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[56]

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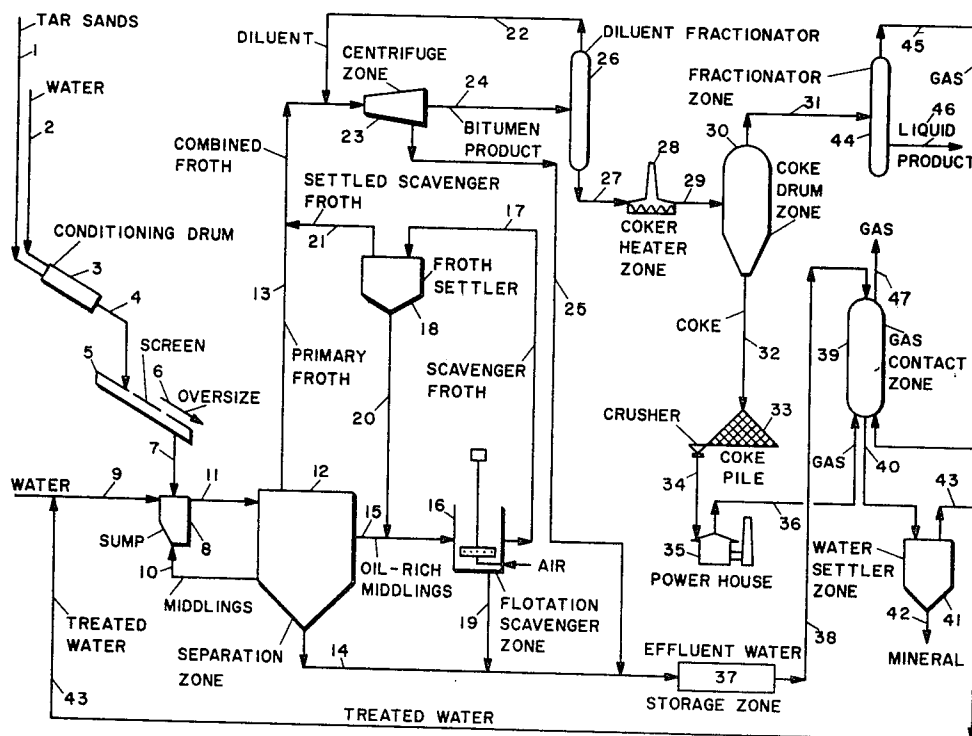
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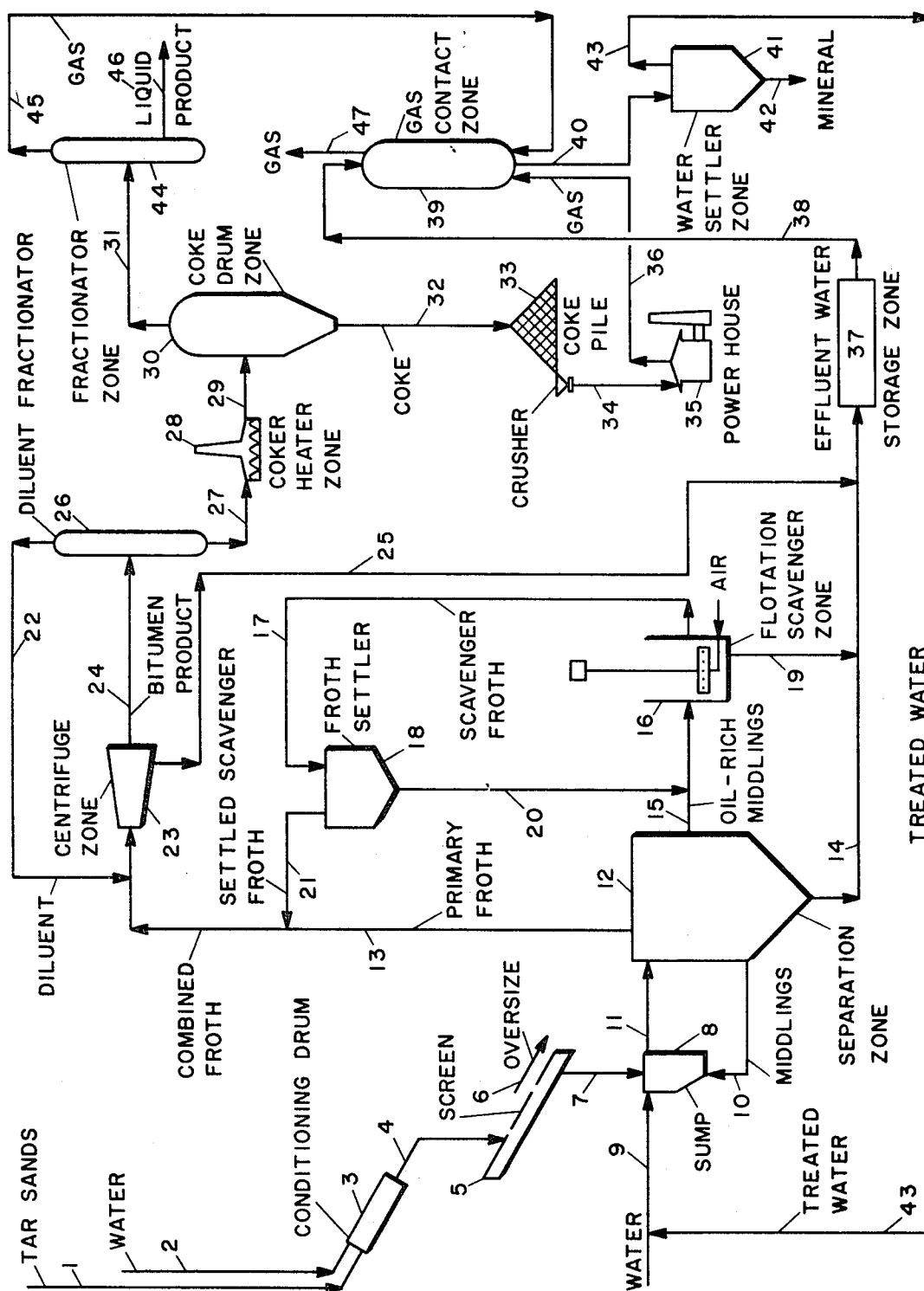
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[54] **HOT WATER PROCESS IMPROVEMENT**
9 Claims, 1 Drawing Fig.

