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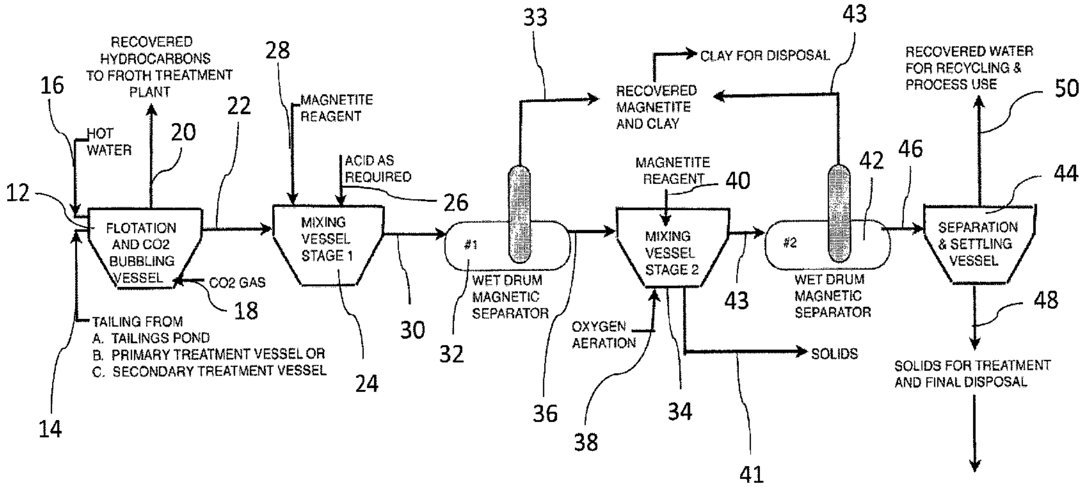
(54) Titre : TRAITEMENT DE RESIDUS AU MOYEN DE PARTICULES MAGNETIQUES
(54) Title: TREATMENT OF TAILINGS WITH MAGNETIC PARTICLES



(57) Abrégé/Abstract:
A method of treating tailings using magnetic particles comprising the steps of: obtaining tailings from a mining operation, the tailings comprising at least water, suspended clay particles, and hydrocarbons; removing at least a portion of the hydrocarbons from the tailings; adjusting the tailings to a pH range that results in a surface charge difference between the suspended clay particles and magnetic particles; mixing the magnetic particles into the tailings and permitting the magnetic particles and clay particles to agglomerate; and removing the agglomerated clay and magnetic particles from the tailings.

ABSTRACT OF THE DISCLOSURE

A method of treating tailings using magnetic particles comprising the steps of: obtaining tailings from a mining operation, the tailings comprising at least water, suspended clay particles, and hydrocarbons; removing at least a portion of the hydrocarbons from the tailings; adjusting the tailings to a pH range that results in a surface charge difference between the suspended clay particles and magnetic particles; mixing the magnetic particles into the tailings and permitting the magnetic particles and clay particles to agglomerate; and removing the agglomerated clay and magnetic particles from the tailings.

TREATMENT OF TAILINGS WITH MAGNETIC PARTICLES

TECHNICAL FIELD

[0001] This relates to a method of removing clay particles from waste tailings generated by mining operations, such as the removal of clay particles from tailings generated by heavy oil extraction, using magnetic particles.

BACKGROUND

[0002] Small clay particles are a problem in waste tailings from various mining operations and typically lead to difficult waste management issues. An example is the tailings ponds of Northern Alberta associated with oil sands operations. These waste tailings are a complex matrix of chemicals including water, hydrocarbons, clay, heavy metals, ammonia and others. These tailings, referred to as a stable emulsion, have resisted efforts for decades to acceptably separate the solids from the water and hydrocarbons.

[0003] It is generally believed in the oil industry that the mixed clays found in the raw oil sands of Northern Alberta are mainly responsible for the resistance of this emulsion to separation when treatment methods are applied. Clay fines and the interaction with added caustic soda used in the bitumen extraction process also contribute to the gel-like structure in the tailings. Current settling time for the clay/solids in the Fort McMurray tailings ponds is estimated to be many hundreds of years.

