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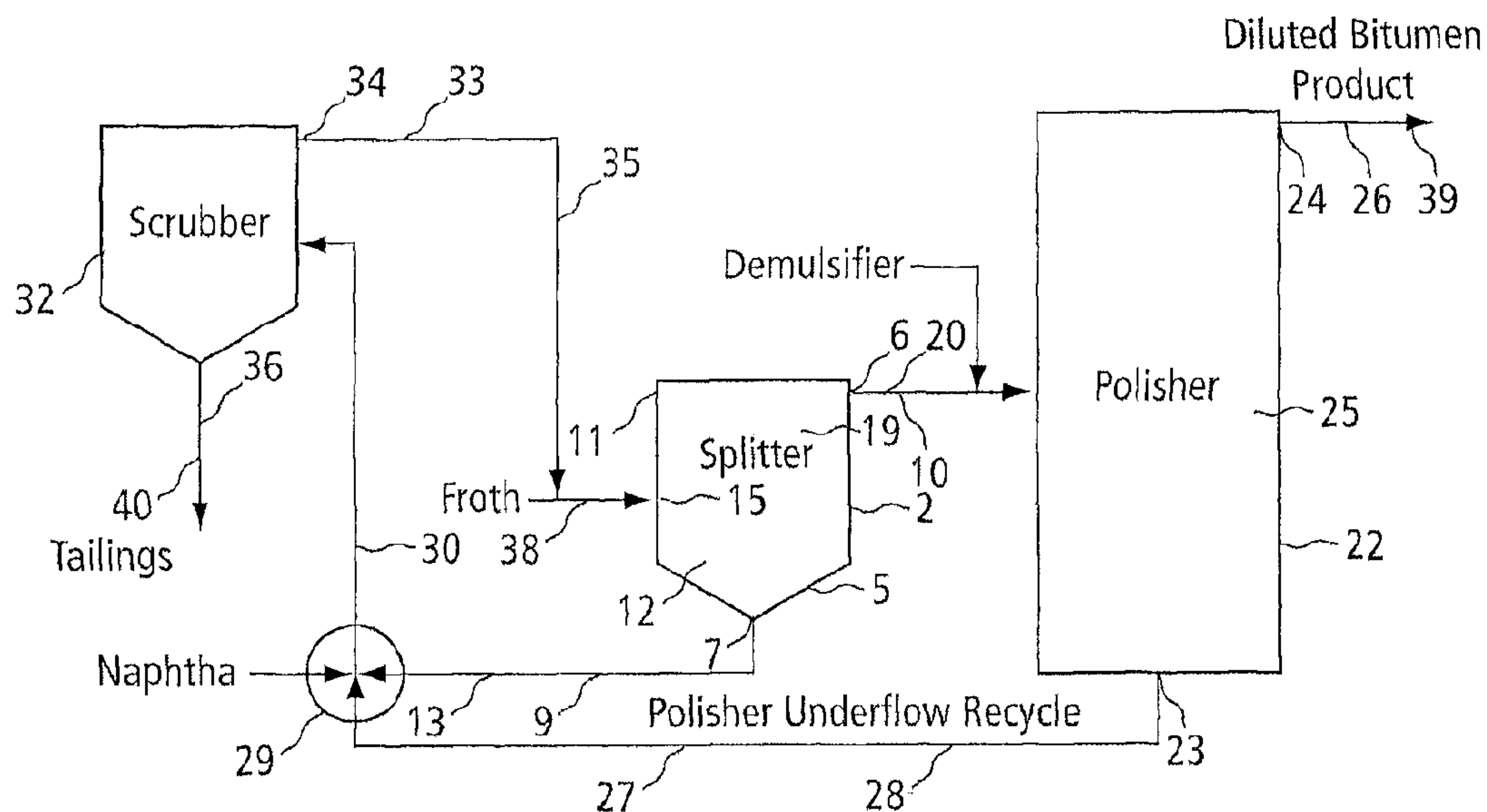
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(54) **Titre : METHODE DE TRAITEMENT DE MOUSSE DE BITUME COMPRENANT L'AJOUT DE SILICATES**

(54) **Title: SILICATES ADDITION IN BITUMEN FROTH TREATMENT**



(57) **Abrégé/Abstract:**

A method for processing a bitumen froth comprising bitumen, water and solids including fine solids for reducing the solids concentration in diluted bitumen is provided comprising diluting the bitumen froth with a hydrocarbon diluent to form a dilfroth; adding a sufficient amount of a silicate to the dilfroth to cause a substantial amount of fine solids to associate with the water instead of the diluted bitumen; and allowing the diluted bitumen to separate from the water containing the substantial amount of fine solids to produce a dilbit having less than 3 percent by weight solids.

ABSTRACT

A method for processing a bitumen froth comprising bitumen, water and solids including fine solids for reducing the solids concentration in diluted bitumen is provided comprising diluting the bitumen froth with a hydrocarbon diluent to form a dilfroth; adding a sufficient amount of a silicate to the dilfroth to cause a substantial amount of fine solids to associate with the water instead of the diluted bitumen; and allowing the diluted bitumen to separate from the water containing the substantial amount of fine solids to produce a dilbit having less than 3 percent by weight solids.

