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R. J. STEGEMEIER ET AL

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OIL RECOVERY FROM BITUMINOUS SAND

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2 Sheets-Sheet 1

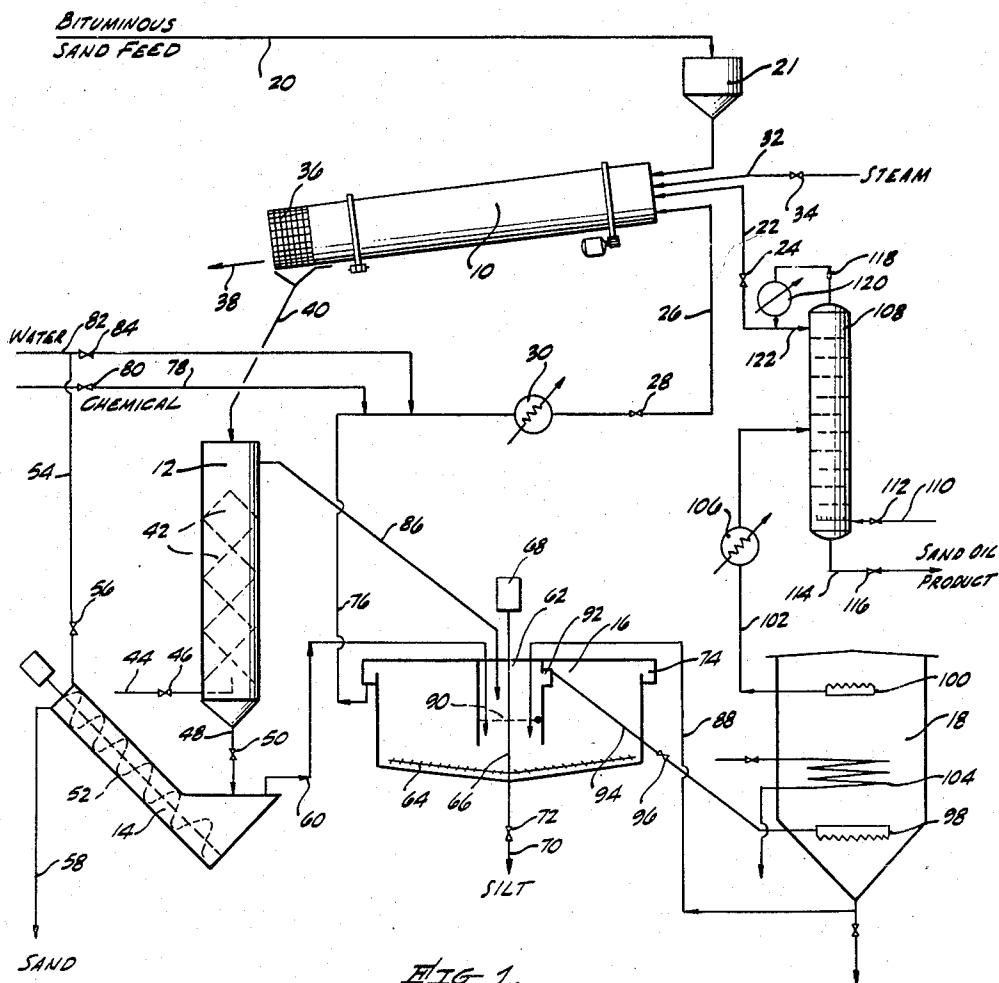


FIG. 1.

INVENTOR.

RICHARD J. STEGEMEIER
PAUL W. FISCHER

BY
Richard C. Hartman
ATTORNEY.