[52] U.S. Cl. **208/11,**
209/5, 209/166
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167; 208/11; 210/68

ABSTRACT: The specification discloses an improvement to the hot water process for treating bituminous tar sands. By the invention water discharged from the hot water process is contacted with a gaseous effluent from the upgrading of bitumen to synthetic crude, the gaseous effluent containing sulfur dioxide, carbon dioxide, hydrogen sulfide, or mixtures of these gases. The contacting between the water and the effluent followed by settling produces clarified water which can be reused in the hot water process.





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HOT WATER PROCESS IMPROVEMENT

This invention relates to an improvement to the hot water process for treating bituminous tar sands. Numerous deposits of these 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 and contains typically 4.5 percent sulfur and 38 percent aromatics. Its specific gravity at 60° F. ranges typically from about 1.00 to about 1.06. The tar sands also contain clay and silt. Silt is defined a 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 rise 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 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 produce a gaseous product containing carbon dioxide and hydrogen sulfide and a high quality crude suitable for further processing.

The hot water process is described in detail in Floyd et al. U.S. application Ser. No. 509,589. Floyd et al. and now U.S. Pat. No. 3,401,110 issued Sept. 10, 1968 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 discarding 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 froth 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 sand 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 present invention relates to a process whereby the silt and clay containing water can be made suitable as at least a portion of the hot water process feed. Additionally the im-

provement of the present invention produces steam which can be used as a heat or power source in the hot water process, thus providing an integrated scheme of operation for preparing hydrocarbon products from tar sands.

