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Office de la Propriété Intellectuelle du Canada

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Canadian Intellectual Property Office

CA 2871395 C 2019/02/05

(11)(21) 2 871 395

(12) BREVET CANADIEN
CANADIAN PATENT

(13) C

(22) Date de dépôt/Filing Date: 2014/11/17

(41) Mise à la disp. pub./Open to Public Insp.: 2016/05/17

(45) Date de délivrance/Issue Date: 2019/02/05

(51) Cl.Int./Int.Cl. *B01J 19/06* (2006.01),
E21B 43/24 (2006.01), *E21B 43/34* (2006.01),
C02F 1/04 (2006.01)

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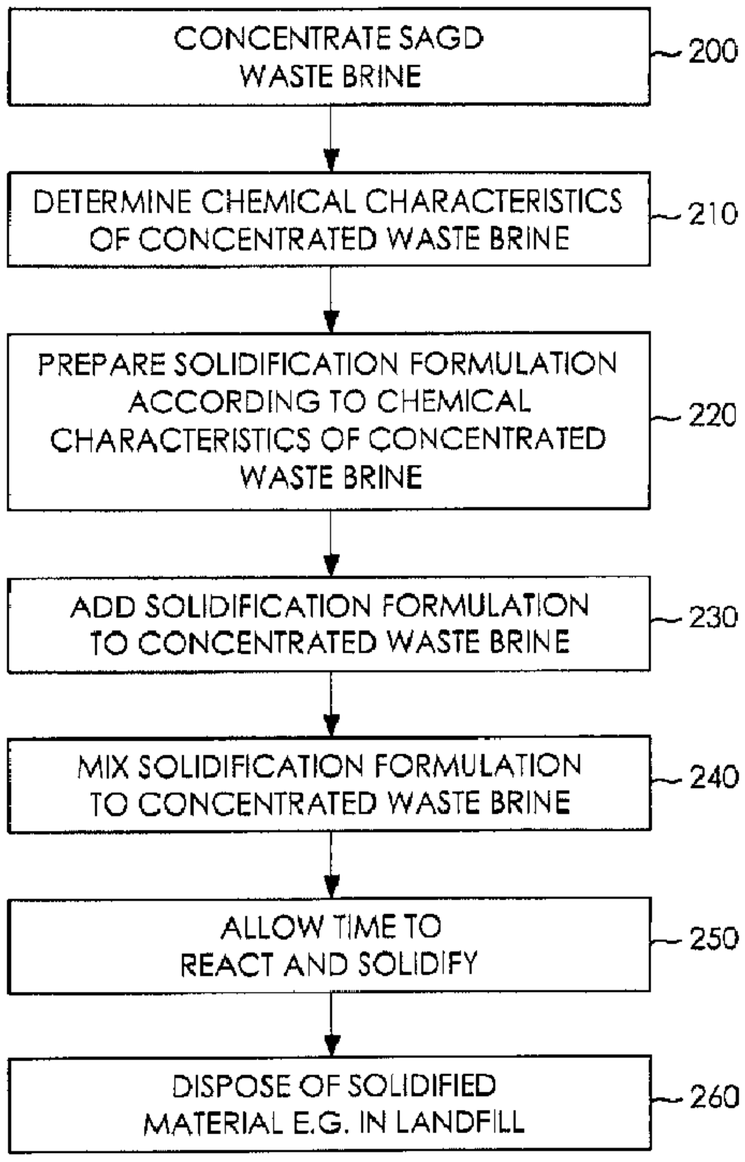
(54) Titre : SOLIDIFICATION DE SAUMURE RESIDUELLE DES OPERATIONS DE RECUPERATION D'HYDROCARBURE SUR PLACE

(54) Title: SOLIDIFICATION OF WASTE BRINE FROM IN SITU HYDROCARBON RECOVERY OPERATIONS



(57) Abrégé/Abstract:
There is provided a process and solidification formulation for treating waste brines derived from a thermal in situ hydrocarbon recovery operation. The waste brines can be from a SAGD operation, a crystallizer blowdown stream, an evaporator blowdown

CA 2871395 C 2019/02/05

(11)(21) 2 871 395

(13) C

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(57) Abrégé(suite)/Abstract(continued):
stream, and/or an OTSG blowdown stream. The process includes addition of the solidification formulation to the waste brine to produce a solidified waste that can be disposed of in landfills. The solidification formulation can be prepared according to the chemical characteristics of the waste brine. The solidification formulation added to the waste brine can include fly ash having high carbon content, such as fly ash derived from petroleum-coke. Calcium-containing compounds and silica-containing compounds can also be included in the solidification formulation.

ABSTRACT

There is provided a process and solidification formulation for treating waste brines derived from a thermal in situ hydrocarbon recovery operation. The waste brines can be from a SAGD operation, a crystallizer blowdown stream, an evaporator blowdown stream, and/or an OTSG blowdown stream. The process includes addition of the solidification formulation to the waste brine to produce a solidified waste that can be disposed of in landfills. The solidification formulation can be prepared according to the chemical characteristics of the waste brine. The solidification formulation added to the waste brine can include fly ash having high carbon content, such as fly ash derived from petroleum-coke. Calcium-containing compounds and silica-containing compounds can also be included in the solidification formulation.

SOLIDIFICATION OF WASTE BRINE FROM IN SITU HYDROCARBON RECOVERY OPERATIONS

TECHNICAL FIELD

[0001] The technical field generally relates to thermal in situ hydrocarbon recovery operations, and more particularly to techniques for solidifying waste brines generated in such operations.

BACKGROUND

[0002] Thermal in situ hydrocarbon recovery operations generate steam for injection into the hydrocarbon-bearing reservoir in order to heat and reduce the viscosity of the hydrocarbons to facilitate recovery. Production fluids that are recovered from the reservoir are separated into produced hydrocarbons and produced water.

[0003] The produced water is then treated, e.g. in an evaporator, to remove contaminants as an evaporator blowdown stream and provide treated water for use as boiler feed water. The boiler feed water can then be supplied to steam generators that produce steam, which can include wet steam streams. Wet steam streams can further be sent to separators to produce dry steam streams suitable for injection and boiler blowdown streams.

[0004] Evaporator and boiler blowdown streams are generally disposed as waste brines in deep injection wells. The waste brines can also be concentrated in a crystallizer and then dried to form a dried salt residual or the concentrate can be transported by truck for third-party waste management.

[0005] Disposal of solidified waste brines in an on-site landfill would be economically beneficial. Concentrated waste brine can be solidified using a gas-fired dryer. However, the resulting dried brine is water soluble, and can be difficult to handle in industrial landfills when exposed to water from precipitation. Alternatively, solid waste material can be obtained by adding a solidification

reagent formulation to the waste brine. Examples of solidification reagents typically used include Portland cement, quicklime, hydrated lime, cement kiln dust, silicates, blast furnace slag and coal fly ash. However, the solidified material is not always stable and generation of contaminated leachate can prevent disposing thereof in a landfill.

[0006] There are various challenges associated with efficient and effective disposal of waste brines produced in thermal in situ hydrocarbon recovery operations.

SUMMARY

[0007] In some implementations, there is provided a process for treating waste brine derived from a thermal in situ hydrocarbon recovery operation, including:

> adding a solidification formulation to the waste brine, the solidification formulation including fly ash having a carbon content of at least 25 wt%.

[0008] In some implementations, the carbon content of the fly ash is at least 50 wt%.

[0009] In some implementations, the fly ash has a Loss-On-Ignition (LOI) value of at least 50% or at least 60%.

[0010] In some implementations, the fly ash has a carbon content sufficiently high to interact with organic components of the waste brine and promote solidification of the waste brine. In some other implementations, the carbon in the fly ash interacts with organic components of the waste brine to promote solidification of the waste brine.

[0011] In some implementations, the solidification formulation further includes at least one calcium-containing reagent.

[0012] In some implementations, the calcium-containing reagent includes calcium oxide, calcium hydroxide, Portland cement, cement kiln dust, calcium silicate, Class C fly ash, Class F fly ash and/or ground-granulated blast-furnace slag.

[0013] In some implementations, the solidification formulation is added to the waste brine in the form of a powder.

[0014] In some implementations, the waste brine is derived from a SAGD operation, a crystallizer blowdown stream, an evaporator blowdown stream, and/or an OTSG blowdown stream.

[0015] In some implementations, there is provided a formulation for solidifying waste brine derived from a thermal in situ hydrocarbon recovery operation, including:

fly ash having a carbon content of at least 25 wt%; and
at least one calcium-containing reagent.

[0016] In some implementations, the carbon content of the fly ash is at least 50 wt%.

[0017] In some implementations, the fly ash has a Loss-On-Ignition (LOI) value of at least 50% or at least 60%.

[0018] In some implementations, the calcium-containing reagent includes calcium oxide, calcium hydroxide, Portland cement, cement kiln dust, calcium silicate, Class C fly ash, Class F fly ash and/or ground-granulated blast-furnace slag.

[0019] In some implementations, there is provided a process for treating waste brine derived from a thermal in situ hydrocarbon recovery operation and including water, solids, salts, and organic components that include dissolved organics and emulsified oils, the process including:

adding a solidification formulation to the waste brine, the solidification formulation including fly ash including carbon compounds that interact with

the organic components of the waste brine to promote solidification of the waste brine, wherein the carbon compounds of the fly ash are derived from combustion of petroleum coke.

[0020] In some implementations, the carbon compounds of the fly ash are derived from combustion of petroleum coke produced by delayed coking of bitumen feedstocks.

[0021] In some implementations, the solidification formulation further includes at least one calcium-containing reagent.

[0022] In some implementations, the calcium-containing reagent includes calcium oxide, calcium hydroxide, Portland cement, cement kiln dust, calcium silicate, Class C fly ash, Class F fly ash and/or ground-granulated blast-furnace slag.

[0023] In some implementations, the solidification formulation is added to the waste brine in the form of a powder.

[0024] In some implementations, the waste brine is derived from a SAGD operation, a crystallizer blowdown stream, an evaporator blowdown stream, and/or an OTSG blowdown stream.

[0025] In some implementations, there is provided a process for treating SAGD waste brine, including:

adding a solidification formulation to the waste brine, the solidification formulation including fly ash derived from combustion of petroleum coke produced by delayed coking of bitumen feedstocks.

[0026] In some implementations, the fly ash includes ash obtained from electrostatic precipitation associated with the combustion of the petroleum coke.

[0027] In some implementations, the solidification formulation further includes at least one calcium-containing reagent.

[0028] In some implementations, the calcium-containing reagent includes calcium oxide, calcium hydroxide, Portland cement, cement kiln dust, calcium silicate, Class C fly ash, Class F fly ash and/or ground-granulated blast-furnace slag.

[0029] In some implementations, the solidification formulation is added to the waste brine in the form of a powder.

[0030] In some implementations, the waste brine is derived from a crystallizer blowdown stream, an evaporator blowdown stream, and/or an OTSG blowdown stream.

[0031] In some implementations, there is provided a process of integrating a thermal in situ recovery operation and an upgrading operation, including:

recovering hydrocarbons and producing waste brine from the thermal in situ recovery operation;

supplying at least a portion of the hydrocarbons recovered from the thermal in situ recovery operation to the upgrading operation;

producing upgraded hydrocarbons and petroleum coke from the upgrading operation;

combusting at least a portion of the petroleum coke to produce energy and fly ash; and

combining at least a portion of the fly ash with at least a portion of the waste brine.

[0032] In some implementations, the upgrading operation includes delayed coking for producing the petroleum coke.

[0033] In some implementations, the fly ash has a carbon content of at least 25 wt%.

