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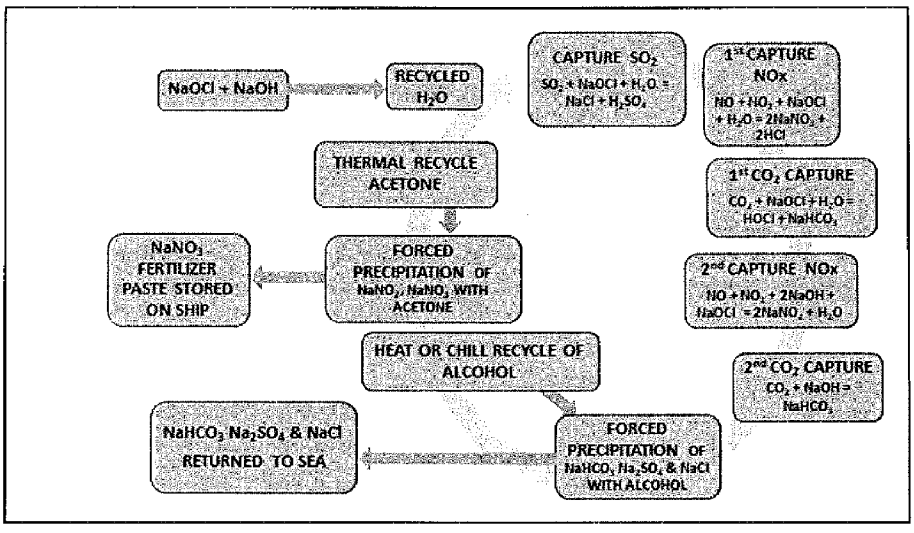
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(54) **Title:** CHEMICAL SEQUESTERING OF CO2, NOX AND SO2

FIGURE 1



(57) **Abstract:** The disclosure provides seven integrated methods for the chemical sequestration of carbon dioxide (CO_2), nitric oxide (NO), nitrogen dioxide (NO_2) (collectively NO_x, where x = 1, 2) and sulfur dioxide (SO_2) using closed loop technology. The methods recycle process reagents and mass balance consumable reagents that can be made using electrochemical separation of sodium chloride (NaC1) or potassium chloride (KC1). The technology applies to marine and terrestrial exhaust gas sources for CO_2, NO_x and SO_2. The integrated technology combines compatible and green processes that capture and/or convert CO_2, NO_x and SO_2 into compounds that enhance the environment, many with commercial value.

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CHEMICAL SEQUESTERING OF CO_2, NOx and SO_2

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of priority under 37 U.S.C. § 119(e) to U.S. Provisional Patent Application No. 62/797,468, titled "CHEMICAL SEQUESTERING OF CO_2 USING CLOSED LITHIUM TECHNOLOGY," filed on January 28, 2019, the entire disclosure of which is hereby incorporated by reference in its entirety for all purposes.

TECHNICAL FIELD OF THE INVENTION

[0002] The present disclosure generally relates to sequestering of atmospheric gases, and more particularly, to the chemical sequestration of carbon dioxide (CO_2), nitric oxide (NO), nitrogen dioxide (NO_2) [collectively "NO_x" where x = 1 or 2], and sulfur dioxide (SO_2) using closed loop technology.

BACKGROUND OF THE INVENTION

[0003] Atmospheric gases such as CO_2, NO_x and SO_2 are internationally recognized as being toxic and may cause dangerous global warming. There have been and continue to be many technologies focused on the reduction in the production and sequestering of these gases. The chemical characteristics of these gases, however, contribute to the difficulty in the development of a low-cost sequestering technology. These gases are stable entities, which require either large amounts of expensive chemical or mechanical energy to entice them into a chemical reaction.

[0004] Scientific research has confirmed greenhouse gas accumulation in the atmosphere and ocean is causing a dramatic change to the life supporting environment on earth. Most governments around the world recognize this and are taking steps to reverse the trend and mitigate the damage. Events that occurred during 23 September 2019 are examples of this

commitment. The following resolutions and commitments were made at the United Nations Climate Change Summit:

[0005] The European Union announced at least 25% of the next EU budget will be devoted to climate-related activities.

[0006] France announced that it would not enter into any trade agreement with countries that have policies counter to the Paris Agreement.

[0007] Germany and 65 other countries committed to carbon neutrality by 2050.

[0008] 12 countries made financial commitments to the Green Climate Fund, the official financial mechanism to assist developing countries in adaptation and mitigation practices to counter climate change. This includes Norway, Germany, France and the United Kingdom's recent doubling of their previous contributions.

[0009] The United Kingdom made a major additional contribution, doubling its overall international climate finance to L11.6 billion for the period from 2020 to 2025.

[0010] India pledged to increase renewable energy capacity to 175GW by 2022 and then continue increasing its capacity to 450GW.

[0011] 80 countries have joined the International Solar Alliance.

[0012] China said it would cut emissions by over 12 billion tons annually and would pursue a path of high-quality growth and low carbon development.

[0013] The Russian Federation announced that they will ratify the Paris Agreement, bringing the total number of countries that have joined the Agreement to 187.

[0014] Pakistan said it would plant more than 10 billion trees over the next five years.

[0015] The United Nations Intergovernmental Panel on Climate Change issued a 1170-page report that documents effects of climate change that confirms the climate emergency on 23 September.

[0016] A third meeting held in London also culminated on 23 September that is directly relevant to the marine shipping industry. Leading ports, banks, oil and shipping companies met on Monday 23 September and launched an initiative which aims to have ships and marine fuels with zero carbon emissions on the high seas by 2030. This is another step by the maritime sector to reduce CO_2.

[0017] Sixty commercial groups including shipping companies such as A.P. Moller Maersk (MAERSKb.CO), which owns the world's biggest container shipping line, commodities players such as COFCO International, Cargill, Trafigura, mining group Anglo American (AAL.L) as well as banks such as Citigroup (C.N), ABN AMRO (ABNd.AS) and Societe Generale (SOGN.PA) have committed to the "Getting to Zero Coalition." The coalition is pushing for vessels and fuels to be ready by 2030 and supported by the required infrastructure.

[0018] While there has been progress in the reduction of the generation of these gases, there has been limited success in capturing these gases once released into the atmosphere. Therefore, there remains a need in the art for new methods and technologies to effectively and economically sequester atmospheric gases such as CO_2, NO_x and SO_2.

SUMMARY OF THE INVENTION

[0019] The disclosed methods provide for technologies that effectively sequester gases such as CO_2, NO_x and SO_2 (Target Gases) with high removal efficiency from point source gas streams or the atmosphere, and then convert them into commercially viable products like sodium bicarbonate ($NaHCO_3$), a compound that can protect the oceans from CO_2 acidification, and

sodium nitrate ($NaNO_3$), a fertilizer, in an energy efficient way with net zero carbon footprints for all of these gases.

[0020] The disclosed processes recycle its intermediate reagents in an energy efficient way using forced alcohol precipitation. The alcohols remove salts made from CO_2, NOx & SO_2 that are repurposed from the methodologies' process liquid at pre-determined points to avoid unwanted equipment clogging. The alcohol(s) selected for this methodology have the unique ability to be recycled through evaporation at 70°C with waste heat from combustion or recaptured through solidification at temperatures below 25°C, available from seawater for example.

[0021] The disclosure describes a combination of seven strategically selected primary processes that are synergistically paired in two different cyclic process groups. The groups are identified as the 1-Loop Process and the 2-Loop Process. Both process loops are linked through a novel integrated sensor and control logic. This combination of processes and control technology encompasses several novel CO_2, NOx or SO_2 sequestration and reuse method features.

[0022] All seven of the primary CO_2, NOx and SO_2 repurposing reactions were strategically chosen to work collaboratively and thereby minimize reactant usage. There are several examples where the byproducts of one reaction are used as a reactant in another reaction.

[0023] This methodology uniquely solves a space problem associated with applications that have limited space for example the treatment of exhaust gases from marine vessels. This is done in two ways: First, there is no need to store process reagents aboard the ship. The seven strategically chosen main processes in this methodology also have the novel ability to supply their primary consumable reagents from the electrochemical treatment of seawater. Second, the integrated processes minimize the need for reaction chamber size and thereby make the

technology equipment size compatible with the limited space available on marine vessels or in congested terrestrial industrial facilities.

[0024] The process combination is novel because all of the reactions are rate determined by the consumption of either sodium hydroxide (NaOH) or sodium hypochlorite (NaOCl).