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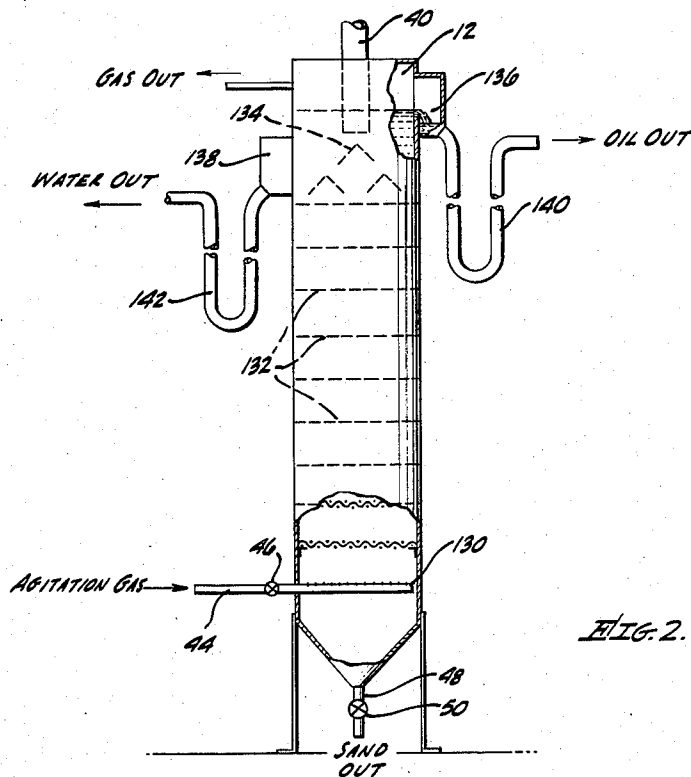


FIG. 2.

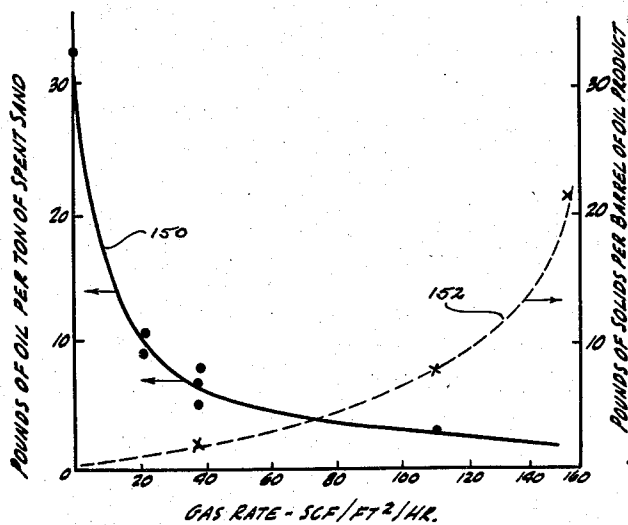


FIG. 3.

INVENTORS.
RICHARD J. STEGEMEIER,
PAUL W. FISCHER,

BY

Joseph J. Lawrence Jr.
ATTORNEY.

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OIL RECOVERY FROM BITUMINOUS SAND

Richard J. Stegemeier, Fullerton, and Paul W. Fischer, Whittier, Calif., assignors to Union Oil Company of California, Los Angeles, Calif., a corporation of California

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3 Claims. (Cl. 208—11)

This invention relates to the recovery of hydrocarbons from hydrocarbon-containing solids such as tar sand, oil-soaked diatomite, and the like. This invention particularly relates to an improved process and apparatus for treating such materials at relatively low temperatures and which may utilize particularly efficient storage pretreatment together with sand washing and separation steps to effect a substantially complete recovery of the hydrocarbon material present.

Extensive deposits of tar sands or bituminous sands are known to exist at widely separated places in the world. These materials are essentially a silicious material, such as sands, loosely agglomerated sandstones, or diatomaceous earth, saturated with relatively heavy or viscous hydrocarbon materials resembling low gravity crude petroleum. They exist near the surface of the earth and are generally discovered through location of their outcroppings. Extensive deposits of such materials have been discovered in the Athabaska region of Northern Alberta, Canada, in the Uinta Basin near Vernal in Northeastern Utah, and in the Santa Maria area of Southern California about 130 miles northwest of Los Angeles. In this area extensive deposits are found in the Sisquoc River Valley, near Casmalia, and elsewhere.

Surveys of these deposits have revealed that they contain tremendous quantities of hydrocarbon materials very similar to low gravity crude petroleum and individual deposits have been estimated to contain on the order of 60 to 70 million barrels of tar sand oil. Extensive recovery of these oils has not been achieved, primarily because of the expense in relation to crude petroleum in spite of the fact of the accessibility of the material near the earth's surface. However with rising costs of crude petroleum due to production and depletion of known petroleum reserves, an efficient and economical process and apparatus for the treatment of such bituminous sands has become highly desirable.