[0034] In some implementations, the carbon content of the fly ash is at least 50 wt%.

[0035] In some implementations, the process further includes combining a calcium-containing reagent with the waste brine.

[0036] In some implementations, the calcium-containing reagent includes calcium oxide, calcium hydroxide, Portland cement, cement kiln dust, calcium silicate, Class C fly ash, Class F fly ash and/or ground-granulated blast-furnace slag.

[0037] In some implementations, there is provided a process for solidifying waste brine derived from a thermal in situ recovery operation and including water, solids, salts, and organic components that include dissolved organics and emulsified oils, the process including:

determining chemical characteristics of the waste brine including silica, calcium and organics content; and

adding a solidification formulation to the waste brine, the solidification formulation including reagents which in combination provide organic carbon, silica and calcium to the solidification formulation; and

wherein the reagents are selected and provided in amounts according to the determined calcium, silica and organics content of the waste brine in order to promote solidification of the waste brine.

[0038] In some implementations, the solidification formulation includes fly ash.

[0039] In some implementations, the fly ash includes ash derived from combustion of petroleum coke produced by delayed coking of bitumen feedstocks.

[0040] In some implementations, the solidification formulation further includes calcium oxide, calcium hydroxide, Portland cement, calcium silicate, Class C fly ash, Class F fly ash and/or ground-granulated blast-furnace slag.

[0041] In some implementations, the waste brine is determined to be calcium depleted, and the solidification formulation has a high-calcium content. In some other implementations, the waste brine is determined to be calcium rich, and the solidification formulation has a low calcium content.

[0042] In some implementations, the waste brine is determined to be calcium depleted or calcium rich, and the solidification formulation added to the waste brine that is calcium depleted has a higher calcium content than the solidification formulation that is added to the calcium rich waste brine.

[0043] In some implementations, the waste brine is determined to have a solids content between 35 wt% and 65 wt%, and the solidification formulation is provided in an amount from 0.3 to 1.0 kg/L of waste brine.

[0044] In some implementations, the process further includes:

providing first and second waste brines having different chemical characteristics, the first waste brine being derived from a lime-softened stream and a second waste brine being derived from a non-lime-softened stream;

treating the first waste brine with a first solidification formulation including higher amounts of calcium;

treating the second waste brine with a second solidification formulation including lower amounts calcium.

In some other implementations, the process further includes:

providing first and second waste brines having different chemical characteristics, the first waste brine being derived from a lime-softened stream and a second waste brine being derived from a non-lime-softened stream;

treating the first waste brine with a first solidification formulation;

treating the second waste brine with a second solidification formulation;

wherein an amount of calcium in the first solidification formulation is higher than the amount of calcium in the second solidification formulation.

[0045] In some implementations, the solidification formulation is provided to have:

an increased amount of carbon-containing compound for higher organics-to-calcium ratios in the waste brine; and

an increased amount of calcium-containing compound for lower calcium contents in the waste brine.

In some other implementations, the solidification formulation is provided to have:

an increased amount of carbon if the waste brine is determined to have a content of organics that is higher than a calcium content; and

an increased amount of calcium if the waste brine is determined to be calcium-depleted.

[0046] In some implementations, there is provided a process for solidifying waste brine derived from blowdown of an evaporator used to treat produced water from a thermal in situ recovery operation, the process including:

adding a solidification formulation to the waste brine, the solidification formulation including a calcium-containing reagent;

wherein the calcium-containing reagent is provided in a solidification dosage enabling solidification of the waste brine, the solidification dosage being lower compared to a corresponding dosage of the calcium-containing reagent required to enable solidification of a corresponding waste brine derived from a lime-softened stream.

[0047] In some implementations, the solidification dosage enabling solidification of the waste brine derived from the evaporator blowdown is less than 0.5 kg solidification formulation per liter of waste brine.

[0048] In some implementations, the solidification formulation includes cement kiln dust and fly ash.

[0049] In some implementations, the solidification formulation comprises a content of cement kiln dust that is higher than a content of fly ash. In some implementations, the solidification formulation includes about 75 wt% cement kiln dust and about 25 wt% fly ash.

[0050] In some implementations, the fly ash includes fly ash deriving from combustion of petroleum coke.

[0051] In some implementations, the fly ash derives from combustion of petroleum coke produced by delayed coking of bitumen feedstocks.

[0052] In some implementations, there is provided a process for solidifying waste brine derived from a thermal in situ recovery operation, including:

generating blowdown from an evaporator used to treat produced water from the thermal in situ recovery operation, and deriving a first waste brine therefrom;

generating OTSG blowdown from lime-softened boiler feed water, and deriving a second waste brine therefrom;

combining the first and second waste brines to produce a combined waste brine; and

adding a solidification formulation comprising calcium and silica to the combined waste brine;

wherein the solidification formulation is provided with a calcium and silica solidification dosage enabling solidification of the combined waste brine, the solidification dosage being lower compared to a corresponding dosage of calcium and silica required to enable solidification of the second waste brine.

[0053] In some implementations, there is provided a process for treating SAGD waste brine, including:

concentrating the SAGD waste brine to produce a concentrated waste brine having a solids content between 35 wt% and 65 wt% total solids;

determining chemical characteristics of the concentrated waste brine, including organics content, calcium content, silica content and solids content;

providing a solidification formulation according to the chemical characteristics of the concentrated waste brine, the solidification formulation including:

a calcium-containing reagent for undergoing solidification reactions with components of the concentrated waste brine;

and

a carbon-containing reagent including fly ash derived from combustion of petroleum coke produced by delayed coking of bitumen feedstocks, for enhancing solidification of the concentrated waste brine;

adding the solidification formulation to the concentrated waste brine, in an amount from 0.3 to 1.0 kg/L of waste brine; and

disposing of the treated waste material.

[0054] In some implementations, the solidification formulation includes silica for undergoing solidification reactions with components of the concentrated waste brine.

[0055] In some implementations, the carbon content of the fly ash is at least 50 wt%.

[0056] In some implementations, the fly ash has a Loss-On-Ignition (LOI) value of at least 50% or at least 60%.

[0057] In some implementations, the fly ash has a carbon content sufficiently high to interact with organic components of the waste brine and promote solidification of the waste brine.

[0058] In some implementations, the calcium-containing reagent includes calcium oxide, calcium hydroxide, Portland cement, cement kiln dust, calcium silicate, Class C fly ash, Class F fly ash and/or ground-granulated blast-furnace slag.

[0059] In some implementations, the waste brine is derived from a SAGD operation, a crystallizer blowdown stream, an evaporator blowdown stream, and/or an OTSG blowdown stream.

[0060] In some implementations, the SAGD waste brine is originated from an OTSG blowdown stream from lime-softened boiler feed water and the solidification formulation comprises approximately equal part of calcium oxide and fly ash.

[0060a] In some implementations, there is provided a process for solidifying waste brine derived from an oil sands hydrocarbon recovery operation, the waste brine comprising water, solids, salts, and organic components that comprise dissolved organics and emulsified oils, the process comprising:

determining chemical characteristics of the waste brine; and

adding a solidification formulation comprising a calcium-containing reagent to the waste brine;

wherein the calcium-containing reagent is selected and provided in amounts according to the determined chemical characteristics of the waste brine in order to promote solidification of the waste brine.

[0060b] In some implementations, there is provided a process for solidifying waste brines derived from an oil sands hydrocarbon recovery operation, comprising:

generating a first waste brine and a second waste brine, wherein a concentration in calcium and silica in the second waste brine is lower than in the first waste brine;

adding a solidification formulation comprising calcium and silica to the first and second waste brines;

wherein an amount of the solidification formulation added to the first waste brine is lower than the amount of the solidification formulation added to the second waste brine.

[0060c] In some implementations, there is provided a process for solidifying waste brine derived from an oil sands hydrocarbon recovery operation, comprising:

generating a first waste brine and a second waste brine, wherein a concentration in calcium and silica in the second waste brine is lower than in the first waste brine;

combining the first and second waste brines to produce a combined waste brine; and

adding a solidification formulation comprising calcium and silica to the combined waste brine;

wherein the solidification formulation is provided with a calcium and silica solidification dosage enabling solidification of the combined waste brine, the solidification dosage being lower compared to a corresponding dosage of calcium and silica required to enable solidification of the second waste brine.

[0060d] In some implementations, there is provided a process for solidifying waste brine derived from an oil sands hydrocarbon recovery operation, comprising:

concentrating the waste brine to produce a concentrated waste brine having a solids content between 35 wt% and 65 wt% total solids;

providing a solidification formulation comprising a calcium-containing reagent for undergoing solidification reactions with components of the concentrated waste brine;

adding the solidification formulation to the concentrated waste brine, in an amount from 0.3 to 1.0 kg/L of waste brine, to produce a treated waste material; and

disposing of the treated waste material.

BRIEF DESCRIPTION OF THE DRAWINGS

[0061] Fig 1 is a process flow diagram of a thermal in situ hydrocarbon recovery operation including a water blowdown treatment and solidification system.

[0062] Figs 2 and 3 are process flow diagrams of a waste brine treatment and solidification operation.

[0063] Figs 4a-4b are process flow diagrams of two different modes of waste brine solidification treatment and disposal.

[0064] Fig 5 is a process flow diagram of a petroleum coke fly ash production.

[0065] Figs 6a-6b are process flow diagrams of solidification treatment of various waste brines.

[0066] Fig 7 is a process diagram of a SAGD waste brine solidification treatment.

DETAILED DESCRIPTION

[0067] Waste brine generated during in situ hydrocarbon recovery operations, e.g. in oil sands SAGD operations, can be treated with a solidification formulation to facilitate disposal thereof in landfills. However, in some implementations, the solidification process can be used for solidifying waste brines from any suitable oil sands brine source, such as basal water desalination or utility water desalination brines, or from other industrial sources. Various aspects, implementations and applications regarding waste brine solidification treatment will be discussed further below.

In situ hydrocarbon recovery operations and production of waste brines

[0068] Fig 1 shows an illustrative example of a thermal in situ bitumen or heavy hydrocarbon recovery operation 10 which can include Steam-Assisted Gravity Drainage (SAGD) where injection-production well pairs are used to exploit a bitumen containing reservoir. Each well pair 12a, 12b includes an injection well employed to inject steam into the reservoir and a production well to recover condensate and mobilized hydrocarbons as production fluid 14a, 14b. The production fluid 14a, 14b is supplied to an oil-water separator (SEP) 16a, 16b to produce a produced hydrocarbons stream 18a, 18b (e.g., produced bitumen) and

produced water 20a, 20b. Diluent can be added to enhance the separation of the oil from the water, and in such scenarios the produced hydrocarbons stream 18a, 18b is diluted.

[0069] Still referring to Fig 1, an illustrative example of a water treatment system for treating produced water and generating steam include a first water treatment train 22 and a second water treatment train 24. The first train 22 receives de-oiled produced water stream 20a and second train 24 receives de-oiled produced water 20b. It should be noted that there may be a single water treatment train or multiple trains that include the same or different treatment units and processes.

[0070] Still referring to Fig 1, in this example system, the first train 22 can include a softening unit receiving the de-oiled produced water stream 20a. The softening unit can include a Warm Lime Softener (WLS) 26 as illustrated or a Hot Lime Softener (HLS). A chemical additive that includes lime and other chemicals, e.g. lime and soda ash, can be added to the WLS 26 to produce a softened water stream 28 and a WLS sludge. Depending on the operation of the WLS 26, different amounts of divalent cations, such as calcium and magnesium, as well as silica can be removed from the de-oiled produced water stream 20a. The softened water stream 28 can be subjected to additional softening that is particularly directed to reducing divalent cation concentration. For example, the softening unit can further include a cation exchange unit 30 for receiving the softened water stream 28 to produce a further treated water stream 32 further depleted in divalent cations. The cation exchange unit 30 can be a Weak Acid Cation (WAC) exchanger, for example, which can use a sodium based medium to remove the divalent cations. In some implementations, the softened water stream 28 can be filtered through membrane filters (not illustrated), e.g. microfilters, before entering the cation exchange unit 30.