[0004] In the case of tailings from oil sands, the tailings also contain a residual amount of un-extracted bitumen, which adds operational complexity to the tailings treatment problem. This residual bitumen, related hydrocarbons and naphthenic acid have created a growing environmental liability issue for the heavy oil industry. In addition, the tailings ponds contain an average of close to 50% water by weight and therefore could be a significant source of water for bitumen production if the water could be extracted.

SUMMARY

[0005] According to an aspect, there is provided a method of treating tailings using magnetic particles, the method comprising the steps of obtaining tailings from a mining operation, the tailings comprising at least water, suspended clay particles, and hydrocarbons, removing at least a portion of the hydrocarbons from the tailings, adjusting the tailings to a pH range that results in a surface charge difference between the suspended clay particles and magnetic particles, mixing the magnetic particles into the tailings and permitting the magnetic particles and clay particles to agglomerate, and removing the agglomerated clay and magnetic particles from the tailings.

[0006] According to another aspect, removing at least a portion of the hydrocarbons may comprise aerating the mixture to generate a froth of the hydrocarbons prior to adding the magnetic particles.

[0007] According to another aspect, aerating the mixture may comprise injecting CO_2 gas.

[0008] According to another aspect, the hydrocarbons may be reduced to less than about 100 ppm.

[0009] According to another aspect, the magnetic particles have a size of about 1 nm to about 100 nm.

[0010] According to another aspect, the magnetic particles may be magnetite.

[0011] According to another aspect, the method may further comprise the step of adjusting the pH of the mixture to between about 6 - 7.

[0012] According to another aspect, the magnetic particles may be added in a stable or semi-stable aqueous solution.

[0013] According to another aspect, the magnetite may be in solution.

[0014] According to another aspect, the temperature of the mixture may be maintained within a range of about 45°C to about 65°C.

[0015] According to another aspect, the magnetite and the bound clay particles may be removed by applying a magnetic or electromagnetic field to the mixture.

[0016] According to another aspect, the tailings may be obtained from a tailings pond or from an output of a bitumen extraction plant.

[0017] In other aspects, the features described above may be combined together in any reasonable combination as will be recognized by those skilled in the art.

BRIEF DESCRIPTION OF THE DRAWINGS

[0018] These and other features will become more apparent from the following description in which reference is made to the appended drawings, the drawings are for the purpose of illustration only and are not intended to be in any way limiting, wherein:

FIG. 1 is a schematic diagram of a process for treating tailings using magnetic particles.

DETAILED DESCRIPTION

[0019] The method described below relates to the removal of clay fines from waste tailings generated by mining operations, such as tailings from heavy oil mining operations, in order to allow the tailings and the various components to be disposed of. In some circumstances, the components may be separated and recovered. The primary components to be recovered or separated include bitumen or other hydrocarbons, clay, and water. Other components may also be separated out, and may require other separation or treatment steps. For example, harmful chemicals, heavy metals, etc. may be neutralized such as by oxidation or removed using known techniques in addition to those described herein.

[0020] Generally speaking, the method involves the use of magnetic particles to agglomerate with other suspended solids in the tailings, allowing the solids to be removed more readily. In order for the magnetic particles to be effective, the tailings must be in a suitable condition. This generally involves reducing the amount of hydrocarbons and adjusting the pH to suitable levels, as will be described herein.

[0021] In a preferred embodiment, the magnetic particles will be magnetite as it is naturally occurring and generally cost-effective to use as there are known techniques to producing magnetite in the scale of sizes required. However, other particles may be used that are either naturally charged or induced with a charge, as will be recognized by those skilled in the art. The charge will be opposite the charge of the particles to be removed. A common type of clay found in oil sands tailings is negatively charged, in which case a positively charged magnetic particle would be used. Preferably, the magnetic particles are in the range of 1 nm to 10 μm, but preferably in the range of 1 nm – 100 nm. It has been found that the surface of the magnetite may be positively charged on these size scales and in the conditions described below. Preferably, the magnetic particles will be prepared to be in a stable or semi-stable aqueous solution to allow them to be mixed into the tailings being treated.