The principal disadvantage in previous processes lay in the extensive requirement of reagent and in the difficulty of separating the very heavy oil from the sand or other solid grains after the pulping or treating step. The present invention successfully overcomes these disadvantages, and is based upon the discovery of a particularly efficient method of treating the pulped material to effect sand separation while avoiding oil rewetting.

In the following description the phrases "bituminous sand" or "tar sand" are used to refer generally to all granular solid materials soaked with a usually highly viscous liquid or semi-liquid hydrocarbonaceous material, although it specifically refers to a characteristic type of bituminous solid consisting of discrete particles of sand bound together by a continuous viscous hydrocarbon oil phase. This terminology is used for the sake of simplicity of description, and it should be understood that the process and apparatus herein described may be applied to other solids similarly containing a bituminous or viscous hydrocarbon coating.

The present invention is directed to a low temperature

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process using a warm aqueous solution of a special alkali metal silicate, with or without other reagents, and a moderately heavy hydrocarbon diluent to separate the heavy oil from the bituminous sands, and in which process special procedures and apparatus are used in handling the effluent from the mixing step in which these materials are heated and agitated with one another to effect the separation of the heavy oil from the sand.

It is a primary object of this invention to provide an improved process for the separation and recovery of heavy oil from bituminous solids such as tar sand and the like.

It is a more particular object of this invention to provide a tar sand treating process involving an immediate treatment of the tar sand with an aqueous material immediately after mining the sand so as to prevent water evaporation therefrom, oil wetting of the sand, and in some cases to effect a partial digestion of the mined material during preliminary storage.

It is a particular object of this invention to provide in this process a preliminary separation step applied to the pulp flowing from a pulper or mixer to produce substantially clean sand and a mixture of the aqueous chemical and the oil phase, together with the step of treating the sand to free from it all of the mechanically occluded oil.

It is a further object of this invention to provide an improved apparatus adapted to effect the foregoing objects.

Other objects and advantages of this invention will become apparent to those skilled in the art as the description and illustration thereof proceed.

Briefly, the present invention comprises an initial step of feeding the tar sand in chunks continuously through a feed hopper which controls the rate of flow to a mixer. Here it is mixed and pulped with an aqueous sodium silicate solution and a hydrocarbon solvent at a slightly elevated temperature. This mixing continues for a period of between about 0.2 and about 2.0 hours and at a temperature of between about 160° F. and about 250° F. Preferably this mixer is of the rotary kiln type provided with internal baffles and conveyor flights so as to control the residence time of the material in the mixer. This treatment reduces the tar sand chunks to a heavy slurry or pulp of sand, water, and oil.

The effluent from the mixer or pulper is a slurry or pulp of treated sand, aqueous chemical solution, and a hydrocarbon phase including the separated bitumen and the relatively light diluent oil. This slurry or pulp is discharged immediately to a primary separation zone in which a very rapid separation of the treated solids is effected. This leaves a stream of fluid including the hydrocarbon and aqueous phases. Since there is a considerable quantity of sand present at all times in this processing step, it is essential that some slight sand agitation be effected during the dropout of the sand grains from the fluid phases in order to liberate residual oil droplets which are trapped in the downwardly progressing sand. The sand is discharged at the bottom of the primary separator into a washer-drier in which a considerable quantity of the water present in the sand stream is recovered for recirculation. If desired, makeup water to the process may be added at this point to recover residual silicate solution from the sand as well.

From the top of the primary separator are discharged the aqueous and hydrocarbon phases substantially free of sand grains, but containing variable amounts of very fine solids such as silt and clay. In the separator thickener zone, to which these phases are sent, a substantially complete removal of these silt-like solids is effected from the aqueous phase and a clean water stream is produced for recirculation. A concentrated wet oil phase is discharged therefrom into a settling zone such as a wash tank in

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which the material is allowed to stand for periods of between about 5 and 25 hours to produce essentially water and silt-free oil, the oil being a dilute mixture of hydrocarbon diluent and the relatively heavy hydrocarbon or bitumen separated from the sand in the process. This oil phase is at some point treated as by distillation to recover the diluent oil for recirculation to the pulper. An aqueous phase containing this silt is recirculated from the wash tank back to the thickener zone to produce clear water. From the thickener zone is removed a concentrated slurry of silt and water which is discharged to outdoor settling basins.

