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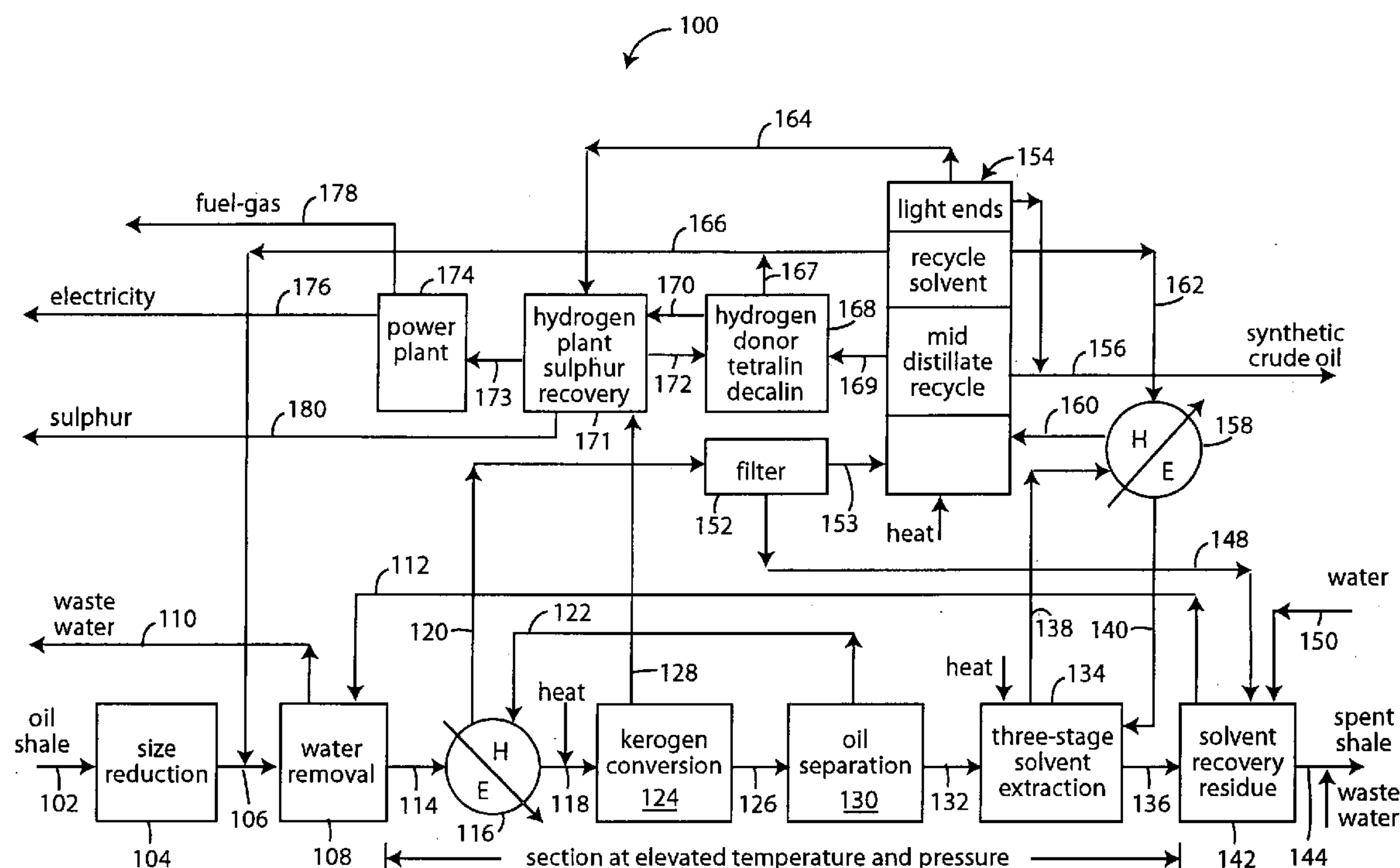
(57) **ABSTRACT**

A method and apparatus for the extraction of hydrocarbon products, alumina and soda ash from oil shales including various amounts of such chemicals, all based on solvent extraction of most of the hydrocarbons at temperatures around 400° C. Such enables the alumina and soda ash values to be leached out with aqueous sodium carbonate leaching at reduced temperatures of around 150° C. with a corresponding reduced pressure. The soda ash monohydrate values are precipitated from the leach liquor at around 100° C. with the alumina values precipitated using CO₂. Alternatively recycled fine aluminum trihydrate at 65° C. is used to produce alumina. Aluminum hydroxide is converted to acid alumina by an acid recycle stream that dissolves the alumina so any silica contaminant can be filtered out. Basic aluminum sulfate is then precipitated at about 200° C. and 250 PSIG for subsequent calcination at around 900° C. This produces alumina and sulphate oxide gasses are recycled via a sulphuric-acid plant.

(22) Filed: **Apr. 13, 2006**

Related U.S. Application Data

(60) Division of application No. 10/247,868, filed on Sep. 19, 2002, which is a continuation-in-part of application No. 09/490,254, filed on Jan. 24, 2000, now abandoned.