By the present invention, clay-containing water discharged from the process is intimately contacted with a gaseous effluent from the upgrading of bitumen product to synthetic crude. The carbon dioxide, hydrogen sulfide and/or sulfur dioxide contained in this gaseous ejection dissolves in the water and causes flocculation of the contained clay. The clay is separated by settling and the clarified water is recycled back into the process. Additionally, some of the water is vaporized by contact with gas. This steam can be used as a source of heat or power to aid in making the process self-sustaining.

In this specification the term "gaseous effluent" is any gas product produced in any steps of the processing of the bitumen produced in the hot water separation. These gas products are further defined as containing gas selected from the groups consisting of carbon dioxide, sulfur dioxide, hydrogen sulfide, and combinations thereof. The flue gas produced in the burning of coke and the sour gas separated from coker distillate both as described infra are examples of gaseous effluent.

The invention can be described as an improvement to a process for treating bituminous tar sands where the 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, finely divided mineral, and bitumen, and a sand tailings layer; removing the bitumen froth layer, middlings layer, and sand tailings layer from the separation zone; resolving the bitumen froth layer to a liquid bitumen product; and treating the bitumen product to produce an upgraded synthetic crude oil and gaseous effluent containing carbon dioxide, sulfur dioxide, hydrogen sulfide, or mixtures of these gases. The improvement is describable as passing at least a portion of a hot gaseous effluent into intimate contact with at least a portion of the middlings to thereby flocculate the finely divided mineral in the middlings portion, and settling the middlings portion to produce a clarified water substantially reduced in mineral content.

In a preferred embodiment, the invention involves a process for treating bituminous tar sand which 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, finely divided mineral, and bitumen, and a sand tailings layer; removing the bitumen froth layer, middlings layer, and sand tailings layer from the separation zone; resolving the bitumen froth layer to a liquid bitumen product; and coking the bitumen product to produce coke and a coker distillate, combusting the coke to produce a hot flue gas comprising carbon dioxide and sulfur dioxide. The improvement is describable as passing the hot flue gas product into intimate contact with at least a portion of the middlings to dissolve carbon dioxide and sulfur dioxide in the portion, thereby flocculating the finely divided mineral in the portion, and settling the middlings portion to produce a clarified water substantially reduced in mineral content.

The process of the present invention is advantageous in two respects. Firstly, the steam formed by contact between the water and hot gaseous effluents can be used as a source of power and heat to provide a more self-sufficient overall hot water process. Secondly, the contacting with hydrogen sulfide, carbon dioxide, or sulfur dioxide containing gaseous effluents causes flocculation of clay in the discharge water. The flocculated clay can then be settled from the water and the treated water reused in the hot water process or discarded.

It is quite surprising that contact with gaseous effluents followed by settling clarifies the discharge water in view of its unique composition, i.e., water containing about 0.1 to 1.5 weight percent bitumen and up to about 20 weight percent mineral between 80 and 100 percent of which is fine clay of a size small than 2 microns. A substantial portion (about 50 percent by weight) of this mineral is fines of a size smaller than 0.2 micron. This fine clay has extremely poor settling charac-

teristics. It is this material in combination with other components of the water which makes this water portion difficult to clarify to a degree such that the water is suitable for reuse or discard.

The present invention is described in more detail with reference to the drawing which is a schematic representation of a preferred embodiment and an alternative embodiment of the present invention.

