(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
21 August 2008 (21.08.2008)

PCT

(10) International Publication Number
WO 2008/100737 A2

(51) International Patent Classification: Not classified

(21) International Application Number:
PCT/US2008/053005

(22) International Filing Date: 5 February 2008 (05.02.2008)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/890,357 16 February 2007 (16.02.2007) US
60/913,100 20 April 2007 (20.04.2007) US

(71) Applicant *(for all designated States except US)*: **ALBEMARLE CORPORATION** [US/US]; 451 Florida Street, Baton Rouge, LA 70801 (US).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **SAUER, Joe, D.** [US/US]; 15553 Waywood Avenue, Baton Rouge, LA 70816 (US). **COOK, George, W.** [US/US]; 10852 North Shoreline, Baton Rouge, LA 70809 (US). **HALL, Tyson, J.** [US/US]; 2000 Myrtle Avenue, Baton Rouge, LA 70806 (US).

(74) Agents: **EYMARD, Frank, C.** et al.; Albemarle Corporation, 451 Florida Street, Baton Rouge, LA 70801-1765 (US).

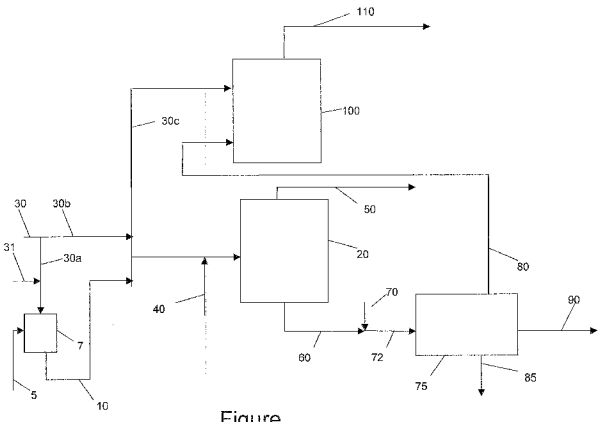
(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:
— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*
— *of inventorship (Rule 4.17(iv))*

Published:
— *without international search report and to be republished upon receipt of that report*

(54) Title: PROCESSES FOR CONJOINTLY PRODUCING BROMINE AND CALCIUM CHLORIDE



Figure
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(57) Abstract: Processes are provided for conjointly producing Br_2 and a concentrated aqueous solution containing at least about 5 wt% $CaCl_2$, based on the weight of the concentrated aqueous solution, from an HBr-rich recycle stream and a feed brine dilute in $CaCl_2$. wherein the aqueous HBr-rich stream is produced from an HBr-rich recycle stream and a portion of the feed brine. Such processes can comprise feeding the HBr-rich recycle stream and a liquid comprising a portion of the feed brine, either together or separately to an HBr absorption tower; producing an aqueous HBr-rich stream in the HBr absorption tower; feeding the aqueous HBr-rich stream and, optionally, a portion of the feed brine to a bromine tower; oxidizing bromide moieties within the bromine tower with Cl_2 to produce Br_2; recovering Br_2 from the bromine tower; removing a bromide- depleted bottoms from the bromine tower, such bottoms containing HCl; adding a Ca++ source to the bromide-depleted bottoms to convert substantially all of the HCl in the bottoms to $CaCl_2$, and, as necessary, removing water from the treated bottoms to produce the concentrated aqueous solution.

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PROCESSES FOR CONJOINTLY PRODUCING BROMINE AND CALCIUM CHLORIDE

BACKGROUND

[0001] The present invention relates to processes for conjointly producing bromine and a concentrated aqueous solution of calcium chloride.

[0002] Bromine is useful in a wide range of industries. For example, bromine is used in the manufacture of brominated flame retardants such as tetrabromobisphenol, decabromodiphenylethane, decabromodiphenyloxide, and brominated polystyrenes. Bromine is also used, e.g., in the manufacture of 1,2-dibromoethane, which is used as a petrol additive, in the manufacture of compounds used in photography (e.g. silver bromide, which is the light sensitive material in film), in the manufacture of dyestuffs and drugs, in analytical laboratory in testing for unsaturation in organic compounds, as a disinfectant, and in gold extraction. Calcium chloride is also useful in numerous applications, e.g., as a drying agent, in ice and dust control, in oil well drilling, in food processing, in concrete mixtures to speed up setting, as an additive in plastics, and as a drainage aid for wastewater treatment.