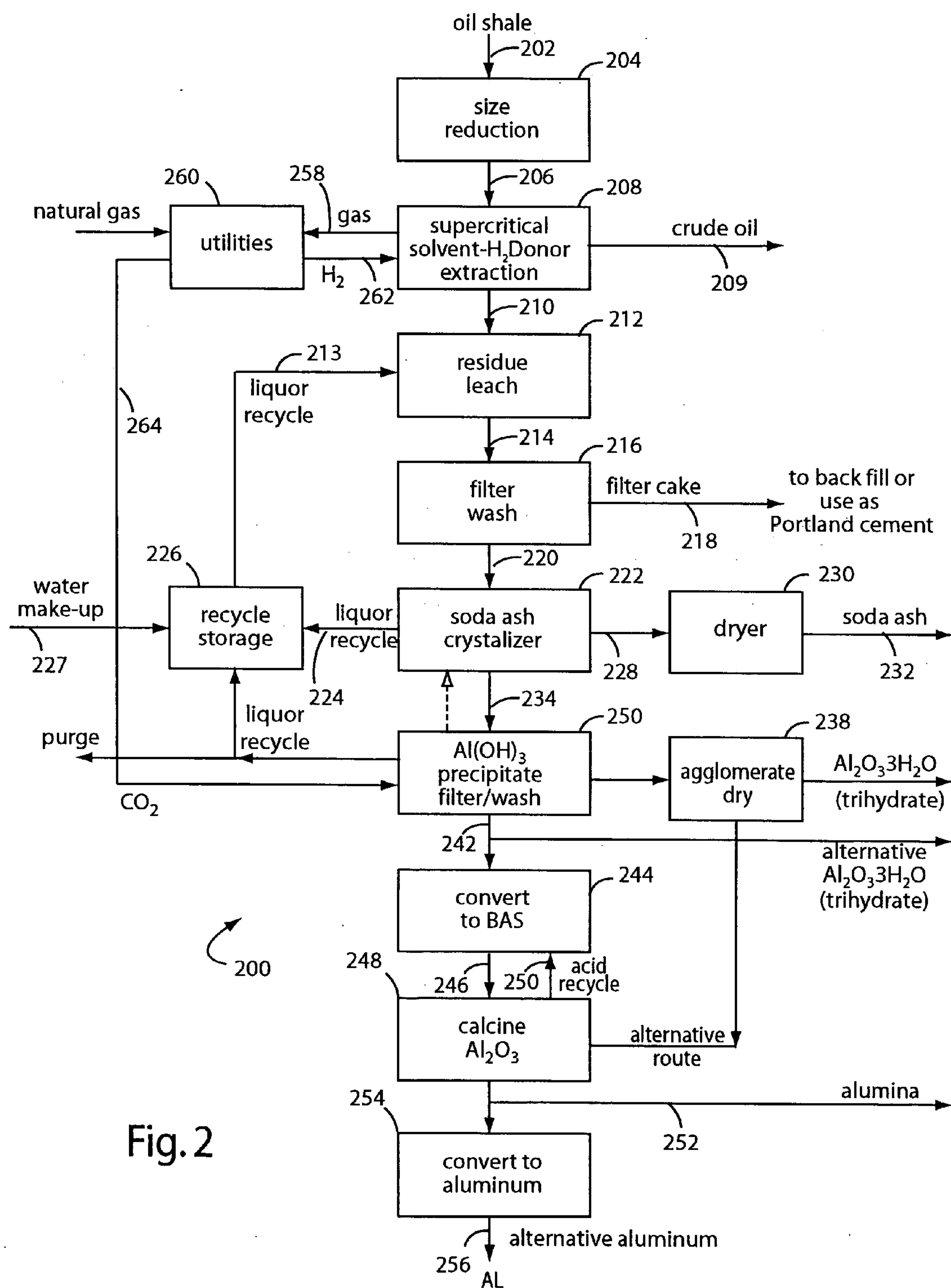


Fig. 2

PRODUCING CRUDE OIL FROM OIL SHALE

RELATED PATENT APPLICATIONS

[0001] This patent application is a divisional of U.S. patent application Ser. No. 10/247,868, filed Sep. 19, 2002 which is a continuation-in-part of U.S. patent application Ser. No. 09/490,254, filed Jan. 24, 2000, and titled APPARATUS AND METHOD FOR THE SUPERCRITICAL HYDRO EXTRACTION OF KEROGEN FROM OIL SHALE.

BACKGROUND OF THE INVENTION

[0002] 1. Field of the Invention

[0003] The present invention relates to processes for extracting the kerogen bituminous matter from oil shale to produce a pipelineable crude oil, and more particularly to extraction processes and apparatus that depend on supercritical hydrogen-donating (H-donating) solvents applied to carbonaceous oil shales with high kerogen contents and low Fischer Assay yields.

[0004] The present invention further relates to processes for extraction of associated minerals (such as alumina and soda ash in the oil shale) by aqueous means, and a residue for production of Portland cement. More particularly, to processes and apparatus that depend on the use of supercritical hydrogen-donatives (H-donor) solvents to remove the oil, and to aqueous leach processes that remove the alumina and soda ash values at temperatures of 400° C. And in particular, to processes in which alumina and soda ash values are removed by precipitation/crystallization in order to maintain an equilibrium of such values from an aqueous leaching circuit in alumina production.

[0005] 2. Description of the Prior Art

[0006] Known oil shale deposits are immense, they are found on all the major continents of the world in massive deposits. The presently estimated oil shale reserves exceed known crude-oil resources by orders of magnitude. The oil shale reserves in the United States alone are estimated to represent over seven trillion barrels of oil. Such reserves are concentrated in the Green River formation of Utah, Colorado, Wyoming, and also in the Devonian-Mississippian Eastern Shale Deposits between the Appalachian and Rocky Mountains.

[0007] Retort and solvent processes are conventionally applied to the job of extracting the kerogen from the oil shales. Retorting processes are divided into in-situ and surface types. All such conventional processes require large amounts of heat. Retorting especially requires expensively high temperatures up to 574° C., and the gaseous heat transfer media used in surface retorting also need very large processing vessels for efficient production.

[0008] Such heating of oil shales creates an environmental problem because some of the constituents are swelled and the whole is too large to put back into the pit from which it came. Such spent oil shale can have a volume that is 103% of the original shale ore. Therefore, easy disposal of the spent shale in the original mine is not possible.

[0009] Retort reaction times and conditions must be carefully controlled to avoid visbreaking or cracking the heavy oil into hydrocarbon products with molecular weights that

are too low. If the retort reaction times and conditions get too far out of control, largely unusable residual carbon output increases. The important hydrocarbons bound in oil shale are collectively called kerogen and have a mixture of high molecular weight components.

[0010] Kerogen is conventionally converted to more convenient forms by heating it to 350° C., or higher, to yield a range of hydrocarbons with lower molecular weights, e.g., methane to light oil. Retorting processes normally operate near 500° C. Extended reaction time leads to conversion of primary bitumen products to other lower molecular weight products and residual carbon. Retorting also typically produces unacceptable environmental emissions, relatively low yields of bitumen and requires heavy water usage.

[0011] The challenges in the processing of oil shale include limiting the production of gas products like methane to enough to fuel the process, and keeping the production of unusable carbon residue at a minimum. Thus, it is without the conversion to secondary lighter products. Upgrading to the desired final products is more efficient in downstream processing.

[0012] Kerogen in oil shale is relatively insoluble in most organic solvents at or below their normal boiling points. But if the environmental pressure is increased to raise the boiling point to higher than 600° K, solvents like toluene will dissolve the kerogen. Solvent extraction separates shale oil from spent shale without vaporization. The converted hydrocarbon products result from dissolution under reaction conditions, e.g., heating the oil shale and a solvent to 380° C.-540° C. Sometimes hydrogenation is also needed for good conversion. In general, solvent processes have better yields than retorting processes.

[0013] Although there are a number of solvent process variations, none efficiently separate spent-shale particles from the solvent and bitumen. And apparently no prior art processes have thought to use supercritical pressures to keep the solvents in their liquid phases at temperatures that would otherwise cause them to boil away.

[0014] Pao, et al., describe in U.S. Pat. No. 4,737,267, the difficulties associated with trying to use supercritical toluene as an extractant. For example, such process did not address stability issues, potentially lower yields of "carbonaceous" oil shales, nor did it address the olefin content of the produced oil.

[0015] Oil removal from oil shale and its residue from retorting has been leached for recovery of alumina and other values as described in several patents including multi mineral products such as superior oil U.S. Pat. No. 3,821,353, issued Jun. 28, 1974.

[0016] In multi-mineral research for such products from oil shale, it has been a prerequisite that the oil shale be retorted generally at temperatures around 500° C. in order to effectively remove oil and also release the alumina and sodium values from subsequent aqueous leaching systems. Since alumina values release with soda ash from dawsonite (in oil shale) at temperatures around 370° C., good temperature control is needed to process oil shales from the Green River Basin of Colorado, Wyoming and Utah. Some processing temperatures exceed 600° C., which locks up the minerals especially when some coke residue is burnt to supply the heat of the retorting process which vaporizes the oil product.

[0017] However in the United States, and elsewhere, retorting processes are unlikely to be used due to environmental and political constraints. In general, the CO₂ production inherent in coking produces about 0.3T CO₂ per barrel of oil, uses up to three barrels of water, and has reclamation problems due to increased spent shale volume.

[0018] Known oil shale deposits are immense, they are found on all major continents of the world in massive deposits. The presently estimated oil shale reserves exceed known crude oil resources by orders of magnitude. The oil shale reserves in the United States alone are estimated to represent over seven trillion barrels of oil. Such reserves are concentrated in the Green River formation of Utah, Colorado, Wyoming, and the Devonian-Mississippian Eastern Shale deposits between the Appalachian and Rocky Mountains.