In the FIGURE, bituminous tar sands are fed into the system through line 1 where they first pass to a conditioning drum or muller 3. Water and steam are introduced from 2 and mixed with the sands. The total water so introduced is a minor amount based on the weight of the tar sands processed and generally is in the range of 10 to 45 percent by weight of the total mixture. Enough steam is introduced to raise the temperature in the conditioning drum to within the range of 130° to 210° F. and preferably to above 170° F. Monovalent alkaline reagents can also be added to the conditioning drum, usually in amount of from 0.1 to 3.0 tons per ton of tar sand. The amount of such alkaline reagent preferably is regulated to maintain a pH of the middlings layer in separation zone 12 within the range of 7.5 to 9.0. Best results seem to be obtained at a pH value of 8.0 to 8.5. The amount of the alkaline reagent that needs to be added to maintain a pH value of the middlings layer in separation zone 12 within the range of 7.5 to 9.0 may vary from time to time as the composition of the tar sands as obtained from the mine site varies. The best alkaline reagents to use for this purpose are caustic soda, sodium carbonate or sodium silicate, although any of the other monovalent alkaline reagents can be used if desired.

Mulling of the tar sands produces a pulp which then passes from the conditioning drum as indicated by line 4 to a screen indicated at 5. The purpose of screen 5 is to remove from the tar sand pulp any debris, rocks or oversized lumps as indicated generally at 6. The pulp then passes from screen 5 as indicated by 7 to a sump 8 where it is diluted with additional water from 9 and a middlings recycle stream 10. In the event the clay content of the tar sands is high, a relatively high rate of fresh or treated feed water introduction through 9 can be employed to compensate for the high clay introduction while a correspondingly high rate of transfer of middlings layer through line 15 can be maintained.

Modifications that may be made in the process as above described include sending a minor portion of the middlings recycle stream from line 10 through a suitable line (not shown) to the conditioning drum 3 to supply all or 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 5 to flush the pulp therethrough and into the sump. As a general rule the total amount of water added to the natural 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 15 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 16 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 gallons per ton when from 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 11 into the separation zone 12. 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 13, and a sand tailings layer which settles to the bottom to be withdrawn through line 14. An aqueous middlings layer between the froth and tailings layer contains silt and clay and some bitumen which failed to form froth. In order to prevent the buildup of clay in 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 in the system, the viscosity of the middlings layer will increase. Concurrently with such increase, an increase in the proportions of both the bitumen and the sand retained by the middlings will occur. If the clay and silt content is allowed to build up too high in the system, 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 separation step is operating properly, the middlings layer withdrawn through line 15 will contain a substantial amount of bitumen which did not separate. Hence the middlings layer withdrawn through line 15 is, for purpose of description, herein referred to as "oil-rich" or "bitumen-rich" middlings.

The oil-rich middlings stream withdrawn from separator 12 through line 15 is sent to a scavenger zone 16 wherein an air flotation operation is conducted to cause the formation of additional bitumen froth. The processing conducted in the scavenger zone 16 involves air flotation by 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 amounts. 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 16 through line 17 to a froth settler zone 18. A bitumen-lean middlings stream is removed from the bottom of the scavenger zone 16 via line 19.

In the settler zone 18, the scavenger froth forms into a lower layer of settler tailings which is withdrawn and recycled via line 20 to be mixed with bitumen-rich middlings for feed to scavenger zone 16 via line 15. In the settler zone an upper layer of upgraded bitumen froth forms above the tailings and is withdrawn through line 21 and is mixed with primary froth in line 13. The combined froths are at a temperature of about 160° F. The combined froths are further heated with steam and diluted with naphtha or another hydrocarbon diluent from line 22 to reduce the viscosity of the bitumen for centrifuging in centrifuge zone 23. This step is carried out in a battery of centrifuges operating in parallel. The bitumen-naphtha phase is discharged under pressure via line 24 while the water and mineral is discharged through line 25 and is passed to an effluent storage zone 37, along with the sand tailings from line 14 and the oil-lean middlings from line 19. The dilute bitumen product passes to a diluent fractionator zone 26 where the naphtha is removed and recirculated via line 22 to be mixed with froth prior to centrifuging. A resolved bitumen product, preferably containing less than 5 weight percent water and 1 weight percent of mineral, passes from the diluent fractionator zone via line 27. The bitumen product is heated up to about 900° F. in fired heaters 28 and is then charged via line 29 into coke zone 30. A coker distillate is produced from the bitumen in the coke zone. This distillate passes via 31 onto further processing. Coke is deposited as a solid which is cut from the coke drums in the zone 30 and is removed via line 32 to coke