SILICATES ADDITION IN BITUMEN FROTH TREATMENT

FIELD OF THE INVENTION

5 The present invention relates generally to a bitumen froth treatment process for reducing the fine solids concentration in hydrocarbon diluent-diluted bitumen ("dilbit"). In particular, silicates, such as sodium silicates, are added during bitumen froth treatment stage(s) to aid in the removal of fine solids such as clays with the water phase.

BACKGROUND OF THE INVENTION

10 Oil sand, as known in the Athabasca region of Alberta, Canada, comprises water-wet, coarse sand grains having flecks of a viscous hydrocarbon, known as bitumen, trapped between the sand grains. The water sheaths surrounding the sand grains contain very fine clay particles. Thus, a sample of oil sand, for example, might
15 comprise 70% by weight sand, 14% fines, 5% water and 11% bitumen (all % values stated in this specification are to be understood to be % by weight except where otherwise provided).

For the past 25 years, the bitumen in Athabasca oil sand has been commercially recovered using a water-based process. In the first step of this process, the oil sand
20 is slurried with process water, naturally entrained air and, optionally, caustic (NaOH). The slurry is mixed, for example in a tumbler or pipeline, for a prescribed retention time, to initiate a preliminary separation or dispersal of the bitumen and solids and to induce air bubbles to contact and aerate the bitumen. This step is referred to as "conditioning".

25 The conditioned slurry is then further diluted with flood water and introduced into a large, open-topped, conical-bottomed, cylindrical vessel (termed a primary separation vessel or "PSV"). The diluted slurry is retained in the PSV under quiescent conditions for a prescribed retention period. During this period, aerated bitumen rises and forms a froth layer, which overflows the top lip of the vessel and is

conveyed away in a launder. Sand grains sink and are concentrated in the conical bottom. They leave the bottom of the vessel as a wet tailings stream containing a small amount of bitumen. Middlings, a watery mixture containing solids and bitumen, extend between the froth and sand layers.

5 The wet tailings and middlings are separately withdrawn, combined and sent to a secondary flotation process. This secondary flotation process is commonly carried out in a deep cone vessel wherein air is sparged into the vessel to assist with flotation. This vessel is referred to as the TOR vessel. The bitumen recovered by flotation in the TOR vessel is recycled to the PSV. The middlings from the deep
10 cone vessel are further processed in induced air flotation cells to recover contained bitumen.

The bitumen froths produced by the PSV and flotation cells are combined and subjected to cleaning, to reduce water and solids contents so that the bitumen can be further upgraded. More particularly, it has been conventional to dilute this
15 bitumen froth with a light hydrocarbon diluent, for example, with naphtha, to increase the difference in specific gravity between the bitumen and water and to reduce the bitumen viscosity, to thereby aid in the separation of the water and solids from the bitumen. This diluent diluted bitumen froth is commonly referred to as "dilfroth". It is desirable to "clean" dilfroth, as both the water and solids pose fouling and corrosion
20 problems in upgrading refineries. By way of example, the composition of naphtha-diluted bitumen froth typically might have a naphtha/bitumen ratio of 0.65 and contain 20% water and 7% solids. It is desirable to reduce the water and solids content to below about 3% and about 1%, respectively.

25 Separation of the bitumen from water and solids may be done by treating the dilfroth in a sequence of scroll and disc centrifuges. Alternatively, the dilfroth may be subjected to gravity separation in a series of inclined plate separators ("IPS") in conjunction with countercurrent solvent extraction using added light hydrocarbon diluent. However, these treatment processes still result in bitumen often containing undesirable amounts of solids and water.

More recently, a staged settling process (often referred to as Stationary Froth Treatment or SFT) for cleaning dilfroth was developed as described in U.S. Patent No. 6,746,599, whereby dilfroth is first subjected to gravity settling in a splitter vessel to produce a splitter overflow (raw dilbit) and a splitter underflow (splitter tails) and then the raw dilbit is further cleaned by gravity settling in a polisher vessel for sufficient time to produce an overflow stream of polished dilbit and an underflow stream of polisher sludge. Residual bitumen present in the splitter tails can be removed by mixing the splitter tails with additional naphtha and subjecting the produced mixture to gravity settling in a scrubber vessel to produce an overhead stream of scrubber hydrocarbons, which stream is recycled back to the splitter vessel.

The froth treatment product stream is naphtha-diluted bitumen (dilbit) that is specified to contain less than 2 % water and less than 0.9 %. High solids content in the diluted bitumen is detrimental to upgrading process equipment. Fine solids are believed to be nucleation sites for coke formation that will foul equipment such as heat exchangers. Solids have been shown to plug the interstitial spaces between catalysts, accelerating their loss of activity. Some typical streams that are fed to process units that utilize a catalyst, and have been identified as being prone to carrying high solids content are the LGO drawn off the DRUs, the feed to the LC-Finer, and even the HGO coming off the Coker, which is due to fine clay solids passing through the Coker. Solids in all of these streams can accelerate the fouling of the catalysts in their respective processing units.

The amount of solids present in dilbit can vary depending on the type of ore used, as some ores may have more solids and fines content than others. Without being limited to theory, it is further believed that alterations in the wettability of the fine clay materials that are being processed in the froth treatment plant may also contribute to an increase in fines. Thus, in some instances, it appears that more fines may reporting to the froth treatment product stream relative to the water content – a deviation from the ‘rule of thumb’ that states the water-to-solids ratio in diluted-bitumen rich streams is about four.