[0019] The Green River formation is known to contain about two million barrels of oil associated with several billion tons of alumina and soda ash. In fact, several million tons per year of soda ash is commercially produced which leaves behind kerogen and alumina/soda ash values in the oil shale dawsonite. U.S. Pat. No. 6,010,672, issued Jan. 4, 2000, and others, describe mining techniques to access soda ash values which may occur independent of the kerogen and dawsonite in the shale.

[0020] The supercritical solvent extraction described by Pao in U.S. Pat. No. 4,737,267, uses toluene to convert kerogen to solvent-soluble oil products at 380° C. to 540° C. almost completely at the supercritical pressure of over 500 PSIG, while more or less completely washing the carbon off the residue. Such makes the residue suitable for aqueous leaching out the alumina and soda ash values contained in the associated dawsonite of the Green River oil shales. Other ore bodies have alumina and molybdenum which are extractable by high temperature, high pressure, aqueous leach. The residue in kerogenous are bodies where calcium carbonate predominates (such as oil shales in Green River, USA; Julia Creek, Australia, and Estonia) is usable in the production of Portland cement.

[0021] However, U.S. Pat. No. 4,737,267, did not address the stability issues connected to the olefin content of the produced oil. Separate hydrotreating was essential for a stable pipelineable crude. In addition, lower yields of oil from oil shale resulted in particular from "carbonaceous" oil shales.

SUMMARY OF THE PRESENT INVENTION

[0022] It is therefore an object of the present invention to provide a process for the efficient extraction of kerogen (as a stable oil product) from oil shale.

[0023] It is another object of the present invention to provide a system apparatus for the efficient extraction of kerogen (as a stable oil product) from oil shale.

[0024] It is a further object of the present invention to provide a process for the efficient removal of kerogen from oil shale while simultaneously converting dawsonite and nacholite associated with ore-body oil shale into alumina and soda ash.

[0025] Briefly, a first process embodiment of the present invention is a method for producing pipelineable synthetic

crude oil from oil shales. Such process combines a low-boiling-point organic solvent fraction with an H-donating mid-distillate fraction and raises temperature to make kerogen in oil shales soluble, and raises pressure conditions to keep the solvents in their liquid phase at those temperatures. The solvent is recovered from the extracted kerogen in a three-stage solvent-recovery unit that is followed by a flash recovery that uses a pressure letdown and draws off the resulting solvent vapors.

[0026] A second process embodiment of the present invention is another method for producing pipelineable synthetic crude oil from oil shales. Such combines a low-boiling-point organic solvent fraction with an H-donating-mid-distillate fraction with temperatures raised to 370-420° C. Such makes any kerogen in the oil shales soluble. The pressure conditions are raised keep the solvents in their liquid phase or appropriate critical phase density at those temperatures, bearing in mind the ratio of light ends, mid distillate, and kerogen converted to a stable pipelineable crude oil, in the mixture associated with the residue after kerogen extraction.

[0027] This oil mixture is separated from the residue at appropriate high temperature and pressure by water (not steam). The oil, mid distillate and solvent proceeds to distillation system to separate oil, mid distillate and light ends. Recovered solvent is removed from the extracted kerogen in a solvent-recovery unit. Such is followed by a flash recovery that uses a pressure letdown and draws off the resulting solvent vapors. Preferred embodiments borrow the pressure and temperatures of the slurry residue after solvent extraction. And such includes the final "mixed oil" recovery from aqueous leach system with staged pressure relief down to atmospheric from around 500 PSIG.

[0028] An advantage of the present invention is that a process for kerogen extraction from oil shale is provided that produces higher yields of oil with reduced gas production.

[0029] Another advantage of the present invention is that a process for kerogen extraction from oil shale is provided that produces hydro-visbroken crude oil which is stable enough for conventional pipeline transfer to refineries.

[0030] An advantage of the present invention is that a process for kerogen extraction from oil shale is provided that allows for the recovery of aqueous solutions of alumina and soda ash by simple leaching.

[0031] A still further advantage of the present invention is that a process for kerogen extraction from oil shale is provided that produces a minimum of environmental contamination. In addition to calcium carbonate rich oil shales, the residue is suitable for the direct production of Portland cement.

[0032] Another advantage of the present invention is that a process for kerogen extraction from oil shale is provided that recycles its solvents and heat.

[0033] These and other objects and advantages of the present invention will no doubt become obvious to those of ordinary skill in the art after having read the following detailed description of the preferred embodiment as illustrated in the drawing figure.

IN THE DRAWINGS

[0034] FIG. 1 is a functional block diagram of an oil-shale processing plant embodiment of the present invention that implements a process for kerogen extraction from oil shale;

[0035] FIG. 2 is a functional block diagram of oil shale processing plant embodiment of the present invention. Such implements a process for extraction of alumina, soda-ash, and other mineral values from the aqueous leach liquor after oil is removed from the oil shale. The residue is useful in the production of Portland cement; and

[0036] FIG. 3 is a functional block diagram of another oil-shale processing plant in a second process embodiment of the present invention that is modified from that shown in FIG. 1.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

[0037] An oil-shale processing plant embodiment of the present invention is diagrammed in FIG. 1 and is referred to herein by the general reference numeral 100. The principle product produced is synthetic crude oil that is suitable for pipeline transportation. An oil shale input feed 102 is crushed by a size reducer 104. A crushed oil shale flow 106 is mixed with a recirculating solvent and input to a water remover 108. Any waste water 110 is removed from the system. A recovered solvent vapor flow 112 is added, condensed for heat recovery and a slurry flow 114 is output. A heat exchanger 116 provides a recovered-heat flow 118 and outputs an oil product flow 120. Hot oil product flow 122 is received from further down the process and is stripped of its elevated heat for recovered-heat flow 118, and the remainder is the cooler oil product flow 120. A kerogen converter 124 outputs a slurry 126. Reaction gases are drawn off in a flow 128. An oil separator 130 outputs an oily solids flow 132 and the oil product flow 122. A solvent extractor 134 outputs a solids flow 136 and an oil/solvents mixture 138. Any heat that can be removed from mixture 138 is returned in a heated solvents flow 140. A last solvent recovery stage 142 outputs a spent shale flow 144 and is assisted with a waste water wash. A filter cake flow 148 is added to the last solvent recovery stage 142 with a wash water flow 150. Such filter cake flow 148 is produced by an extracted-oil solids filter 152 that removes solids from the oil product flow 120 and forwards filtered product oil flow 153.

[0038] The final solvent recovery from the aqueous leach system preferably includes a staged pressure relief let-down to atmospheric from around 500 PSIG

[0039] A distillation column 154 outputs a final-product synthetic crude oil 156. A heat exchanger 158 outputs a flow 160 and receives a flow 162. A flow 164 is forwarded for hydrogen production and sulphur recovery. A recycle solvent 166 is provided by the distillation column 154 to the pulverized oil shale flow 106. An H-donor flow 167 is added to flow 166 from an H-donor generator 168. A mid-distillate flow 169 from the distillation column 154 is sent to the H-donor generator 168. A hydrogen sulfide (H_2S) flow 170 is sent to a hydrogen plant sulfur recovery unit 171. Such produces a hydrogen flow 172, a pair of sulfur-free fuel-gas flows 173 and 178, and a sulfur flow 180. A fuel flow 173 is provided to run a power plant 174. One output from the power plant 174 is electricity 176. A sulphur flow 180 is output from the sulphur plant 171.