[0071] The treated water 32 of the first water treatment train 22 can be fed to a first boiler feed water tank (BFWT) 34, from which a first boiler feed water stream 36 can be sent for steam generation to a first Once Through Steam Generator

(OTSG) 38. In some example systems, the first boiler feed water stream 36 can be sent to a deaerator to remove non-condensable gases and oxygen from the stream before entering the first OSTG 38. The first OTSG produces wet steam 40 that is sent to a separator 42 for separating into substantially dry steam 44 and a first boiler blowdown (BBD_{WLS}) stream 46 that has a concentrated level of impurities relative to the concentration in the first boiler feed water stream 36. Steam generation has the effect of concentrating impurities in the blowdown stream. For example, an OTSG often produces wet steam including about 20% water and 80% steam and once the water is removed from the wet steam, the impurities concentration in the blowdown can be about five times greater than the concentration in the boiler feed water. The dry steam 44 can be used as the steam injected into the injection well of the well pair 12a.

[0072] Still referring to Fig 1, in this example system, the second water treatment train 24 has an alternative configuration to the first train 22. The second water treatment train 24 can include an evaporator (EVAP) 48 for receiving a second de-oiled produced water stream 20b, which can be identical, similar or different compared to the first de-oiled produced water stream 20a and can come from the same or a different source. For instance, the first de-oiled produced water stream 20a can come from a SAGD well pad operating in a given reservoir area, while the second de-oiled produced water stream 20b can come from a different SAGD well pad or other recovery operation operating in another reservoir area. The produced water stream 20b can be pre-heated before being sent to the evaporator 48. It should also be understood that there can be several evaporators arranged in parallel, and that the evaporators can be, for example, vapour compression distillation and/or multiple effect distillation type evaporators. The evaporator 48 produces a distillate stream 50 and an evaporator blowdown (EBD) stream 52. The distillate stream 50 is depleted in calcium, magnesium, silica and dissolved solids and is a relatively clean, high quality water stream.

[0073] The distillate stream 50 of the second water treatment train 24 can be supplied to a second boiler feed water tank 54. A second boiler feed water

stream 56 can be sent from the tank 54 to a second steam generator, which can include a second OTSG 58 and a second separator 62. The second OTSG 58 produces wet steam 60 and the second separator 62 receives the wet steam 60 and produces substantially dry steam 64 and a second boiler blowdown (BBD_{EVAP}) stream 68. The dry steam 64 can be used as the steam injected into the injection well of the well pair 12b.

[0074] In some example systems, a portion of the BBD_{WLS} stream 46 can be disposed of directly or stored as a BBD_{WLS} disposal stream 66. A portion of the EBD stream 52 can be recycled as recycled EBD stream 70 to other processing units. A portion of BBD_{EVAP} stream 68 can also be disposed of directly or stored as a BBD_{EVAP} disposal stream 72.

[0075] The BBD_{WLS} stream 46, EBD stream 52 and BBD_{EVAP} stream 68 can be sent as waste brines to a blowdown treatment and solidification (BDTS) operation 74 where the streams, either independently or in combination, can be treated with a solidification formulation 76 resulting in a solid material which can be disposed in a landfill. A portion of the produced water 20a, 20b can also be sent as waste brine stream 78a, 78b to the BDTS operation 74. Waste brine stream 78a, 78b can also be combined with one or more of the BBD_{WLS} stream 46, EBD stream 52 and BBD_{EVAP} stream 68 to form a single brine to be subjected to the solidification operation. The BBD_{WLS} stream 46, EBD stream 52, BBD_{EVAP} stream 68 and waste brine stream 78a, 78b can also be stored independently or in combination in holding tank(s) before being sent to the BDTS operation 74.

Waste brine treatment and solidification implementations

[0076] As mentioned above, any one of the BBD_{WLS} stream 46, EBD stream 52 and BBD_{EVAP} stream 68, as well as produced water stream 78a, 78b, or any combination thereof, can be sent directly as waste brines to a solidification operation to facilitate their disposal in a landfill.

[0077] In some implementations, these blowdown streams can be subjected to additional treatments before the solidification operation itself, as will be now described referring to Figs 2 and 3.

[0078] In some implementations as illustrated in Fig 2, the BDTS operation 74 can include sending any one of the first and second boiler blowdown streams (BBD_{WLS}, BBD_{EVAP}) and evaporator blowdown stream (EBD), or any combination thereof, to a brine evaporator 80 to recover a water stream 82 and discharge a concentrated waste water brine stream 84. At this stage, the concentrated waste brine stream 84 is either mixed with a solidification formulation 76 in solidification operation 96 to form a solid waste material or sent to a crystallizer 86. In the crystallizer 86, the concentrated waste brine 84 can be further concentrated to produce water stream 88 and crystallizer waste brine stream 90. As was the case for the concentrated waste brine stream 84, the crystallizer waste brine stream 90 can either be sent to a solidification operation 96 or further fed to other water-removal devices or concentrators 92 to produce an even more concentrated waste brine stream 94. In the solidification operation 96, waste brine stream 84, 90 or 94 (or any combination of these streams) is mixed with a solidification formulation 76, to form solidified waste material 98 which can be disposed in a landfill 100, for example.

[0079] In some implementations, the waste brine stream which is sent to solidification operation 96 can contain approximately 35 wt% to 65 wt% total solids. Since the total solids (suspended and dissolved solids) content of the concentrated waste brine stream 84 can vary depending on the blowdown stream source (BBD_{WLS}, BBD_{EVAP} or EBD), further concentrating waste brine 84 in crystallizer 86 and/or other potential water-removal devices or concentrators 92 can be done to reach a suitable weight percentage of total solids in the waste brine to be solidified. In some implementations, the concentrated waste brine 84 is thus further concentrated to reach a minimum content of total solids content of approximately 35 wt% in crystallizer waste brine stream 90 or waste brine stream 94. The waste brines generated by the in situ hydrocarbon recovery operation

can be monitored for total solids content and other properties, such as composition, temperature, and so on, and the waste brines can be blended or pre-treated in order to achieve a desired state, such as a minimum total solids concentration of 35 wt%. The pre-treatment of the waste brines and the addition of the solidification reagent can be adjusted depending on the monitored properties.

[0080] Monitoring of the total solids content of the waste brines can be performed at different stages of the process. For instance, the solids content of the concentrated waste brine 84 can be measured at the exit of the evaporator 80 or the solids content of the crystallizer waste brine stream 90 can be measured after the crystallizer 86. Monitoring of the solids content can also be performed at different other positions during the process, for example at the exit of any other additional water-removal devices or concentrators 92. The total solids content can be measured for any one of the concentrated waste brines either in-situ or a brine sample can be collected and analyzed in a laboratory.

[0081] Referring now to Figs 4a and 4b, two different possible ways of adding the solidification formulation to the waste brine to form a solidified waste material will be described.

[0082] As illustrated in Fig 4a, the solidification formulation can be added in-line to the concentrated waste brine 84, 90, 94 upstream of the solidification unit 102. Alternatively, as illustrated in Fig 4b, addition of the solidification formulation to the waste brine can be done directly into the solidification unit 102. The waste brine(s) to be treated with the solidification formulation are generally hot due to the process upstream of solidification. The temperature of the waste brine(s) can be about 90-100°C when the solidification formulation is added thereto. In solidification unit 102, the mixture waste brine and solidification material is further blended to form a paste consisting of “solidified” waste material 98 which can further be sent for disposal, e.g. in landfills. It should be noted that the reaction occurring when the solidification reagents are mixed with the waste brine

produces a thickened waste material which will eventually become fully solid after disposal thereof, for example in a landfill. Solidification unit 102 can include an inline mixer or a tank provided with a mixer, for instance a ribbon mixer or a pug mill, which facilitates thorough mixing of the solidification reagents and the waste brine. Upon thorough mixing, the reagents of the solidification formulation can be incorporated into the waste brine and reactions between the reagents and the components of the waste brine can occur to promote solidification of the waste brine.

[0083] It should also be noted that the solidification formulation can include a single component or a mixture of components. When a mixture of components makes up the solidification formulation, they can be added together or separately to the waste brine. In some implementations, the solidification formulation can be a mixture of dry components that can be added together as a powder to the waste brine in the mixer. In some implementations, the mixer can be designed so that the dry ingredients of the solidification formulation are wetted before incorporation into the waste brine with reduced or no soak time. Hence, in some implementation the solidification formulation can be in the form of a liquid or a slurry when added to the waste brine.

[0084] After addition of the solidification formulation to the waste brine and mixing, the resulting solidified waste material which is in the form of a paste, slurry or solid, can be discharged from the solidification unit 102 through a pipe or chute for disposal into containers for later disposal to the landfill, or can be pumped directly to the landfill where it is left to sit, e.g. in sloped lifts, and where it is allowed to fully solidify. The addition/mixing/discharge process can be run in a continuous, batch or semi-batch mode. When the slurry is disposed of in containers, it can be left to sit therein for several hours or days during which the slurry can further solidify, before being transported to the landfill. It should be noted that final strength development of the solidified waste material can take several weeks, and there is no specific requirement that final strength be achieved before initial placement in the landfill.

[0085] The solidification process not only allows the formation of solid products which can be easily disposed in landfills, but the chemical reactions between the solidification reagent(s) and the waste brine can also allow stabilizing the solidified waste by reducing the amount of material that can be leached therefrom when it is exposed to water. Further detail will be provided below on the solidification/stabilization process itself.

[0086] The nature of the solidification formulation, which will be described in more detail below, and the quantities thereof to be added to the waste brine to achieve proper solidification, can depend on the waste brine chemistry and its solids content, and process operating parameters. As previously mentioned, the waste brine can originate from different water treatment processes used in the SAGD operation, and, the waste brine chemistry is influenced by these treatments. For instance, the waste brine originating from the first boiler blowdown stream BBD_{WLS} which has been treated with lime softening and ion exchange processes has a concentration in calcium, magnesium and silica which is lower than the concentration of these elements/components in the waste brines originating from evaporator blowdown streams (BBD_{EVAP} or EBD). Also, the amount of organic compounds present in the waste brines can be different depending on their origin. These differences can affect the type and amount of solidification formulation that can be used. Hence, in some implementations, testing can be performed to determine the proper quantity of solidification formulation that is required to solidify a given waste brine. Testing can also confirm that the nature of the solidification formulation is adapted to achieve a proper solidification or can be used to adjust the solidification formulation recipe.

[0087] In some implementations, testing can first be performed to determine the chemical characteristics of the concentrated waste brine. For instance, one can determine the Total Organic Carbon (TOC) content and the Loss-On-Ignition (LOI) of the waste brine to be treated as well as the content in calcium, magnesium, sulfur and/or silica which will provide an indication of the type and quantity of solidification reagent(s) to be used to achieve proper solidification.

More details will be provided below regarding the choice of the solidification reagent(s) depending on the chemical characteristics of the concentrated waste brine.