For a naphtha-based gravity settling froth treatment process, such as SFT, fine clays have been hypothesized to cause process instabilities, particularly the formation of emulsions stabilized by fine clays. In addition, these fine clay particles may contribute to the rag layer formation, a persistent multiple emulsion that forms as a low quality neutral-density phase in the splitter. Further, fines in the polisher vessel underflow may assist in the development of complex rheology that encumbers recovery of bitumen and the efficient transport of tailings. The adsorption of surface-active solids at the water-diluted bitumen interface is postulated as one of the main contributors to rag formation and stable water-in-oil emulsions in froth treatment.

SUMMARY OF THE INVENTION

Oil sand clays (interburden clays) are found to consist mainly of the kaolinite and illite clays by X-ray diffraction analysis. It was originally believed that oil sand clays were water wet solids and thus would partition in water phase. Surprisingly, however, it was discovered that a portion of the interburden clay material also appeared to preferentially partition into the oil. Without being bound to theory, it is believed that the reason for the interburden clays having a hydrophobic behavior might be due to the presence of naphthenic acid in oil sand. In general, process water contains 100 ppm or 0.01% naphthenic acid and oil sand contains up to 500 ppm. Thus, the presence of naphthenic acid may change the wettability of water wet clays such as kaolinite into oil wet clay.

The concept of using silicates such as sodium silicates as a process aid in the oil sand industry is not new. However, the prior patents and publications on sodium silicates addition for oil sand processing have only focused their use in the primary extraction process and not the upgrading of bitumen froth.

Thus, in one aspect, the present application is directed to the use of silicates, such as sodium silicates, in a continuous process as an additive in a diluted bitumen froth feed to promote the association of fine solids with the water phase.

A method for processing a bitumen froth comprising bitumen, water and solids including fine solids for reducing the solids concentration is provided, comprising:

- diluting the bitumen froth with a hydrocarbon diluent to form a dilfroth;
- adding a sufficient amount of a silicate to the dilfroth to cause a substantial amount of fine solids to associate with the water instead of the diluted bitumen; and
- allowing the diluted bitumen to separate from the water containing the substantial amount of fine solids to produce a dilbit having less than about 3% by weight solids.

10 In one embodiment, the dilbit produced has a solids concentration of less than about 1% by weight solids.

15 In one embodiment, the bitumen froth is diluted with naphtha to give a naphtha to bitumen ratio of about 0.5:1 to about 1:1. It is understood that the diluted bitumen in the dilfroth can be separated from the water containing the fine solids by any number of processes, such as gravity settling in staged gravity settlers, a sequence of scroll and disc centrifuges, gravity separation in a series of inclined plate separators ("IPS"), optionally, in conjunction with countercurrent solvent extraction using added light hydrocarbon diluent, etc.

20 By "silicate" is meant any of a wide variety of compounds containing silicon, oxygen and one or more metals with or without hydrogen, for example, a sodium silicate having the general formula $x\text{Na}_2\text{O} \cdot y\text{SiO}_2$.

25 Without being bound to theory, it is believed that during processing of diluted bitumen froth, stable water-in-oil emulsions may persist due to the presence of fine clay solids. Further, much of the fine clay solids, for example, kaolinite and illite, were found to be partially oil-wet, thereby tending to associate with the bitumen phase rather than the water phase. The addition of silicates, for example, sodium meta silicate Na_2SiO_3 , is believed to change the wettability of these clay solids from

oil-wet to water-wet. This allows the clay solids to settle into the aqueous phase rather than the oil phase. Further, it is believed that the silicates also may break up the water-in-oil emulsions, which may be stabilized by the partially oil-wet clay solids, and thus release more clay solids to the aqueous phase.

5 In addition, for gravity settling froth treatment processes, for example, SFT, a rag layer tends to form between the bitumen phase and the tailings phase. It is believed that this rag layer is stabilized by the presence of fine clays. The addition of silicates can reduce the rag layer, which may also result in better recovery and quality of dilbit.

10 DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic showing one embodiment of a bitumen froth treatment process useful in the present invention.

15 FIGS. 2(a), 2(b) and 2(c) are graphs showing the effect on the mass percent of fine solids in raw dilbit when dilfroth was treated with increasing amounts (0.0001, 0.01 and 0.1%) of sodium silicate.

DESCRIPTION OF THE PREFERRED EMBODIMENT

20 In one aspect, the invention is concerned with a bitumen froth treatment process for reducing the fine solids content of hydrocarbon diluent-diluted bitumen. In the embodiment shown in FIG. 1, the hydrocarbon diluent is process naphtha. It is understood, however, that other low molecular weight hydrocarbon diluents could also be used.

25 FIG. 1 shows a stationary bitumen froth treatment facility comprising gravity settlers, which can be used in one embodiment of the present invention. It is understood that other bitumen froth treatment facilities can also be used, for example, facilities comprising scroll centrifuges, disc centrifuges, inclined plate separators, or various combinations thereof. For example, a sequence of scroll and disc centrifuges or a series of inclined plate separators can be used.

Bitumen froth is initially received from an extraction facility (not shown), which extracts bitumen from oil sand using a water extraction process known in the art. The bitumen froth, as received, typically comprises about 60% bitumen, about 30% water and about 10% solids.