[0022] In one example, the waste tailings to be treated may be obtained from heavy oil operations in Northern Alberta, where the clay fines portion of the solids in the tailings is primarily kaolinite clay in the range of 22 – 76% by volume. The size of clay particles in these tailings has been characterized and is generally known by those skilled in the art. When "fines" are referred to in the context of oil sands, they are generally on the micron scale, such as between 1 – 50 μm, although particles of up to 1 mm in size may be present and the particles may be smaller as well. The small size of the fines results in a relatively stable emulsion in water. In addition, the tailings generally contain hydrocarbons, such as a certain amount of bitumen that remains after the extraction process and may contain other particles, such as heavy metals, chemical additives, etc. as is known in the art. It has been found that the residual bitumen and other hydrocarbons reduce the effectiveness of the reaction between the clay and the nano-magnetite. Accordingly, as a first step, the method preferably removes as much residual bitumen from the tailings as is practical, balancing the difficulty in removing the bitumen with the increase in effectiveness as the amount of bitumen is reduced. In one example, beneficial results may be obtained by reducing the amount of hydrocarbons to about 100 ppm or less. Once a sufficient amount of hydrocarbons has been removed, the method then removes negatively charged micro-clay by adding positively charged nano-magnetite and allowing them to agglomerate with the clay fines. This occurs based on the differences in the surface charge of the various particles, referred to as the Zeta potential. In the case of kaolinite clay, it was found that the Zeta potential of the clay particles at a pH range of between 6.0 and 7.0 was about 30 mV in this pH range, which provided beneficial results. Once the clay and magnetite particles have agglomerated, an electromagnetic field may be used to recover the magnetite/clay mix and remove it from the tailings. Once removed, the magnetite may be recovered by filtering off the clay from the magnetite using known techniques and reused. Preferably, the process steps are performed in a vessel, which allows greater control over the volumes of materials, temperature, pH level, and operational steps such as the injection and removal of the various components. The vessel may be designed to process tailings in a batch or as a continuous flow.

[0023] Once the level of clay fines and bitumen has been reduced, it becomes easier to treat the remaining components in the tailing, for example, by reducing the time required for the solids to settle. A second or third nano-magnetite treatment may be used to remove additional clay fines in order to enhance the tailings emulsion separation and the recovery of water. The number of treatments will depend on the amount of clay fines present and the amount removed by the magnetite in each step, which in turn will relate to the amount of magnetite used. In addition, each additional step may be modified to account for the reduction in components. For example, beneficial results may be had by aerating with oxygen or an oxygen-containing gas in subsequent steps. It is believed that the use of nano-magnetite in the separation of clay fines, which may be recovered and reused, provides economic advantages relative to other recovery processes, and also reduces the treatment costs for the remaining waste tailings solids. It is also believed that the method may also reduce an operator's environmental liability and future risks related to toxic leachate associated with the permanent resting place of tailings.

[0024] Referring to FIG. 1, one example of a process used to treat tailings from heavy oil extraction is shown. In a first step, tailings are injected into a floatation vessel 12 through line 14. Some of the bitumen and other hydrocarbons may be removed from the tailings by mixing in additional fresh hot water injected through line 16 and aerating the slurry with CO_2

bubbles injected through line 18 while simultaneously mixing the tailings. This will cause the bitumen to rise to surface as a froth, which can be collected and sent to a regular froth treatment plant, represented by line 20. Once the hydrocarbons have been reduced to a suitable level, the tailings are transferred through line 22 to a first mixing vessel 24. While other gases could be used, using CO_2 gas maintains a non-explosive environment with the hydrocarbon off-gassing. In addition, the CO_2 gas bubbles may be used to reduce the pH of the slurry. It has been found that the pH of tailings from oil sands operations in Northern Alberta is generally around 8.2 or higher. However, as will be discussed below, a preferred pH range for the steps described below is around 6.5 to 7.0, as will be described below. In some circumstances, it may be desirable to retain the tailings in floatation vessel 12 until a suitable pH has been achieved. Alternatively, the pH may be adjusted in other ways, such as by adding acid or other additives through line 26 to first mixing vessel 24 to reach the desired pH range. While it is believed that, in most situations, the pH will need to be lowered, similar steps with different additives may also be used to raise the pH if necessary.

