bicarbonate mineral having the formula $NaHCO_3$. Nahcolite, until recently, has not been of significant importance. With the recently recognized need for controlling air pollution and the unavailability of a low cost scrubbing agent, however, nahcolite can be provided as a low cost and effective scrubbing agent for the greatest contaminants, namely oxides of sulfur, nitrogen and other elements. At present nahcolite is not available to industry because it is known to exist in quantity only in the oil shale of the Piceance basin in northwest Colorado. Nahcolite exists as bedded and nonbedded rosettelike and coarse bladed crystal aggregates. The aggregates range in diameter from less than an inch to a few feet. Many of the bedded forms of nahcolite contain finely crystalline layers along with the aggregates to form discontinuous beds of nahcolite in the oil shale.

Whereas nahcolite as a natually occurring sodium bicarbonate is an efficient scrubbing agent, an even more efficient scrubbing agent can be produced by decomposing nahcolite into sodium carbonate. Sodium carbonate produced by decomposing nahcolite is also a more efficient scrubbing agent than commercial sodium carbonate because of the nature of the decomposition process. Nahcolite decomposes according to the formula:

$$2NaHCO_3 + \text{Heat} \rightarrow Na_2CO_3 + CO_2 + H_2O$$

The water is forced out of the nahcolite causing a molecular change. This molecular change results in the sodium carbonate having a crystalline structure which is more efficient in scrubbing sulphur oxides and other contaminates than sodium carbonate produced by the Solvay process or from trona.

An economical and practical process to mine and retort oil shale could also produce sodium carbonate at a cost far less than mining sodium carbonate alone. The production of sodium carbonate by a low cost method described herein could provide industry with economical sodium carbonate in a form which could be used as a scrubbing agent for controlling air pollution.

The process of FIG. **5** is the same as that of FIG. **1** and **3** except for the treatment of the crushed shale between the crushing step **11** and the retort **20.** In the process of FIG. **5** for the recovery of nahcolite from oil shale the mined material is crushed in step **11** to about minus ½ inch diameter and roasted in a shale heater **40** to a temperature of about 130°C. to 475°C. This roasting temperature is important because nahcolite decomposes rapidly at the proper temperature range, depending on the particle size. By virtue of the weight loss without particle size reduction, a lower bulk density results for the sodium carbonate. The sodium carbonate from the output of shale heater **40** is much more brittle than the remaining minerals in the oil shale.

In the roasting operation **40,** the decomposition of nahcolite occurs rapidly; that is, particles of nahcolite less than ½ inch in diameter decompose in about 15 minutes when subjected to a temperature in excess of 150°C. This allows the residence time in the shale heater **40** to be short and not sufficiently long enough to cause significant pyrolization of the oil shale or breakdown of other minerals. The decomposition is also dependent upon the rate at which heat (greater than 150°C.) is applied to each particle.

The material from the output of shale heater **40** is passed to an impact crusher **41** where the particles of sodium carbonate are mechanically disintegrated to a smaller size, leaving the remaining minerals in the material substantially unchanged in particle size. The impact crusher **41** may operate, for example, by rotary

impact or by blowing the crushed oil shale including the sodium carbonate with an air or gas stream against impact plates. Rotary impact crushing can be effected by conventional rotary impact crushing apparatus. Upon impact, the sodium carbonate particles, being very brittle, will disintegrate whereas the remainder of the material will not. Most of the sodium carbonate particles and the remaining shale will fall to the bottom or out of the impact crusher **41,** but the very fine particles of sodium carbonate laden in the air stream are passed to a filter such as a filter house **42.** The fine particles of sodium carbonate are removed from the air stream removed in filter house **42** under clean air specifications. Filtering of the fine particles of sodium carbonate may also be effected by use of a dry cyclone.

The particles of sodium carbonate which fall to the bottom of or out of the impact crusher are separated from the remainder remaining shale by passing the material over a screen **43,** preferably having **10** to **200** mesh. The most efficient size or mesh of the screen **43** depends upon the amount of nahcolite in the raw oil shale which will govern the amount of fines in the material.

The sodium carbonate may also be separated from the oil shale after crushing by conventional floatation or other methods or combinations thereof.

The dried and pre-heated remainder of the oil shale from the screening process **43** is now fed into the retort process **20** for recovery of hydrocarbon products as described above. It is noted that no burning or grinding step prior to leach is shown in FIG. **5,** emphasizing that these steps are not always needed.

While the invention has been described with reference to particular embodiments, this description is not meant to be construed in a limiting sense. Various modifications of the disclosed embodiments, as well as other embodiments of the invention, may be apparent to persons skilled in the art upon reference to this description. It is therefore contemplated that the appended claims will cover any such modifications or embodiments as fall within the true scope of the invention.