[0025] At least one CO_2 treatment process and one NOx treatment process are rate controlled by the dosing of NaOH and at least one process in each group is rate controlled by the concentration of sodium hypochlorite (NaOCl) as a reactant. This feature allows the process control system to regulate the rate of each of the seven primary processes in a way that balances the use of chemistry that can be supplied from an electrochemical treatment of sodium chloride (NaCl).

[0026] A second feature of the novel process control logic is its ability to utilize pre and post treatment gas concentrations for the CO_2, NOx and SO_2 and other variables to proactively and reactively adjust the rates of individual reactions by selectively supplying only the as needed amounts of reactants required to treat the concentration of CO_2, NOx or SO_2 in the gas stream. This "as required" chemical dosing feature minimizes the overall chemical use by eliminating any wasted chemicals. The novel process control also selects which of the seven processes are favored in the overall treatment of gaseous CO_2, NOx and SO_2.

[0027] A third feature is available because the seven processes are strategically selected with at least one CO_2 treatment process and one NOx treatment processes utilizing NaOH as its reaction controlling reagent and at least one other process in each group using NaOCl as the reaction controlling reagent. This strategic selection of primary process allows the integrated process control logic to balance the overall consumption of NaOH and NaOCl by responding to sensor data and then preferentially prioritizing either the NaOH or NaOCl processes for CO_2

treatment and/or NOx treatment as required to balance the overall chemical production from the electrochemical generator.

[0028] A fourth feature of the integrated combination of processes and process control system is its ability to treat the gaseous CO_2, NOx and SO_2 using mist or gas phase reactions within ducting that can be oriented in any direction. This feature results in a small physical size when compared to conventional treatment methodologies for these gases. Large reaction chambers can be used but are not required. The small equipment size allows this integrated gas treatment technology to be used in small space requirements of marine vessels and congested industrial facilities where conventional gas treatment process will not fit.

[0029] A fifth feature of this strategically selected group of seven processes and novel process control technology is the ability to individually adjust the reaction rates of all of the processes as required to compensate for variations in the CO_2, NOx and SO_2 compound ratio and overall concentrations of the compounds in exhaust gas in real time.

[0030] The previously described CO_2 repurposing process utilized NaOH to regenerate lithium hydroxide (LiOH). The process has a high CO_2 removal efficiency and effectively cooperates with other CO_2 capture and repurposes technologies that utilize sodium hypochlorite (NaOCl) as the consumable reagents. The use of two compounds that can be made from NaCl provides a clever method for balancing the consumable reagent requirement as previously described. This is an attribute when this methodology is used on a marine vessel or other application that benefits from onsite manufacturing of consumable reagents with electrochemical conversion of NaCl from seawater or brine.

[0031] This patent also describes an additional methodology for CO_2 capture and repurposes technology. The consumable reagent in this lithium hydroxide based CO_2 capture process is

potassium hydroxide (KOH). The KOH is used to regenerate the LiOH. This process does not provide an ability to balance reactants made on site by electrochemical processes, but it does have smaller piping systems than the LiOH based CO_2 capture system using NaOH as its consumable reagent. This equipment sizing difference is the result of increased secondary step reactant solubility in the KOH based CO_2 capture technology.

[0032] Irrespective of the reagent used to recycle LiOH in the CO_2 capture technology, it provides 99.0% CO_2 removal efficiency and produces sodium bicarbonate ($NaHCO_3$), a compound that dramatically benefits ocean stability. However the process is compromised by NOx in the gas stream and slowed by the presence of large amounts of SO_2. That is why the LiOH based CO_2 capture process is included in the group of processes previously described that treat NOx, SO_2 and CO_2. The group also provides the ability to balance the NaOH and NaOCl consumption.

[0033] The LiOH based CO_2 capture process utilizing KOH as its consumable reagent, also requires a gas or liquid stream with minimal levels of SO_2 and NOx, but must, because of chemical compatibility, use a method other than that shown above to accomplish this objective. An unrelated process is ideal for this application. It utilizes non-ionic chlorine dioxide (ClO_2^o) to remove 99.5% of NOx and SOx from a gas or liquid stream.

[0034] BRIEF DESCRIPTION OF THE DRAWINGS

[0035] The disclosure, in accordance with one or more various embodiments, is described in detail with reference to the following figures. The drawings are provided for purposes of illustration only and merely depict exemplary embodiments of the disclosure. These drawings are provided to facilitate the reader's understanding of the disclosure and should not be

considered limiting of the breadth, scope, or applicability of the disclosure. It should be noted that for clarity and ease of illustration these drawings are not necessarily made to scale.

[0036] FIGURE 1 illustrates an embodiment of an integrated closed loop system (1-Loop Process), which collaboratively captures CO_2, NO_x and SO_2;

[0037] FIGURE 2 illustrates an embodiment of the NaOCl/NaOCl percent speciation at different pH environments in an integrated closed loop system (1-Loop Process);

[0038] FIGURES 3A and 3B illustrate other embodiments of an integrated closed loop system (2-Loop Process), which collaboratively captures CO_2;

[0039] FIGURES 4A and 4B illustrates an embodiment of how the 1-Loop Process and the 2-Loop Process can be configured;

[0040] FIGURE 5 illustrates an embodiment of the reagent generation, conversion and distribution technology for the 1-Loop Process and 2-Loop Process;

[0041] FIGURE 6 illustrates an embodiment of the process flow instruments used in the 1-Loop Process; and

[0042] FIGURE 7 illustrates an embodiment of the process flow instruments used in the 2-Loop Process.

DETAILED DESCRIPTION OF EXEMPLARY EMBODIMENTS

[0043] The following description is presented to enable a person of ordinary skill in the art to make and use embodiments described herein. Descriptions of specific devices, techniques, and applications are provided only as examples. Various modifications to the examples described herein will be readily apparent to those of ordinary skill in the art, and the general principles defined herein may be applied to other examples and applications without departing from the

spirit and scope of the disclosure. Thus, the disclosure is not intended to be limited to the examples described herein and shown but is to be accorded the scope consistent with the claims.

[0044] The word "exemplary" is used herein to mean "serving as an example illustration." Any aspect or design described herein as "exemplary" is not necessarily to be construed as preferred or advantageous over other aspects or designs.

[0045] Reference will now be made in detail to aspects of the subject technology, examples of which are illustrated in the accompanying drawings, wherein like reference numerals refer to like elements throughout.

[0046] The specific order or hierarchy of steps in the process disclosed herein is an example of exemplary approaches. Based upon design preferences, it is understood that the specific order or hierarchy of steps in the processes can be rearranged while remaining within the scope of the disclosure. Any accompanying method claims present elements of the various steps in a sample order and are not meant to be limited to the specific order or hierarchy presented.

[0047] The disclosed technology presented herein is relevant to the objectives and tasks of the above groups that are focused on enhanced environmental stewardship. The technology provides a new resource for terrestrial and sea applications for CO_2 capture and repurposing NO_x abatement and SO_2 destruction. For example, the byproduct of the CO_2 capture processes described herein is sodium bicarbonate ($NaHCO_3$), which is the compound the oceans use to maintain the chemical equilibrium necessary for life. If this product is shared with the sea, it will reverse the acidification that CO_2 is causing when it unavoidably transfers from the atmosphere into oceans and other bodies of water.

[0048] The disclosed technology can be applied to marine and terrestrial exhaust gas sources for CO_2, NOx and SO_2 or directly treat these compounds in the atmosphere. This integrated

technology provides a combination of compatible and very green processes that capture and/or convert these gases into compounds that enhance the environment, many with commercial value.

[0049] The disclosed combination of chemical processes using NaOH and NaOCl as consumable reactants has been verified through bench scale testing, to remove 99% CO_2, 90% NO_x and 99%SO_2 from combustion and chemical process exhaust gas. The ClO_2^o based NOx removal technology has a 99.5% removal efficiency. The results are based on testing of gas streams including but are not limited to diesel exhaust, heavy fuel oil combustion exhaust and exhaust from chemical digestion processes.

[0050] The disclosed technology applies to terrestrial and ocean vessel applications. It also requires a small physical "footprint" and is carbon neutral when treating exhaust generated from the production of electricity the processes use. The technology is also carbon neutral when it uses electricity generated from solar or wind sources. All of the target gases are removed in a continuous mist, dry / wet aerosol, gas phase or liquid phase reaction(s) within vessels that can be not much larger in diameter than conventional duct for a given exhaust gas flow.