[0003] One source used in production of bromine and calcium chloride is brine. Brine is an aqueous solution nearly saturated with halide salts and which is produced in several areas of the United States. Such produced brines typically contain at least sodium chloride, sodium bromide and calcium chloride. Additionally, certain processes, such as processes for producing brominated flame retardants, generate substantial quantities of hydrogen bromide as a by-product, which can be converted to bromine.

[0004] Processes for production of bromine from these and other bromide-containing solutions are well know. For example, bromine can be produced by a bromine steaming out process, such as Kubierschky's distillation method; see, e.g., Kirk-Othmer, Encyclopedia of Chemical Technology, Fourth Edition, volume 4, pages 548 through 553. Other methods for recovering bromine from bromide-containing solutions are described, e.g., in US 3181934, US 4719096, US 4978518, US 4725425, US 5158683, and US 5458781.

[0005] Processes for production of calcium chloride from brines and other sources are also well known. See, e.g., US 4704265, WO 03/035550, and US 6524546.

[0006] Even in view of these and other published methods for production of bromine and for production of calcium chloride, it would be commercially beneficial to have processes for conjointly producing bromine and calcium chloride.

THE INVENTION

[0007] This invention meets the above-described needs by providing processes for conjointly producing Br_2 and a concentrated aqueous solution comprising from about 5 wt% $CaCl_2$ to about 40 wt% $CaCl_2$, based on the weight of the concentrated aqueous solution, from an HBr-rich recycle stream and a feed brine dilute in $CaCl_2$, which processes can comprise: (a) feeding the HBr-rich recycle stream and a liquid comprising at least a portion of the feed brine, either together or separately to an HBr absorption tower; (b) producing an aqueous HBr-rich stream in the HBr absorption tower; (c) feeding (i) at least a portion of the aqueous HBr-rich stream, and optionally (ii) a portion of the feed brine, either together or separately to a bromine tower; (d) oxidizing bromide moieties within the bromine tower with Cl_2 to produce Br_2; (e) recovering Br_2 from the bromine tower; (f) removing bromide-depleted bottoms from the bromine tower, such bottoms comprising less than about 35 wt% HCl; (g) adding a Ca^{++} source to the bromide depleted bottoms to convert substantially all of the HCl in the bottoms to $CaCl_2$; and (h) as necessary, removing water from the treated bottoms from (g) to produce the concentrated aqueous solution. In such processes, in (h) heat can be used in removing water from the treated bottoms in the form of steam and the steam can be recycled for use in a bromine steaming out process. Also provided are such processes wherein the HBr-rich recycle stream comprises amines. Also provided are improvements to processes for producing Br_2 from an HBr-rich recycle stream and, optionally, a feed brine dilute in $CaCl_2$, which processes comprise: (a) feeding the HBr-rich recycle stream, and optionally the feed brine, either together or separately to a bromine tower; (b) oxidizing bromide moieties within the bromine tower with Cl_2 to produce Br_2; (c) recovering Br_2 from the bromine tower; (d) removing bromide-depleted bottoms from the bromine tower, such bottoms comprising less than about 35 wt% HCl; and (e) adding ammonia or a caustic to the bromide-depleted bottoms to neutralize substantially all of the HCl; and the improvements can comprise: replacing (a) with (a1) feeding the HBr-rich recycle stream and a liquid comprising at least a portion of the feed brine, either together or separately to an HBr absorption