5 With reference now to FIG. 1, a hydrocarbon diluent such as naphtha is mixed with bitumen froth, for example, in a mixer (not shown) to provide diluent-diluted bitumen froth (dilfroth). In one embodiment, the naphtha may at least partly be supplied by recycling scrubber naphtha, produced as described below. The naphtha is supplied in an amount such that the naphtha to bitumen ratio of the dilfroth is preferably in the
10 range 0.5-1.0, most preferably about 0.65. A silicate, for example, sodium silicate, is also added to the dilfroth at a concentration ranging between about 0.0001 to about 0.1% wt/wt or more.

The dilfroth 38 is then fed into the chamber of a gravity settler vessel, referred to in FIG. 1 as splitter 2, for example, through an inlet means (not shown). In this
15 embodiment, splitter 2 has a conical bottom 5. It has underflow and overflow outlets 7, 6 at its bottom and top ends, respectively. The diluted bitumen froth is temporarily retained in the splitter 2 for a sufficient length of time to allow a substantial portion of the solids and water to separate from the diluted bitumen. The splitter overflow is referred to heretofore as raw dilbit 20. Line 9 withdraws a stream of splitter tails
20 13 through the underflow outlet 7. Splitter overflow line 10 collects an overflow stream of raw dilbit 20.

As previously mentioned, it is believed that silicates change the surface properties of the fine solids, causing them to associate with the water phase, rather than the oil phase. This will result in the fine solids leaving the primary settler with the water in
25 the tailings streams, not the product, effectively reducing the solids content in the diluted bitumen (dilbit).

The rate at which dilfroth 38 is fed to the splitter 2 and the diameter of the cylindrical section 11 of the splitter 2 are selected to ensure a preferred flux of <10 m/h, for example, in a range between about 3 to about 9 m/h. The bottom layer 12 of splitter

tails 13 comprises mainly sand and aqueous middlings, said tails containing some hydrocarbons, and the top layer 19 of raw dilbit 20 comprises mainly hydrocarbons containing some water and a reduced amount of fines (clay particles). Preferably, the incoming dilfroth 38 may be introduced into the middlings 15 across the cross-section of the splitter 2, at an elevation spaced below the top layer of raw dilbit 20 and well above the underflow outlet 7.

Preferably, the rates of feeding dilfroth 38 and withdrawing splitter tails 13 are controlled to maintain the elevation of the interface generally constant. It is of course desirable to keep the interface away from the bottom of the splitter 2, to minimize hydrocarbon losses with the splitter tails 13. For example, one may monitor the composition of the splitter tails 13 and vary the rates with the objective of keeping the splitter tails hydrocarbon content below a predetermined value, usually less than 35% hydrocarbon (i.e., naphtha plus bitumen), or less than 20% bitumen.

The raw dilbit 20 produced through the splitter overflow outlet 6 routinely comprises less than about 3% solids. However, it may be desirable to decrease the solids concentration even more. Thus, in one embodiment, the raw dilbit 20 is pumped through line 10 to a second gravity settler vessel, preferably a flat-bottomed, vapor-tight tank, referred to as the polisher 22, and subjected to further gravity settling therein. It is understood that a cone bottomed tank could also be used. A demulsifier as known in the art may be added to the raw dilbit 20 as it moves through the line 10. In this embodiment, the polisher 22 has a bottom underflow outlet 23 and a top overflow outlet 24.

The raw dilbit and optional demulsifier is temporarily retained for a prolonged period (for example, <24 hours) in the polisher chamber 25. Water droplets coalesce and settle, together with most of the remaining fine solids. Polisher dilbit 39 is removed as an overflow stream from the polisher 22 through line 26. The polisher dilbit 39 is found to comprise hydrocarbons, typically containing <3.0 wt. % water and <1.0 wt. % solids. Polisher sludge 27, comprising water, solids and typically between about

20-70% hydrocarbons, or 12-40% bitumen, is removed from the polisher 22 as an underflow stream through line 28.

The splitter tails 13 produced through the splitter underflow outlet 7 are pumped through line 9, optionally first to a mixer/vessel 29, where it is mixed with polisher sludge 27 and naphtha to produce a gravity settler feed 30 preferably having a naphtha:bitumen ratio in the range 4:1 to 10:1, more preferably about 6:1 to about 8:1 or greater. Additional sodium silicate may be added to the gravity settler feed 30 prior to introducing the feed to a third gravity settler vessel, scrubber 32. In one embodiment, less than 0.1% wt/wt sodium silicate is added. The gravity settler feed 30 (with or without additional sodium silicate) is then temporarily retained in the scrubber 32 (for example for 20 to 30 minutes) and subjected to gravity settling therein.

The scrubber overflow stream 33 of hydrocarbons, mainly comprising naphtha and lighter bitumen, is removed through an overflow outlet 34 and in one embodiment may be recycled through line 35 to splitter 2. Scrubber underflow stream of scrubber tails 36, comprising water and solids containing some hydrocarbons, is removed via line 40 and forwarded to a naphtha recovery unit (not shown).