What is claimed is:

1. An integrated process for producing hydrocarbon products, sodium carbonate products, and aluminum compounds from oil shale containing oil, nahcolite, and dawsonite, comprising the steps of:

mechanically separating a major portion of the nahcolite from the oil shale by crushing the oil shale to produce fine nahcolite particles and relatively coarser oil shale particles and screening the fine nahcolite from coarser shale to recover nahcolite as a first sodium carbonate product;

leaching the shale with an aqueous leach to dissolve a portion of the remaining nahcolite and recovering a second sodium carbonate product from the aqueous leach liquor by evaporation;

heating the shale in a non-combustion type retort at a temperature of from about 450°C. to about 550°C. to recover hydrocarbon products and to convert the dawsonite to a more soluble aluminum compound;

subjecting the spent shale from the retort to a caustic leach to dissolve the aluminum compound, the caustic leach being maintained at a pH not exceeding about 12.2 and not below about 11, the caustic leach comprising a solution of sodium carbonate not exceeding about 0.5 Normal, and having a molar ratio of sodium to available aluminum of less than about 6;

separating the spent shale from the caustic leach liquor containing the dissolved aluminum compound; and

precipitating aluminum hydroxide from the leach liquor of the caustic leach.

2. A process according to claim **1** further comprising the step of converting the aluminum hydroxide to alumina by calcining.

3. A process according to claim **1** wherein precipitating the aluminum hydroxide from the caustic leach liquor includes the adding of CO_2.

4. A process according to claim **1** wherein precipitating the aluminum hydroxide includes seeding of the leach liquor

5. A process according to claim **1** wherein the spent shale from the retort is burned at a controlled heat at a temperature ranging from above about 450°C. to about 600°C. before being subjected to the caustic leach.

6. A process according to claim **1** wherein the caustic leach comprises a solution of sodium carbonate of a concentration in a range of about 0.1 to 0.5 Normal.

7. A process according to claim **1** wherein the caustic leach also contains sodium hydroxide to maintain the pH not exceeding about 12.2 and not below about 11.

8. A process according to claim **1** wherein the spent shale from the retort is burned after the caustic leach to provide heat to the process and to provide a source of CO_2 for precipitating the aluminum hydroxide from the leach liquor of the caustic leach.

9. A process according to claim **8** wherein the spent shale is subjected to grinding before the caustic leach, to remove carbon coating the shale particles.

10. A process according to claim **1** wherein the oil shale includes aluminum in the form of a major portion of dawsonite and a minor portion of at least gibbsite.

11. A process according to claim **1** wherein sodium carbonate is recovered from the leach liquor of the caustic leach by filtering and evaporating the caustic leach liquor to recover sodium carbonate.

12. A process according to claim **1** wherein the quantity of nahcolite remaining in the shale after the aqueous leach does not exceed an amount sufficient to cause the sodium carbonate concentration in the caustic leach to be greater than about 0.5 Normal.

13. A process according to claim **1** wherein at least about three-fourths of the original nahcolite is removed from the oil shale by screening, and at least about three-fourths of the then remaining nahcolite is removed by by aqueous leach.

14. A process according to claim **1** wherein the step of mechanically separating includes a two-stage crushing sequence, with the screening being done between crushing steps.

15. A process according to claim **1** wherein the step of mechanically separating includes at least a two-stage crushing sequence followed by screening.

16. An integrated process for producing hydrocarbon products, sodium carbonate, and aluminum compounds from oil shale containing oil, nahcolite, and dawsonite, comprising the steps of:

initially heating the oil shale at a temperature less than pyrolizing temperature to decompose the nahcolite to sodium carbonate;

impacting the heated shale to disintegrate the particles of sodium carbonate relative to the host shale;

segregating the sodium carbonate from the host shale on the basis of particle size, and collecting the particles of sodium carbonate;

retorting the crushed shale to recover hydrocarbon products and to convert the dawsonite to a more soluble aluminum compound;

leaching the spent shale from the retort in a weak caustic leach containing no more than about 0.5 Normal solution of sodium carbonate, and having no more than about **6** moles of sodium per mole of available aluminum, to dissolve the aluminum compound;

separating the spent shale from the caustic leach liquor containing the dissolved aluminum compound;

precipitating aluminum hydroxide from the caustic leach liquor;

separating the aluminum hydroxide precipitate from the caustic leach liquor; and

removing sodium carbonate from the caustic leach liquor by evaporation.

17. A process according to claim **16** wherein the particles of sodium carbonate are further separated from the host shale by a floatation step following the segregating step.

18. A process according to claim **16** further comprising converting the aluminum hydroxide to alumina by calcining.

19. A process according to claim **16** wherein precipitation of aluminum hydroxide includes adding CO_2 to the leach liquor.

20. A process according to claim **16** wherein precipitation of aluminum hydroxide includes seeding.

21. A process according to claim **16** wherein the initial heating is at a temperature of from about 100°C. to about 475°C. for a time less than would cause significant pyrolizing of the oil shale.

22. A process according to claim **16** wherein the retorting is in a non-combustion type retort at a temperature not greater than about 550°C.

23. A process according to claim **16** wherein the spent shale from the retort is burned at a temperature not exceeding about 600°C. prior to leaching.

24. A process according to claim **16** wherein the caustic leach has a pH not exceeding about 12.2.

25. A process according to claim **16** wherein part of the sodium carbonate in the leach liquor is from nahcolite passing through the crushing and retorting steps.

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