[0088] In some implementations, testing can also include determining the properties of the solidified waste material to insure that the solidification formulation is adapted for properly solidifying a given waste brine. A preliminary visual assessment can be performed followed by one or more further tests including for example a standard concrete industry slump test, a standard Paint Filter test, rheology measurements (such as Unconfined Strength Test) and hydraulic permeability, to ensure that the desired solidification has occurred. Testing can also be performed on the solidified waste material left to sit for several hours to few days. For instance, the confined compressive strength of the solidified material can be measured with a pocket penetrometer within few hours of mixing and/or after 1 to 7 days. The results of these tests can be used as a solidification indicator to adjust the amounts of solidification formulation added, the types or reagents added, the mixing intensity provided, or other process parameters.

[0089] Unconfined compressive strength and hydraulic permeability are other properties of the solid waste material that can be determined. They are usually measured on solidified waste material left to cure for few days, e.g. 7, 14 and/or 28 days. The unconfined compressive strength can be measured to determine if the solidified waste material has a desired strength to be able to support loads such as heavy equipment moving over the deposited materials in a landfill. Hydraulic conductivity can be measured to determine the ability of the solidified waste material to shed water in response to an applied hydraulic gradient and to determine the contaminant leachability.

Solidification formulation recipes

[0090] The waste brine to be solidified is generally in the form of a concentrate liquid or a slurry which contains solids, both of organic and mineral nature, salts,

including contaminants suspended or dissolved in water. Addition of the solidification formulation into this waste slurry generates a reaction between the waste components and the solidification formulation resulting in the formation of a solid. Moreover, chemical reactions can arise whereby the contaminants are converted into less soluble and less mobile forms. This results in a reduction of the leachability of the waste which is thus "stabilized". Therefore, addition of the solidification formulation can induce two reactions: solidification which changes the physical nature and handling characteristics of the waste, and stabilization which chemically reduces the hazard potential of the waste. The solidification formulation can be in various forms and can include various possible reagents as will be now described in greater detail.

Solidification formulation including fly ash having high carbon content

[0091] In some implementations, the waste brine resulting from the thermal in situ hydrocarbon recovery operation can be treated with a solidification formulation including fly ash having substantial carbon content. An example of fly ash having high carbon content includes fly ash generated during the combustion of petroleum coke (pet-coke). Details on the production of pet-coke fly ash will be provided below. Other types of fly ash containing substantial carbon content can also be obtained in certain power plants that produce coal fly ash, such as power plants where powdered activated carbon is added to the flue gas stream of the coal combustion process as a way of removing mercury from emissions. This can result in a larger fraction of the produced coal fly ash being of the high-carbon variety.

[0092] In some implementations, the carbon content of the fly ash to be used in the solidification formulation can be at least about 25 wt%, or even at least at least about 50 wt%. The fly ash used in the solidification formulation can also be characterized by its Loss-On-Ignition (LOI) value. In some implementations, the fly ash as a LOI of at least about 50% or at least about 60%.

[0093] It should be noted that the carbon-containing compounds present in the pet-coke fly ash, such as organic carbon present in pet-coke fly ash, can interact with the organic components of the waste brine to promote solidification of the waste brine. It should also be noted that other components present in the pet-coke fly ash, such as calcium oxide, calcium sulfate and silica can also contribute to the solidification process.

[0094] Fig 5 illustrates a process for obtaining pet-coke fly ash that can be used in waste brine solidification operation 96. A petroleum feedstock stream 103, that need to be upgraded can be fed to a coking unit 104 to produce a hydrocarbon stream 106 containing higher-value products and pet-coke stream 108. In some implementations, the petroleum feedstock can be bitumen, such as bitumen recovered from a thermal in situ recovery operation, e.g. SAGD, and the higher-value product can be synthetic crude oil. Use of pet-coke fly deriving from petroleum feedstock produced in a SAGD operation to solidify waste brine deriving from the same SAGD operation, rather than buying and transporting commercial solidification reagents, can be economically and environmentally beneficial.

[0095] In coking unit 104, thermal cracking of the petroleum feedstock allows breaking down the long hydrocarbon molecules into lighter hydrocarbon products, such as gas oils, and kerosene distillates. Coking also concentrates extra carbon into the pet-coke by-product. In some implementations, the coking process can be delayed coking. In delayed coking, large reactors called coke drums are used to hold the heated petroleum feedstock while the cracking takes place. Pet-coke is deposited in the coke drum as a solid which builds up during cracking. In order to facilitate the removal of the pet-coke, by hydraulic cutting, the hot petroleum feedstock is diverted from one coke drum to another, alternating the drums between pet-coke removal and the cracking part of the process. The so-produced pet-coke can contain over about 80 wt% carbon. In some implementations, pet-coke 108 can be conveniently stored in storage facility 110 before being used for the production of pet-coke fly ash.

[0096] Still referring to Fig 5, in some implementations, pet-coke 108 resulting from the coking process can be used as pet-coke fuel to heat water 112 in steam/heat production unit 114 and generate steam stream 116 and heat 118. Unit 114 can include one or more boilers where combustion of pet-coke, e.g. circulating fluidized bed combustion, produces heat which can be used to boil water 112 and produce steam 116. Steam 116 can then be used to drive large turbines to produce electricity. The flowing gas containing fine solid particles resulting from the pet-coke combustion can be captured and recovered as fly ash 120. In some implementations, an electrostatic precipitator (ESP) (not illustrated) is used to collect pet-coke fly ash 120. It should be noted that fly ash resulting from circulating fluidized bed combustion of pet-coke can have very large amounts of unburned carbon as well as high amounts of calcium and sulfur. It should also be noted that the chemical compositions of the fly ash can depend on the origin of the pet-coke being burned. In some implementations, an analysis of the pet-coke fly ash can be performed to determine the quantity of some of its chemical constituents, for instance the carbon, calcium or sulfur content, as well as its LOI.

[0097] Still referring to Fig 5, pet-coke fly ash 120 obtained from the combustion of pet-coke can be used as a solidification reagent, either alone or admixed with further reagents, to treat waste brines produced in a hydrocarbon recovery operation. In some implementations, pet-coke fly ash 120 can be stored, for example in silos, before being used in solidification operation 96.

[0098] As previously mentioned, fly ash containing high amount of carbon, at least about 25 wt% carbon, can be used as a waste brine solidification reagent alone or can be part of a solidification formulation including further solidification reagents. In some implementations, high carbon content fly ash can be used in combination with one or more calcium-containing reagents. The addition of a calcium-containing reagent can improve solidification for certain type of brines, for example brines having lower calcium content, such as brines deriving from water streams which have been treated with warm lime softening process. The

relative quantities of fly ash and other calcium-containing compounds in the solidification formulation can be determined depending on the chemistry of the waste brine. Solidification bench tests can be performed if required to provide a proper formulation. Examples of calcium-containing reagents that can be used in the solidification formulation in combination with the high carbon-containing fly ash include for example calcium oxide (quicklime), calcium hydroxide, Portland cement, cement kiln dust, ground-granulated blast-furnace slag, calcium silicate and Class C or Class F fly ash.

Solidification formulation according to waste brine chemistry

[0099] As previously mentioned, the waste brines derived from thermal in situ recovery operation, e.g. SAGD, can have different chemistries depending on their origin. Referring to Figs 6a and 6b, waste brine originating from evaporator blowdown streams 52, 68 can have a concentration in calcium and/or silica which is higher than the concentration of these constituents in waste brine originated from boiler blowdown stream 46 which has been treated with warm lime softening. The difference in calcium and/or silica content of the waste brines can affect the type and amount of solidification reagents containing calcium and/or silica required for solidification to occur. The chemistry of the waste brines can also vary in terms of the amount of organic compounds it contains, which can also be different depending on the origin of the waste brine. The difference in organics content can also affect the type and amount of solidification reagents required for solidification to occur.

[0100] Hence, solidification of the waste brines generated during thermal in situ recovery operation can require solidification formulations including various solidification reagents and/or amounts of solidification reagents to reach proper solidified material, as will be described below.

[0101] Still referring to Fig 6a, in some implementations, waste brine 46 originating from warm lime softener stream can be concentrated, for instance in one or more evaporators and/or crystallizers, to give concentrated waste brine

stream 122. Concentrated waste brine stream 122 can have a solids content of about 35 to 65 wt%. This concentrated waste brine is usually depleted in calcium and silica. Hence, in some implementations, concentrated waste brine stream 122 can be treated with solidification formulation 124 including calcium- and silica-reagent(s), for solidification to occur. In some implementations, the solidification formulation is provided to have an increased amount of calcium for lower calcium contents in waste brine 122.

[0102] Referring now to Fig 6b, in some implementations, waste brine derived from an evaporator blowdown 52, 68 can be concentrated, for instance in one or more evaporators and/or crystallizers, to give concentrated waste brine stream 126. Concentrated waste brine stream 126 can have a solids content of about 35 to 65 wt%. This concentrated waste brine 126 usually has a higher calcium and/or silica content compared to the content of these constituents in corresponding waste brine 122 derived from lime-softened stream. Hence, in some implementations, solidification of concentrated waste brine stream 126 can be performed by adding solidification formulation 128 which includes a calcium-containing reagent, but in a dosage which is lower compared to a corresponding dosage of the same calcium-containing reagent required to enable solidification of corresponding concentrated waste brine 122 derived from lime-softened stream. It should be noted that solidification formulation 128 can also contain silica in addition to calcium. Calcium and silica can be present in a same reagent or can be provided to the solidification formulation through two or more reagents.

[0103] In some implementations, various waste brines derived from a thermal in situ recovery operation can be combined to be solidified together and disposed of in landfills as a single solidified waste material. For instance, waste brine 52 and/or waste brine 68, derived from evaporator blowdown streams, can be combined with waste brine 46 derived from lime-softened blowdown stream to be subjected to solidification together. In some embodiment, the combined waste brines can be concentrated before addition of the solidification formulation. Alternatively, concentrated waste brine 122 derived from lime-softened stream

can be combined with concentrated waste brine 126 derived from evaporator blowdown, to produce a concentrated combined waste brine to be subjected to solidification. In these implementations, solidification of the combined waste brine can be performed by addition of a calcium- and silica-containing solidification formulation. The calcium and silica solidification dosage to enable solidification of the combined waste brine can be lower compared to a corresponding dosage of calcium and silica required to enable solidification of waste brine 122 derived from lime-softened stream.

[0104] In some implementations, proper solidification of the waste brine, either derived from lime-softened stream, derived from an evaporator blowdown, or the combined waste brine, having a solids content between 35 wt% and 65 wt%, can be achieved by addition of the solidification formulation in an amount of between 1:3 and 1:1 of the solidification formulation to waste brine on a total weight basis. In some implementations, the amount of solidification formulation required to achieve proper solidification of waste brine derived from lime-softened stream can be higher compared to the amount of solidification formulation required to achieve solidification of waste brine derived from evaporator blowdown stream.

[0105] As previously mentioned, not only the calcium and silica content of the waste brine can affect solidification, but its organics content can also play a role in the solidification process. In some implementations, the solidification formulation can include carbon compounds, particularly organic carbon-containing compounds, which can react with organic compounds in the waste brine to enhance solidification of the waste brine. In some implementations, the solidification formulation can be provided to have an increased amount of carbon for higher organics-to-calcium ratios in the waste brine.

[0106] Hence, in some implementations, the solidification formulation can include an organic carbon-containing reagent. An example of such organic carbon-containing reagent can be fly ash produced from petroleum coke, such as petroleum coke deriving from a SAGD operation. The organic-carbon containing

compounds such as those present in pet-coke fly ash can interact with organics present in the waste brine to be treated and can enhance its solidification. Hence, fly ash derived from petroleum coke, e.g. fly ash produced by delayed coking of bitumen feedstocks, can be used, either alone or in combination with other reagents, in the solidification formulation. For example, further calcium containing reagents can be used in the solidification formulation, in addition to the fly ash containing organic carbon-containing compounds, to provide additional amounts of calcium as required depending on the chemistry of the waste brine. Examples of calcium containing reagents can include quicklime (CaO), calcium hydroxide (CaOH), Portland cement, calcium silicate, Class C fly ash, Class F fly ash, cement kiln dust and/or ground-granulated blast-furnace slag. The reagents can be used in various quantities which can be calculated depending on the chemistry of the waste brine.

