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UNITIZING ON EXCHANGE TO REDUCE FRESH WATER REQUIREMENT OF HOT WATER PROCESS

Frederick W. Camp, West Chester, Pa., assignor to Great Canadian Oil Sands Limited, Toronto, Ontario, Canada, a corporation of Canada

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7 Claims

ABSTRACT OF THE DISCLOSURE

This invention relates to an improvement to a hot water process for treating bituminous tar sands. The improvement results in reduced fresh water requirement for the process. By the improvement, at least a portion of the clay-containing water fractions discharged from the hot water process is contacted with a cationic exchange material to substantially reduce the divalent and trivalent cations in the portion. The portion is then recycled to serve as at least a part of the water used to form the tar sands water mixture which is charged into the process separation zone.

The present invention relates to an improvement in the hot water process for treating bituminous tar sands.

Numerous deposits of bituminous tar sands exist throughout the world. The most extensive deposits are found in northern Alberta, Canada. The sands are composed of a siliceous material, generally having a size greater than that passing a 325 mesh screen, saturated with a relatively heavy, viscous bitumen in quantities of from 5 to 21 weight percent of the total composition. More typically the bitumen content of the sands is between about 8 to 15 percent. This bitumen is quite viscous—6° to 8° API gravity—and contains typically 4.5 percent sulfur and 38 percent aromatics. Its specific gravity at 25° C. ranges typically from about 1.00 to about 1.06. The tar sands also contain clay and silt. Silt is defined as mineral which will pass a 325-mesh screen but which is larger than 2 microns. Clay is mineral smaller than 2 microns including some siliceous material of that size.

There are several well-known processes for effecting separation of bitumen from the tar sands. In the hot water method, the bituminous sands are jetted with steam and mulled with a minor amount of hot water at temperatures in the range of 140° to 210° F. The resulting pulp is conducted to a sump where it is diluted with additional hot water and carried to a separation cell maintained at a temperature of about 150° to 200° F. In the separation cell, sand settles to the bottom as tailings and bitumen rises to the top in the form of an oil froth. An aqueous middlings layer containing some mineral and bitumen is formed between these layers. A scavenger step may be conducted on the middlings layer from the primary separation step to recover additional amounts of bitumen therefrom. This step usually comprises aerating the middlings as taught by K. A. Clark, "The Hot Water Washing Method," Canadian Oil and Gas Industries 3, 46 (1950). These froths can be combined, diluted with naphtha and centrifuged to remove more water and residual mineral. The naphtha is then distilled off and the bitumen is coked to a high quality crude suitable for further processing.

The hot water process is described in detail in Floyd et al., United States application Ser. No. 509,589 now Patent No. 3,401,110. Floyd et al. disclose that froth formation in the process separation cell is dependent upon the viscosity of the middlings layer, and that the viscosity is dependent upon the middlings clay content. It is thought that increasing viscosity retards the upward settling of bitumen flecks. When this occurs, the smaller bitumen flecks and those that are heavily laden with mineral matter stay suspended in the water of the cell and are removed with the middlings layer, or lost altogether with the sand tailings.

Upon discharge from the separation zone the water from the middlings must eventually be stored, disposed of, or recycled back into the process. Because this water contains bitumen emulsions, finely dispersed clay with poor settling characteristics and other contaminants, water pollution considerations prohibit discharging the water into rivers, lakes or other natural bodies of water. It has been proposed that the water be stored in evaporation ponds but this proposal would involve large space requirements and the construction of expensive enclosure dikes. It has also been suggested that the water in the effluent discharge be recycled back into the process as an economic measure to conserve both heat and water. Floyd et al. teach that some of this water can be recycled but that the amount of recycle is limited by the dispersed silt and clay content of the water which can reduce the water yield by increasing the viscosity of the middlings layer and retarding the upward settling of bitumen flecks as pointed out supra. A proportion of water in the diluted tar sands pulp fed into the separation cell must therefore be fresh water—water which is substantially free of the clay and silt found in middlings water. In fact, with some high clay content tar sands feeds, all of the water in the diluted pulp must be added as fresh water.