tower; (a2) producing an aqueous HBr-rich stream in the HBr absorption tower; (a3) feeding (i) at least a portion of the aqueous HBr-rich stream, and optionally (ii) a portion of the feed brine, either together or separately to a bromine tower; and replacing (e) with (e1) adding a Ca^{++} source to the bromide depleted bottoms to convert substantially all of the HCl in the bottoms to $CaCl_2$. Also provided are processes for conjointly producing Br_2 and a concentrated aqueous solution comprising from about 5 wt% $CaCl_2$ to about 40 wt% $CaCl_2$, based on the weight of the concentrated aqueous solution, which processes can comprise: (a) feeding an HBr-rich recycle stream either together or separately with a liquid comprising a portion of a feed brine dilute in $CaCl_2$ to an HBr absorption tower, wherein the HBr-rich recycle stream comprises amines and has a pH of less than about 4 and the feed brine comprises at least about 10 wt% NaCl, based on the total weight of the feed brine; (b) producing an aqueous HBr-rich stream in the HBr absorption tower; (c) feeding the aqueous HBr-rich recycle stream either together or separately with a portion of the feed brine dilute in $CaCl_2$ to a bromine tower; (d) oxidizing bromide moieties within the bromine tower with Cl_2 to produce Br_2; (e) recovering Br_2 from the bromine tower; (f) removing bromide-depleted bottoms from the bromine tower, such bottoms comprising less than about 5 wt% HCl, based on the weight of the bromide-depleted bottoms; (g) adding a Ca^{++} source to the bromide depleted bottoms to convert substantially all of the HCl in the bottoms to $CaCl_2$; and (h) as necessary, removing water from the treated bottoms from (g) to produce the concentrated aqueous solution.

Figures

[0008] The invention will be better understood by reference to the Figure, which is a flow diagram representative of processes according to this invention.

Process Description

[0009] Referring to the Figure, in one process according to this invention HBr-rich recycle stream **5** and at least a portion of feed brine stream **30**, via stream **30a**, are fed to HBr absorption tower **7**. Optionally, water stream **31** is also fed to HBr absorption tower **7**, either combined with feed brine stream **30a** (as shown) or separately. Streams **5** and **30a** may be fed to HBr absorption tower either together or separately. Aqueous HBr-rich stream **10** is fed to tower **20**. Optionally, a portion of feed brine stream **30**, dilute in $CaCl_2$, is fed to tower **20** via stream **30b**. Stream **40** comprising source of Cl_2

is also fed to tower **20**. Streams **10**, **40**, and optionally **30b**, can be fed together or separately to tower **20**. Inside tower **20**, bromide moieties are oxidized with Cl_2 to produce Br_2 and HCl. Stream **50** comprising produced Br_2 is recovered from tower **20**. Stream **70** comprising Ca^{++} source is combined with stream **60** comprising bromide-depleted bottoms to convert substantially all of the HCl in the bottoms to $CaCl_2$; i.e., stream **72** comprises $CaCl_2$ and essentially no HCl. As necessary, stream **80** comprising water in the form of steam is removed from the Ca^{++} treated bottoms via device **75** to produce stream **90** comprising a concentrated aqueous solution of at least about 5 wt% $CaCl_2$, based on the weight of the concentrated aqueous solution. Device **75** can be any device suitable for the process, such as a tank, filter, or centrifuge, to name a few.

[0010] In another such process according to this invention, stream **80** comprising water in the form of steam is removed from the Ca^{++} treated bottoms via device **75** and is cycled to tower **100** to be used as a heat source for a bromide steaming out process. A portion of stream **30** comprising feed brine dilute in $CaCl_2$ can be fed to tower **100** via stream **30c**. Stream **110** comprising produced Br_2 can be recovered from tower **100**.

[0011] In known processes for producing Br_2, stream **60** comprising bromide-depleted bottoms can be treated with ammonia or a caustic such as NaOH, MgOH, or the like, to neutralize substantially all of the HCl. In an improvement to such a process according to this invention, stream **70** comprising Ca^{++} source is combined with stream **60** comprising bromide-depleted bottoms to convert substantially all of the HCl in the bottoms to $CaCl_2$. Thus stream **72** comprises $CaCl_2$ and essentially no HCl. This improvement is beneficial in that the cost to treat with a Ca^{++} source is typically less than the cost to treat with ammonia or a caustic, and treatment with a Ca^{++} source produces $CaCl_2$, which can be sold commercially.