[0025] Once the desired pH range has been reached, magnetite is added to the slurry in first mixing vessel 24 through line 28. As noted elsewhere, while the examples are described as using magnetite, it will be understood that any suitable particle with the necessary magnetic properties may be used. Magnetite may be added in various ways, such as by adding it directly in a powder form, or in an aqueous carrier, such as in a reagent or aqueous solution. The preferred delivery medium will depend on the preferences of the user and available resources. It has been found that the pH of the tailings has an effect on the removal of clay particles. If pH is too high or too low, the Zeta potential between the clay particles and the magnetite is too low for agglomeration to occur. For example, in one experiment, it was found that the Zeta potential between kaolinite clay particles and magnetite was about 30 mV when the pH was between 6.0 and 7.0, but that the Zeta potential dropped to near zero at the normal pH range of 8.2, which is the normal pH range of tailings from heavy oil mining operations in Northern Alberta. It is thus beneficial to achieve the right conditions to enhance the magnetite/clay attraction. Alternatively, the pH may be adjusted simultaneously with the addition of magnetite, or the mixture may be monitored and the pH adjusted as necessary. Once the clay and magnetite particles are sufficiently agglomerated, the tailings are passed from first mixing vessel 24 through line 30 into a separator 32, which removes the agglomerated particles, such as by using a wet drum magnetic separator as is known in the art. The magnetite may then be separated from the clay using known techniques to recover the magnetite for reuse in the process.

[0026] Depending on the amount of material removed and the composition of the tailings, the steps in removing clay particles using magnetite may be repeated, and other treatment steps may be taken to treat other components in the tailings. As shown, the tailings stream is passed from separator 32 to a second mixing vessel 34 through line 36. An oxidative additive, such as oxygen, may be added to second mixing vessel 34 through line 38, and a magnetite reagent may be added to second mixing vessel 34 through line 40. At this stage, the pH level may again require adjustment, and sensors may be used to monitor the pH for adjustment. The oxygen aeration progresses the separation and settling of solids as well as breaking down some components in an oxidative reaction. The magnetite further removes clay fines, along with other components such as heavy metal volunteers or other elements that may have a suitable surface charge and that may be present in the tailings. Solids may be removed from second mixing vessel 34 through line 41. The tailings may then be passed through line 43 to a second separation vessel 42 to remove additional agglomerated particles, and may then be passed either to additional vessels for additional treatment, or to a separation and settling vessel 44 through line 46 as shown. A portion of the magnetite and clay may be recovered from separators 32 and 42 through lines 33 and 43 respectively. The solids are then recovered through line 48 and water is recovered through line 50. Each stream may require additional treatment before disposal or recovery. As the treatment of the tailings proceeds and at various stages, the tailings may be dewatered when appropriate. This allows for preferred water treatment for recycling of the recovered water.

[0027] This method may be particularly useful in treating heavy oil tailings waste in Northern Alberta, which is primarily kaolinite clay (22-76%). Chemical conditions in the tailings waste stream make separation very difficult, therefore the present method does not rely on a chemical methodology. Rather, this method takes advantage of the magnetic attraction of kaolinite and nano-magnetite (Fe_3O_4) in certain conditions. One important condition to control is the pH of the tailings, which can enhance the attraction between magnetite and clay particles in a specific range. It has been found that, at a pH of between about 6.0 to 7.0, the surface charge difference (Zeta potential) between the kaolinite and the magnetite provides beneficial results. It is generally believed that the pH of the solution affects the ability of the charged particles to agglomerate with the clay particles because of the change in the concentration of H+ in solution and that the agglomeration may be optimized by choosing an appropriate H+ concentration. In one experiment, it was found that their charge difference at this pH range was about 30 mV. Furthermore, it was found that, at the typical pH of Northern Alberta tailings waste of about 8.2 or higher, the Zeta potential between kaolinite clay and magnetite was sufficiently low that there was insufficient attraction to allow separation to occur in any meaningful way. In these conditions, magnetite would do little to assist in disturbing the tailing emulsion.