The amount of this required fresh water can be related to the feed fines content according to the following relationship:

\[
\text{Tons fresh water} = \frac{0.00254 \times (P)}{\text{Tons tar sand}} \times \text{Clay/total water}
\]

where P is the percent material in the mineral portion of the tar sands feed which is smaller than 44 microns. Tons fresh water/Tons tar sand is the ratio of fresh water to tar sands required in the diluted pulp passing to the separation zone and Clay/Total water is the operable ratio of clay to total water in the middlings zone layer.

The limiting factor in this relationship is the clay to total water ratio in the middlings which cannot exceed about 0.1 in usual operation. It has surprisingly been observed in the present invention that an operable middlings viscosity can be maintained in the separation cell with a greater proportion of clay-containing water recycle in the diluted tar sands pulp than before possible. By the present invention the operable clay to total water ratio may be raised above 0.1 and the required fresh water makeup rate correspondingly reduced.

It has been observed that at a fixed Clay/Total water ratio, the viscosity of the hot water process middlings depends on the soluble salt content of the system, particularly on divalent and trivalent cation concentration. It has been found that the clay present in the tar sands contains exchangeable cations and is actually the major source of these ions in the process streams. Table I shows typical cationic constituents of bituminous tar sands clay:

<table>
<thead>
<tr>
<th>TABLE I.—CATIONIC CONSTITUENTS OF ABATASCA CLAY</th>
</tr>
</thead>
<tbody>
<tr>
<td>Milligram moles cation/100 g. clay</td>
</tr>
<tr>
<td>Cation</td>
</tr>
<tr>
<td>----------------</td>
</tr>
<tr>
<td>Calcium</td>
</tr>
<tr>
<td>Magnesium</td>
</tr>
<tr>
<td>Potassium</td>
</tr>
<tr>
<td>Sodium</td>
</tr>
<tr>
<td>Hydrogen</td>
</tr>
</tbody>
</table>

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It is proposed by the process of the present invention to treat the clay containing water fractions from the hot water process separation zone with a cation exchange resin to substantially reduce the concentration of divalent and trivalent cations in the fractions. This exchange makes the fractions suitable for recycle back into the process to replace fresh water added thus allowing operation at higher clay to total water ratios. The reduction in fresh water required in the process is made possible through the substitution therefor of a treated clay-containing water stream. This stream has been treated in an ion exchange to remove all exchangeable Ca++ and Mg++ ions. The stream serves as a reservoir to absorb di- and trivalent ions contained in the tar sand feed.

The invention can be described as an improvement to the hot water process where the hot water process comprises; forming a mixture of tar sands and water, passing the mixture into a separation zone to form an upper bitumen froth layer, a middlings layer comprising water, mineral and bitumen and containing divalent and trivalent cations and a sand tailings layer, and recovering the bitumen froth layer. The improvement comprises; removing at least a portion of the middlings layer from the separation zone, contacting the portion with a cationic exchange material to substantially reduce the divalent and trivalent cations in the portion and recycling that portion, substantially reduced in divalent and trivalent cations as at least a portion of the water utilized to form the tar sands and water mixture.

The steps of contacting the portion of middlings with the cationic exchange material can utilize any well-known exchange material which will substantially reduce the divalent and trivalent cation concentration in the portion. The natural and synthetic inorganic zeolites are less preferred in the present process than the synthetic organic resins. Typical solid cation exchange resins which can be employed in the present invention include the divinylbenzene-styrene copolymer type, the acrylic type, the sulfonated coal type and the phenolic type. These can be used in the sodium, hydrogen, ammonium or hydradine forms. Such resins are sold, for example, under the trademarks of Amberlite 200 which is a sulfonated styrene-divinylbenzene copolymer, manufactured and sold by Rohm and Haas Company; Amberlite IR-120 which is a nuclear sulfonic acid type exchange also manufactured and sold by Rohm and Haas Company; and Permolt Q which is a sulfonated styrene type resin manufactured and sold by the Permutit Company.

The process of the present invention can be described in detail with reference to the drawing which shows a preferred embodiment of the invention.

Mulling of the tar sands produces a pulp which then passes from the conditioning drum as indicated by line 3 to a screen indicated at 24. The purpose of screen 24 is to remove from the tar sand pulp any debris, rocks or oversized lumps as indicated generally at 4.