[0051] The combined CO_2, NOx and SO_2 abatement processes are collaborative. Chemical use is minimized because reaction products from one process are often reagents in another. For example, in the reaction sequence shown in FIGURE 1, the HOCl formed in the first capture of CO_2 is used to generate NaOCl in the two subsequent capture process of NO_x.

[0052] The primary consumable for all of these processes is sodium chloride (NaCl) or potassium chloride (KCl). The energy required to convert NaCl or KCl into other consumables used in the processes is included in the mass balance and energy study shown below.

[0053] Most of the chemicals used in the CO_2, NOx and SO_2 capturing and repurposing processes can be recycled. The entire reagent recycling only requires 70°C that can be supplied

from combustion waste heat or chilling to below 25°C that can be supplied by seawater or other liquid of equal or lesser temperature.

[0054] The electrical power required for equipment operation is also included in the provided energy study and mass balance. This process can treat the CO_2, NOx and SO_2 made from generating the electricity required for this process if the generation source is local, for example a ship or power plant application.

[0055] The process control system logic program used to collaboratively manage processes described herein has the ability to individually adjust the reaction rates of all of the processes independently as required to compensate for variations in the CO_2, NOx and SO_2 compound ratio and overall concentrations of the compounds in exhaust gas in real time. This is done by sensing the concentration of CO_2, NOx and/or SO_2 and then dosing only the requisite amount of reagent necessary to treat the desired amount of CO_2, NOx or SO_2.

[0056] The disclosed methods provide for technologies that effectively sequester point source and atmospheric gases including CO_2, NO_x and SO_2. The technology can be applied at the point source for these gases, for example, from the exhaust stack of a combustion source, or a chemical reaction that generates these gases. These gases may also be present in the liquid phase, such as when they are dissolved into an aqueous solution. This technology is also applicable for gases that have been released into the atmosphere or are present in water. This technology is also environmentally responsible because it generates non-hazardous reaction by products such as sodium bicarbonate ($NaHCO_3$), which is also known as baking soda and has commercial value.

[0057] The disclosure provides seven synergistically related chemical processes for the removal of CO_2, NOx and SO_2 (target gases). The disclosure also describes the supporting reactions and reveals the useful aspects of the integrated chemical process methodology. The

seven chemical processes and their supporting reactions share multifaceted chemical synergy that results in reduced reaction chamber volume, decreased residence time, compounds recycled with low energy and efficient production of commercially viable products. For example, the five chemical reactions described in FIGURE 1 can occur in a single reaction chamber. The rate of reactions for all five reactions can be individually regulated by varying the concentrations and pH of solutions that contain only three chemicals. The products of some reactions are also the reactants for subsequent reactions.

[0058] The process control techniques can use data from strategically placed sensors with data that is confirmed accurate through comparisons between sensors with known chemical axioms, the Process Logic Control (PLC) program employs sophisticated "if then" logic and algorithms that adroitly regulate the reaction rates of all reactions in a way that:

[0059] Adjusts for changes in the ratios of the three target compounds.

[0060] Adjusts for changes in concentrations of the target compounds.

[0061] Determines as needed chemical dosing necessary to individually obtain a predetermined CO_2 and NOx and SO_2 removal efficiency. This approach eliminates excess chemical use.

[0062] Balances the molar ratios of the two primary reactants: NaOH and Cl_2/NaOCl for all seven reactions.

[0063] The multi-variable if then logic of the PLC can accomplish these tasks because the seven principal reactions to treat the target compounds were deliberately chosen with CO_2 and NO_x reactions that use NaOH/NaOCl as their primary rate determining reagent. This ability to treat CO_2 or NOx or SO_2 with either group of compounds allows the PLC program to adjust the reaction rates of the seven equations as required to balance the chemical demand for NaOH and

NaOCl. The entire group of seven processes can also act as a "polishing scrubber" that follows a less efficient CO_2, NOx, SO_2 or other scrubber for another compound(s) where desired.

[0064] The emphasis on balanced reagent usage is important because it allows a single electrochemical (E-Chem) process to generate the two major reagents for all seven processes described in this document through the conversion of NaCl into NaOH and Cl_2. The Cl_2 is immediately converted to NaOCl and HOCl using a conventional subordinate reaction that requires a portion of the NaOH generated by the E-Chem process. This step of selecting 7 equations that have chemically symbiotic stoichiometry and easily managed reaction mechanics is commercially valuable because it eliminates or reduces the need for reagent storage containers. This feature is of significance when the integrated process is used aboard a vessel that chooses to generate its reactants from seawater using an electrochemical process rather than utilize ship cargo space for chemical reagents. The electrochemical process can also be used with sodium chloride brine aboard a vessel or in terrestrial applications.

[0065] There is a very important justification for returning the $NaHCO_3$ to the sea, it compensates for CO_2 adsorbed by the sea from the atmosphere. The sea utilizes $NaHCO_3$ as its primary buffering compound to hold the ocean pH stable at approximately 8.1. The CO_2 enters the sea from the atmosphere as part of a natural effort to equalize the concentrations of CO_2 within the gas phase atmosphere and liquid phase ocean water. At this time, the world's oceans are using more $NaHCO_3$ to compensate for the adsorbed CO_2 than they can make through dissolving of $CaCO_3$ from shells and other materials within the sea. If this process is not balanced in some way, the oceans will lose their ability to maintain their pH. The resulting rapid change in pH will kill the algae that produce approximately 70% of the world's oxygen introduced into the atmosphere. If that happens, humans and everything else that relies on

oxygen in the atmosphere will die! That would cause the world's 6th extinction process. Unfortunately, there is already so much CO_2 in the atmosphere from natural and anthropomorphic sources that even if we immediately stopped introducing more CO_2 into the atmosphere from combustion and other sources, the worlds' oceans will run out of available $NaHCO_3$ before the equilibrium between CO_2 in the atmosphere and oceans is reached.

[0066] Therefore, intervention is required to prevent an ocean pH catastrophe. Fortunately, the CO_2 capture processes disclosed herein creates one mole of $NaHCO_3$ byproduct for every mole of CO_2 that it sequesters from any source. The processes disclosed herein are part of the solution to prevent the oceans from losing their ability to maintain the life-saving pH equilibrium.

[0067] Thus, in one embodiment, the disclosure provides technology that combines processes for the removal of CO_2, NOx and SO_2 from an exhaust gas or liquid stream using three or more sequential reaction stages within a single reactor or combination of three or more separate reaction stages. The gas/mist or gas/(wet or dry aerosol) or liquid/liquid phase reaction technology allows individual and collective scrubbing stages to treat any gas/liquid volume from less than 500 m^3/minute to any size that can be built. The reaction rates can be fast enough to facilitate reaction vessel sizing that is small enough for mobile applications as well as terrestrial applications with limited space. The methodology can also be made much larger to accommodate an exceptional target gas treatment requirement. Although not commercially offered for sale or sold, the methodology has been successfully sized for a challenging marine vessel application where space is limited. The mass balance for this exercise is included in this document. The process can easily be sized for a much larger terrestrial applications.

[0068] As shown in FIGURE 1, 1-Loop Process technology involves the initial capture of SO_2. This process can occur when gas containing SO_2 is introduced into an aqueous mist containing

sodium hypochlorite (NaOCl or NaClO, also known as "bleach") or moving gas containing SO_2 through a countercurrent packed bed scrubber, bubble tray scrubber or equal that is recirculating a solution that contains NaOCl or by reacting a solution that contains SO_2 with a solution that contains NaOCl. In all cases the reaction forms sodium chloride (NaCl) and sulfuric acid (H_2SO_4). As shown below in equation [1], 1 mole of NaOCl can react with 1 mole of SO_2 and 1 mole of H_2O to form 1 mole of NaCl and 1 mole of H_2SO_4:

[0069] $SO_2 + NaOCl + H_2O \rightarrow NaCl + H_2SO_4$ [1].

[0070] Next, as shown in FIGURE 1, the first capture of NO_x (both NO and NO_2) can occur through their reaction with NaOCl and H_2O to form sodium nitrate ($NaNO_3$) and hydrochloric acid (HCl). As shown in equation [2], 1 mole of NO and 1 mole of NO_2 can react with 1 mole of NaOCl and 1 mole of H_2O to form 2 moles of $NaNO_3$ and 2 moles HCl:

[0071] $NO + NO_2 + NaOCl + H_2O \rightarrow 2\ NaNO_3 + 2\ HCl$ [2].