As illustrated by the following examples and as described herein the specific steps taken in the separator and settling zones to prevent contact of the sand with separated oil and to recover mechanically trapped oil from the settling sand have been found to be extremely important in the successful recovery of up to 99.9% of these heavy oils and in the production of clean sand containing less than 0.10% of the original oil.

The process of the present invention is best described and illustrated by reference to the accompanying drawings in which:

Figure 1 is a schematic flow diagram showing portions of the apparatus in elevation view.

Figure 2 is an elevation view in partial cross section of the primary settling zone into which the digested pulp of sand, oil, and water is discharged, and

Figure 3 shows the critical effect of aeration rate variation on the contamination of the oil and sand products.

Referring now more particularly to Figure 1, the essential equipment elements employed in the process and apparatus of the present invention include pulper or mixer 10, primary separator 12, sand washer and drier 14, thickener 16, and product settler 18. The subsequent discussion of the invention in connection with Figure 1 will be conducted as a typical example of the process and apparatus of this invention applied to the treatment of Sisquoc bituminous sand at a rate of approximately 200 t./d. (tons per day). Although the tar sand may contain between 20 and 40 gallons of oil per ton and have a gravity of from 2 to 10° API, typical bituminous sand contains about 30 gallons per ton of about 4° API gravity bitumen.

The freshly mined bituminous sand is introduced into pulper 10 by means of conveyor 20 at a rate of 200 t./d. controlled by solids feeder 21. A light coker gas-oil as diluent oil is introduced at a rate of 191 b./d. (barrels per day) and a temperature of 180° F. through line 22 at a rate controlled by valve 24. Also introduced into the pulper is the aqueous alkali metal silicate solution (with or without other reagents) which flows through line 26 at a rate of 286 b./d. controlled by valve 28. This material is maintained at a temperature of about 180° F. by means of heater or exchanger 30. To maintain a pulper temperature of about 180° F. within pulper 10, steam at the rate of 482 pounds per hour is also introduced through line 32 at a rate controlled by valve 34.

The relative rates at which the foregoing ingredients are introduced into pulping zone 10 are specific to one typical operation. In general however they are preferably maintained within certain limits in order to effect the most rapid and efficient liberation of the bituminous material from the sand or other solid grains. Pursuant to this the diluent hydrocarbon rate is that sufficient to produce an oil phase having an API gravity above 10° and is preferably maintained between limits of about 0.1 and about 2.5 b./t. (barrels per ton) of raw bituminous sand feed. The aqueous silicate solution is introduced at a rate maintained between about 0.75 and about 5.0 b./t. of raw sand feed, and preferably between about 1.0 and 1.5 b./t. This aqueous solution contains between about 0.5 and 20 and preferably between about 0.75 and about 10.0 pounds of an aqueous sodium silicate

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concentrate per barrel. This concentrate is a 34% by weight aqueous solution and is a special material marketed commercially under the name "Silicate 120." It has an Na_2O to SiO_2 ratio of about 0.55 mol per mol. Other high basicity sodium silicates may be substituted provided this ratio is above about 0.4 and preferably greater than about 0.5. The commercial water glass of commerce is not satisfactory since it has a ratio of about 0.25.

The pulping temperature must be maintained higher than about 160° F. and preferably is maintained above 180° F., although it ordinarily should not run above about 250° F. The operation of the pulping zone is controlled relative to the set rate and the size of the pulper so that the raw bituminous sand is subjected to the action of steam, the aqueous silicate, and the hydrocarbon diluent within the pulping zone for a period of between about 0.1 and 2.0 hours. Under the conditions given previously a pulping time of about 0.25 hour will liberate substantially all of the bitumen from the sand and produce a spent sand containing less than about 3 pounds of hydrocarbon per ton.