pile zone 33 where it is crushed into a material suitable for combustion in powerhouse zone 35. The crushed coke is conveyed via 34 to the powerhouse zone 35 where it is combusted in boilers to produce steam, and a flue gas 36 containing carbon dioxide and sulfur dioxide.

The oil-lean middlings in line 19, the sand tailings from the separation zone 12, and the water and mineral from the centrifuge zone 23 are combined to form an effluent discharge which is delivered via line 14 to an effluent water storage zone 37. The effluent contains between 25 and 50 weight percent sand and silt material which is larger than about 2 microns. Preferably, the effluent storage zone is a pond area surrounded by deposited sand. The water in the effluent discharge percolates down through and over the deposited sand to the pond 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.

In a preferred embodiment of the present invention, pond water is withdrawn from storage zone 37 and is fed via 38 into contact zone 39 where it is contacted with flue gas from powerhouse zone 35. For the purpose of this invention, "pond water" is effluent water discharge from a hot water process which effluent has been settled to give a composition comprising water containing up to about 20 percent solids, between 80 percent and 100 percent of which is fine clay of a size smaller than 2 microns. The effluent discharge from a hot water process comprises middlings material of depleted bitumen content which has undergone final treatment, the sand tailings layer from the process, and other discharged water containing fractions which are not the primary products of the hot water process. The discharge is removed from the process areas as a slurry of about 25 to 60, typically 45, percent solids by weight. The effluent contains virtually all of the clay material which was present in the feed. Typically, the amount is 2 to 10 weight percent of the feed. This material is smaller than 2 microns and has extremely poor settling characteristics.

The contacting step conducted in zone 39 can comprise any procedure which will scrub the carbon dioxide and sulfur dioxide from the flue gas into the water. For example, the operation in zone 39 can be vertical countercurrent flow of the gas and the water through packed, plate or spray towers. The contact with the sulfur dioxide and carbon dioxide containing flue gas causes flocculation of the mineral contained in the pond water. Flocculation of mineral occurs through the formation of insoluble salts in the water which cause mineral flocs to form and also through the change in pH of the water below about 7.5. The effluent discharge from a hot water process has a pH ranging from about 7.5 to 9.0 typically about 8.3. In this range, the contained mineral material does not flocculate; however, lowering the pH below about 7.5 does cause flocculation.

After contact with the flue gas, the flocculated mineral is settled from the water. In a batch contacting operation, the settling can be conducted by merely discontinuing gas flow to the gas contact zone 39, permitting the fines to settle and recovering clarified water from the zone top and flocculated mineral from the zone bottom. In a continuous operation the water, treated with sulfur dioxide and carbon dioxide, can be continuously withdrawn from zone 39 via line 40 to settler zone 41 where the water is permitted to settle into flocculated mineral which is removed via 42 and discarded and into a clarified water fraction which can be introduced, via line 43, back into the system as all or a portion of the water in line 9 to the sump as shown or can be alternatively introduced into the system via lines 2 or 10 or as a screen wash or at any desired point of introduction into the process.

In another embodiment of the present invention, the distillate material from the coke drums 30 is fractionated in fractionator zone 44 into a sour gas fraction 45 containing hydrogen sulfide and a liquid product fraction 46. The sour gas fraction is then contacted with pond water in the gas contact zone 39. This contacting step flocculates mineral in the pond water and allows separation in a subsequent settling step in zone 41. Additionally in this embodiment, a significant amount of hydrogen sulfide is removed from the sour gas to give a gas product 47 more suitable for further use or processing.