[0107] In some implementations, the waste brine to be solidified can be analyzed to determine its chemical characteristics to enable preparation of a proper solidification formulation according to these chemical characteristics. In some implementations, at least the silica content, calcium content and organics content of the waste brine can be determined. Once the silica, calcium and organics content of the waste brine has been determined, a proper solidification formulation can be prepared by mixing reagents which, in combination, will provide organic carbon, silica and calcium in amounts enabling solidification of the waste brine. The amounts of reagents providing organic carbon, silica and calcium can be determined according to the calcium, silica and organics contents of the waste brine.

[0108] In some implementations, the waste brine to be subjected to solidification can be determined to be calcium depleted and the solidification formulation can be provided to include high calcium content. In some implementations, waste brine originated from a warm lime softener stream, such as stream 122 in Fig 6a, can be subjected to solidification using a calcium-rich solidification formulation.

[0109] In some implementations, the waste brine to be subjected to solidification can be determined to be calcium rich, and the solidification formulation can be provided to include a low calcium content. In such implementations, the solidification formulation can be prepared using calcium-containing reagents including a lower proportion of calcium and/or using a lower proportion of the calcium-containing compounds. As previously mentioned, waste brine originated from evaporator streams, such as stream 126 in Fig 6b, can be calcium rich and can therefore be subjected to solidification using a low calcium content solidification formulation.

[0110] It should be noted that depending on the nature of the waste brine, including its calcium, silica and organics content, and the nature of the compounds present in the solidification formulation, different type of reactions can be involved to achieve solidification of the waste brine. As mentioned above, waste brine derived from evaporator blowdown, which has not been subjected to warm lime-softening, contain higher concentrations of calcium and silica compared to the brines that have undergone softening. Solidification of such waste brine can be achieved using cement chemistry and traditional solidification reagents. For instance, cement kiln dust and fly ash (Class C or Class F), which can contain various amounts of silica, calcium oxide, as well as aluminum oxide and iron oxide, can be used to make up a formulation enabling solidification of waste brine originated from evaporator blowdown. In some implementations, the formulation for solidifying waste brine derived from evaporator blowdown can include a large amount of cement kiln dust and a lesser amount of fly ash. A cementitious reaction can occur between the compounds in the solidification formulation and the constituents of the waste brine with the formation of various minerals including calcium aluminum silicate. Differently, waste brine derived from warm lime-softened streams, contain low concentrations of calcium and a solidification formulation with high calcium content can be required to achieve solidification. For example, a formulation including calcium oxide and fly ash (either Class C or pet-coke fly ash) can provide high calcium content but with lower concentrations of aluminum, silica and iron. In this case, it is supposed that

the solidification mechanism can include precipitation with the sulfates contained in the waste brine, resulting in the formation of gypsum, ettringite and other calcium aluminum sulfate minerals.

[0111] Referring now to Fig 7, the various steps implemented in the treatment of a given waste brine generated in a SAGD operation will be described. In step 200, the waste brine, which can be any waste brine derived from water produced in the SAGD operation, including for example waste brine derived from lime-softened blowdown streams and/or streams which have not been subjected to lime-softening, can be concentrated to reach a minimum content of suspended solids in the waste brine. For example, the waste brine can be concentrated to achieve a content of total suspended solids between about 35 wt% and 65 wt%. Concentration of the waste brine can be achieved in one or more evaporator and/or crystallizer or any other suitable water-removal devices.

[0112] In following step 210, the concentrated waste brine can be subjected to various analyses in order to determine its chemical characteristics. The chemical analysis can provide information on the constituents present in the concentrated waste brine and their relative amounts. For instance, the chemical analysis can provide information on the calcium and/or silica content in the concentrated waste brine, and also on its organics content. As previously mentioned, this information on the chemical characteristics of the waste brine can be useful to prepare a suitable solidification formulation.

[0113] The preparation of the solidification formulation in step 220 can thus be performed based on the result of the chemical analysis of the concentrated waste brine. In some implementations, the solidification formulation can be prepared to include carbon, silica and calcium which will interact with the constituents of the waste brine to promote solidification thereof. The content of each of calcium, silica and carbon can thus be selected according to the determined calcium, silica and organics content of the waste brine. In some implementations, the SAGD concentrated waste brine can be determined to have a high ratio of

organics compared to calcium and/or silica and the solidification formulation can be prepared to provide a high carbon content reagent, such as pet-coke fly ash. In some implementations, the concentrated waste brine can be determined to contain low concentrations of calcium, e.g. waste brine derived from a lime-softened stream, and a solidification formulation containing high content of calcium can thus be prepared.

[0114] The solidification formulation can be in the form of a powder which can be added to the concentrated waste brine. If a combination of reagents is required to prepare the solidification formulation, these reagents can be mixed together prior to being added to the waste brine in step 230. In some implementations, the dry reagents can be blended together to result in a more homogenized powder.

[0115] Analysis of the waste brine chemistry can also provide information on the quantity of solidification reagents to be added to the concentrated waste brine in step 230 to favor solidification. In some implementations, the solidification formulation can be added to the concentrated waste brine in step 230, in an amount of approximately 0.3 to 1.0 kg per liter (kg/L) of waste brine. In some implementations, the concentrated waste brine can be determined to have low calcium and/or silica content, such as when the waste brine is derived from a lime-softened blowdown stream, and the solidification formulation can be added in an amount close to the higher dosage rate range stated above. In some implementations, such as when the waste brine is derived from a stream which has not been subjected to lime-softening, the solidification formulation can be added in an amount closer to the lower dosage rate range stated above.

[0116] As previously mentioned, the solidification formulation can be added to the concentrated waste brine as a powder to promote solidification. Addition of the solidification formulation can be carried out in a tank provided with a mixer. In some implementations, the mixer can be designed so that the dry ingredients of

the powder can be wetted before incorporation into the waste brine without a soak time.

[0117] In step 240 the mixture of waste brine and solidification reagents is blended to allow incorporation of the solidification reagents into the waste brine to enhance reaction between the solidification reagents and the waste brine components in step 250. The mixing step 240 can be performed in any mixer suitable to thoroughly blend the waste brine and the solidification reagents, e.g. a ribbon mixer, pug mill or any other suitable device. In steps 240, the components of the waste brine and solidification reagent can start to react to initiate solidification upon contact during mixing and can continue reacting over time in step 250 and even in step 260 as explained below.

[0118] The waste material obtained in step 250 can be in the form of a paste or slurry which can be pumped directly for disposal in a landfill in step 260. Then, in the landfill, the slurry is left to sit, e.g. in sloped lifts, and is allowed to fully solidify. Alternatively, the slurry resulting from step 250 can be discharged from the mixer into disposal containers in step 260. Then, the slurry in the containers can be left to sit therein for several hours to few days during which the slurry can further solidify, before being transported to the landfill.

EXAMPLES

[0119] SOLIDIFICATION PERFORMANCE CRITERIA

[0120] Addition of chemical solidification reagents to SAGD brines was intended to result in a solid waste that was suitable for disposal in a regulated industrial

landfill in the Province of Alberta. A series of performance criteria were developed, and are summarized in Table 1.

[0121] Table 1: Performance Criteria

Test	Goal
Paint Filter Test	Pass
Unconfined Compressive Strength (UCS)	≥ 10 psi
Early Compressive Strength Development (Penetrometer)	≥ 2.5 ton/ft^2
TCLP (leachability)	Pass
Hydraulic Conductivity	1x10^{-6} cm/s

[0122] SAGD BRINE SAMPLES

[0123] Waste brines from four operating SAGD facilities were used for bench-scale solidification experiments. Brine 1 was an OTSG blowdown crystallizer concentrate, Brine 2 was a produced water evaporator concentrate, Brine 3 was an OTSG blowdown and Brine 4 was a de-oiled produced water.

[0124] Samples of each of the brines were heated and mixed at 180°F (82°C). Total suspended solids measurements were taken. The hot brines were then filtered through 25 µm paper filters and the concentrations of various chemical species measured in the filtrate. The chemical characteristics of the brines, as received, are summarized in Table 2. Although complete speciation is not shown, cations and anions balanced to within 90 to 110% for brines 3 and 4, whereas difficulties with some analyses were found for the higher salinity brines 1 and 2, in which the ions balanced only within +/- 25%. Total organic carbon (TOC) was measured using a thermal combustion technique and also measured as loss on ignition (LOI). Silica and sulfur were measured by inductively coupled plasma (ICP). The alkalinity results, which were determined using a standard pH titration, include a large contribution from the organic acids present within the samples. This can be seen in brine 4, where the standard alkalinity titration results were compared to a measurement of total inorganic carbon (TIC). The TIC results

provide a more realistic measure of the carbonate / bicarbonate species present. TIC measurements were not done on brines 1 through 3.

[0125] As can be seen in Table 2, the chemistry of the brines varied from site to site. However, some trends are evident. The inorganic chemistry of each brine was influenced by whether or not warm lime softening (WLS) was used in the water treatment process upstream of the sample point. Brine 4 (a de-oiled produced water) and brine 2 (the concentrate from an evaporator treating de-oiled produced water) were not treated by a WLS and contained, therefore, significant concentrations of Ca, Mg, and SiO_2. On the other hand, brines 1 and 3 were OTSG blowdown streams that had Ca, Mg, and Si removed by upstream WLS treatment and were, therefore, low in Ca, Mg, and SiO_2 concentrations.

[0126] Organics concentrations also differed amongst the brines. Table 2 includes a calculated TOC:TDS ratio, which provides an estimate of the relative amount of organic material present. The organics present in SAGD produced water are highly water soluble and include hundreds of different individual compounds.

[0127] Table 2: Composition of SAGD waste brines (concentrations given on a mg/kg of filtrate basis, except for TSS, as noted)

	Brine 1 OTSG Blowdown Crystallizer Concentrate	Brine 2 Produced Water Evaporator Concentrate	Brine 3 OTSG Blowdown	Brine 4 De-oiled Produced Water
Bulk Parameters pH TSS (mg/L)	 13.6 326,000	 13.5 360	 12.2 12	 8.1 65
Filtrate Concentrations				

TDS (105°C)	409,000	133,000	56,000	2,190
Na	128,000	34,200	18,500	461
Ca	50	94	2	3
Mg	16	<5	0.5	1
SiO_2	3,200	12,700	161	120
Cl	104,000	6,800	24,800	440
Total S	2,200	5,500	680	25
TIC	-	-	-	69
TOC	58,400	21,500	5,000	480
Total Alkalinity (as $CaCO_3$)	75,900	44,400	5,820	405
TOC/TDS ratio	0.14	0.16	0.09	0.22

[0128] To facilitate the direct comparison of the different brines, Table 3 shows the concentrations of key constituents normalized to the total solids of brine 1, which was the most concentrated.

[0129] Table 3: Composition of SAGD Brines Normalized to Brine 1 Total Solids

Brine	Concentration Factor	Total Solids (mg/kg)	TOC (mg/kg)	SiO_2 (mg/kg)	Ca (mg/kg)
1	1	676,000	58,400	3,200	50
2	5	676,000	109,313	64,571	478
3	12	676,000	60,376	1,941	24
4	309	676,000	148,211	37,053	1,019

[0130] SOLIDIFICATION REAGENTS

[0131] SAGD brines are highly alkaline, and can contain significant amounts of Ca and Si. Therefore, solidification agents that would augment the CaO and SiO_2 content of the brines were selected for evaluation. These included Portland cement, cement kiln dust, lime, fly ash (including fly ash with high carbon content), clays, and sodium silicate.