[0012] In one process according to this invention, aqueous HBr-rich stream **10** that is fed to tower **20** contains amines and can be available in streams that also contain NaBr. The amines can be by-products from other commercial processes. For example, amines in recycle stream **5**, which are passed through to stream **10** in tower **7**, can result from production of alkyldimethylamine, which is useful, e.g., in production of quatenary amines, amine oxides, and betaines, which are useful in cleaners, disinfectants, wood treatments, personal care products, oilfield products, and water treatment products. A recycle stream from production of alkyldimethylamine can comprise amines and sodium bromide. Bromine in the presence of amine compounds

can lead to production of by-products that are shock sensitive. In this process, however, feed brine stream **30** comprises at least about 10 wt% NaCl up to about 25 wt% NaCl (typically about 20wt% to about 25 wt%) based on the total weight of feed brine stream **30**; also, aqueous HBr-rich stream **10** has a pH of less than about 4, or less than about 2, or even less than about zero. The tendency of bromines in solution with amines to produce shock sensitive by-products is significantly reduced in this process due to the combination in tower **20** of stream **30a** comprising at least about 10 wt% NaCl and stream **10** having a pH of less than about 4. Thus, bromines and amines in tower **20** do not tend to produce shock-sensitive by-products; and amines can be removed from tower **20** with bromine in stream **50**. NaCl from stream **30** (**30a**) can be removed via device **75** via stream **85** comprising NaCl.

Aqueous HBr-rich stream

[0013] Aqueous HBr-rich stream **10** that is fed to tower **20** comprises at least about 3 wt% HBr, based on the total weight of stream **10**, up to the HBr saturation limit of stream **10**, e.g., up to about 60 wt% HBr, based on the total weight of stream **10**. Stream **10** can also comprise varying amounts of other components such as NaBr. In this invention, HBr-rich recycle stream **5** and feed brine stream **30a** are fed to tower **7** to produce aqueous HBr-rich stream **10**. Optionally, water stream **31** is also fed to tower **7**, either combined with feed brine stream **30a** (as shown) or separately. Water stream **31** can comprise water from any suitable source, such as fresh water or another water source. The HBr-rich recycle stream can be any stream comprising HBr.

Feed brine dilute in $CaCl_2$

[0014] Feed brine stream **30** dilute in $CaCl_2$ comprises at least about 5 wt% $CaCl_2$ based on the total weight of stream **30**. The upper limit of $CaCl_2$ in stream **30** depends upon the feed brine source, and can be based on whatever amount of $CaCl_2$ naturally occurs in the brine, which typically will be no more than about 15 wt% $CaCl_2$ based on the weight of the brine. Stream **30** can also comprise varying amounts of other components such as NaBr and NaCl.

Source of Cl_2

[0015] Stream **40** comprising source of Cl_2 can comprise essentially 100 wt% elemental chlorine, and can also comprise some water, e.g., up to about 5 wt% or

more. Cl_2 can be purchased from commercial providers or can be produced from, e.g., a feed brine, through electrolysis, as will be familiar to those skilled in the art.

Oxidation of bromide moieties with Cl_2

[0016] As is familiar to those skilled in the art, oxidation of bromide moieties with Cl_2 to produce Br_2 in tower **20** can occur, e.g., due to the reaction: $2HBr + Cl_2 \rightarrow Br_2 + 2HCl$ and/or the reaction: $2NaBr + Cl_2 \rightarrow Br_2 + 2NaCl$, among others. Tower **20** can be any suitable tower for oxidizing bromide moieties with Cl_2 to produce Br_2, as will be familiar to those skilled in the art. In processes according to this invention, the acidic pH of aqueous HBr-rich stream **10** provides an economic benefit in that the feed brine in stream **30** typically contains impurities such as NH_3 and H_2S, which react with Cl_2. These reactions are inhibited at low pH, e.g., pH less than about 4, thereby improving Cl_2 utilization.