The pulp then passes from screen 24 as indicated by line 5 to a sump 5 where it is diluted with additional water from 6 to a middling recycle stream 7. In the event the clay content of the tar sands is high, a relatively high rate of fresh or treated feed water introduction through 6 can be employed to compensate for the high clay introduction while a correspondingly high rate of transfer of middlings layer through line 11 is maintained. Under these circumstances recycling of the other stream of middlings through line 7 to the sump is not required.

Modifications that may be made in the process as above described include sending a minor portion of the middlings recycle stream from line 7 through a suitable zone (not shown) to the conditioning drum 23 to supply all or a part of the water needed therein other than that supplied through condensation of the steam which is consumed. Also, if desired, a stream of the middlings recycle can be introduced onto the screen 24 to flush the pulp therethrough and into the sump. As a general rule the total amount of water added to the water insoluble bituminous sands as liquid water and as steam prior to the separation step should be in the range of 0.2 to 3.0 tons per ton of the bituminous sands. The amount of water needed within this range increases as the silt and clay content of the bituminous sand increases. For example, when 15 percent by weight of the mineral matter of the tar sands has a particle size below 44 microns, the fresh water added generally can be about 0.3 to 0.5 ton per ton of tar sands. On the other hand, when 30 percent of the mineral matter is below 44 microns diameter, generally 0.7 to 1.0 ton of water should be used per ton of tar sands. Correspondingly the amount of bitumen-rich middlings removed through line 11 will vary depending upon the rate of fresh water addition. As a general rule the rate of withdrawal of bitumen-rich middlings to scavenger zone 27 will be 10 to 75 gallons per ton of tar sands processed when 15 percent by weight of the mineral matter is below 44 microns and 150 to 250 gallon per ton of tar sands when 25 to 30 percent of the mineral is of this fine particle size.

Further following the process, the pulped and diluted tar sands are pumped from the sump through line 8 into the separation zone 26. This zone comprises a cell which contains a relatively quiescent body of hot water. In the cell, the diluted pulp forms into a bitumen froth layer which rises to the cell top and is withdrawn via line 9, and a sand tailings layer which settles to the bottom to be withdrawn through line 10. An aqueous middlings layer between the froth and tailings layers contains silt and clay and some bitumen which failed to form froth. In order to prevent the build up of the system it is necessary to continually remove some of the middlings layer and supply enough water in the conditioning operations to compensate for that so removed.

The rate at which the middlings need to be removed from the system depends upon the content of clay and silt present in the tar sands feed and this will vary from time to time as the content of these fines varies. If the clay and silt content is allowed to build up too high, effective separation no longer will occur and the process will become inoperative. This can be avoided by regulating the recycling and withdrawal of middlings and input of fresh water per the invention disclosed and claimed in the Floyd et al. application. However, even when the separ-
The oil-rich middlings stream withdrawn from separator 26 through line 11 is sent to a scavenger zone 27 wherein an air flotation operation is conducted to cause the formation of additional bitumen froth. The process involves introducing air into the scavenger zone 27 through any of the air flotation procedures conventionally utilized in processing of ores. This involves providing a controlled zone of aeration in the flotation cell at a locus where agitation of the middlings is being effected so that air becomes dispersed in the middlings in the form of small bubbles. The drawing illustrates a flotation cell of the subaeration type wherein a motorized rotary agitator is provided and air is fed thereto in controlled amount. Alternatively the air can be fed in through the shaft of the rotor. The rotor effects entraining of the air in the middlings. This air causes the formation of additional bitumen froth which passes from the scavenger zone 27 through line 12 to a froth settler zone 28. A bitumen-lean middlings stream is removed from the bottom of the scavenger zone 27 via line 13.

In the settler zone 28, the scavenger froth forms into a lower layer of settler tailings which is withdrawn and recycled via line 14 to be mixed with bitumen-rich middlings for feed to the scavenger zone 27 via line 11. In the settler zone an upper layer of upgraded bitumen froth forms above the tailings and is withdrawn through line 15 and is mixed with primary froth in line 9. The combined froths are at a temperature of about 160°F. They are heated with steam and diluted with sodium hydroxide to produce a sodium bitumen in zone 16 to reduce the viscosity of the bitumen for centrifuging in zone 29 to produce a bitumen product 17 suitable for further processing.