[0132] SOLIDIFICATION EXPERIMENTS

[0133] A three-tier approach was used for the bench-scale solidification tests reported here. Tier 1 was a general screening of various brine and reagent

combinations. Typically, 20 to 40 combinations of reagents were tested for each brine sample. Paint filter and pocket penetrometer tests were performed on each sample after curing at ambient temperature in the lab. The best results from Tier 1 were used to select Tier 2 mix formulations, where 10 to 15 combinations of reagents were tested. In addition to the paint filter and pocket penetrometer tests, UCS and TCLP tests were also performed. In the Tier 3 tests, a larger volume of sample was mixed to minimize heat loss during the reaction phase, and to allow more extensive analyses to be performed. An overview of the tiered testing program is shown in Table 4. While the brine formulations were mixed at about 90°C, the landfill samples were blended at ambient laboratory temperature.

[0134] Table 4: Overview of Tiered Bench-Scale Test Procedures

Tier	Analytical Tests
1	Paint Filter Test – after 24 hours of curing Pocket Penetrometer – after 1, 3, 5, 7 days of curing
2	Paint Filter Test - after 24 hours of curing Pocket Penetrometer – after 1, 3, 5, 7 days of curing UCS after 7 days of curing TCLP after 7 days of curing
3	Paint Filter Test - after 24 hours of curing Pocket Penetrometer – after 1, 3, 5, 7 days of curing UCS after 7, 14, 18 days of curing TCLP after 7 days of curing Permeability after 28 days of curing

[0135] Prior to each tier of the solidification experiments, the as-received brines were heated and mixed to a uniform consistency, then concentrated in the laboratory by thermal evaporation until they were similar in total solids to what would be expected in an operating crystallizer. As shown in Table 3, the brines were boiled down to the degree necessary to make them approximately of the same TS concentration as the brine 1 crystallizer blowdown. The SAGD landfill test materials were not heated or concentrated. They were mixed and cured at ambient room temperature.

[0136] RESULTS

[0137] Highlights of the brine solidification tests are shown in Table 5. The total dosages of combined reagents added to the various samples to meet the stated solidification goals ranged from a low of 0.3 to a high of 0.8 kg per liter of brine and 0.5 to 0.7 kg per liter of landfill matrix.

[0138] Due to shipping logistics, brine 2 was the first brine to be analyzed. Tier 1 testing began with the use of Portland cement, alone, and with various fly ashes, Calciment, and blast furnace slag. Only Portland cement in combination with Calciment and combinations of fly ash and cement kiln dust (CKD) achieved penetrometer readings above 2.5 ton/ft^2 in Tier 1 testing. Tier 2 and 3 tests further refined these combinations. Cement kiln dust in combination with fly ash at relatively moderate additive levels was found to achieve UCS readings above 10 psi. For many formulations, greater than 25% of the final strength was developed after 4 hours of curing. This represents a relatively short curing time before the material is suitable for landfill placement.

[0139] Brine 1 was analyzed next. Tier 1 and 2 testing was conducted. It was found that the use of calcium-rich additives such as quicklime (CaO) in combination with fly ash at additive levels of about twice the brine 2 level.

[0140] Combinations of quicklime and CKD, silicates, or fly ash were found to be successful for brines 3 and 4, although higher reagent dosages were required for brine 3.

[0141] The above results indicate that solidification processes are effective for the conversion of waste SAGD brine to a solid waste suitable for landfill disposal. The results also indicate that lower additive dosages were adequate for brines that were not pre-treated with WLS. The type and amount of solidification reagents required can be adapted to reach the desired strength of the solidified product.

[0145] Table 5: Reagent formulations and test results for concentrated brines

Sample	Reagents Dosage	Reagents	Paint Filter Test	Pentrometer @ 7 days	UCS @ 14 days	UCS @ 28 days	Hydraulic Permeability	TCLP
	Kg/L Brine			(tons/ft^2)	(psi)	(psi)		
			EPA SW-846 Method 9095		ASTM D 2216		ASTM 5084	EPA SW-846 Method 1311
Brine 1: Crystallizer Concentrate from WLS Pre-treated OTSG Blowdown								
1	Moderate	Quicklime + Flyash	Pass	> 4.5	17	-	-	Pass
2	Moderate (+5%)	Quicklime + Flyash	Pass	> 4.5	20	-	-	Pass
3	Moderate (-5%)	Quicklime + Flyash	Pass	> 4.5	14	-	-	Pass
Brine 2: Produced Water Evaporator Concentrate – Concentrated to Crystallizer TS								
1	Low	CKD + Flyash	Pass	3.25	12.3	64	4.5×10^{-6}	Pass
2	Low (+10%)	CKD + Flyash	Pass	2.75	20	-	1.9×10^{-7}	Pass
Brine 3: WLS Pre-treated OTSG Blowdown – Concentrated to Crystallizer TS								
1	High	Quicklime + CKD	Pass	4.5	-	-	-	-
2	High (-5%)	Quicklime + CKD	Pass	> 4.5	-	-	-	-
3	High (-35%)	Quicklime + Silica	Pass	> 4.5	-	-	-	-
Brine 4: Produced Water– Concentrated to Crystallizer TS								
1	Low	Quicklime + Flyash	Pass	> 4.5	-	-	-	-
2	Low	Quicklime + Flyash	Pass	> 4.5	-	-	-	-
3	Low (+5%)	Quicklime + Flyash	Pass	> 4.5	-	-	-	-

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CLAIMS

1- A process for solidifying waste brine derived from a thermal in situ recovery operation, comprising:

generating blowdown from an evaporator used to treat produced water from the thermal in situ recovery operation, and deriving a first waste brine therefrom;

generating OTSG blowdown from lime-softened boiler feed water, and deriving a second waste brine therefrom;

combining the first and second waste brines to produce a combined waste brine; and

adding a solidification formulation comprising calcium and silica to the combined waste brine;

wherein the solidification formulation is provided with a calcium and silica solidification dosage enabling solidification of the combined waste brine, the solidification dosage being lower compared to a corresponding dosage of calcium and silica required to enable solidification of the second waste brine.

2- A process for solidifying waste brines derived from an oil sands hydrocarbon recovery operation, comprising:

generating a first waste brine and a second waste brine, wherein a concentration in calcium and silica in the second waste brine is lower than in the first waste brine;

adding a solidification formulation comprising calcium and silica to the first and second waste brines;

wherein an amount of the solidification formulation added to the first waste brine is lower than the amount of the solidification formulation added to the second waste brine.

3- A process for solidifying waste brine derived from an oil sands hydrocarbon recovery operation, comprising:

generating a first waste brine and a second waste brine, wherein a concentration in calcium and silica in the second waste brine is lower than in the first waste brine;

combining the first and second waste brines to produce a combined waste brine; and

adding a solidification formulation comprising calcium and silica to the combined waste brine;

wherein the solidification formulation is provided with a calcium and silica solidification dosage enabling solidification of the combined waste brine, the solidification dosage being lower compared to a corresponding dosage of calcium and silica required to enable solidification of the second waste brine.

4- The process of claim 2 or 3, wherein the first and second waste brines are derived from a SAGD hydrocarbon recovery operation.

5- The process of any one of claims 2 to 4, wherein the first and second waste brines are derived from a SAGD water treatment system.

6- The process of any one of claims 2 to 5, wherein the first and second waste brines are derived from de-oiled produced water streams.

7- The process of any one of claims 2 to 6, wherein the first and second waste brines are independently derived from a crystallizer blowdown stream, an evaporator blowdown stream, and/or an OTSG blowdown stream.

8- The process of any one of claims 1 to 7, wherein a total solids content of the waste brine to which the solidification formulation is added, is comprised between 35 wt% and 65 wt%.

9- The process of any one of claims 1 to 8, wherein calcium and silica are provided in the solidification formulation in a same reagent.

10- The process of any one of claims 1 to 8, wherein calcium and silica are provided in the solidification formulation through two or more reagents.

11- The process of any one of claims 1 to 10, wherein the solidification formulation comprises calcium oxide, calcium hydroxide, Portland cement, cement kiln dust, calcium silicate, Class C fly ash, Class F fly ash and/or ground-granulated blast-furnace slag.

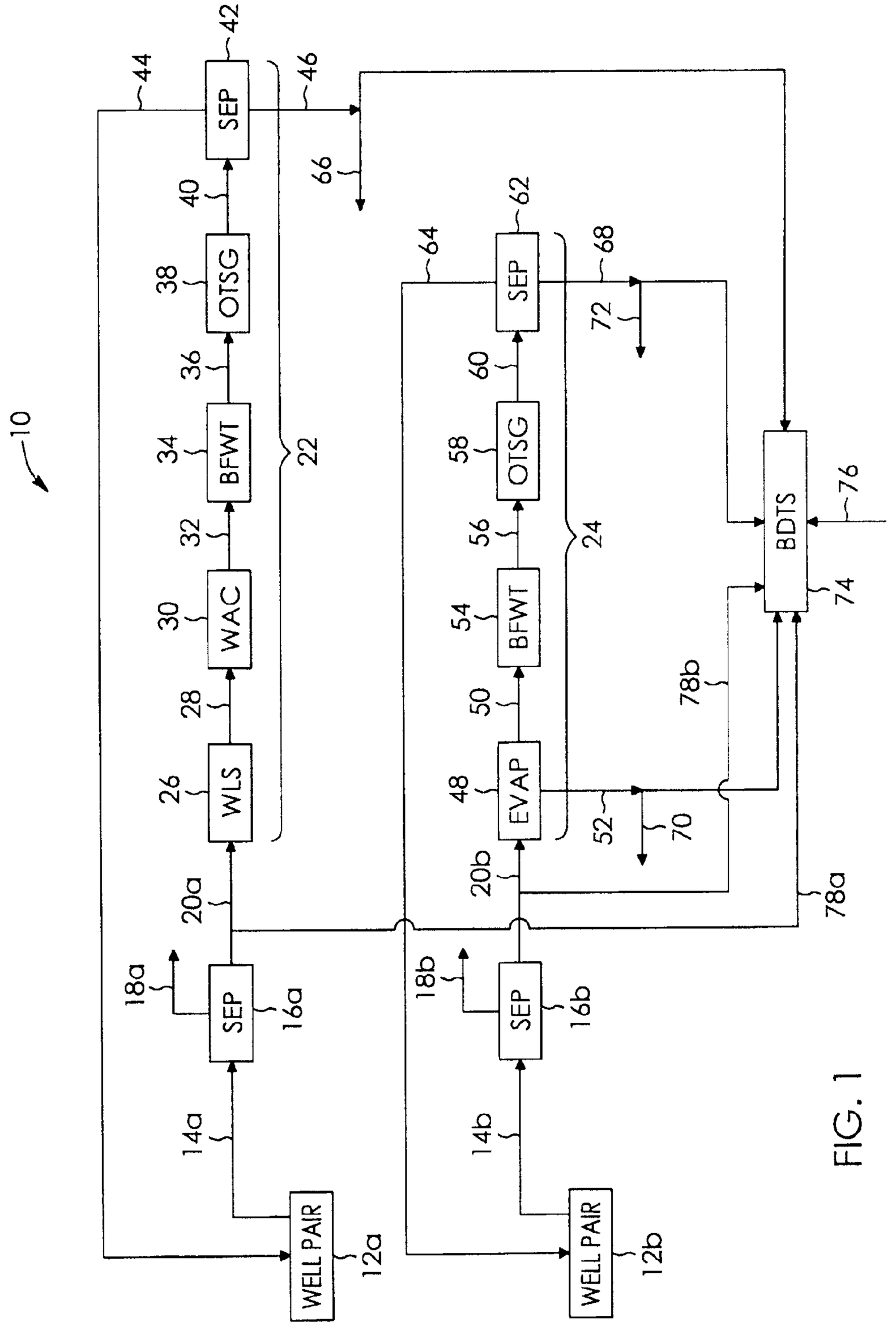
12- The process of any one of claims 1 to 11, wherein the solidification formulation is provided in an amount from 0.3 to 1.0 kg/L of waste brine.