Bromide-depleted bottoms

[0017] Stream **60** comprising bromine-depleted bottoms can comprise water, HCl, NaCl, $CaCl_2$, and other components that result from the oxidation of bromide moieties with Cl_2 to produce Br_2 and that may pass through tower **20** from stream **10**, stream **30**, or stream **40** unchanged. Typically, stream **60** comprises essentially no bromide moieties to very small amounts of bromide moieties, e.g., from about 50 ppm to about 400 ppm bromide moieties. Stream **60** comprising bromide-depleted bottoms typically comprises less than about 5 wt% HCl based on the total weight of stream **60**, and can comprise 1 wt% HCl to about 5 wt% HCl. In some commercial applications, stream **60** can comprise up to about 35 wt% HCl.

Ca^{++} source

[0018] Stream **70** comprising Ca^{++} source can comprise any suitable source of Ca^{++} that is now known or comes to be known, including without limitation lime, CaCO, $Ca(OH)_2$, and $CaCO_3$, as will be familiar to those skilled in the art.

Conversion of HCl to $CaCl_2$

[0019] Once stream **70** comprising Ca^{++} source is combined with stream **60** comprising bromide-depleted bottoms, $CaCl_2$ can be generated, e.g., by the reaction $2HCl + CaCO_3 \rightarrow CaCl_2 + H_2O + CO_2$, and/or the reaction $2HCl + CaO \rightarrow CaCl_2 + H_2O$,

and/or the reaction $2HCl + Ca(OH)_2 \rightarrow CaCl_2 + 2H_2O$, among others. Thus stream **72** comprises essentially no HCl, and comprises more $CaCl_2$ and more H_2O than stream **60**. Stream **72** can consist essentially of H_2O, NaCl and $CaCl_2$.

Removing H_2O from Ca^{++} treated bottoms

[0020] Stream **80** comprising water that is removed from the Ca^{++} treated bottoms via device **75** comprises primarily water in the form of steam. The water can be removed by heating of the contents of device **75**, generally with steam, or via any other heating means, as will be familiar to those skilled in the art.

Concentrated aqueous solution

[0021] Stream **90** comprising a concentrated aqueous solution of at least about 5 wt% $CaCl_2$, based on the weight of the concentrated aqueous solution, can comprise $CaCl_2$ up to the saturation limit of the concentrated aqueous solution. Typically, the concentrated aqueous solution comprises at least about 5 wt% $CaCl_2$, and can comprise from about 5 wt% $CaCl_2$ to about 40 wt% $CaCl_2$. The concentrated aqueous solution can be further processed to produce a substantially 100% composition of $CaCl_2$, which will typically be flaked $CaCl_2$.

EXAMPLE

[0022] The following example is illustrative of the principles of this invention. It is understood that this invention is not limited to any one specific embodiment exemplified herein, whether in the examples or the remainder of this patent application.

[0023] Referring to the Figure, HBr-rich recycle stream **5** comprises 5838 lbs/hour HBr. Feed brine stream **30** comprises about 0.4 wt% NaBr, about 63.6 wt% H_2O, about 25 wt% NaCl, and about 11 wt% $CaCl_2$, based on the total weight of stream **30**. Stream **30a** comprises about 120 lbs/hour NaBr, about 19180 lbs/hour H_2O, about 7528 lbs/hour NaCl, and about 3312 lbs/hour $CaCl_2$. In this example, no water from water stream **31** is fed to tower **7**. Aqueous HBr-rich stream **10** comprises 5838 lbs/hour HBr, 360 lbs/hour NaBr, and 19194 lbs/hour H_2O; i.e., stream **10** comprises about 23 wt% HBr, about 1 wt% NaBr, and about 76 wt% H_2O, based on the total weight of stream **10**. In this example, HBr-rich recycle stream **5** is comprised of streams from various processes, some of which make brominated flame retardants and some of which comprise amines; thus, aqueous HBr-rich stream **10** comprises amines. Feed brine