The discharge end of pulping zone 10 is provided with trash screen 36 by means of which rocks and nondisaggregated lumps of tar sand are discharged from the system by means of conveyor 38. The fluid pulp discharges through the screen 36 and flows by means of line 40 into the top of primary separation zone 12. This stream contains approximately 58 t./d. of water, 55 t./d. of oil and 172 t./d. of sand. Primary separation zone 12 operates at a temperature a few degrees below that of the pulper. This is attained by making line 40 as short as possible and providing for the immediate transfer of the pulp from the pulper into the primary separator. Preferably line 40 is an inclined pipe having a slope of not less than 60° relative to the horizontal.

The interior of primary separation zone 12 is provided with a plurality of baffles 42 over which the settling sand progresses in sequence to provide the gentle agitation necessary to liberate mechanically trapped oil drops from the sand stream. Additional agitation is provided by introducing fluid, hereinafter more fully described, into the bottom of primary separation zone 12 through line 44 at a rate controlled by valve 46.

From the bottom of primary separation zone 12 the treated sand discharges through line 48 at a rate controlled by valve 50, which may be a density valve responsive to the density of the sand and water slurry collecting in the bottom of primary separation zone 12. In any event, the sand discharges at a rate of 172 t./d. into washer 14 along with 193 b./d. of water. The sand is picked up and conveyed upwardly by means of conveyor 52 whereby a gravity separation of the aqueous phase is provided. Preferably, part or all of the makeup water to the system is introduced by means of line 54 controlled by valve 56 as wash water to the washer-drier. The clean oil-free sand is discharged from washer-drier 14 by means of line 58 and is conveyed to a suitable disposal point.

The aqueous phase removed with the sand from the primary separation zone 12 is separated from washer-drier 14 through line 60 and is discharged into the central well 62 of thickening zone 16. This stream flows at about 160° F. at a rate of about 1168 b./d., containing about 5 t./d. of sand and 1 b./d. of oil.

Thickener 16 is an essentially cylindrical vessel provided internally with a coaxial central well 62 into which all of the fluids for treatment are introduced. The floor of thickener 16 is provided with a plurality of radial rake arms 64 rotated by means of a vertical central shaft 66 or by other means, driven by rotating means 68. In the present example the central well is such that the fluid residence time is about one hour devoted to the settling of silt from the oil phase as well as the separation of the oil and water phases. The annular volume outside well 62 is sized to give a water residence time of about 6-8

hours during which time substantially all of the silt settles from the aqueous phase. Rake arms 64 are provided with rakes inclined at such an angle so that rotation of the rakes move the settled silt as a thickened sludge radially inward toward silt outlet 70. The thickened silt is removed through line 70 at a rate controlled by valve 72, the silt concentrate containing about 87 b./d. of water and 15.0 t./d. of solids.

The clear water effluent is removed from collector 74 surrounding the upper periphery of thickener 16 by means of line 76 at a rate of 1821 b./d. This material actually constitutes the aqueous silicate solution to which makeup aqueous silicate concentrate is introduced by means of line 78 at a rate of 2.5 gallons per hour controlled by valve 80. Fresh water is introduced by means of line 82 at a rate of about 355 b./d. controlled by valve 84. This may, if desired, flow into the clear aqueous stream in line 76. As previously indicated this is preferably employed, wholly or partly, as wash water for the spent sand and is introduced through line 54 previously described. The total aqueous stream from thickener 16 continues through heat exchanger 30. It is heated to about 180° F. and is introduced into pulping zone 10 through line 26 as previously stated.

The overflow of the wet oil phase from primary separator zone 12 passes through line 86 also into central well 62 of thickener 16. This stream flows at a rate of about 1081 b./d. and includes 754 b./d. of water, 327 b./d. of oil, and 12 t./d. of silt and sand. The temperature of the stream is about 175° F.

Also introduced into the central well 62 at a temperature of about 155° F. is a relatively small stream of water from the bottom of settling zone 18. This passes through line 88 into central well 62 and contains 67 b./d. of water, 1 b./d. of oil, and a trace of silt and sand.