[0040] Guo Shu-Cai, et al., described some conversion steps like those of the oil-shale processing plant 100 for an experiment they conducted. Such experiment was reported

in "Conversion of Chinese Oil Shales to Liquid Products using Supercritical Extraction," pp. 311-316, German Publication: *Erdol und Kohle-Erdgas-Petrochemie vereinigt mit Brennstoff-Chemie*, Bd. 39, Haft 7, Juli 1986. Guo Shu-Cai, et al., found that the supercritical extraction of oil shale with toluene can give up to twice the oil yield over conventional retorting. When an H-donor was added to the supercritical solvent, complete recovery of the oil-shale kerogen and high liquid-product yields was possible. But their paper did not describe a practical or complete system that recovered the solvent from the synthetic crude oil. What was described was that with a toluene/donor-solvent mixture with a tetralin content of about twenty percent, the oil yield (extract and liquids) can be enhanced as high as 200% of the Fischer Assay.

[0041] Earlier, in 1980, John Pratzer, II, was issued U.S. Pat. No. 4,238,315, (Pratzer '315) which describes the recovery of oil from oil shale. Such patent is incorporated by reference and may be helpful to the reader in implementing embodiments of the present invention. Pratzer '315 describes the extraction of oil from oil shale with the aid of elevated temperatures and pressures so that solvents with tetralin may be employed for highly efficient oil shale processing. The reactor effluent is described as being filtered, and the resulting filter cake rinsed with toluene. Again, such did not describe a practical or complete system that recovered the solvent from the synthetic crude oil.

[0042] The recovery and recycling of solvents with H-donors is described by Marvin Green, et al., in U.S. Pat. No. 4,325,803, (Green '803) titled "Process For Hydrogenation/Extraction Of Organics Contained In Rock," and issued Apr. 20, 1982. A hydrogen transfer agent in its liquid phase is used to separate kerogen from oil shale. The oil separation occurs in a reactor at elevated pressure and temperature that keeps the solvent liquid. A slurry flash releases pressure and an adiabatic flash vaporization of the organic materials occurs. A portion of the vaporized materials is recycled as hot recycle oil vapors. Green '803 is also incorporated herein by reference as it may be helpful to the reader in implementing embodiments of the present invention.

[0043] In embodiments of the process of the present invention, the H-donor generator 168 starts with a mid-distillate fraction of naphthalene ($C_{10}H_8$) with a molecular-weight-128, e.g., in flow 169, and chemically reacts this with hydrogen using a catalyst. Such produces H-donor products in flow 167 like decalin ($C_{10}H_{18}$) (molecular-weight-138) and tetralin ($C_{10}H_{12}$) (molecular-weight-132) with boiling points of 190-220° C. Up to eight percent by weight of hydrogen is available for such chemical reaction. Typical oil-shale production requires about two percent by weight hydrogen for the benefits described. About twenty percent of the total solvent mix used in the extraction/conversion is preferably H-donor mid-distillate fraction.

[0044] Method embodiments of the present invention combine crushed oil shale with a mixture of toluene or other low-boiling-point range organic solvent, and tetralin/decalin or other mid-distillate. Such is then fed into a slurry mixer and heated by a solvent recovery from a spent shale. Any water in the oil shale is eliminated. The slurry is then pumped with a recycle product oil stream into an autoclave where moderate temperatures and elevated pressures are used to convert substantially kerogen to a hydro visbroken

stable crude oil with some gas production. The oil product is then separated from the spent shale under similar temperature and pressure conditions.

[0045] After separation, some of the oil product is used for recycling. The rest is distilled for the solvent mix by a low-boiling-point fraction and a mid-distillate fraction. Such mid-distillate fraction is hydrotreated and recycled to make up for any hydrogen used up. The spent shale is washed by a counter-current with low-boiling-point solvent fractions under elevated, e.g., supercritical, pressure and temperature conditions. Such enables easy separation of the solids and continued conversion of the residual kerogen. The final residue of spent shale with clean low-boiling-point solvent at supercritical temperature/pressure conditions is let-down gradually in stages with almost all the low-boiling-point solvent evaporating for recovery and reuse with the final stage sprayed with water to release any remaining solvent through steam stripping. The oil product is filtered before storage and is eventually piped to a commercial market.

[0046] Such gas produced is rich in methane, and thus is easily employed in the hydrogen production needed for mid-distillate hydrotreating. The hydrogen is used for heating and powering the rest of the process.

[0047] Some embodiments of the present invention include the use of at least one autoclave wherein high pressure leaching is used to convert kerogen to oil. The autoclave preferably includes an internal venturi draft tube to keep the slurry mixed. A pressurized extraction vessel continues the conversion process and acts to solubilize the converted oil. A series of pressurized solvent washing shale decanters are used in which shale moves counter-current to the solvent. Distillation columns, settling tanks and a plurality of pumps and heat exchangers are used to transfer and recycle components.

[0048] Referring again to FIG. 1, the plant 100 begins with the oil shale input feed 102 that preferably ranges in size up to forty inches. Such is forwarded to conventional commercial size reduction equipment to obtain a resulting ore of about $\frac{3}{8}$ -inch screen mesh. The crushed shale is fed by flow 106 into a slurry mixer system water remover 108, e.g., as described in Rendall '267, and incorporated herein by reference. The system water remover 108 receives heated solvent vapors from the solvent recovery stage 142 and the heat received helps maintain an operating temperature near the boiling point of water. Any water vapor is condensed and drawn off in waste water flow 110 which is flushed out in spent shale flow 144. The slurry is heated by heat exchanger 116 and the pressure is increased to 600 PSIG.

[0049] More heat can be added to flow 118 to raise the temperature of the flow 118 entering the kerogen converter 124 to about 400° C. The kerogen converter 124 preferably includes an autoclave and provides residence times of five to thirty minutes, depending on the oil shale ore. The kerogen is converted by pyrolysis with an H-donor distillate providing hydrogen to deal with olefin formation and unsaturated hydrocarbons. Some sulphur will detach as hydrogen sulfide.

[0050] The reaction is chemical and continues through the entire section under elevated temperature and pressure, e.g., kerogen converter 124, oil separator 130, and three-stage solvent extractor 134. The gas flow 128 produced by the

reaction comprises methane, ethane, hydrogen, and some hydrogen sulfide. The oil flow 126 is separated in oil separator 130 by a pressure vessel.

[0051] The three-stage solvent extractor 134 can be implemented similar to the three pressure decanters 712, 730, and 740, in FIG. 2 of Rendall '267.

[0052] The oil is removed in flow 122. The oil separator 130 agglomerates the fines which settle out with the solids output flow 132. The hot product oil is fed to distillation column 154 via a heat exchanger 116 to heat the incoming slurry then through an extracted-oil solids filter 152 before the pressure is let down to provide the energy needed for distillation. The solids with oil exit in flow 132 to a three-stage solvent extractor 134, wherein fresh hot solvent at about 400° C. and about 700 PSIG is fed from flow 140 counter-current to the output spent shale.

[0053] Most of the remaining product oil output with the solvent in flow 138 via a heat exchanger 158 (for the incoming solvent) to the distillation column 154. The solids residue with some solvent leaves three-stage solvent extractor 134 via flow 136 to a solvent recovery solvent-residue solvent recovery unit 142. The solvent-residue solvent recovery unit 142 consists essentially of depressurizing the residue in a vessel fed from flow 136 thereby releasing most of the low-boiling-point solvent via flow 112 as a vapor to heat the incoming slurry at water removal water remover 108. The residue of spent shale is further cooled from about 200° C.-300° C. in a rotary drum with the remaining solvent from flow 148 joining flow 112. Filter residue from extracted-oil solids filter 152 feeds the depressurizing vessel in solvent-residue solvent recovery unit 142. The water from hydrogen plant 171 and/or waste water from water remover 108 can be used to cool the solids and dampen the spent shale residue for dust control during mine backfill. The solvent-residue solvent recovery unit 142 is any such system as described in Rendall '267 including depressurizing vessels and a cooling (rotary drum). The heat from the flow 136 is transferred via solvent and water (steam) vapors to the water removal water remover 108. It would aid water disposal to use acid water from the hydrogen/sulfur plant hydrogen plant 171 to cool the hot spent shale while waste water flow 110 is disposed of in flow 144 for dust control.