stream **30b** comprises 320 lbs/hour NaBr, 58134 lbs/hour H_2O, 22834 lbs/hour NaCl, and 10047 lbs/hour $CaCl_2$. Stream **40** comprises at least about 2593 lbs/hour elemental chlorine and only trace amounts of water. Streams **10**, **30**, and **40** are combined and input to tower **20**. Inside tower **20**, bromide moieties from streams **10** and **30** are oxidized with Cl_2 from stream **40** to produce Br_2 in a standard steaming out process, and stream **50** comprising about 5844 lbs/hour Br_2 is recovered from tower **20**. Stream **60** is recovered from tower **20** by means known to those skilled in the art, and comprises 58104 lbs/hour H_2O, 2392 lbs/hour HCl, 15288 lbs/hour NaCl, and 6726 lbs/hour $CaCl_2$; i.e., stream **60** comprises about 70.1 wt% H_2O, about 3.0 wt% HCl, about 18.5 wt% NaCl, and about 8.2 wt% $CaCl_2$, based on the total weight of stream **60**. Stream **70** comprises 3323 lbs/hour $CaCO_3$; i.e., stream **70** comprises 100 wt% $CaCO_3$. Stream **72** results from combination of streams **60** and **70** and the conversion of HCl from stream **60** by $CaCO_3$ from stream **70** to $CaCl_2$ and H_2O; and stream **72** comprises 59300 lbs/hour H_2O, 15288 lbs/hour NaCl, and 10379 lbs/hour $CaCl_2$; i.e., stream **72** comprises about 69.5 wt% H_2O, about 18.0 wt% NaCl, and about 12.2 wt% $CaCl_2$, based on the total weight of stream **72**. Stream **72** is input to tank **75**, which is heated by steam (heating means not illustrated). NaCl in stream **72** (carried forward from stream **30**) is removed from tank **75** via stream **85** comprising 22834 lbs/hour NaCl. Stream **80** comprising 43731 lbs/hour H_2O, i.e., essentially 100 wt% H_2O based on the weight of stream **80**, which H_2O is in the form of steam due to the heating of tank **75** with steam, is used to heat tower **100**, or alternatively is used to heat tower **20** or tank **75**. Calcium chloride (comprising produced $CaCl_2$ and $CaCl_2$ carried forward from stream **30**) are recovered from tank **75** via stream **90** which comprises 20552 lbs/hour H_2O and 13702 lbs/hour $CaCl_2$, i.e., about 60 wt% H_2O and about 40 wt% $CaCl_2$, based on the total weight of stream **90**. Economic benefit is derived from the sale of stream **90** as is or by sale of flaked $CaCl_2$ from stream **90**, produced by means familiar to those skilled in the art.

[0024] This invention is economically advantageous. Recovery of $CaCl_2$ during production of Br_2 is cost and energy efficient. Additionally, when feed brine is used in the place of water to absorb HBr from the HBr-rich recycle stream that feeds the Br_2 recovery process, the amount of water that must be boiled off during $CaCl_2$ recovery is reduced, and thus the process is made even more cost and energy efficient.

[0025] It is to be understood that the reactants and components referred to by chemical name or formula anywhere in the specification or claims hereof, whether

referred to in the singular or plural, are identified as they exist prior to being combined with or coming into contact with another substance referred to by chemical name or chemical type (e.g., another reactant, a solvent, or etc.). It matters not what chemical changes, transformations and/or reactions, if any, take place in the resulting mixture or solution or reaction medium as such changes, transformations and/or reactions are the natural result of bringing the specified reactants and/or components together under the conditions called for pursuant to this disclosure. Thus the reactants and components are identified as ingredients to be brought together in connection with performing a desired chemical reaction or in forming a mixture to be used in conducting a desired reaction. Accordingly, even though the claims hereinafter may refer to substances, components and/or ingredients in the present tense ("comprises", "is", etc.), the reference is to the substance, component or ingredient as it existed at the time just before it was first contacted, combined, blended or mixed with one or more other substances, components and/or ingredients in accordance with the present disclosure. Whatever transformations, if any, which occur in situ as a reaction is conducted is what the claim is intended to cover. Thus the fact that a substance, component or ingredient may have lost its original identity through a chemical reaction or transformation during the course of contacting, combining, blending or mixing operations, if conducted in accordance with this disclosure and with the application of common sense and the ordinary skill of a chemist, is thus wholly immaterial for an accurate understanding and appreciation of the true meaning and substance of this disclosure and the claims thereof.