The oil-lean middlings in line 13 and the sand tailings from the separation zone 26 are combined to form an effluent discharge which is delivered via line 18 to a sand pile zone 30 via distribution piping 31. The effluent contains between 25 and 50 weight percent sand and silt material which is larger than about two microns. The distribution piping provides for continuous and uniform delivery of the effluent to the sand pile zones where the sand and silt material is deposited. The water in the effluent discharge percolates through and over the sand pile zone 30 to the pond zone 32 where it collects as pond water containing up to about 12 weight percent suspended solids, between 80 and 100 percent of which is fine clay of a size smaller than 2 microns. The pond water also contains between about 0.1 and 1.5 weight percent bitumen. Because of the particular composition of this pond water, and especially because of the extreme fineness of the suspended clay material which has extremely poor settling characteristics, the water cannot be discarded or to any great extent recycled back into the hot water system.

By the process of the present invention, the pond water is withdrawn from the pond zone 32 by means of pump 33 and fed via 19 to the cation exchange zone 10. This zone can comprise any of the equipment used for ion-exchange contacting. The simplest useable equipment is the batch reactor or single-stage contactor. In this unit the resin is intimately mixed in a stirred vessel with the pond water for removal of the divalent and trivalent ions. Another contactor in general use is the fixed-bed column. The essential requirements for a fixed-bed column are sufficient free space above the resin bed for expansion, a good liquid distribution system, and a good bed support and collecting system. Operation of a fixed bed can be controlled manually or automatically. Countercurrent contactors are also suitable for use in zone 34.

When the ion exchange material has absorbed all of the exchangeable divalent and trivalent ions it can hold, it can be regenerated as generally indicated at 35 by contacting with a salt solution introduced via line 20 with discharge of divalent and trivalent salts indicated at 21. The treated water can be introduced via line 22 into the system as all or a portion of the water in line 6 to the sump as shown or can be alternatively introduced into the system via lines 7 or 2 or as a screen wash or at any desired point of introduction into the process. Although the invention has been described supra with reference to the treatment of pond water from the hot water process effluent discharge it should be pointed out that the invention can be practiced on any water stream from the separation cell. For example, referring again to the drawing, the bitumen-lean middlings line 13 from the flotation scavenger zone can be directly treated by the invention to remove divalent and trivalent cations contained therein to make these middlings suitable for recycle back into the process. Also the middlings in line 7 can be treated to remove cations before recycle into sump 25 for dilution of the tar sands pulp.

The following examples illustrate the process of the present invention.

**EXAMPLE I**

On an hourly basis sufficient amount of tar sands to give 1000 tons in the feed after screening is mixed with 382 tons of fresh water and steam, mulled in a conditioning drum, and changed into a separation cell. The tar sands contain mineral, 15 weight percent of which is fines material (material passing a 325-mesh screen). Of this fines material about 38 tons are clay. About 0.67 pound of NaOH per ton of tar sands is added to the feed before it is fed to the cell. The caustic is sufficient to raise the pH of the separation cell middlings from about 6.5 to 7 to about 8.5.

In the cell the tar sands separate into a bitumen froth, a sand tailings and a water middlings containing mineral and some bitumen. The viscosity of the middlings in the separation cell is determined to be 4 centipoise. One-hundred and fifty-two tons of froth product are recovered and a middlings and tailings effluent discharge of 1230 tons per hour is removed from the cell to the tailings pond where the effluent is percolated over and through a sand pile down to the pond where about 187 tons of pond water per hour collects. This pond water comprises about 170 tons of water and about 17 tons of clay per hour while the sand pile "beach" accumulates about 210 tons of water and about 833 tons of mineral. If the proportion of fresh water input in the process feed is decreased, it is observed that the middlings viscosity increases. Thus it is determined that 4 centipoise is about the maximum operable viscosity for this system. Above this value, froth recovery begins to decrease as the upward settling of separated bitumen flocks is impeded by the increased middlings viscosity. Operating as described above at 4 centipoise, viscosity accumulates 187 tons per hour of pond water discharged from the process.