[0072] Next, as shown in FIGURE 1, the first capture of CO_2 can occur through its reaction with NaOCl and H_2O to form hypochlorous acid (HOCl) and $NaHCO_3$. As shown in equation [3], 1 mole of CO_2 can react with 1 mole of NaOCl and 1 mole of H_2O to form 1 mole of HOCl and 1 mole of $NaHCO_3$:

[0073] $CO_2 + NaOCl + H_2O \rightarrow HOCl + NaHCO_3$ [3].

[0074] Next, as shown in FIGURE 1, the second capture of NO_x can occur through their reaction with NaOH and NaOCl to form sodium nitrite ($NaNO_2$) and H_2O. As shown in equation

[4], 1 mole of NO and 1 mole of NO_2 can react with 2 moles of NaOH and 1 mole of NaOCl to form 2 moles $NaNO_2$ and 1 mole of H_2O:

[0075] $NO + NO_2 + 2\ NaOH + NaOCl \rightarrow 2\ NaNO_2 + H_2O$ [4].

[0076] Finally, as shown in FIGURE 1, the second capture of CO_2 can occur through its reaction with NaOH to form $NaHCO_3$. As shown in equation [5], 1 mole of CO_2 can react with 1 mole of NaOH to form 1 mole of $NaHCO_3$:

[0077] $CO_2 + NaOH \rightarrow NaHCO_3$ [5].

[0078] The first forced precipitation of the products can occur upon addition of an alcohol including but not limited to methanol, ethanol, propanol, butanol including tert-butanol, and the like, to the reaction mixture containing products $NaHCO_3$, Na_2SO_4 and NaCl. Once the precipitated material has been separated from the aqueous/alcohol phase, the alcohol (methanol) can be thermally separated and recycled and the solid $NaHCO_3$, Na_2SO_4 and NaCl products can be stored for commercial use or returned to the sea. Alternatively, once precipitated material is removed from the aqueous/alcohol liquor, the alcohol (tert-butanol) can be separated from the aqueous phase and recycled by chilling the mixture with seawater or other cold trap of 25°C or lower temperature plus separation of the jell or solid by any appropriate means. The solid $NaHCO_3$, Na_2SO_4 and NaCl products can be stored for commercial use or returned to the sea.

[0079] The second forced precipitation of the products can occur upon addition of a dialkyl ketone, including but not limited to acetone, methyl ethyl ketone, diethyl ketone and the like, to the aqueous reaction mixture containing $NaNO_2$, $NaNO_3$. Once precipitated material is separated from the aqueous/acetone mixture, the acetone can be thermally recycled and the solid $NaNO_3$ product can be stored for use as fertilizer.

[0080] In addition, as shown in FIGURE 1, NaOCl and NaOH and any recycled H_2O can be added back into the loop sequence to maintain the reaction cycle.

[0081] The reaction sequence shown in FIGURE 1 uses a process control sequence based on multiple algorithms that effectively regulate the interrelated reaction rates of five slightly overlapping sequential reactions by varying reagent dosing parameters. The process control can integrate data from multiple sensors using multi-variable simultaneous equations that employ if-then logic and references known kinetic reaction parameters to determine the validity of the sensor data. This process control also regulates reagent injection timing into the single reaction chamber. The process control also involves regulation of the mass of reagents injected and pH of the reagent mixtures used. This multivariable process control of five reactions can be accomplished by the regulation of just three reactants: NaOCl, NaOH and HCl.

[0082] The synergistic choice of reactions within the loop sequence allows the reaction products in early stages of the process to act as reagents in subsequent reactions that occur in semi-overlapping environments within the same vessel. For example, in the reaction sequence shown in FIGURE 1, the HOCl formed in the first capture of CO_2 is used to generate NaOCl in the two subsequent capture process of NO_x.

[0083] Precise process control is possible for the reactions shown in FIGURE 1 because the unique and different reactions chosen for the process have uniquely different kinetic reaction rates and respond differently to the two ions formed when $NaHCO_3$ is speciated in response to the pH of its environment.

[0084] Knowledge of reaction sequence and deliberately varying the pH, timing and amount of the NaOCl reagent dosed into the reaction chamber as described previously provides a

predictable way to selectively capture and/or remove SO_2, NOx and CO_2 in the process sequence.

[0085] The fifth reaction in the FIGURE 1 loop utilizes NaOH as its reagent. The rate and timing of the introduction of NaOH as specified by the PLC program in response to pre-determined sensor data regulates that process too.

[0086] The process control logic used in this system requires reliable data from sensors. Non-specific sensors like Oxidation Reduction Potential (ORP) can provide unreliable process information. For example, if ORP is used to regulate the dosing of NaOCl into a reaction mixture, a change in ORP would accompany the addition of NaOCl, and that would be a valid process control variable if NaOCl was the only compound that could influence the solution ORP value. But data from an ORP probe can be unreliable because ORP is not exclusively sensing the HClO and ClO^- ions in the reaction mixture. Other chemical compounds or ions in the reaction mixture can also influence the ORP value of the reaction liquid. This problem is not resolved by utilizing two or more of the same sensors. Therefore, the process control logic used for the regulation of the reactions disclosed herein does not rely on non-specific sensors where process confusion is possible. The process control described in this patent application relies on comparison between information from two uniquely different sensors in each situation where process sensor confusion is possible.

[0087] For example, the dosing of NaOCl can be confirmed by data from two dissimilar sensors: the pH of process liquid and the concentration of Cl_2 gas in the reaction chamber. The two sensor values are compared against known speciation of NaOCl as shown in FIGURE 2. The combination just described is used to provide reliable process variable data for each area where the addition of NaOCl is a part of process chemistry.

[0088] The concept of verifying sensor data applies to other process variables too. The FTIR data for the identity and concentrations of gases in specific sections of the reaction chamber can be compared with known relationships between gas ratios such as the presence of SO_2 against the pH of the process liquid mist.

[0089] The monitored and regulated integration of multiple processes within a single reactor is the primary reason the reaction chambers are much smaller than would be required if the seven processes were completed in separate reaction chambers and regulated with conventional process control.

[0090] The alternative methodology for removing SO_2 and NOx from a gas or liquid stream prior to LiOH based CO_2 capture is based on chlorine dioxide (ClO_2^o).

[0091] The key to this process is generating non-ionic chlorine dioxide distinguished with a superscripted "o" as shown here: ClO_2^o. This can be done by several methods that are described in the previously referenced patent. Process control that meters the ClO_2^o addition into a reaction chamber(s) as required to react with known quantities of nitrogen monoxide (NO) and nitrogen dioxide (NO_2) provided by FTIR or other sensors capable of sensing these compounds and ClO_2^o in a gas or liquid stream. The ClO_2^o reacts with the NO and NO2 according to equations [6] and [7]:

[0092] $5\ NO + 2\ (ClO_2)^o + H_2O \rightarrow 5\ NO_2 + 2\ HCl$ [6]

[0093] $5\ NO_2 + (ClO_2)^o + 3\ H_2O \rightarrow 5\ HNO_3 + HCl$ [7]

[0094] The HCl and HNO_3 generated by equations [6] and [7] are neutralized with KOH as described in equations [8] and [9]:

[0095] $HCl + KOH \rightarrow KCl + H_2O$ [8]

[0096] $HNO_3 + KOH \rightarrow KNO_3 + H_2O$ [9]

[0097] The KCl and KNO_3 products shown in equations [8] and [9] can be removed with forced precipitation using ethanol or equal.

[0098] In another embodiment, the disclosure provides 2-Loop Process technology of an integrated closed two loop system, which collaboratively captures CO_2 and converts it to $NaHCO_3$. During this sequence, the primary reactants include lithium hydroxide (LiOH), which can be regenerated and recycled back into the loop. The rate controlling consumable that is introduced into the loop includes sodium hydroxide (NaOH). A by-product, sodium carbonate (Na_2CO_3) can be generated, and can be used for further conversion of CO_2 into $NaHCO_3$. This technology has many applications including use in space crafts, ships, submarines, and anesthesia.

[0099] As shown in FIGURES 3A and 3B, Loop 1 of the 2-Loop Process involves the initial capture of CO_2 and a second capture of CO_2. This process occurs when CO_2 is introduced to lithium hydroxide (LiOH) or sodium carbonate (Na_2CO_3). The contact and subsequent reaction between LiOH and/or Na_2CO_3 and CO_2 can occur in several ways: gas containing CO_2 can be exposed to an aqueous mist containing LiOH and/or Na_2CO_3 resulting in the CO_2 transfer through the membrane between the gas phase and the liquid droplet where it reacts with the LiOH and/or Na_2CO_3 in the droplet. Gas containing CO_2 can impact a thin liquid film containing LiOH resulting in the CO_2 transfer through the membrane between the gas phase and the liquid film where reacts with the LiOH and/or Na_2CO_3 in the liquid film.