[0054] The recycle solvent to three-stage solvent extractor 134 flow 140 is fed from the distillation column 154 via flow 162 to a heat exchanger 158. Such is necessary at elevated pressure of about 400 PSIG. The heat can be provided by the oil/solvent output three-stage solvent extractor 134 via flow 138 at about 400° C. and leaves the heat exchanger 158 at flow 160 with temperatures about 150° C. to the distillation column 154. Auxiliary heat to flow 140 can also be provided by flow heat fuel gas from power plant 174. The hot oil from kerogen conversion from oil separator 130 flows at about 600 PSIG and 400° C. Flow 122 heats incoming slurry in heat exchanger 116 from which it leaves at about 600 PSIG and 150° C. An oil product flow 120 is forwarded via an extracted-oil solids filter 152. The filter residue is fed via flow 148 to the solvent recovery solvent-residue solvent recovery unit 142, for disposal of the fines. The filter can be of the metal porous cartridge type such as are readily commercially available, a pressurized rotary drum filter with engineered fabric for high temperatures about 150° C. such as supplied by CJ (Zyex Hi tech yarn) or any other suitable

for process conditions. All are used in refineries for removal of catalyst fines before oil product distillation. The preferred route is a metal porous cartridge type. The distillation column **154** is fed the product oil flow **153** and recycle solvent at about 150° C. Flow **153** is a depressurized flow and additional heat can be provided by a fuel gas flow **178**.

[0055] The distillation column **154** is conventional system with a mid-distillate metered off-take at about 200° C. in flow **169** for hydrotreating in H-donor **168**. The recycle solvent off take at about 120° C. is metered to flow **166** feeding the slurry of the incoming raw oil shale for water removal in water remover **108**. The ratio of mid-distillate flow **169** hydrotreated in H-donor **168** mixing with the recycle solvent flow **166** via flow **167** is about twenty percent of mid-distillate H-donor in the flow **114** proceeding under elevated temperature about 400° C. and pressure about 600 PSIG to the kerogen converter **124**. The H-donor **168** for hydrotreating the mid-distillate from flow **169** is practiced by industry today, as referenced books for catalysts including, "Oil and Gas Journal Refining-Catalyst Compilations". Such catalysts usually use alumina support with combinations of cobalt molybdenum nickel etc. as active agents. The technologies are similar to those described in "Petroleum Processing Handbook" edited by John S. Meketta, published by Marcel Dekken, June 1992 or "Upgrading Petroleum Residue and Heavy Oils" by Murray S. Greg, published by Marcel Dekker Inc., NY, N.Y. 1994. The hydrogen plant **171** receives hydrogen, hydrocarbon gases, including some light ends, some ammonia (NH₄) and hydrogen sulfide H₂S from flow **170**.

[0056] The hydrogen is separated, concentrated, and reused by compressors. The hydrogen sulfide is converted to sulfur by a conventional Claus plant. Some of the fuel gas is used for further hydrogen production via a reformer for methane/light ends, and the rest for heat needed for process and electric power. About six to fifteen percent by weight of the kerogen is converted gases dependant on the source of the oil shale and the processing conditions for extraction of the kerogen. About two percent by weight of the produced oil is the hydrogen necessary for chemical reactions to produce a suitable pipelineable oil with the required viscosity and stability. Up to four percent by weight hydrogen has also been reported on particularly aromatic kerogens, producing more gas. The whole hydrogen system produces electric power. All these items in power plant **174** via flow **173** can only be quantified in specificity depending on the oil shale source and the size of the facility by those skilled in the art.

[0057] The Fischer Assay was developed for the oil shale industry to determine the efficiency of oil extraction processes. The Fischer Assay measures the recovery ratio of hydrocarbons from the oil shale. In prior art retorting processes, a Fischer Assay recovery of 80-100% is typical, and recoveries exceeding 100% are difficult to achieve.

[0058] Rendall '267, describes fifteen batch runs in which oil shale was treated with toluene under supercritical conditions ranging up to 400° C. and 1200 PSIG pressure for recovery of up to 120% of Fischer Assay of hydrocarbons.

[0059] In the batch runs, oil shale has been slurried in toluene in a batch stirred reactor and heated to temperatures up to 400° C. and held for periods ranging from zero minutes up to two hours.

[0060] Other data referenced on "carbonaceous" oil shales in which an H-donor mid-distillate has been used with the supercritical toluene shows kerogen conversion almost complete (about 95%). Such data clearly shows oil production with negligible olefins and hydrogen consumption from the H-donor mid-distillate at two to three percent by weight of the produced oil.

[0061] Method embodiments of the present invention for "carbonaceous" oil shales allow almost all of the kerogen to be produced as oil and gas (a 5-15% fraction). For example, Julia Creek, Queensland, Australia, oil shales, CRA report **1967-1988**, show an average of 17-18% kerogen. The Fischer Assay yield is about H-donor 70 liters/ton, 14-15 gallons, representing about seven percent kerogen which is only 30% of what potentially could be available from the recovery method of the present invention. Such is adequately borne out by independent research on other Chinese, Australian and Eastern US shales shown in the references. The decrepitation observed on Colorado oil shales does not appear to occur in carbonaceous oil shales. However, continuous operation may change this phenomenon.

[0062] Some process embodiments of the present invention produce pipelineable synthetic crude oil from oil shales. A low-boiling-point organic solvent fraction is combined with an H-donating mid-distillate fraction. The temperature is raised to 370° C.-420° C. to make kerogen in oil shales soluble, and pressure conditions are raised to keep the solvents in their liquid phase or appropriate critical phase density at those temperatures. The solvent is recovered from the extracted kerogen in a solvent-recovery unit that is followed by a flash recovery that uses a pressure letdown and draws off the resulting solvent vapors.

[0063] It is important to use a one-quarter inch feed in cases of kerogen removal which do not powder or otherwise decrepitate the host rock, e.g., as with Mahogany zone oil shales. Slurry pumpability under supercritical conditions will dictate. The process described in U.S. Pat. No. 4,737, 267, can be used without the H-donor system.

[0064] A preferred embodiment to use the pressure and temperature of slurry residue after solvent extraction involves the final solvent recovery from aqueous leach system with staged pressure relief down to atmospheric from around 500 PSIG.

[0065] A pressure let-down efficiently recovers solvent and simultaneously leaches out mineral values with aqueous recycles. So most of the heat from the system can be recovered this way. The dry and damp residues can be used with the aqueous recycle for leaching out the mineral values.

[0066] A second preferred embodiment does not use solvents to wash the oil mixture from the residue, and instead uses high pressure, temperature hot water to separate the oil mixture from the residue.

[0067] The pressure let-down of the aqueous recycle efficiently recycles heat and residual solvent from the system. The residue is available for Portland cement production after washing in a pressure filter. The pressure and temperature reduction of the residue will release most of the water remaining in the solids.