In central well 62 broken line 90 indicates the approximate position of the oil emulsion-aqueous phase interface. This is maintained at a distance about two-thirds of the way down in the central well. The aqueous streams flowing through lines 60 and 88 from washer-drier 14 and settling zone 18 respectively are introduced below this level because they contain only slight quantities of oil. The primary separator effluent flowing through line 86 and containing about 30% by volume of oil is introduced above level 90 into the supernatant phase consisting of separated oil and possibly a layer of oil-water emulsion. Preferably the interface denoted by line 90 is detected continuously and the rate of removal of the supernatant wet oil phase from weir box 92 or other removal means is controlled so as to maintain a substantially constant position of the interface. In any event, the residence time for the oil phase is approximately one hour and the wet oil stream is removed from weir box 92 through line 94 at a rate of 409 b./d. controlled by valve 96 or other means. The temperature of this stream is approximately 168° F., and it contains 328 b./d. of oil, 81 b./d. of water, and 2 t./d. of sand.

This wet oil stream is discharged into separator zone 18 by means of distributor 98 disposed in the lower portion of the settling zone. Heating coil 104 is provided within settling zone 18. Preferably the volume of settling zone 18 is sufficient to give the wet oil a residence time of about 12 hours permitting it to separate into dry oil and aqueous phases. The separated aqueous phase is removed from the bottom of settling zone 18 through line 88 and contains a trace of solids, but is otherwise essentially all water. The dry oil is removed from the top of settling zone 18 by means of take-off weir 100. This stream is pumped by means of a pump not shown through line 102 to distillation facilities which may be located at the plant site or at a remote area where it is associated with oil refining facilities for treating the recovered oil. This stream flows

at a temperature of about 153° F. and contains 321 b./d. of oil, 2 b./d. of water and 0.1 t./d. of solids. The effluent dry oil is heated in exchanger means 106 and is distilled in distillation column 108. A stripping gas such as steam is introduced into the bottom of distillation column 108 through line 110 at a rate controlled by valve 112. The overhead vapor flowing through line 118 from still 108 is condensed in condenser 120, part of the condensate is returned through line 122 as reflux, and the remainder is pumped by means of a pump not shown through line 22 into pulping zone 10. The stripped diluent oil-free bitumen is removed through line 114 at a rate of 137 b./d. controlled by valve 116. This product oil has the following properties:

TABLE I

Product oil characteristics

Viscosity, SUS at 180° F.-----	50,200
Carbon Residue, percent by wt.-----	16.05
Sulfur, percent by wt.-----	4.4
Nitrogen, percent by wt.-----	0.95
Gravity, ° API.-----	4.4

By means of the above-described process, bituminous sands are readily treated to effect better than 96% by volume of the bitumen contained therein at moderate temperatures and pressures and with only slight consumption of chemicals. The sand discharged from the system contains less than 5 pounds per ton of residual oil.

Referring now more particularly to Figure 2, an enlarged detail drawing of primary separator 12 is shown in which the details of the internals and particularly the baffles are shown. As previously described, a lower outlet line for treated sand is provided in the form of line 48 controlled by valve 50. Also a lower inlet line 44 controlled by valve 46 is further provided with a distributor 130 by means of which an aeration gas is introduced and broken up into small bubbles distributed uniformly throughout the entire cross sectional area of the primary separator zone.

In primary separator vessel 12 there is superimposed above each other a series of transverse perforated baffles, such as relatively small-meshed screens 132 having mesh sizes between 0.1 and about 1.0 inch, supported internally from the walls of the column. As a specific example, excellent success was attained in removing residual oil from the sand in a column which was 10 feet in height, and 22 inches in diameter which contained 9 screens having 0.25 inch mesh spaced apart from one another by a distance of about 10 inches, or between about 0.25 and 1.0 column diameters. The pulp introduced from pulping zone 10 flows through line 40 into the top of separator 12 wherein it contacts several conical distributors 134. From the distributors the sand flows downwardly successively through the superimposed screens countercurrent to a rising stream of aeration gas bubbles. If desired, the aqueous and oil phases may be removed together in the manner shown in Figure 1 by means of line 86. However, in the specific apparatus shown it was found that an excellent separation of the aqueous and oil phases could be obtained and accordingly separate weir boxes 136 for the oil and 138 for the aqueous phases were provided. A gooseneck line 140 opens from weir box 136 through which the oil discharges as fast as it accumulates at the top of separator 12. A second gooseneck take-off line 142 opens from weir box 138 by means of which the aqueous phase is removed at a controlled liquid level within the column.