Example 1

A bench-scale pilot plant of a continuous naphtha-based froth treatment gravity setting operation with a configuration similar to that shown in FIG. 1 was used in the following example. Varying amounts of sodium silicate (0.0001, 0.01 and 0.1% sodium silicate, wt/wt based on bitumen froth) were added to bitumen froth diluted with naphtha. In this example, bitumen froth contained an average of about 60.1 wt% bitumen, about 28.4 wt% water and about 11.5 wt% solids. The naphtha to bitumen ratio was 0.6.

The treated dilfroth was then fed to a splitter vessel and the splitter overflow (raw dilbit) was analyzed as to the mass percent of fine solids that are present in the splitter overflow versus the diameter (μm) of the fines. FIGS. 2(a) to 2(c) show that

the addition of sodium silicate resulted in less fine solids (e.g., solids having a diameter less than 10 μm) present in the raw dilbit when compared to no addition of sodium silicate. Further, the reduction in fine solids was shown to be dose dependent. Thus, a total reduction in solids was shown to be $\sim 0.1\%$ absolute or $\sim 10\%$ solids reduction in splitter overflow product (raw dilbit). The amount of solids in the raw dilbit is further reduced in the polisher, resulting in a polisher overflow product (polished dilbit) having less than 3%, and more likely, less than 1% solids.

Example 2

Bench-scale batch tests were also performed to see what effect the addition of sodium silicates would have on the stable rag layer that forms between the diluted bitumen layer and the water layer in the splitter vessel during gravity settling of the diluted bitumen froth. It is believed that the rag layer may be a result of stable water-in-oil emulsions persisting, primarily due to the clay solids present in the diluted bitumen froth. The rag layer is a mixture of partially oil-wet solids, oil and water-in-oil emulsions. Much of the clay solids are kaolinite and illite. The formation of such a rag layer prevents complete separation of the diluted bitumen from the water and solids.

In this example, bitumen froth containing water and fine solids including clays (approximately 60% bitumen, 30% water and 10% fine solids) was first diluted with naphtha to give a dilfroth having a naphtha to bitumen ratio of about 0.7:1. Sodium meta silicate (Na_2SiO_3) from a 10^{-4}M solution was then added to the dilfroth to increase the pH from about 8.2 to about 8.5 and the dilfroth was allowed to stand for several minutes to allow the diluted bitumen to collect at the top and the water and fine solids collect at the bottom.

When compared to untreated dilfroth, Na_2SiO_3 -treated dilfroth had a much less pronounced rag layer. Without being bound to theory, it is believed that the addition of Na_2SiO_3 makes the clay solids more water-wet, which can enhance the coalescence of emulsions. Further, if the clay solids become more water-wet, in the rag layer, some of the adsorbed oil on the solid surface can be replaced by water,

and the density of the rag material will be greater than that of water, causing it to settle to the bottom.

WE CLAIM:

1. A method for processing a bitumen froth comprising bitumen, water and solids including fine solids for reducing the solids concentration in diluted bitumen, comprising:

diluting the bitumen froth with a hydrocarbon diluent to form a dilfroth;

adding a sufficient amount of a silicate to the dilfroth to cause an amount of the fine solids to associate with the water instead of the diluted bitumen; and

allowing the diluted bitumen to separate from the water containing the amount of fine solids to produce a dilbit having less than 3 percent by weight solids.

2. The method as claimed in claim 1 wherein the produced dilbit comprises less than 1 percent by weight solids.

3. The method as claimed in claim 1 wherein the hydrocarbon diluent is naphtha.

4. The method as claimed in claim 1 wherein the silicate is sodium silicate.

5. The method as claimed in claim 1 wherein hydrocarbon diluent is added to the bitumen froth to give a diluent to bitumen ratio of about 0.5:1 to about 1:1.

6. The method of claim 1 wherein the diluted bitumen is separated from the water and fine solids in a gravity settler vessel.

7. The method of claim 1 wherein the diluted bitumen is separated from the water and fine solids in at least one scroll centrifuge, at least one disc centrifuge or at least one sequence of scroll and disc centrifuges.

8. The method of claim 1 wherein the diluted bitumen is separated from the water and fine solids in at least one inclined plate separator.

9. A method for processing a bitumen froth comprising bitumen, water and solids including fine solids for reducing the solids concentration in diluted bitumen, comprising:

diluting the bitumen froth with a hydrocarbon diluent to form a diluted bitumen froth;

adding a sufficient amount of a silicate to the diluted bitumen froth to cause an amount of fine solids to associate with the water instead of the diluted bitumen;

subjecting the diluted bitumen froth to gravity separation in a first gravity settler vessel to produce a first diluted bitumen overflow having less than 3 percent by weight solids and a solids underflow; and

subjecting the first diluted bitumen overflow to gravity separation in a second gravity settler vessel to produce a second diluted bitumen overflow having less than 1 percent by weight solids.

10. The method as claimed in claim 9 wherein the hydrocarbon diluent is naphtha.

11. The method as claimed in claim 9 wherein the silicate is sodium silicate.

12. The method as claimed in claim 9 wherein hydrocarbon diluent is added to the bitumen froth to give a diluent to bitumen ratio of about 0.5:1 to about 1:1.

13. The method as claimed in claim 9, further comprising:

diluting the solids underflow from the first gravity settler vessel with hydrocarbon diluent and subjecting the diluted solids underflow to gravity separation in a third gravity settler vessel to produce a third diluted bitumen overflow.