[0068] The process continues in the removal of the washed residue by any suitable system such as pressure filters. The

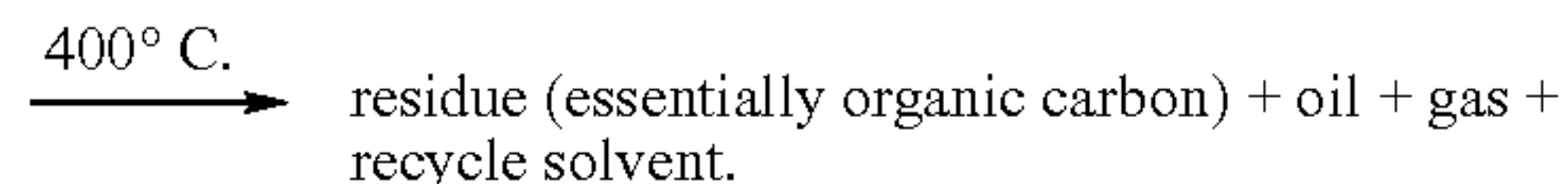
filtered leach liquor now contains the alumina and soda ash values ready for precipitation of the sodium carbonate monohydrate and of the aluminum trihydrate as is practiced today in industry both for specialty grade aluminum hydrates or metallurgical grade alumina for smelters.

[0069] The preferred requirement of the aqueous leach circuit leaving the pressure leach section of the residue is that it contains a saturated solution of the alumina and soda ash values, adjusted by water dilution of the recycle spent liquor. E.g., after primary removal of soda ash and alumina values). The recovery of soda ash values by crystallization as a mono hydrate is preferable at about 150° C. as is practiced industrially today. (ref. Isonex, Jun. 11, 1997) The alumina values are then recovered with an alumina to sodium carbonate ratio of about 0.7 and an alumina concentration around 165 grams-per-liter as is practiced in the Bayer process today (in notes of Don Donaldson Mar. 11, 1997). Alternatively the alumina (as aluminum trihydrate) is precipitated by sparging with CO₂.

[0070] The filtration particle size is critical. The industry has developed the art of precipitation control using recycle of fine aluminum hydrates as a seeding mechanism to control yield and size. Experimentation shows that the silica content of the produced alumina meets aluminum smelter industry requirements. Leaching with sodium carbonate, as opposed to caustic, will also reduce the aluminum sodium silicate formation. Free sodium hydroxide levels in leach liquor can also be controlled by converting to the carbonate with CO₂ sparging.

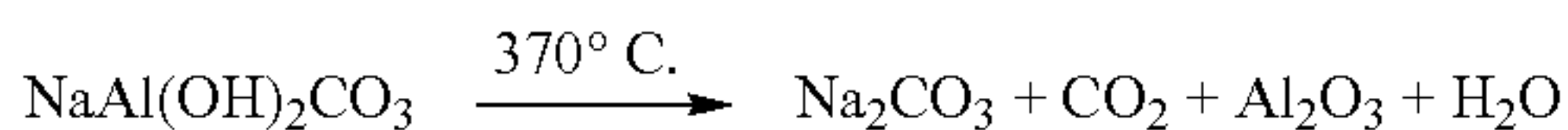
[0071] The chemistry involved in embodiments of the present invention is represented in the following Table.

A. Oil shale and H₂ Donor solvent

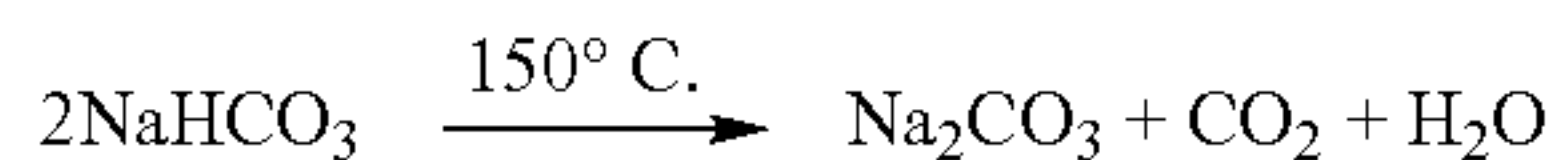


B. Residue including alumina and soda ash formed at around 400° C. as follows:

Dawsonite NaAl(OH)₂CO₃



Nacholite NaHCO₃



C. Residue including alumina and soda ash leached at temperatures between 125° C. and 200° C. but typically about 150° C. with sodium carbonate (or CO₂) provides leach liquor at 150° C. Wherein Na₂CO₃H₂O, the monohydrate, is removed at concentrations around thirty percent by evaporative crystallization at temperatures around 100° C.

D. The leach liquor at around 70° C. including alumina: sodium carbonate ratio of around 0.7 and with an alumina content of about 165 grams-per-liter can be reduced to about 80 grams-per-liter for recycle by seeding with fine hydrate crystals (about 50% @ 44 u or 825 mesh) at about 30 grams-per-liter. This removes half of original alumina in the leach liquor, and then the liquor is recycled for further leaching to replenish the alumina soda ash values.

E. The residue in limestone-predominant kerogenous ore bodies has unconverted carbon that is then calcined at over 1000° C. with requisite amount of limestone to yield a Portland cement equivalent. About 5% of the original kerogen will be unconverted carbon. The calcining results in a clinker that can be ground to the consistency of dry Portland cement.

[0072] FIG. 2 represents a process plants and method embodiment of the present invention for extracting multiple mineral products from oil shale, and is referred to herein by the general reference number 200.

[0073] Process 200 extracts crude oil from oil shale using supercritical extraction temperatures 370-420° C., with a preferred temperature of 400° C. The overall residence time at such temperatures is preferably 15-60 minutes. Process 200 further extracts soda ash from any dawsonite and nacholite associated with oil shale, and aluminum hydroxide clumps in various sizes. Bayer-type alumina and acid alumina can also be obtained from the hydroxides obtained in process 200. Aluminum metal is obtainable by reductive smelting of such alumina.

[0074] Process 200 begins with an oil shale feed material 202 that naturally and typically includes kerogen, dawsonite, nacholite, alumina and soda ash. Such oil shale is mined and transferred to a conventional particle-size reducer 204. The reduction is preferred to be less than one-quarter inch for easy slurry processing. A crushed oil shale 206 enters a supercritical solvent extractor 208, e.g., an extractor as described in U.S. Pat. No. 4,737,267. A hot residue 210 is then transferred to a pressure leach 212. Such receives a recycle 213 of leach liquor. Preferably, a temperature of 150° C. is used in pressure leach 212 with a residence time of about half hour, or at least in the range of 15-60 minutes. An output flow 214 is sent to a wash and pressure filter 216.

[0075] A washed filter cake output 218 can be returned to the oil shale mine for back fill. Such washed filter cake output 218 may instead be mixed and crushed with limestone in proportionate amounts to produce a material equivalent to dry Portland cement. A good commercial market exists for such materials. Conventional Portland cements are a type of hydraulic cement usually made by burning a mixture of clay and limestone in a kiln.

[0076] A leach liquor 220 is forwarded that includes alumina and soda ash values. A soda ash crystallizer 222 returns a liquor recycle flow 224 through a recycle storage 226. The soda ash crystallizer 222 also separates out a soda ash slurry 228 which is sent to a dryer 230. The concentration values are preferred to be greater than 300 grams-per-liter at 150° C. A typical dryer 230 uses evaporative crystallization at around 100° C., to yield sodium carbonate monohydrate crystals. Such crystals are centrifuged, washed, and dried to produce sodium carbonate, e.g., soda ash. A soda ash product 232 is output from process 200.

[0077] The concentration of the recycled saturated leach liquor is adjusted with a fresh water input 227, and is made dependent on the soda ash content of the residue available for leaching.