[0028] In one example, a reagent solution of nano-magnetite may be prepared using various methods that are known in the industry. The tailings are preferably treated initially by introducing CO_2 aeration into the slurry while adding hot recycled water at a ratio of about 1:1 to the slurry volume, although the ratio of added hot water may vary based on tailings composition. The time required for aeration will vary for the same reason. The maximum temperature of slurry at this stage should be maintained at 60°C. It has been found that the added water promoted demulsification of the tailings and also reduced pH. Some mixing is generally required during aeration. In addition, the water that is added may be prepared with an additive that helps address the charged particles in the tailings or for other purposes. For example, sodium silicate may be added as is known in the art to change surface charges of particles for better emulsion separation. The process may be done in a continuous or batch format, and will affect the type of vessel design chosen. One result of the aeration step is a drop of pH. Another result is separation of bitumen and other hydrocarbons as a rising froth which is removed to existing facility for recovery/processing.

[0029] Sensors may be used to monitor the slurry and measure the adjusted pH in the vessels and the temperatures. If pH reduction is required, an additive, such as a small amount of acid, may be injected into the slurry. Suitable acids are known in the art, and may include sulfuric acid or acetic acid. Temperature is preferably maintained at a maximum of 65°C at the aeration stage and allowed to drop to a low of 45°C later in the treatment.

[0030] Preferably, the process described herein may be applied to warm tailings waste at the discharge source beside the bitumen extraction plant. At the extraction plant, there will generally be a primary, secondary and middlings extraction waste stream. Each of these three waste streams are hot and have their own more consistent chemical characteristics, such as pH, temperature, etc. By treating the waste streams while they are still hot, energy may be conserved, and as each stream has separate characteristics, the process steps may be tailored to match the treatment requirements of the specific waste stream.

[0031] When the aeration is stopped and the hydrocarbon froth is removed, a nano-magnetite aqueous reagent is added and mixed vigorously in the remaining cooler slurry until the suitable sediment rates by the agglomeration of clay and magnetite has been reached. It is anticipated that this will be in the range of 5 to 10 minutes. The actual time will preferably be based on sensor data obtained by detecting sediment rates. The reagent volume may vary, but will generally be less than 1% by volume of slurry and may be based in part on the previous volume of clay removed.

[0032] Once added, the positively charged magnetite is attracted to and surrounds the negatively charged clay particles. This heterocoagulation then precipitates and is attracted to an applied magnetic or electromagnetic field, preferably at the bottom of the vessel. This settled material may then be removed, and the magnetite separated from the clay. For example, the settled material may be moved as a thick liquid to a flow path over a wet drum magnetic separator, which recovers the magnetite and removes the clay from the process for final placement. Generally speaking, the amount of magnetite recovered will be in the range of 85% to 95%, but will depend on the recover y steps taken. The wet drum separator is a well known technology and is commonly used in non-related industry processes.

[0033] At this stage, the remaining slurry is more easily treated for further demulsification due to the removal of a significant portion of the clay fines and the hydrocarbons. Additional aeration, preferably oxygen, and strong stirring may be applied to the remaining slurry. The oxygen will promote new reactions in the mixed slurry and further demulsification will occur. A second treatment of nano-magnetite may then be applied and any clay and heavy metal volunteers that agglomerate with the magnetite may then be removed and magnetite is recovered. It should be noted that heavy metal volunteers may also be removed in the first separation stage, however it is anticipated that the primary component that is removed will be clay, as it will have the highest concentration in the tailings.

[0034] In the final stage of the process, where settling time is important, the large amount of separated water may be treated using known techniques. For example, the water may be treated for desalination such as with a "desalination hydrocylone" and recovered for use again in the tailing treatment plant or in the main bitumen extraction plant. The remaining concentrated brine may then be pumped into a disposal well or salt cavern.

[0035] The remaining dewatered solids are then ready for final treatment and disposal, such as placement for disposal at the mine site.

[0036] In this patent document, the word "comprising" is used in its non-limiting sense to mean that items following the word are included, but items not specifically mentioned are not excluded. A reference to an element by the in definite article "a" does not exclude the possibility that more than one of the elements is present, unless the context clearly requires that there be one and only one of the elements.