[00100] In another example CO_2 can be dissolved or suspended in an aqueous solution which is mixed with a solution containing dissolved LiOH and/or Na_2CO_3 where it subsequently reacts with the LiOH and/or Na_2CO_3. In a final example, a gas containing CO_2 can be exposed to an aerosol conveying dry or moist LiOH granules or nano-granules that contact gas phase CO_2 or

CO_2 dissolved/suspended in liquid droplets resulting in a reaction as described in equations [10A and 10B]. The reaction product and excess reactants are subsequently captured in a mist or liquid that is ultimately recirculated in this process sequence.

[00101] This capture of CO_2 used in this methodology as described above is uniquely different from the well-known and industry practiced "dry" method that captures CO_2 by exposing the gas to stationary beds of granular LiOH or granular material impregnated with LiOH or other lithium materials.

[00102] All of the examples of CO_2 capture used in this methodology, described on FIGURE 3A, ultimately transfer the CO_2 into an aqueous phase where it reacts according to the equations as shown below.

[00103] As shown below in equation [10A], 2 moles of LiOH can react with 1 mole of CO_2 to form 1 mole of lithium carbonate (Li_2CO_3) and 1 mole of water (H_2O). In addition, as shown in equation [10B], 2 moles of lithium hydroxide monohydrate ($LiOH{\cdot}H_2O$) can react with 1 mole of CO_2 to form 1 mole of Li_2CO_3 and 3 moles of H_2O:

[00104] $2\ LiOH + CO_2 \rightarrow Li_2CO_3 + H_2O$ [10A]

[00105] $2\ LiOH{\cdot}H_2O + CO_2 \rightarrow Li_2CO_3 + 3\ H_2O$ [10B]

[00106] That is, CO_2 can be captured from the atmosphere and/or from an aqueous solution and then sequestered into a solid Li salt, i.e. Li_2CO_3. The CO_2 captured described in equations [10A] and [10B] can occur in either the gas or liquid phase.

[00107] Next, as shown in FIGURES 3A and 3B, the Li_2CO_3 generated in equations [11A or 11B] is converted into sodium carbonate (Na_2CO_3) or potassium carbonate (K_2CO_3) by treatment with NaOH or potassium hydroxide (KOH), respectively.

These reactions are shown below in equations [11A] and [11B], 1 mole of Li_2CO_3 can react with 2 moles of NaOH or 2 moles of KOH to form 2 moles of LiOH and 1 mole of sodium carbonate (Na_2CO_3) or 1 mole of potassium carbonate (K_2CO_3):

[00108] $Li_2CO_3 + 2\ NaOH \rightarrow 2\ LiOH + Na_2CO_3$ [11A]

[00109] $Li_2CO_3 + 2\ KOH \rightarrow 2\ LiOH + K_2CO_3$ [11B]

[00110] In addition to regenerating LiOH, the generated Na_2CO_3 or K_2CO_3 can be used in the next step to capture more CO_2 (see equations [8A] and [8B] below).

[00111] The reaction of Li_2CO_3 with NaOH/KOH to generate LiOH and Na_2CO_3/K_2CO_3 as shown in equations [11A] and [11B] occurs in the liquid phase.

[00112] Next the reaction products from equations [11A and 11B] are exposed to CO_2 again using the gas/liquid or liquid/liquid or gas/solid mass transfer methodology described above.

[00113] The mass transfer results in reactions wherein 1 mole of Na_2CO_3 or 1 mole of $KHCO_3$ can react with 1 mole of CO_2 and 1 mole of H_2O to generate 2 moles of $NaHCO_3$, or 2 moles of $KHCO_3$ as shown in equations [12A] and [12B]:

[00114] $Na_2CO_3 + CO_2 + H_2O \rightarrow 2\ NaHCO_3$ [12A]

[00115] $K_2CO_3 + CO_2 + H_2O \rightarrow 2\ KHCO_3$ [12B]

[00116] This reaction can be perpetuated (subject to solids concentration in the aqueous phase) as long as the pH is elevated to basic by the addition of NaOH or KOH.

[00117] As shown on FIGURES 3A and 3B and described in the Mass Balance (Table 5), the LiOH is recycled and the overall process requires one mole of NaOH or LOH per mole of captured CO_2. The overall reaction produces one mole of $NaHCO_3$ per mole of CO_2 captured.

[00118] The process chemistry uses a method to regulate the process residence time. This involves the flow of liquids through Loop 1 and Loop 2 of the 2-Loop Process sequence. Loop 2

is a slip stream of the Loop 1 process stream. Loop 2 is actually two or more process loops with the same mechanical configurations that may or may not handle the same volume of process liquid. The multiple Loop 2 process equipment systems can have equal or dissimilar reaction vessel cross sectional areas.

[00119] The ratio or percent of the two or more Loop 2 process liquid flow paths can be monitored and regulated as required to provide ideal reaction residence time. The overall Loop 2 process flow cross sectional area is adjusted as required to achieve a liquid flow velocity that slows or increases the residence time within the reactor. The residence time is adjusted to allow the reaction(s) within the loop to achieve the desired percent process completion. The optimum process tuning is achieved by changing the overall cross-sectional area of the Loop 2 process path until any further change in cross-sectional area will adversely affect the desired percent of process completion within Loop 2.

[00120] The Loop 1 process path residence time can also be adjusted as required obtaining the optimum percent completion for processes that occur in that loop. This is done by adjusting the process liquid flow rate through the loop and that is done by varying the split of liquid diverted to the Loop 2 reactors.

[00121] The process control logic effectively monitors and adjusts the number of Loop 2 paths and the split ratio between Loop 1 and Loop 2 by responding to analytical sensors that determine concentrations of compounds in the liquid and gas stream plus flow rate sensor data and known loop cross sectional areas of the loops to create the desired residence time within Loop 1 and Loop 2 to effect the desired reaction completions in both loops. This process automatically adjusts to variations on the ratio of concentrations of the target gases and the total amount of each target gas.

[00122] The disclosure provides methods for the removal of $NaHCO_3$ from the Loop 2 recycling process without removing the LiOH from the same process liquid. This is done through a forced precipitation using an alcohol at the add alcohol to the Loop 2 slip stream step. The selection of a suitable alcohol is critical to the success of this process.

[00123] Two alcohols were identified as ideal for this process. Each has has a unique set of ideal physical characteristics. Methanol is ideal because it is miscible in water without forming an azeotrope, has a low solubility for $NaHCO_3$ when compared to H_2O and a solubility for LiOH that is equal to or higher than that of H_2O. Methanol is the only alcohol that does not form an azeotrope with water, and that feature allows a more complete separation of the alcohol and water during distillation. Methanol has a boiling point of 64.7°C. This low temperature allows recovery of the methanol through distillation using waste heat available from a combustion process. Tert-butanol has a solidification temperature at 25°-26° C. This provides a solution for applications of this methodology that have access to large heat sinks, for example processes that are installed aboard seagoing ships. The ocean can provide chilling required for solidification of the tert-butanol at no cost. This feature allows its subsequent separation from the process stream by centrifuge or filtering.

[00124] This separation sequence utilizes the fact that $NaHCO_3$ has a lower solubility in alcohol than does LiOH. For example, the LiOH solubility in water is between 108 and 128 g/L at process temperatures, and $NaHCO_3$ solubility in water is between 69 and 169g/L at ambient temperatures. However, when an alcohol such as ethanol is added to an aqueous solution of LiOH, its solubility remains around 23g/L, whereas the solubility of an aqueous solution of $NaHCO_3$ in ethanol is 0.

[00125] The difference in solubility between $NaHCO_3$ and LiOH allows for this forced precipitation step: $NaHCO_3$ precipitates leaving the LiOH in solution. Methanol, tert-butanol (or other suitable alcohols) can be added to this slip stream liquid to affect the precipitation of the sodium or potassium salts.

[00126] An alcohol, preferably methanol or tert-butanol, can be added to the Loop 2 liquid. The volume of alcohol is proportional to the Loop 2 liquid flow rate, process liquid temperature and the concentrations of compounds in the process stream that can influence precipitation of the $NaHCO_3$ or $KHCO_3$. The alcohol can be added to the Loop 2 process liquid flow piping using any conventional dosing method that facilitates good liquid mixing with minimal introduction of static pressure in the process flow systems.