13- The process of any one of claims 1 to 11, wherein the solidification formulation is added to the waste brine in a ratio solidification formulation to waste brine between 1:3 and 1:1 on a total weight basis.

14- The process of any one of claims 1 to 13, wherein a temperature of the waste brine before addition of the solidification formulation is between 90-100°C.

15- The process of any one of claims 1 to 14, wherein the solidification formulation comprises dry components added as a powder to the waste brine.

16- The process of any one of claims 1 to 14, wherein the solidification formulation comprises dry components which are wetted before addition to the waste brine.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38
40
SEP
42
44
46
66
22
WELL PAIR
12b
14b
SEP
16b
18b
20b
EVAP
48
50
BFWT
54
56
OTSG
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SEP
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BDTS
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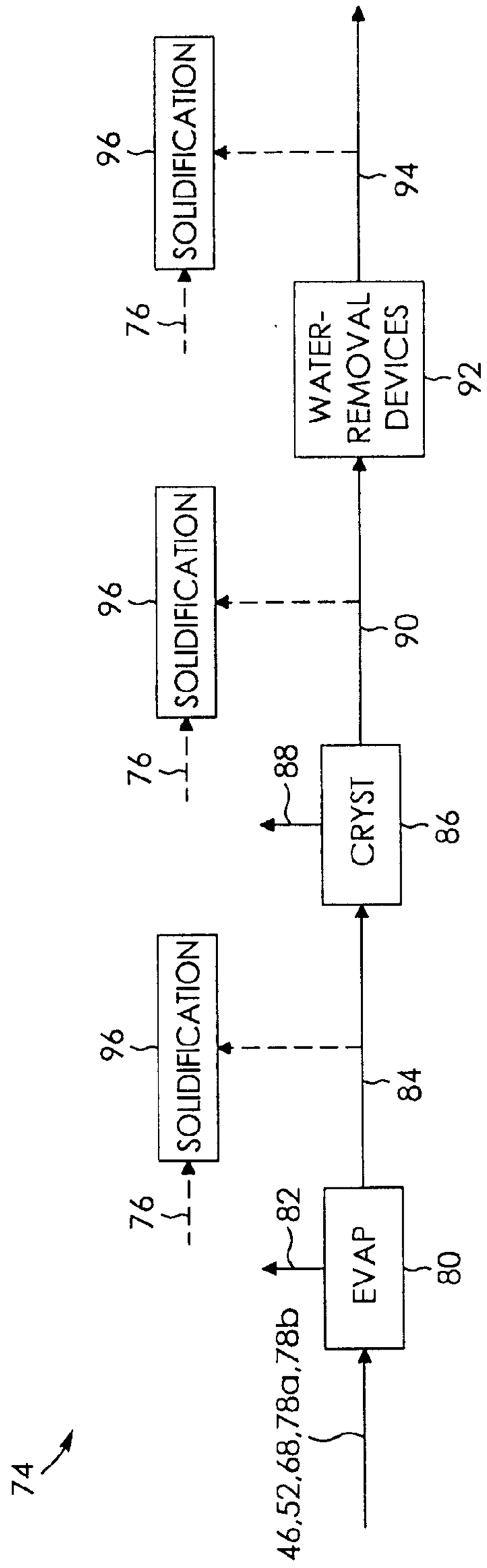
78a
24

FIG. 1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46,52,68,78a,78b
EVAP
80
82
CRYST
86
88
84
90
94
SOLIDIFICATION
96
WATER-REMOVAL DEVICES
92
LANDFILL
100
98
76

FIG. 2

FIG. 3

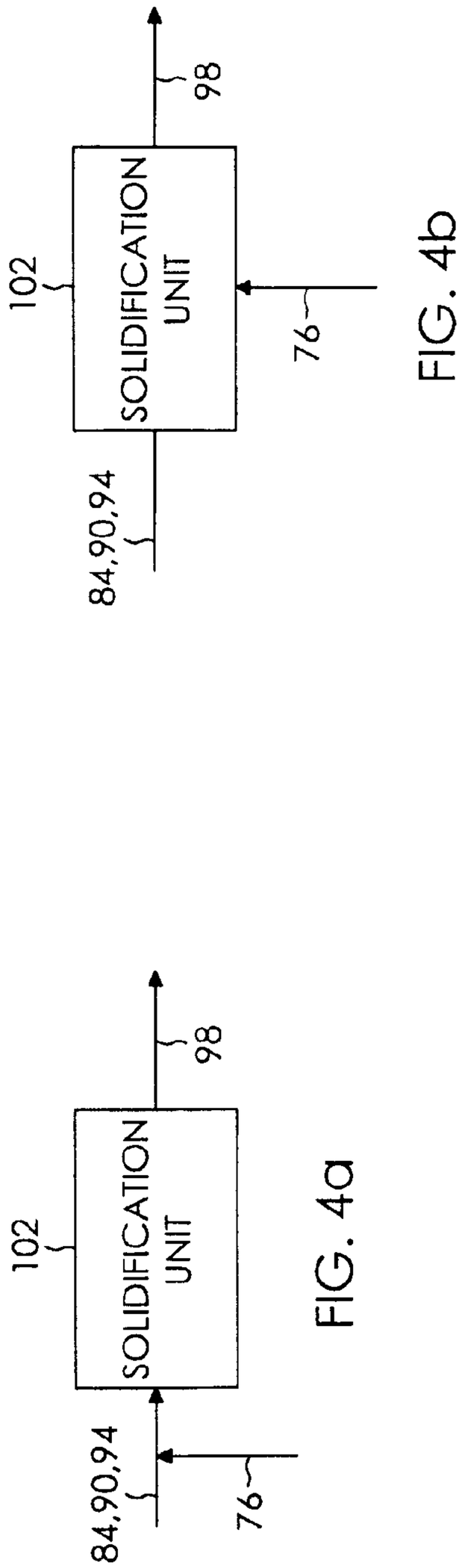
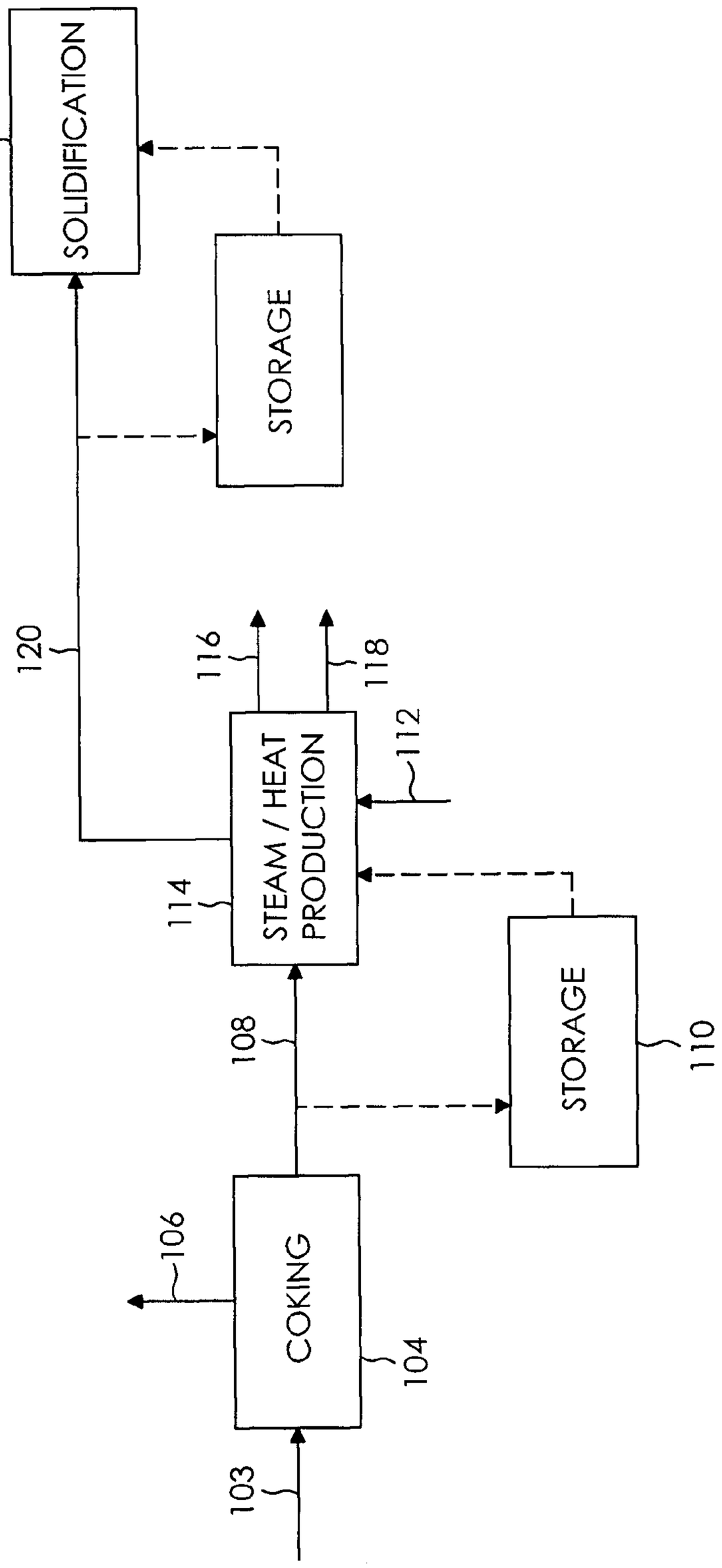

102
SOLIDIFICATION UNIT
98
84,90,94
76

FIG. 4a

102
SOLIDIFICATION UNIT
98
84,90,94
76

FIG. 4b


SOLIDIFICATION
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STORAGE
120
116
118
STEAM / HEAT PRODUCTION
112
114
108
STORAGE
110
COKING
106
104
103