[0078] Such sodium carbonate monohydrate Na₂CO₃H₂O removal in soda ash crystallizer 222 is preferably limited to that necessary for a 0.7 ratio of alumina to sodium carbonate in the liquor. A liquor 234 at around 70° C. is then transferred to a precipitator-filter-washer 236. The feed preferably has concentration of about 30 grams-per-liter alumina, e.g., as aluminum trihydrate fines with 50% less than 44-microns. The concentration of alumina increases from 165-grams-per-liter to 195-grams-per-liter of the aluminum for precipitation at 70° C. This leaves a aluminum hydroxide residue with a concentration of about 80-grams-per-liter.

[0079] In alternative embodiments of the present invention, CO_2 is introduced under pressure at temperatures above 100°C . after the sodium carbonate monohydrate $\text{Na}_2\text{CO}_3\cdot\text{H}_2\text{O}$ is removed at around 100°C . to 200°C . Such precipitates aluminum hydroxide. Crystalline granular aluminum hydroxide will be formed as long as the sodium carbonate values are about equal to the alumina values in the leach liquor. Increasing the residence time up to three hours increases the size of the fine particles in the precipitate. A further variation for use at atmospheric pressures includes seeding with fine aluminum trihydrate.

[0080] An agglomerate drier **238** can be manipulated to produce larger crystals by increasing the residence time up to 24-hours, e.g., as is common in the Bayer process. An output **240** produces dried aluminum trihydrate crystals. Such crystals can be commercially marketed for use as fire retardants, catalysts, and paper-making materials.

[0081] A flow **242** of trihydrate $\text{Al}_2\text{O}_3\cdot\text{H}_2\text{O}$ is both output from process **200** and input to a basic aluminum sulphate (BAS) converter **244**. A BAS output in flow **246** is forwarded to a calciner **248**. Fine crystals from agglomerate drier **238** can also be converted to BAS using sulphuric acid. Such acid is recycled in a flow **250**. The BAS is calcined into an alumina and SO_2/SO_3 flow **252**. The alumina is forwarded for a conversion **254** to aluminum metal, e.g., smelting. An aluminum metal **256** is output as a commercial product.

[0082] The supercritical solvent extractor **208** uses heat around 400°C . and pressures of around 500-PSIG to remove the organic carbon kerogen and breaks it down to a lighter oil **209**. Solvent is recycled after hydrogenation, and a gas product **258** is sent to a utility **260** to produce a hydrogen flow **262** needed. A carbon dioxide gas (CO_2) flow **264** is sent to precipitator-filter-washer **236**.

[0083] **FIG. 3** represents an aqueous mineral extraction process embodiment of the present invention, and is referred to herein by the general reference numeral **300**. The process **300** repeats much of what is illustrated in **FIG. 1** for process **100**. So the 100-series of reference numerals is repeated here for identical components. The differences are concerned with the flows in and out of oil separator **130** and the three-stage solvent extractor **134**.

[0084] In process **300**, the oil separator **130** has hot water **150** injected in remove oil from the solid residue. A barrier forms to float the oil out in flow **122** to heat exchanger **116** for heat removal. Such water causes light-ends in the oil within separator **130** to azeotrope. These are output in flow **112**. This causes heat to be transfer to the incoming oil shale slurry **106** in water remover **108**.

[0085] The residue from oil separator **130** is an aqueous slurry flow **132** forwarded to solvent extractor **134**. Here it sits for the staged residence times necessary to leach out mineral values. The appropriate residence time is determined empirically, as it varies from one ore body to the next. In the case of Green River oil shale, one-half to one hour is adequate. The entire slurry can be sent for filtering in flow **136**. Otherwise, the heat exchanger **158** of **FIG. 1** can be used to conserve the heat in the aqueous supplement liquor. In any case, the liquor and the residue need filtration to provide clean liquor and a cake residue.

[0086] In general, oil shales that include kerogen and with other minerals associated with alumina and soda ash, are

mined and crushed. This provides a slurry feed with solvents to an extraction module operated under supercritical conditions of pressure and temperature for the solvent. Such extracts the organic carbon content as oil. The residue is then leached with an aqueous sodium carbonate solution to remove the alumina and soda ash values. The remainder is washed and returned to the mine as backfill. The leach liquor is processed at around 100°C . to precipitate the soda ash values. The alumina values are recycled and replenished with residue remaining after oil extraction. The soda ash is dried to remove waters of hydration and then sent to market. The aluminum hydrate is then converted to alumina via conversion to a basic aluminum sulphate (BAS). Such is precipitated at around 200°C . at pressure. The BAS is calcined at around 850°C . into alumina. Sulphur oxide gases are recycled from a conversion to sulphuric acid.

[0087] In alternative method embodiments of the present invention, the crushed particle size of the oil shale is preferably one-eighth inch to one-quarter inch in size. The solvent used is a low-boiling type in the range of 100°C . to 140°C . An additional recycle of a hydrogen donor mid-distillate can be used such as tetralin, e.g., from a cut of the produced oil. The temperature is preferably maintained at $370\text{--}420^\circ\text{C}$., with an overall residence time of 15-60 minutes. But typically the residence time is about thirty minutes.

[0088] An aqueous recycle of sodium carbonate is preferably maintained at a temperature of greater than 150°C . at around 200 PSIG for the leaching of the residue. Sodium carbonate is leached into the recycle aqueous sodium carbonate leach liquor from the residue after oil extraction. Sodium carbonate monohydrate is preferably removed by precipitation using evaporative crystallization at temperatures about 100°C . After removal of the sodium carbonate, the leach liquor is sparged with CO_2 to precipitate aluminum trihydrate crystals. The amount of sparging CO_2 used is about equal to that entering from the oil shale residue. Such sodium carbonate monohydrate is preferably dried with the production of dense soda ash.

[0089] The aluminum trihydrate crystals are washed, dried and calcined into alumina at about 850°C . to 950°C . Fine aluminum trihydrate is recycled to for the production of crystalline aluminum trihydrate from the leach liquor. An alternative embodiment precipitates the aluminum trihydrate using fine aluminum trihydrate (1) at a 1:4 ratio, (2) a temperature around 65°C ., (3) a concentration of alumina of about 160 grams per liter, and (4) a ratio of alumina to sodium carbonate of about 0.7.

[0090] The precipitated aluminum trihydrate is preferably agglomerated into larger crystals using starch with a residence time in thickness of about 20-25 hours. The aluminum trihydrate production is preferably directly converted to basic aluminum sulfate using a recycle acid stream from the calciner off-gasses at a temperature of around 200°C . with a corresponding pressure for aqueous systems. The recycle leach liquor is preferably purged after any depletion of soda ash and alumina values to remove accumulation of impurities in the aqueous leach circuit.

[0091] Process embodiments of the present invention extract hydrocarbon products, alumina, and soda ash, from oil shales. Such includes extracting various amounts of such chemicals, all based on supercritical solvent extraction of most of the hydrocarbons at temperatures around 400°C .

The alumina and soda ash values are leached out with aqueous sodium carbonate leaching at reduced temperatures of around 150° C. with a corresponding reduced pressure. The soda ash monohydrate values are precipitated from the leach liquor at around (over) 100° C. with the alumina values precipitated using CO₂ at lower temperatures (or the same) and alternatively using recycled fine aluminum trihydrate at 65° C. under conditions practiced today to produce alumina. Alternatively and especially should silica prove to be a high contaminant the precipitate aluminum hydroxide is preferably converted to acid alumina by an acid recycle stream dissolving the alumina (leaving the silica to be filtered out) and precipitating basic aluminum sulfate at about 200° C. (250 PSIG) for calcination at around 900° C. to produce alumina and recycle of the sulphate oxide gasses via a sulphuric acid plant.