[00127] The regenerated LiOH remains in the aqueous reaction mixture, which can be reused to sequester additional CO_2 through Loop 1, and the solid $NaHCO_3$ can be converted into a paste and washed or dried depending on the desired purity or physical state. For example, a thin film dryer, centrifuge or other similar device can remove the moisture present in the $NaHCO_3$ paste or slurry. The solid $NaHCO_3$ is then packaged for commercial use or deposited in the ocean in exchange for a tax donation.

[00128] In the event the Loop 1 and optional SO_2 pre scrubber did not remove all of the SO_2 from the gas stream, any remaining SO_2 can react with the LiOH to form Li_2SO_3. This is also removed from the recirculated liquor in the forced two step precipitation of $NaHCO_3$ and Li_2SO_3 step of the Loop 2 process. The process follows the following reaction steps shown below in equations [13] through [17]:

[00129] $2\ LiOH\ (saturated) + SO_2 \rightarrow Li_2SO_3 + H_2O$ [13]

[00130] $Li_2SO_3 + H_2O + SO_2 \rightarrow 2\ LiHSO_3$ [14]

[00131] $Li_2SO_3 + H_2SO_4 \rightarrow Li_2SO_4 + SO_2 + H_2O$ [15]

[00132] Li_2SO_4 (conc.) + $Na_2CO_3 \rightarrow Li_2CO_3\downarrow + Na_2SO_4$ [16]

[00133] $Li_2CO_3 + 2\ NaOH \rightarrow 2\ LiOH + Na_2CO_3$ [17]

[00134] The chemistry used in the disclosed CO_2 sequestering process has been checked against other compounds commonly found in combustion exhaust and it was determined that no significant omissions occur that are not remedied in this process.

[00135] FIGURES 4A and 4B illustrate an embodiment of how the CO_2, NOx and SO_2 capture and reuse methodology disclosed herein for the 1-Loop Process and the 2-Loop Process can be configured. The sequence is important, but the steps can occur in one, two or more separate but linked reaction vessels. The process can also occur in two or more parallel reaction vessels provided all of the parallel vessels use the reaction sequence shown here. The 1-Loop Process and 2-Loop Processes can be sequentially combined within a single scrubbing vessel or separated into two or more components.

[00136] FIGURES 4A and 4B also shows how the 1Loop and 2Loop Processes are typically preceded by a SO_2 scrubber and/or exhaust gas cooling/economizer/quenching module when the exhaust gas is above ambient temperatures. The right side of the diagram also shows the generation of reagents and their flow into the 1-Loop Process and the 2-Loop Process.

[00137] FIGURES 4A and 4B illustrate an embodiment of how the sequence of the five processes grouped within the black rectangle named "1 LOOP PROCESSES" of FIGURE 1 can be integrated into a scrubbing process within a single scrubbing vessel. This combination of chemical reactions is defined as the 1-Loop Process. It is designed to treat the effluent exhaust gas either from combustion, or from other chemical and biological sources of CO_2, NOx and SO_2.

[00138] The 1-Loop and 2-Loop Process diagrams on the left side of FIGURES 4A and 4B are displayed in full detail in FIGURES 1, 3A and 3B, respectively. The configuration shown in FIGURES 4A and 4B is only an example of the possible configuration and is not meant to be limiting. The reagent generation, conversion and distribution technology shown in FIGURES 4A and 4B is described in greater detail in FIGURE 5.

[00139] FIGURES 4A and 4B also shows hydrogen gas generated during the electrochemical (E-Chem) production of NaOH and Cl_2 vented to a burner downstream of the 2-Loop Process. This burn module can include a metallic grate across the gas flow. When present, the grate is heated by the hydrogen gas combustion. The hot metallic surface and/or burner flame are designed to combust remaining hydrocarbons and warm the exhaust gas to minimize a condensate cloud at the exhaust stack.

[00140] FIGURE 5 illustrates how seven separate gas scrubbing processes are grouped into two scrubbing groups:

[00141] The SO_2, NOx and CO_2 scrubbing chemical reactions identified as the 1-Loop Process is grouped within a rectangle enclosed in a double solid line.

[00142] Two additional CO_2 capture process identified as the 2-Loop Process is shown within the rectangle enclosed in a dashed line

[00143] FIGURE 5 also shows that a single electrochemical generator can make the primary chemical consumables for all seven processes from seawater or other solution that contains NaCl without other compounds that will interfere with the E-Chem process. The methodology for E-Chem manufacture of NaOH and Cl_2 from NaCl is well practiced in industry. Newer and more energy efficient and less environmentally challenging technology is emerging. The improved

technology is recommended, but the disclosed technology is not dependent upon any one electrochemical methodology.

[00144] The conversion of Cl_2 into NaOCl is also well practiced methodology. This disclosure is not dependent on any one methodology but recommends the most energy efficient and environmentally noninvasive method be employed.

[00145] FIGURE 5 also show how reagent usage made by the E-Chem process can be balanced. Multiple methods for capturing and repurposing CO_2 and NO_x are present; at least one of each type of process uses NaOCl as a reagent and another uses NaOH as a reagent. This dual reagent consumption option allows an allocation of the CO_2 and/or NO_x scrubbing to either or both reagents as required to equalize the overall reagent production by the E-Chem process.

[00146] Only one method for SO_2 capture is shown in FIGURE 5, but it can be augmented with an optional SO_2 pre-scrubbing stage.

[00147] The integration of multiple CO_2, NOx and SO_2 treatment methods within this overall process that use NaOH or NaOCl as consumables make it possible to accommodate fluctuations in the ratios of CO_2, NOx and SO_2 in the waste gas stream without wasting reagents.

[00148] For example, three processes for the removal of CO_2 were deliberately included in this technology package. One of the CO_2 processes utilizes NaOCl as a consumable and the other two use NaOH/KOH. This is important because the CO_2 mass loading in some process gas, for example combustion, is typically 40x higher than the NOx or SOx mass loading so it is essential to treat part of the CO_2 with NaOH/KOH and the rest with NaOCl in order to balance the chemical availability of reagents from the E-Chem conversion of NaCl. Variations in the NOx and SO_2 concentrations are monitored and easily accommodated by adjustments in the overall

ratio selected for the CO_2 reactions. The process control system logic adjusts the percentage of each of the CO_2 sequestration processes through a multifaceted process previously described.

[00149] The 1-Loop Process described herein is designed to operate as a prerequisite for the 2-Loop Process. However, the 1-Loop Process and 2-Loop Process can also be used in a standalone mode.

[00150] The 1-Loop Process can also act as a polishing scrubber. In one example the 1-Loop Process can follow an SO_2 abatement scrubbing device of any design or a NOx abatement scrubbing device of any design. In another example, the 1-Loop Process can follow a quencher that captures waste heat from the exhaust gas stream for use in the recycling reactants used in the 1-Loop Process or for other purposes.

[00151] Furthermore, the 2-Loop Process can be used as a standalone technology if the gas stream does not contain compounds that can react with the process chemicals, for example: SO_2 and NOx.

[00152] EXAMPLES

[00153] Example 1: The process flow instruments used in the 1-Loop Process are described in FIGURE 6 and in Table 2 below:

Table 2

KEY	DESCRIPTION
NOTE	The following summarize reactions that are occurring at each step in the overall reaction sequence. This information is also provided in the 1-Loop Process diagram shown in FIGURE 6.
A	$SO_2 + NaOCl + H_2O \rightarrow NaCl + H_2SO_4$
B	$NO + NO_2 + NaOCl + H_2O \rightarrow 2NaNO_3 + 2HCl$