14. The method as claimed in claim 13, further comprising:

adding a silicate to the diluted solids underflow prior to adding it to the third gravity settler vessel.

FIG. 1

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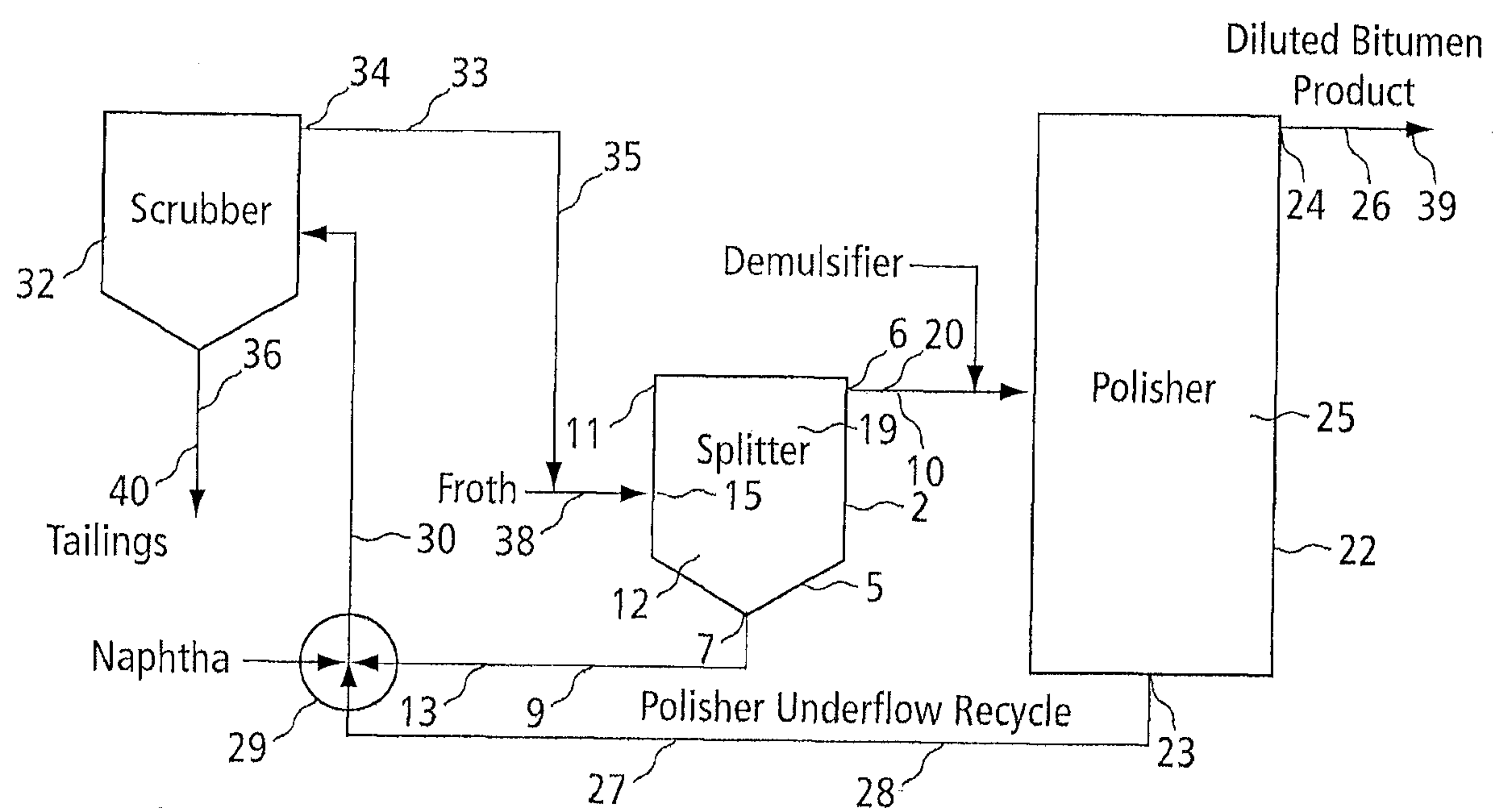