FIG. 5

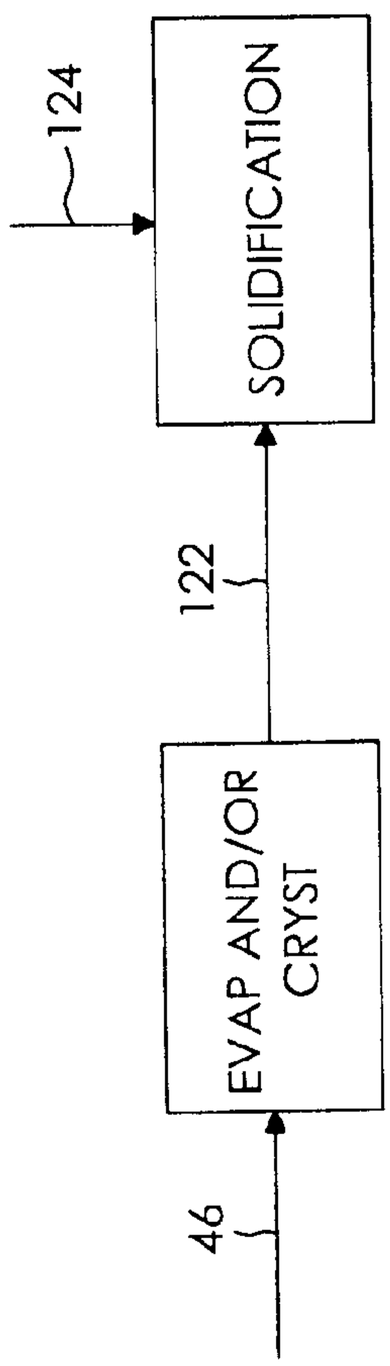

124
SOLIDIFICATION
122
EVAP AND/OR CRYST
46

FIG. 6a

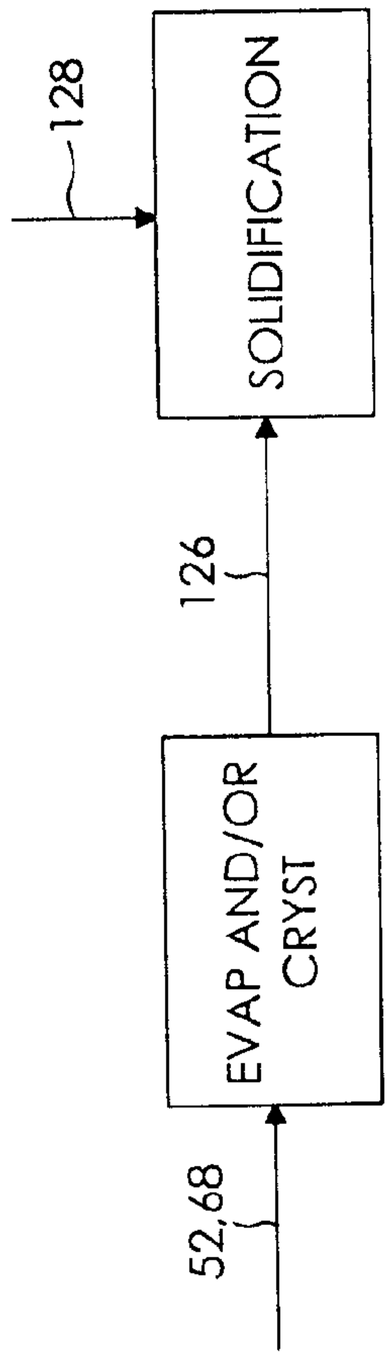

128
SOLIDIFICATION
126
EVAP AND/OR CRYST
52,68

FIG. 6b

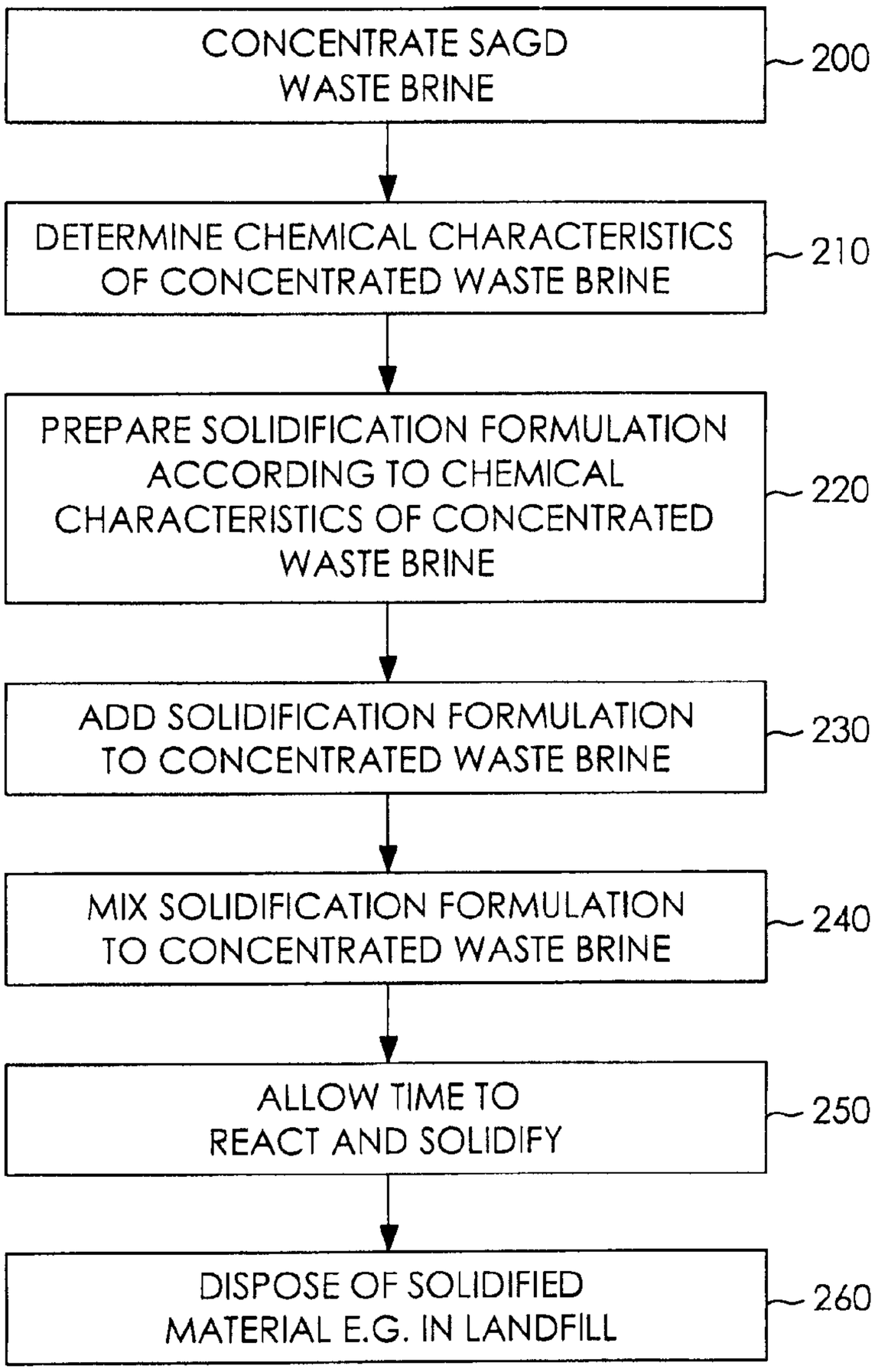
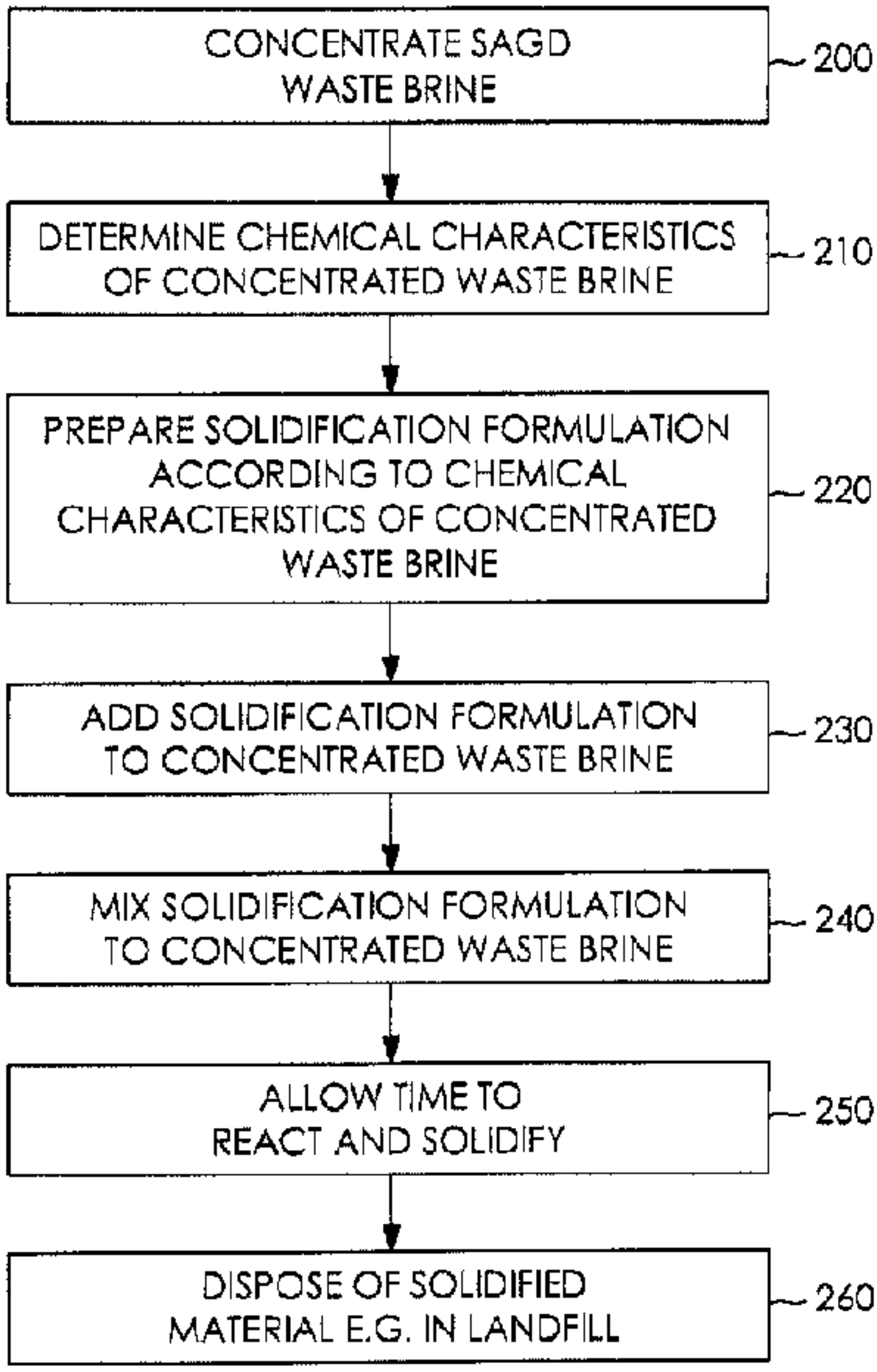

CONCENTRATE SAGD WASTE BRINE
200
DETERMINE CHEMICAL CHARACTERISTICS OF CONCENTRATED WASTE BRINE
210
PREPARE SOLIDIFICATION FORMULATION ACCORDING TO CHEMICAL CHARACTERISTICS OF CONCENTRATED WASTE BRINE
220
ADD SOLIDIFICATION FORMULATION TO CONCENTRATED WASTE BRINE
230
MIX SOLIDIFICATION FORMULATION TO CONCENTRATED WASTE BRINE
240
ALLOW TIME TO REACT AND SOLIDIFY
250
DISPOSE OF SOLIDIFIED MATERIAL E.G. IN LANDFILL
260

FIG. 7


CONCENTRATE SAGD WASTE BRINE
200
DETERMINE CHEMICAL CHARACTERISTICS OF CONCENTRATED WASTE BRINE
210
PREPARE SOLIDIFICATION FORMULATION ACCORDING TO CHEMICAL CHARACTERISTICS OF CONCENTRATED WASTE BRINE
220
ADD SOLIDIFICATION FORMULATION TO CONCENTRATED WASTE BRINE
230
MIX SOLIDIFICATION FORMULATION TO CONCENTRATED WASTE BRINE
240
ALLOW TIME TO REACT AND SOLIDIFY
250
DISPOSE OF SOLIDIFIED MATERIAL E.G. IN LANDFILL
260