C	$CO_2 + NaOCl + H_2O \rightarrow HOCl + NaHCO_3$
D	$NO + NO_2 + 2NaOH + NaOCl \rightarrow 2NaNO_2 + H_2O$
E	$CO_2 + NaOH \rightarrow NaHCO_3$
NOTE	All components and systems described below are assumed to be made from materials that are compatible with the chemicals/reagents, and process pressures, temperatures etc. that are applicable and relevant for the specific application. Pumps and blowers required to move liquids and gases are not shown. There are many sensors and a process control system that are not shown.
1	Reaction vessel – typically cylindrical with one or more inlets for untreated gas at one end (Item 2) and one or more exists for treated gas at the other end (Item 41). The vessel can be of any shape and configuration. It need not be linear as shown. The vessel is designed to operate at the system pressures and meet site requirements. The vessel includes liquid diverters near the inlet end of each reaction vessel stage. This is used to prevent liquid condensate from draining past the entrance end of any reaction vessel. The liquid diverter can be of any design.
2	Gas containing one or more of the following: CO_2, NOx, SO_2. The gas can be at any pressure. Ideally the pressure is slightly negative with respect to the surrounding atmosphere to prevent any exhaust gas from leaking into the atmosphere. The gas can be at any temperature between 10°C and 90°C.
3	Gas sensor array. Local and/or remote instrumentation for qualitative and quantitative analysis of CO_2, NOx, SO_2 and other compounds in the reaction mixtures. Also, instrumentation for gas temperature and pressure.
4	Reagent Injection Array. This proportionally introduces and mixes two or more

	different reagents and sprays the mixture into the reaction chamber.
5	Detail of "4" – Spray nozzle(s) of any type of air or mechanically atomized design in countercurrent and/or co-current and/or tangential orientation with respect to the gas flow. Tangential orientation is typically done at an angle or series of angles that promote gas mixing.
6	Detail of "4" – Wall of Reaction Vessel (Item 1).
7	Detail of "4" – Mixing chamber. This chamber provides an isolated environment for mixing of reagents used at each phase of the chemical reaction within the Reaction Vessel (Item 1).
8	Detail of "4" – Static Mixer of any design.
9	Detail of "4" – Remotely controlled Proportional high-pressure chemical pump of any design. Preferably a pump that provides consistent pressure. The pressure range can be anywhere between 10 and 3000 psi. Preferably 200-300 psi. The device is made of any material that is compatible with the reagents and pressure. Reagents used include but are not limited to a hypochlorite compound, for example sodium hypochlorite ($NaHCO_3$), or an alkaline compound, for example sodium hydroxide (NaOH), or a mineral acid, for example hydrochloric (HCl).
10	Detail of "4" – This is a second two or more Remotely controlled Proportional high-pressure chemical pump of any design. Preferably a pump that provides consistent pressure. The pressure range can be anywhere between 10 and 3000 psi. Preferably 200-300 psi. The device is made of any material that is compatible with the reagents and pressure. Reagents used include but are not limited to a hypochlorite compound, for example sodium hypochlorite ($NaHCO_3$), or an alkaline compound, for example

	sodium hydroxide (NaOH), or a mineral acid, for example hydrochloric (HCl).
11	Detail of "4" – Remotely controlled valve to regulate the addition of a gas into the Mixing Chamber (Item 7). The gas can be added to the reaction chamber in one or more locations. The selection of gas injection point(s) is configured to provide optimum mixing. The location can be before, with or after liquid reagent(s) has/have been introduced into the reaction chamber.
12	Detail of "4" – Chemical storage, transfer pump(s) and interconnecting piping. The reagent is stored in any appropriate quantity within tanks or vessels of material that is compatible with the reagent. The reagents can be but are not limited to a hypochlorite compound, for example sodium hypochlorite ($NaHCO_3$), or an alkaline compound, for example sodium hydroxide (NaOH), or a mineral acid, for example hydrochloric (HCl).
13	Detail of "4" – This is the second of several sets of chemical storage, transfer pump(s) and interconnecting piping. The reagent is stored in any appropriate quantity within tanks or vessels of material that is compatible with the reagent. The reagents can be but are not limited to a hypochlorite compound, for example sodium hypochlorite ($NaHCO_3$), or an alkaline compound, for example sodium hydroxide (NaOH), or a mineral acid, for example hydrochloric (HCl).
14	This is a gas compressor(s), pressure vessel(s) and interconnecting piping. The equipment is made of materials that are compatible with the gas(s) and pressure rated for the application.
15	Drainage from the Reaction Vessel (Item 1). This flow is transferred via pipe with or without pumps and storage tanks.

16	Injection of alcohol, preferably methanol into the 1Loop process liquid stream. The point of introduction includes methods of statically mixing the 1Loop process liquid stream and the alcohol.
17	Separation device to separated precipitated sodium bicarbonate ($NaHCO_3$), sodium sulfate (Na_2SO_4), and sodium chloride (NaCl). The device can use any technology. Examples include, centrifuge and separatory funnel.
18	Storage vessel for separatory sludge. This includes screw conveyor or other device to transport the sludge to next treatment process. Size and material of construction are commensurate with chemistry of stored materials and process flow requirements.
19	Sludge processing process. This includes subsequent separation of the three or more components in the sludge and/or product rinsing as required for end product requirement.
20	Supplemental sludge processing. This includes drying and packaging as required to meet end product requirements.
21	Conveyance device for final product(s). This includes and is not limited to storage, weighing, loading and other steps required for relocating product to a new location.
22	Transport supernatant from precipitate separation device. This includes storage devices, piping, pumps and other equipment required to manage product flow and move liquid into distillation device (Item 23).
23	Distillation device(s) of any type that will separate alcohol from the water and other compounds in the 1Loop process liquid. The temperature is relevant to the alcohol used. Ideally methanol is used. It is one of the few alcohols that do not form an

	azeotrope with water, and therefore is capable of more complete separation from the water of the 1Loop liquid. The device(s) includes all necessary devices to interface this equipment with the rest of the process flow sequence.
24	Transfer of alcohol condensate from the Distillation devices (Item 23). This includes piping, pumps and other devices necessary to integrate this system into the overall process flow.
25	Alcohol storage vessel. This includes any required vents, level control and other devices necessary to integrate the vessel into the overall process flow.
26	Transport the alcohol. This includes all piping, pumps and flow control devices necessary.
27	Remotely controlled proportional metering pump at the required pressure and flow necessary to effectively introduce the alcohol into the 1Loop process flow line (Item 15). Ideally a pump with consistent fluid flow.
28	Injection of acetone into the 1Loop process liquid stream. The point of introduction includes methods of statically mixing the 1Loop process liquid stream and the acetone.
29	Separation device to separated precipitated sodium nitrate ($NaNO_3$). The device can use any technology. Examples include, centrifuge and separatory funnel.
30	Storage vessel for separatory sludge. This includes screw conveyor or other device to transport the sludge to next treatment process. Size and material of construction are commensurate with chemistry of stored materials and process flow requirements
31	Sludge processing process. This includes subsequent separation of the three or more components in the sludge and/or product rinsing as required for end product

	requirement.
32	Supplemental sludge processing. This includes drying and packaging as required to meet end product requirements.
33	Conveyance device for final product(s). This includes and is not limited to storage, weighing, loading and other steps required for relocating product to a new location.
34	Transport supernatant from precipitate separation device. This includes storage devices, piping, pumps and other equipment required to manage product flow and move liquid into distillation device (Item 35).
35	Distillation device(s) of any type that will separate acetone from the water and other compounds in the 1Loop process liquid. The device(s) includes all necessary devices to interface this equipment with the rest of the process flow sequence.
36	Transfer of acetone condensate from the Distillation devices (Item 35). This includes piping, pumps and other devices necessary to integrate this system into the overall process flow.
37	Acetone storage vessel. This includes any required vents, level control and other devices necessary to integrate the vessel into the overall process flow.
38	Transport the acetone. This includes all piping, pumps and flow control devices necessary.
39	Remotely controlled proportional metering pump at the required pressure and flow necessary to effectively introduce the acetone into the 1Loop process flow line (Item 28). Ideally a pump with consistent fluid flow.
40	1Loop process liquid with reduced concentrations of $NaHCO_3$, Na_2SO_4, NaCl and $NaNO_3$.

41	Gas containing lower concentrations of one or more of the following: CO_2, NOx, SO_2. The gas can be at any pressure. Ideally the pressure is slightly negative with respect to the surrounding atmosphere to prevent any exhaust gas from leaking into the atmosphere.

[00154] Example 2: The process flow instruments used in the 2-Loop Process are described in FIGURE 7 and in Table 3 below:

Table 3

KEY	DESCRIPTION
NOTE	The following summarize reactions that are occurring at each step in the overall reaction sequence. This information is also provided in the 2Loop Process diagram.
A	$2\ LiOH + CO_2 \rightarrow Li_2CO_3 + H_2O$
B	$Na_2CO_2 + CO_2 + H_2O \rightarrow 2NaHCO_3$
NOTE	All components and systems described below are assumed to be made from materials that are compatible with the chemicals/reagents, and process pressures, temperatures etc. that are applicable and relevant for the specific application. Pumps and blowers required to move liquids and gases are not shown. There are many sensors and a process control system that are not shown.
1	Reaction vessel – typically cylindrical with one or more inlets for untreated gas at one end (Item 2) and one or more exists for treated gas at the other end (Item 28). The vessel can be of any shape and configuration. It need not be linear as shown. The vessel is designed to operate at the system pressures and meet site requirements. The vessel includes liquid diverters near the inlet end of each reaction vessel stage.