[0092] To summarize, the solvent conversion of kerogen in the oil shale to crude oil using high pressure around 500 psia with temperatures around 400° C. and its separation from the host rock by solvent extraction or aqueous flotation is described in **FIGS. 1 and 3**. The solvent/mid distillate fraction of the oil extracted is recycled, and the gas production is cleaned of ammonia and sulphur in 171 before it is used for hydrogen needs of the process embodiments and for the power plant means 17.

[0093] The process embodiment **FIG. 2** removes the minerals from the residue by high pressure/high temperature (150° C.-300° C.) aqueous means containing soda ash to access valuable minerals in Green River oil shales (alumina and soda ash), Julia Creek oil shales (alumina and molybdenum), Estonia oil shales (alumina) with a residue calcined for production of Portland cement.

[0094] Although the present invention has been described in terms of the presently preferred embodiments, it is to be understood that the disclosure is not to be interpreted as limiting. Various alterations and modifications will no doubt become apparent to those skilled in the art after having read the above disclosure. Accordingly, it is intended that the appended claims be interpreted as covering all alterations and modifications as fall within the true spirit and scope of the invention.

What is claimed is:

1. An improved method for extracting oil products from oil shale, comprising said steps of:

crushing a mined oil shale ore into a pulverized oil shale feed;

mixing said pulverized oil shale feed with a hot organic solvent recycled from a distillation column to form a slurry, wherein said solvent is hot enough to strip water from said slurry;

transferring said slurry for kerogen conversion under supercritical conditions for said organic solvent with an H-donor distillate such that said kerogen is converted into a stable, pipelineable crude oil;

transferring said slurry to recycle solvent extraction stage at a supercritical conditions of temperature and pressure for further reaction, and producing an oil product and a separated solid phase;

filtering at less than supercritical conditions said oil product for distillation of a recycle solvent and a mid-distillate fraction, with said oil product being sent to storage;

hydro-treating a mid-distillate fraction recycled from said distillation to provide an H-donor for kerogen conversion;

withdrawing a spent shale after solvent extraction and desolventizing oil shale solids at less than supercritical conditions, wherein a solvent is flashed off with a water to be recycled to a water removal means; and

providing hydrogen, fuel gas and electric power from any gas products of conversion of said kerogen and from a distillation of said solvents.

2. The process of claim 1, wherein:

the steps are such that a low-boiling-point-solvent supercritical temperature-and-pressure of about 400° C. and 500+PSIG is used;

the steps are such that said oil shale ore is crushed to about $\frac{3}{8}$ inch;

the steps are such that said residence time in said supercritical high pressure/temperature to maintain moisture as liquid region is in a region of five to thirty minutes; and

the steps are such that an H-donor mid-distillate recycle with a boiling point of approximately 200° C. is about twenty percent of a low-boiling-point solvent recycle.

3. The process of claim 1, wherein:

the steps are such that a hydrogen make-up to hydro-treat a mid-distillate recycle is derived from gases produced in said process.

4. The process of claim 1, wherein:

the steps are such that pressure vessels are used for kerogen conversion, oil separation, and solvent extraction.

5. The process of claim 2, wherein:

if there is to be no mineral recovery, the steps are such that a spent shale is cooled for disposal via a rotary drum internally sprayed with water;

6. The process of claim 2, wherein:

the steps are such that a pressure vessel is used to float any solvent from the residue by an aqueous means, and any wet residue is pressure filtered for recovery of leach-liquor mineral values.

7. The process of claim 2, wherein:

the steps are such that a pressure vessel is used to float a mixture of oil, mid distillate, lightened end solvent with an aqueous means, and any wet residue is pressure filtered for recovery of leach-liquor mineral values.

8. The process of claim 4, wherein:

the steps are such that said pressure vessels used include an autoclave with a draft-tube venturi.

9. A process for extracting kerogen and other minerals including alumina and soda ash from mined and crushed oil shales:

subjecting a slurry of oil shales to super critical conditions of pressure and temperature to extract any organic carbon content as oil;

extracting organic carbon from said slurry of oil shales which leaves a residue of oil shales;

leaching said resulting residue of oil shales with an aqueous sodium carbonate solution to create a leach liquor that includes alumina and soda ash values;

washing and returning said residue of oil shales after the steps of extracting and leaching to a mine for use as backfill;

precipitating any soda ash values from said leach liquor at around 100° C.;

recycling any alumina values from said leach liquor to the step of extracting;

drying said soda ash values to remove waters of hydration to yield a commercial soda ash product; and

converting any aluminum hydrate a basic aluminum sulphate (BAS) at around 200° C. and under pressure, wherein said BAS is calcined at around 850° C. into alumina and any of sulphur oxide gases are recycled after being converted to sulphuric acid.

10. The process of claim 9, wherein:

the step of subjecting includes crushing said oil shales for a particle size of about 1/8 inch to 1/4 inch diameter.

11. The process of claim 9, wherein:

the step of subjecting includes a solvent with a low boiling point in the range of 100° C. to 140° C.

12. The process of claim 9, further comprising the step of:

recycling a hydrogen donor mid-distillate equivalent to tetralin from a cut of said oil.

13. The process of claim 9, wherein:

the step of subjecting includes maintaining a temperature of 370-420° C. with an overall residence time of 15-60 minutes.

14. The process of claim 9, wherein:

the step of leaching includes an aqueous recycle of sodium carbonate at a temperature of greater than 150° C. and at a pressure of around 200 PSIG.

15. The process of claim 9, further comprising the step of:

evaporative crystallization of any sodium carbonate monohydrate leached into a recycled aqueous sodium carbonate leach liquor from said residue after oil extraction, and including temperatures above 100° C.

16. The process of claim 9, further comprising the step of:

sparging with CO₂ to precipitate aluminum trihydrate crystals from said leach liquor after any removal of sodium carbonate.

17. The process of claim 15, further comprising the step of:

producing a dense soda ash by drying said sodium carbonate monohydrate.

18. The process of claim 18, further comprising the step of:

washing, drying, and calcining said aluminum trihydrate crystals into alumina at temperatures of 850-950° C.

19. The process of claim 9, further comprising the step of:

recycling a fine aluminum trihydrate for improved production of crystalline aluminum trihydrate from said leach liquor.

20. The process of claim 9, further comprising the step of:

precipitating aluminum trihydrate, after the step of precipitating any soda ash values, by seeding with a fine aluminum trihydrate at a ratio of around 1:4, a temperature around 65° C., keeping a concentration of alumina of about 160 grams-per-liter, and a ratio of alumina to sodium carbonate of about 0.7.

21. The process of claim 20, further comprising the step of:

agglomerating any precipitated aluminum trihydrate into larger crystals using starch and over a residence time of about 20-25 hours.

22. The process of claim 9, further comprising the step of:

directly converting any aluminum trihydrate to basic aluminum sulfate (BAS) using calciner off-gasses in a recycle acid stream, and at a temperature of around 200° C. and under pressure sufficient to keep the constituents in their liquid phases.

23. The process of claim 9, further comprising the step of:

purging a recycle of said leach liquor after a depletion of soda ash and alumina values to remove an accumulation of impurities in an aqueous leach circuit.

24. The process of claim 9, after the step of washing and returning, further comprising the step of:

crushing and calcining said residue with limestone to produce a material equivalent to a Portland cement.

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