[0037] The scope of the following claims should not be limited by the preferred embodiments set forth in the examples above and in the drawings, but should be given the broadest interpretation consistent with the description as a whole.

What is Claimed is:

1. A method of treating tailings using magnetic particles, the method comprising the steps of:

obtaining tailings from a mining operation, the tailings comprising at least water, suspended clay particles, and hydrocarbons;

removing at least a portion of the hydrocarbons from the tailings;

adjusting the tailings to a pH range that results in a surface charge difference between the suspended clay particles and magnetic particles;

mixing the magnetic particles into the tailings and permitting the magnetic particles and clay particles to agglomerate; and

removing the agglomerated clay and magnetic particles from the tailings.

2. The method of claim 1, wherein removing at least a portion of the hydrocarbons comprises aerating the mixture to generate a froth of the hydrocarbons prior to adding the magnetic particles.

3. The method of claim 2, wherein aerating the mixture comprises injecting CO_2 gas.

4. The method of claim 1, wherein the hydrocarbons are reduced to less than 100 ppm.

5. The method of claim 1, wherein the magnetic particles have a size of 1 nm to 100 nm.

6. The method of claim 1, wherein the magnetic particles are magnetite.

7. The method of claim 6, further comprising the step of adjusting the pH of the mixture to between 6 - 7.

8. The method of claim 1, wherein the magnetic particles are added in a stable or semi-stable aqueous solution.

9. The method of claim 1, wherein the magnetite is in solution.

Date reçue/Date Received 2021-12-03

10. The method of claim 1, wherein the temperature of the mixture is maintained within a range of 45°C to 65°C.

11. The method of claim 6, wherein the magnetite and the bound clay particles are removed by applying a magnetic or electromagnetic field to the mixture.