**EXAMPLE II**

The process of Example I is repeated except that the amount of fresh water in the feed is reduced to 210 tons per hour. To make possible this reduction, a treated clay stream (210 tons per hour) is added with the feed. This stream comprises pond water containing 17 tons of clay which has been subjected to contact with a synthetic organic ion exchange resin, Amberlite IR-120, to remove all exchangeable Ca⁺⁺ and Mg⁺⁺ ions contained in the clay in the tar sands feed. One ton of treated clay is added per ton of clay in the feed, so as to reduce the divalent ion concentration in the process streams to about one-half of the concentration in Example I. Operation in the cell is maintained at an operable viscosity of 4 centi-
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poise. It is also noted in the operation of this example that only about 0.38 pound of added caustic per ton of tar sand is needed to maintain middlings pH in the separation cell at about 8.5.

The process of Example I illustrates the operation of a hot water process under conventional conditions to give a viscosity of 4 centipoise in the separation cell, the upper limit for operability. In Example II, a treated clay containing recycle stream is added with the feed. This latter example shows that although a portion of the fresh feed water has been replaced with clay containing recycle water, viscosity of the separation zone is not affected.

Comparison of Examples I and II shows that the process of this invention substantially reduces the amount of water finally disposed from a hot water process by making possible the recycle of this water back into the process after it has been treated in accordance with this invention. The comparison shows that even with recycle of a substantial portion of this treated clay-containing water, viscosity of the separation cell middlings is unaffected.

Another advantage of the present invention illustrated above is the savings in added caustic by the process of Example II. It is thought that some of the caustic, added in Example I, exchanges with Ca\(^{++}\) ions in the tar sands feed clay. With the added treated clay stream of Example II acting as an ion reservoir for the Ca\(^{++}\) ions in the feed clay, added caustic is not consumed in this function.

What is claimed is:

1. In a hot water process for treating bituminous tar sands which comprises; forming a mixture of tar sands and water; passing said mixture into a separation zone to form an upper bitumen froth layer, a middlings layer comprising water, mineral and bitumen and containing divalent and trivalent cations and a sand tailings layer; recovering said froth layer; and passing at least a portion of the middlings layer and tailings layer to a settling pond; the improvement which comprises:

(a) removing at least a part of the water from said settling pond, said part comprising a water layer with suspended mineral and containing divalent and trivalent cations;

(b) contacting said part of said pond water with a cation exchange resin to substantially reduce said divalent and trivalent cations in said part; and

(c) recycling said part, substantially reduced in divalent and trivalent cations to said tar sands as at least a portion of the water utilized to form said mixture.

2. The process of claim 1 in which said cation exchange resin is a sulfonated styrene-divinyl benzene copolymer.

3. In a hot water process for treating bituminous tar sands which comprises; forming a mixture of tar sands and water; passing said mixture into a separation zone to form an upper bitumen froth layer, a middlings layer comprising water, mineral and bitumen and containing divalent and trivalent cations and a sand tailings layer; recovering said froth layer; and passing at least a portion of the middlings layer and tailings layer to a settling pond; the improvement which comprises:

(a) removing at least a portion of the water from said settling pond, said part comprising a water layer with suspended mineral and containing divalent and trivalent cations;

(b) contacting said part of said pond water with a cation exchange resin to substantially reduce said divalent and trivalent cations in said part; and

(c) recycling said part, substantially reduced in divalent and trivalent cations to said tar sands as at least a portion of the water utilized to form said mixture.

4. The process of claim 3 in which said cation exchange resin is a sulfonated styrene-divinyl benzene copolymer.

5. The process of claim 3 in which said mixture is formed by mulling said tar sands with a minor amount of water to form a tar sands-water pulp; and diluting said pulp with additional water to form said mixture.

6. The process of claim 5 in which said water pulp, substantially reduced in divalent and trivalent cations, is recycled as at least a portion of the water utilized to dilute said pulp to form said mixture.

7. The process of claim 6 in which said cation exchange resin is a sulfonated styrene-divinyl benzene copolymer.

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PAUL M. COUGHLAN, Jr., Primary Examiner

T. H. YOUNG, Assistant Examiner

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