Whereas the sand separated by simple settling in an unbaffled tank to which no aeration gas was provided contained 60 pounds of residual oil per ton, and sand from the screen baffled tank with no gas aeration contained 32 pounds of oil per ton, the process of aeration gas agitation in the presence of superimposed screens

described above successfully reduced the residual oil content to about 4 pounds per ton at 150° F. and with a gas rate of 75 s.c.f./ft.²/hr. (standard cubic feet per square foot of column cross section per hour).

Referring finally to Figure 3, experimental data obtained in the semi-commercial size apparatus are shown plotted to illustrate the variation in the degree of contamination of the sand with residual oil and the variation in the degree of contamination of the product oil with solids, each as a function of aeration gas rates.

Curve 150 graphically illustrates the rapid reduction in residual oil content in the spent sand with the introduction of aeration gas into the bottom of separation zone 12. As little as 20 s.c.f./ft.²/hr. aeration gas reduces the residual oil content to about 25% of its original value in the absence of aeration. Further reductions are obtained with moderate increases in the gas rate and contaminations less than 3 pounds per ton are readily obtained at aeration gas rates of about 100 s.c.f./ft.²/hr. In the present process, the increases in gas rate may not be continued indefinitely since simultaneously with the reduction in oil concentration in the sand, there is an increase in the solids or silt contamination of the product oil. This is represented by curve 152 also shown in Figure 3. Accordingly in the process of the present invention the aeration gas rate must be limited between values of about 20 and 140 s.c.f./ft.²/hr. and preferably the aeration rate is restricted to between about 50 and about 100 s.c.f./ft.²/hr. There is also a limitation on the sand rate, and desirably the solid grains have a falling retention time of from about 1.5 to about 5 minutes. The solids rate should be maintained between about 0.5 and about 5.0 tons per square foot of column cross section per hour, and preferably between about 1.5 and about 2.5 tons per square foot per hour.

A particular embodiment of the present invention has been hereinabove described in considerable detail by way of illustration. It should be understood that various other modifications and adaptations thereof may be made by those skilled in this particular art without departing from the spirit and scope of this invention as set forth in the appended claims.

We claim:

1. In a process for the recovery of hydrocarbon values from naturally-occurring hydrocarbonaceous mineral solids wherein said solids are contacted with an aqueous sodium silicate solution and a hydrocarbon diluent at a moderately elevated temperature for a period sufficient to reduce said solids to a homogeneous pulp, and said pulp is then treated to separate it into a solids phase and a liquid phase comprising liquid hydrocarbons and aqueous sodium silicate, the method of effecting said

separation treatment which comprises (1) introducing said pulp into the upper end of a confined vertically elongated separation zone at a rate corresponding to between about 0.5 and about 5 tons of solid per hour per square foot of cross-sectional area of said separation zone, said separation zone being maintained filled with a liquid body consisting of liquid components of said pulp; (2) allowing the solid components of said pulp to descend by gravity down through said liquid body; (3) during the descent of said solids through said liquid body distributing said solids substantially uniformly over the cross-sectional area of said separation zone; (4) simultaneously introducing a stream of air into the lower end of said separation zone at a rate between about 20 and about 140 s.c.f./hr./sq. ft. of cross-sectional area of said separation zone; (5) allowing said air to rise through said liquid body in the form of bubbles passing countercurrent to the solids descending there-through; (6) during the ascent of said air bubbles through said liquid body distributing said bubbles substantially uniformly over the cross-sectional area of said separation zone; (7) withdrawing settled solids from the lower end of said separation zone; (8) withdrawing liquid components of said pulp from the upper end of said separation zone; and (9) withdrawing air from the upper end of said separation zone.

2. A process as defined by claim 1 in combination with the steps of allowing liquid components of said pulp to settle in the upper part of said separation zone into an upper hydrocarbon layer and a lower aqueous layer, and separately withdrawing said upper and lower layer from said separation zone.

3. A process as defined by claim 2 wherein, in step (4), the said air is introduced into said separation zone at a rate of between about 50 and about 100 s.c.f./hr./sq. ft. of cross sectional area of said separation zone, and in step (1), said pulp is introduced into said separation zone at a rate corresponding to between about 1.5 and about 2.5 tons of solids per hour per square foot of cross-sectional area of said separation zone.

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