12. The method of claim 1, wherein the tailings are obtained from a tailings pond.

13. The method of claim 1, wherein the tailing are obtained from an output of a bitumen extraction plant.

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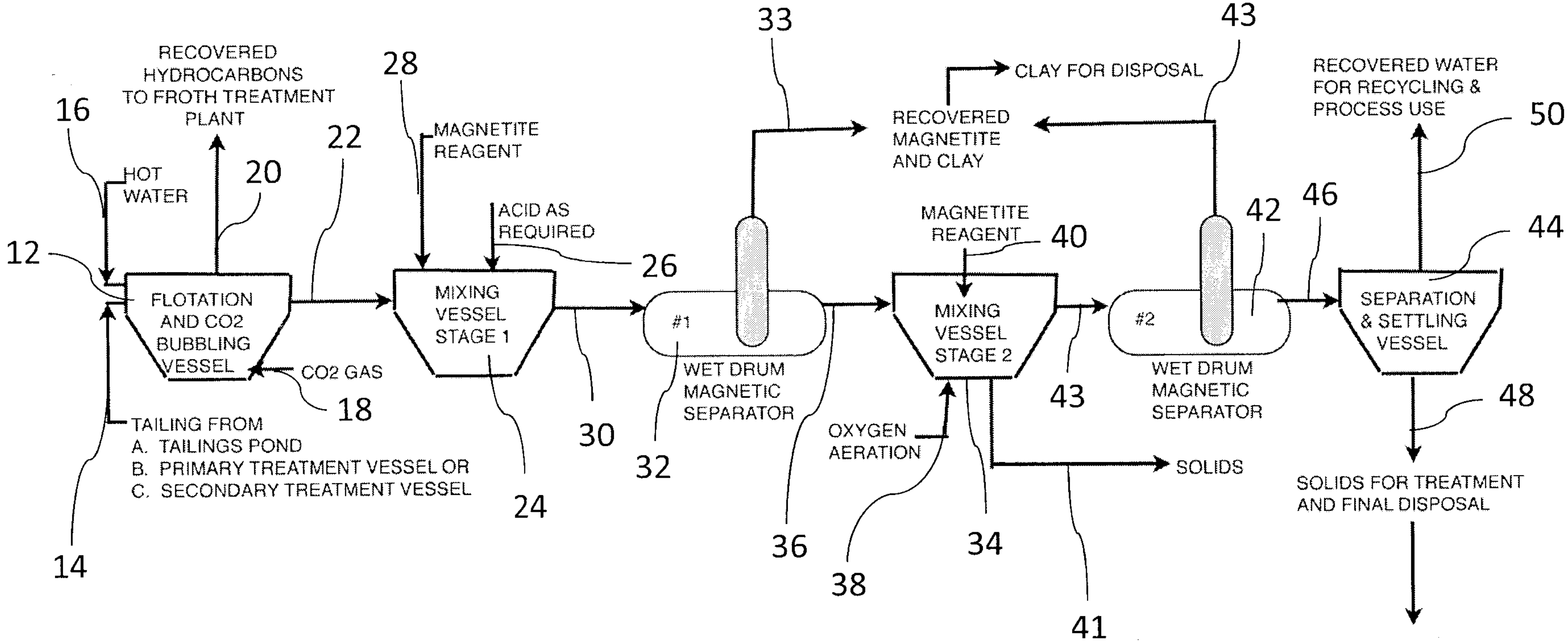
RECOVERED HYDROCARBONS TO FROTH TREATMENT PLANT
HOT WATER
FLOTATION AND CO2 BUBBLING VESSEL
CO2 GAS
TAILING FROM
A. TAILINGS POND
B. PRIMARY TREATMENT VESSEL OR
C. SECONDARY TREATMENT VESSEL
MAGNETITE REAGENT
ACID AS REQUIRED
MIXING VESSEL STAGE 1
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WET DRUM MAGNETIC SEPARATOR
RECOVERED MAGNETITE AND CLAY
CLAY FOR DISPOSAL
MAGNETITE REAGENT
MIXING VESSEL STAGE 2
OXYGEN AERATION
SOLIDS
#2
WET DRUM MAGNETIC SEPARATOR
RECOVERED WATER FOR RECYCLING & PROCESS USE
SEPARATION & SETTLING VESSEL
SOLIDS FOR TREATMENT AND FINAL DISPOSAL
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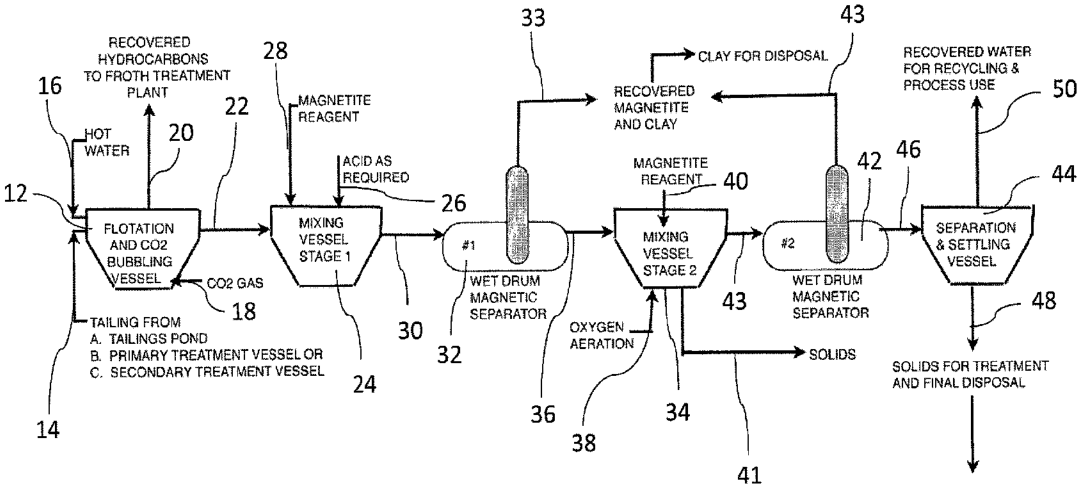
FIG. 1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CLAY FOR DISPOSAL
RECOVERED MAGNETITE AND CLAY
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SEPARATION & SETTLING VESSEL
44
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SOLIDS FOR TREATMENT AND FINAL DISPOSAL
TAILING FROM
A. TAILINGS POND
B. PRIMARY TREATMENT VESSEL OR
C. SECONDARY TREATMENT VESSEL
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