FIG. 2a and 2b

2/3

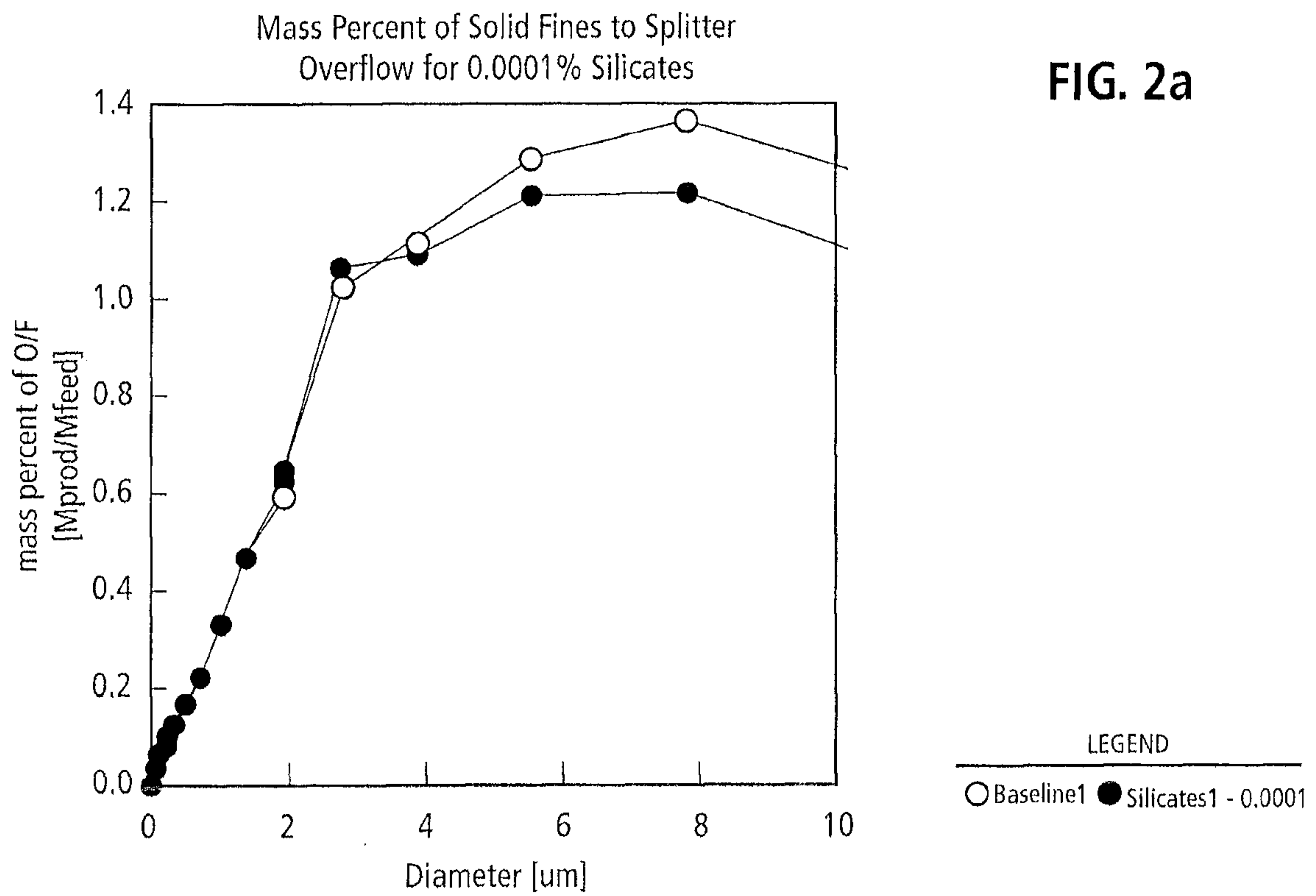


FIG. 2a

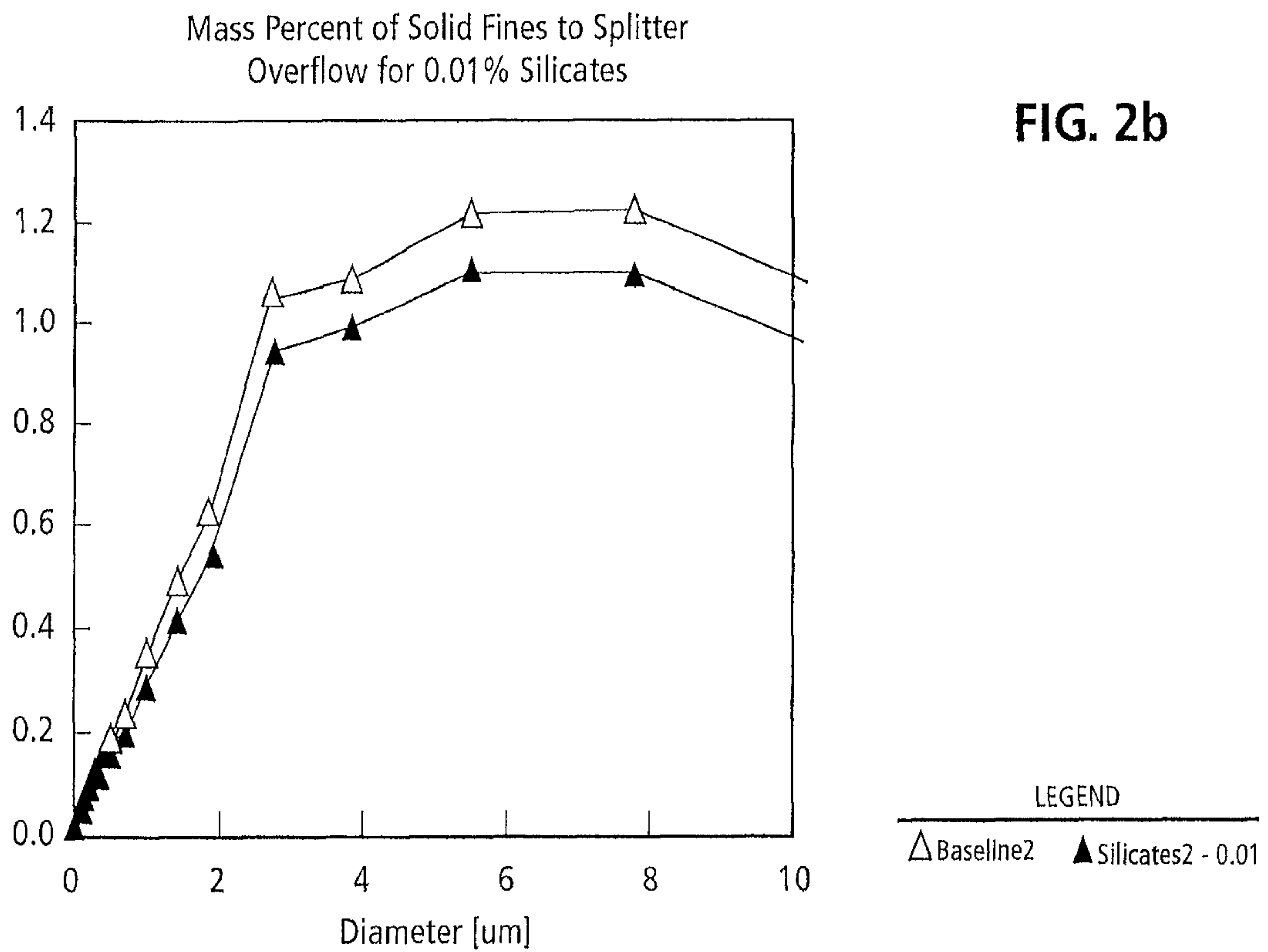
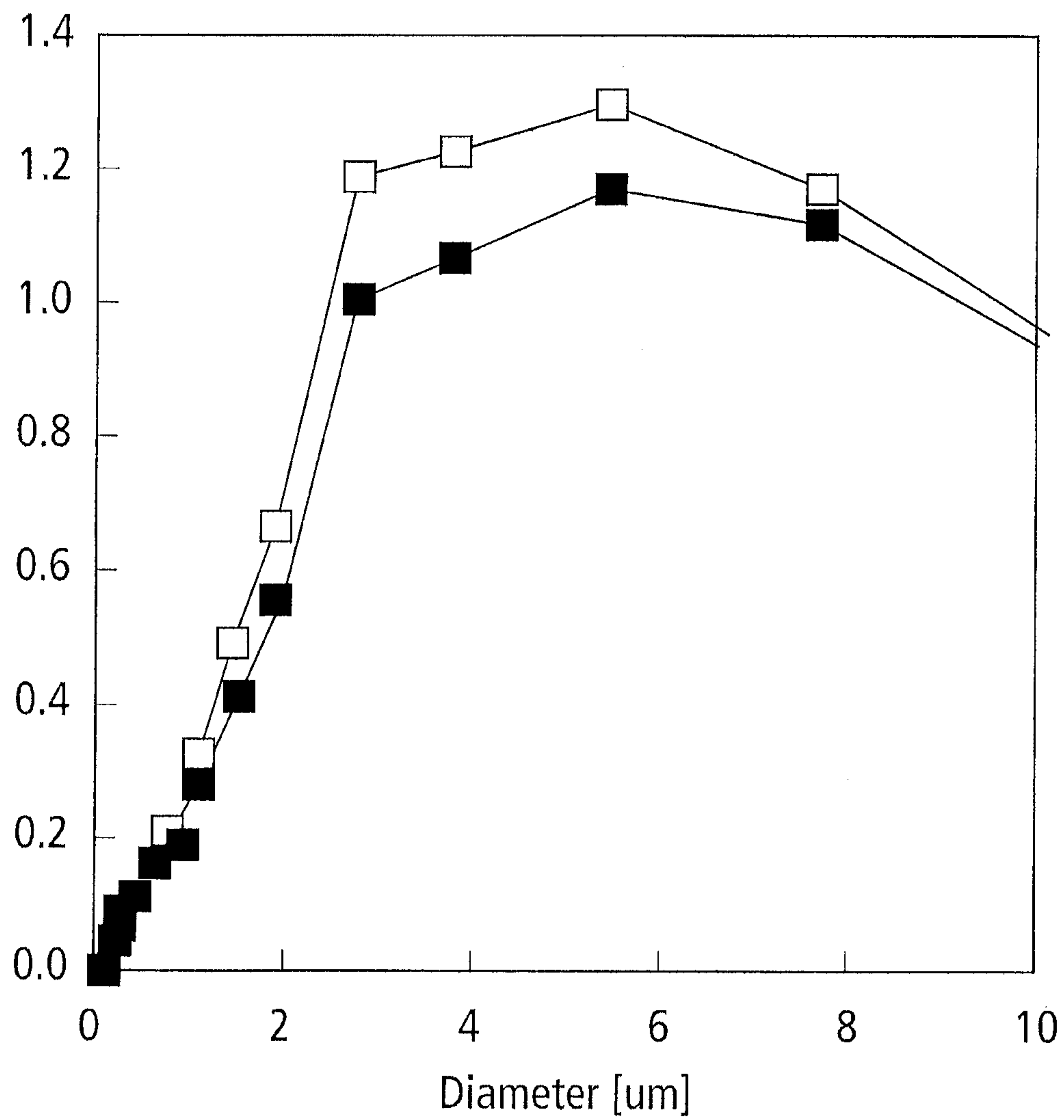


FIG. 2b

FIG. 2c

3/3

Mass Percent of Solid Fines to Splitter
Overflow for 0.1% Silicates



LEGEND

□ Baseline3 ■ Silicates3 - 0.1