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 19 from the flotation scavenger zone 16 can be directly treated by the invention to make these middlings suitable for recycle back into the process. Also the middlings in line 10 can be treated before recycle into sump 8 for dilution of the tar sands pulp.

What I claim is:

1. In a process for treating pond water, discharged from a tar sands treating process for separating bitumen from tar sands, and containing finely divided mineral, the improvement which comprises: treating said separated bitumen to produce an upgraded synthetic crude oil and gaseous effluent containing carbon dioxide, sulfur dioxide, hydrogen sulfide or mixtures of these gases; passing said gaseous effluent into intimate contact with at least a portion of said pond water to thereby flocculate finely divided mineral in said portion; and settling said pond water portion to produce a clarified water substantially reduced in mineral content.

2. The process of claim 1 wherein said tar sands treating process comprises forming a mixture of tar sand and water; passing said mixture into a separation zone to form an upper bitumen froth layer, a middlings layer comprising water, finely divided mineral, and bitumen, and a sand tailings layer; removing said bitumen froth layer, middlings layer, and sand tailings layer from said separation zone; resolving said bitumen froth layer to a separated bitumen product; and wherein said portion of pond water contacted with gaseous effluent comprises at least a portion of said middlings.

3. The process of claim 2 in which said clarified water substantially reduced in mineral content is recycled into the bituminous tar sands treating process as at least a portion of the water utilized to form said mixture of tar sands and water.

4. The process of claim 2 in which said bitumen product is coked to produce coke and a coker distillate; said coke is combusted to produce a hot flue gas containing carbon dioxide and sulfur dioxide; and said hot flue gas is utilized as the gaseous effluent for contact with said middlings portion.

5. The process of claim 4 in which said clarified water substantially reduced in mineral content is recycled into the bituminous tar sands treating process as at least a portion of the water utilized to form said mixture of tar sands and water.

6. The process of claim 2 in which said bitumen product is coked to produce coke and a coker distillate, said coker distillate is fractionated to produce a liquid product and a sour gas containing hydrogen sulfide; and said sour gas is utilized as the gaseous effluent for contact with said middlings portion.

7. The process of claim 6 in which said clarified water substantially reduced in mineral content is recycled into the bituminous tar sands treating process as at least a portion of the water utilized to form said mixture of tar sands and water.

8. In a process for separating bitumen from bituminous tar sands which comprises forming a pulp of said bituminous sands with a minor amount of water in a pulping zone; removing pulp therefrom, and mixing the same with hot water and a hereinafter specified recycle stream in a dilution zone; flushing the mixture from the dilution zone to a separation zone; settling the mixture in the separation zone to form an upper bitumen froth layer, a middlings layer comprising water,

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mineral, bitumen and a sand tailings layer; separately removing the upper bitumen froth layer and the sand tailings layer; removing a stream of middlings layer from the separation zone and passing it to the dilution zone as the aforesaid recycle steam; passing a second stream of middlings layer to a separate recovery zone and therein subjecting it to a flotation to recover additional amount of bitumen froth; removing from said separate recovery zone middlings material of depleted bitumen content comprising mineral dispersed in water; centrifuging said upper bitumen froth layer and said additional amount of bitumen froth to produce a bitumen product substantially reduced in water and mineral content; coking said bitumen product to produce coke and a coker distillate; com-

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busting said coke to produce a flue gas comprising carbon dioxide and sulfur dioxide; the improvement which comprises passing said hot flue gas into intimate contact with at least a portion of said middlings material of depleted bitumen content to dissolve carbon dioxide and sulfur dioxide in said portion thereby flocculating said mineral in said portion; and settling said middlings portion to produce a clarified water substantially reduced in mineral content.

9. The process of claim 8 in which said clarified water substantially reduced in mineral content is recycled into the bituminous tar sands treating process as at least a portion of the water utilized to dilute said pulp and said dilution zone.

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