[0026] While the present invention has been described in terms of one or more preferred embodiments, it is to be understood that other modifications may be made without departing from the scope of the invention, which is set forth in the claims below.

CLAIMS

What is claimed is:

1. A process for conjointly producing Br_2 and a concentrated aqueous solution comprising from about 5 wt% $CaCl_2$ to about 40 wt% $CaCl_2$, based on the weight of the concentrated aqueous solution, from an HBr-rich recycle stream and a feed brine dilute in $CaCl_2$, which process comprises:

(a) feeding the HBr-rich recycle stream and a liquid comprising at least a portion of the feed brine, either together or separately to an HBr absorption tower;

(b) producing an aqueous HBr-rich stream in the HBr absorption tower;

(c) feeding (i) at least a portion of the aqueous HBr-rich stream, and optionally (ii) a portion of the feed brine, either together or separately to a bromine tower;

(d) oxidizing bromide moieties within the bromine tower with Cl_2 to produce Br_2;

(e) recovering Br_2 from the bromine tower;

(f) removing bromide-depleted bottoms from the bromine tower, such bottoms comprising less than about 35 wt% HCl;

(g) adding a Ca^{++} source to the bromide depleted bottoms to convert substantially all of the HCl in the bottoms to $CaCl_2$; and

(h) as necessary, removing water from the treated bottoms from (g) to produce the concentrated aqueous solution.

2. The process according to claim 1, wherein in (h) heat is used in removing water from the treated bottoms in the form of steam and the steam is recycled for use in a bromine steaming out process.

3. The process according to claim 1, wherein the HBr-rich recycle stream comprises amines.

4. An improvement to a process for producing Br_2 from an HBr-rich recycle stream and, optionally, a feed brine dilute in $CaCl_2$, which process comprises:

(a) feeding the HBr-rich recycle stream, and optionally the feed brine, either together or separately to a bromine tower;

(b) oxidizing bromide moieties within the bromine tower with Cl_2 to produce Br_2;

(c) recovering Br_2 from the bromine tower;

(d) removing bromide-depleted bottoms from the bromine tower, such bottoms comprising less than about 35 wt% HCl; and

(e) adding ammonia or a caustic to the bromide-depleted bottoms to neutralize substantially all of the HCl,

the improvement comprising:

replacing (a) with

(a1) feeding the HBr-rich recycle stream and a liquid comprising at least a portion of the feed brine, either together or separately to an HBr absorption tower;

(a2) producing an aqueous HBr-rich stream in the HBr absorption tower;

(a3) feeding (i) at least a portion of the aqueous HBr-rich stream, and optionally (ii) a portion of the feed brine, either together or separately to a bromine tower;

and
replacing (e) with

(e1) adding a Ca^{++} source to the bromide depleted bottoms to convert substantially all of the HCl in the bottoms to $CaCl_2$.

5. A process for conjointly producing Br_2 and a concentrated aqueous solution comprising from about 5 wt% $CaCl_2$ to about 40 wt% $CaCl_2$, based on the weight of the concentrated aqueous solution, which process comprises:

(a) feeding an HBr-rich recycle stream either together or separately with a liquid comprising a portion of a feed brine dilute in $CaCl_2$ to an HBr absorption tower, wherein the HBr-rich recycle stream comprises amines and has a pH of less than about 4 and the feed brine comprises at least about 10 wt% NaCl, based on the total weight of the feed brine;

(b) producing an aqueous HBr-rich stream in the HBr absorption tower;

(c) feeding the aqueous HBr-rich recycle stream either together or separately with a portion of the feed brine dilute in $CaCl_2$ to a bromine tower;

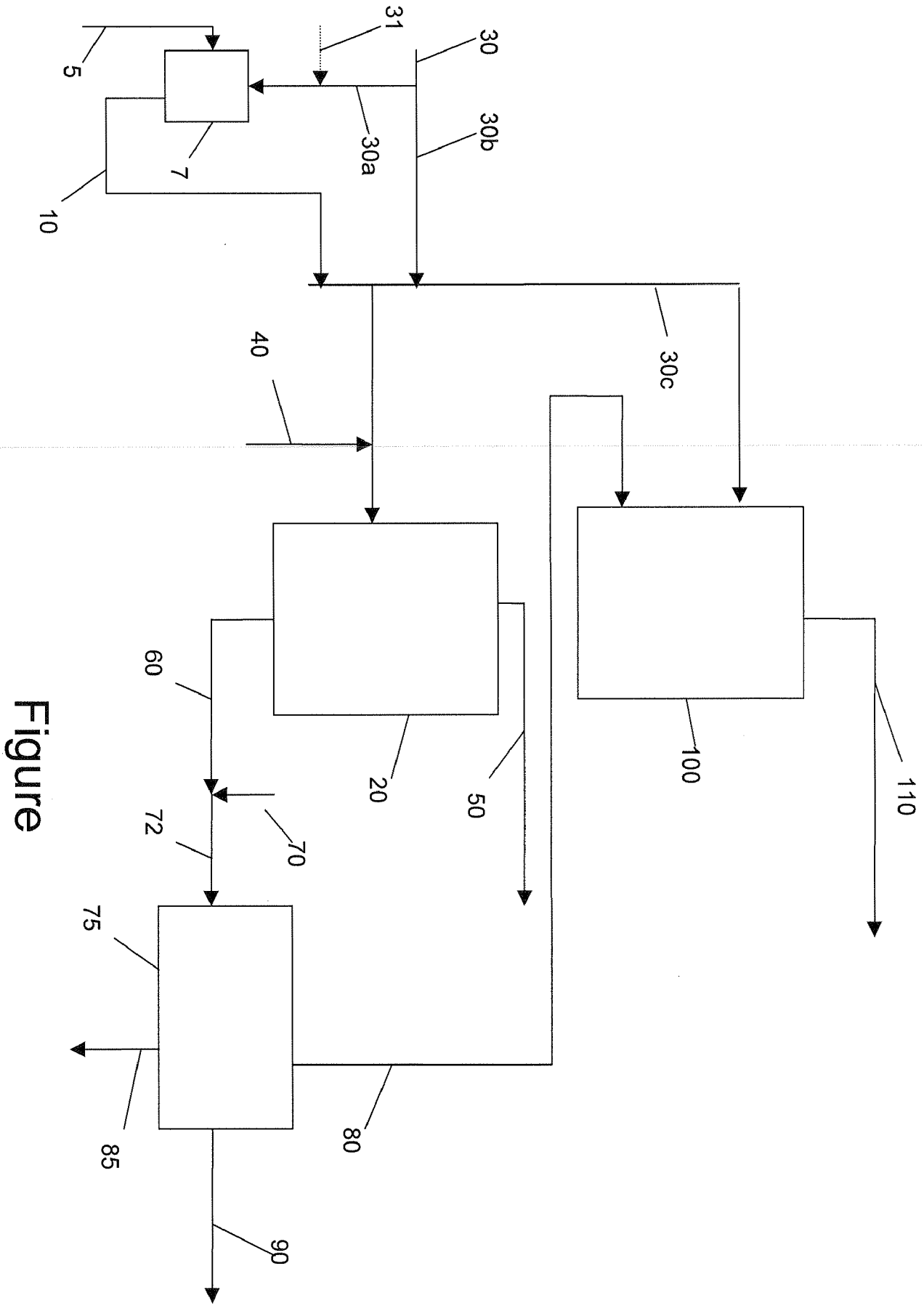
(d) oxidizing bromide moieties within the bromine tower with Cl_2 to produce Br_2;

(e) recovering Br_2 from the bromine tower;

(f) removing bromide-depleted bottoms from the bromine tower, such bottoms comprising less than about 5 wt% HCl, based on the weight of the bromide-depleted bottoms;

(g) adding a Ca^{++} source to the bromide depleted bottoms to convert substantially all of the HCl in the bottoms to $CaCl_2$; and

(h) as necessary, removing water from the treated bottoms from (g) to produce the concentrated aqueous solution.



Figure