	This is used to prevent liquid condensate from draining past the entrance end of any reaction vessel. The liquid diverter can be of any design.
2	Gas containing one or more of the following: CO_2, NOx, SO_2. The gas can be at any pressure. Ideally the pressure is slightly negative with respect to the surrounding atmosphere to prevent any exhaust gas from leaking into the atmosphere. The gas can be at any temperature between 10°C and 90°C.
3	Gas sensor array. Local and/or remote instrumentation for qualitative and quantitative analysis of CO_2, NOx, SO_2 and other compounds in the reaction mixtures. Also, instrumentation for gas temperature and pressure.
4	Drain for liquid reagent and product mix from the lower section of the reaction chamber in the 2Loop Process scrubber stage.
5	Reaction chamber of any shape, cylindrical is preferred with static mixer of any kind. The reaction: $Li_2CO_3 + 2NaOH = 2LiOH + Na_2CO_3$ is occurring in this chamber.
6	The reaction products from equation shown in Item 5 above, LiOH & Na_2CO_3 are sprayed into the upper section of the reaction chamber (Item 1). Spray nozzle(s) of any type of air or mechanically atomized design in countercurrent and/or co-current and/or tangential orientation with respect to the gas flow. Tangential orientation is typically done at an angle or series of angles that promote gas mixing.
7	Drain line for liquid reagent and product mix from the upper section of the reaction chamber in the 2Loop Process scrubber stage.
8	The "B" reaction ($Na_2CO_2 + CO_2 + H_2O = 2NaHCO_3$) occurs in the upper section of the reaction chamber. The $NaHCO_3$ will precipitate but is carried as a colloidal solid

	in the liquid stream to separation Vessel 8. Vessel 8 separates the precipitate from the liquid. The LiOH remains dissolved in the liquid. This separation device can be of any appropriate design.
9	Piping to convey liquid supernatant to distillation device designated as Item 10.
10	Item 10 is a distillation device. Distillation is used to separate the alcohol (preferably methanol) from the liquid supernatant. This can be done by any means. Supernatant without the alcohol leaves the distillation device.
11	Pipe and pump to transfer alcohol vapor to condensation device.
12	Item 12 is an alcohol condensation device. Any technology can be used for this process.
13	Pipe to transfer condensed (liquid) alcohol from condenser to storage vessel Item 14.
14	Storage vessel for alcohol. Any appropriate design.
15	Piping and PLC controlled variable speed pump system to introduce the alcohol into the drainage line #7. Static mixing of any design is/are included downstream of alcohol addition for mixing.
16	Precipitated $NaHCO_3$ storage container. Device can be of any appropriate shape or size.
17	Optional $NaHCO_3$ conditioning system as desired to improve the purity of the compound. This can be a wash and re-precipitation and drying device of any appropriate design. Or the product can be supplied as a paste.
18	Storage of optionally cleaned $NaHCO_3$ product. Vessel can be of any appropriate size and shape.

19	Clean $NaHCO_3$
20	Piping with pump to transfer the alcohol free supinate to the upper chamber of the reaction vessel. The liquid is sprayed into the gas stream within the reaction chamber by any appropriate means. This includes but is not limited to low- or high-pressure nozzles and air assisted nozzles.
21	Pipe with PLC controlled proportionally controlled pump for introduction of NaOH into the drainage liquid from the lower portion of the reaction chamber. A static mixer of any appropriate design is provided downstream of the point where the NaOH is introduced into the liquid.
22	NaOH storage tank. Any appropriate size and shape.
23	Pipe transferring NaOH from Electrochemical Cell (E-Cell).
24	E-Cell designed to convert NaCl into NaOH and Cl_2. Ideally the generator utilizes a design that does not include Hg cells and membranes.
25	H_2 gas produced in the E-Cell is safely vented to atmosphere or utilized in another process.
26	Pipe transferring NaOH from the E-Cell to the NaOCl generator.
27	NaOCl generator of any appropriate design.
28	NaOCl storage tank with vent to safe location or back into a process flow that utilizes NaOCl.
29	NaOCl supplied to the 1Loop processes (Diagram 1 and 1A).
30	Cl2 storage tank. Optionally this is fed directly into the NaOCl generator.
31	Liquid NaCl solution. This can be a high or low concentration brine or sea water.
32	Exhaust gas with little or no CO_2.

[00155] The integrated CO_2, NOx and SO_2 processes disclosed herein are applicable to marine and land based applications. The inherent design of this series of processes provides it with the features necessary for marine applications. These same features can be applied to land applications if desired, or land applications can be segregated in ways that require larger equipment footprints. These features are summarized below:

[00156] The reaction chambers process the exhaust gas at velocities that allow the reaction chambers to be fractionally larger than the volume required for typical exhaust gas flow.

[00157] The reaction chambers can be oriented in any direction because they utilize mist reactions. The upward flow shown in the figures are only examples.

[00158] The process can generate the NaOH and NaOCl from seawater thereby not requiring storage aboard the vessel for NaCl.

[00159] The processes generate $NaHCO_3$ which is naturally used by the oceans for pH control. Direct disposal of this compound from the ship as it is underway will benefit the oceans. This eliminates the need for storage aboard the vessel for the $NaHCO_3$.

[00160] The processes disclosed herein segregate the $NaNO_3$ from the process stream and store it as a commercially viable paste.

[00161] The processes disclosed herein have the ability to treat the exhaust of a generation system required to make the electricity necessary to run the processes thereby emitting essentially no CO_2, NOx and SO_2 as a result of operating the combined group of processes.

[00162] The use of E-Chem generation for NaOH/KOH production would be of concern if it was done using outdated technology. Over the past few years the technology for NaOH/KOH generation has become progressively more environmentally friendly. Upgrades in electrode technology are already used in commercial production. Other recent technological breakthroughs

show how the need for a cell membrane is eliminated. This most recent change is reported to reduce the electrical requirement to between 1/3 and 1/5 of conventional power requirement.

[00163] Table 4 shows the composition chemical composition of seawater that can be used to make the NaOH and NaOCl required for the disclosed processes.

Table 4

Total molar composition of seawater (salinity = 35)[16]

Component	Concentration (mol/kg)
H_2O	53.6
Cl^-	0.546
Na^+	0.469
Mg^{2+}	0.0528
SO_4^{2-}	0.0282
Ca^{2+}	0.0103
K^+	0.0102
C_T	0.00206
Br^-	0.000844
B_T	0.000416
Sr^{2+}	0.000091
F^-	0.000068

Seawater elemental composition (salinity = 3.5%)[citation needed]

Element	Percent by mass
Oxygen	85.84
Hydrogen	10.82
Chlorine	1.94
Sodium	1.08
Magnesium	0.1292
Sulfur	0.091
Calcium	0.04
Potassium	0.04
Bromine	0.0067
Carbon	0.0028
Vanadium	$1.5 \times 10^{-11} - 3.3 \times 10^{-11}$

[00164] The Mass Balance in this study utilizes a 95%NO/5%NO_2 mix in the NOx, but value is approximate. The exact NO/NO_2 ratio will depend upon the actual time between NOx generation and scrubbing, gas temperature, and other compounds in the gas stream. It is also influenced by exposure to mist quenching prior to SOx scrubbing. Some of the NO_2 will dissolve into the quench water.

[00165] The disclosure also presents individual Mass Balance tables for the 1-Loop Process and the 2-Loop Process scrubbing stages. Literature reports widely divergent ratios for NOx and CO_2 in marine exhaust therefore this study calculates Mass Balance for the removal of 1 Kg each of SO_2, NOx and CO and then combines these based on a "typical car carrier type ship" with

defined operational parameters. Table 5 illustrates the amount of CO_2 captured and repurposed based on 1 kg of CO_2 captured in the 2-Loop Process*.

Table 5

Compound	Module	Made/Used	Moles	Kg	Total (Kg)	Net-Made/Used (Kg)
CO_2	Capture	Used	11.36	0.50	1.0	Used (CAPTURED)
CO_2	Product	Used	11.36	0.50		
LiOH	Capture	Used	22.74	0.55	0	
LiOH	Convert	Made	22.74	0.55		
Li_2CO_3	Capture	Made	11.36	0.84	0	
Li_2CO_3	Convert	Used	11.36	0.84		
H_2O	Capture	Made	11.36	0.21	0	
H_2O	Product	Used	11.36	0.21		
NaOH	Convert	Used	22.74	0.91	0.91	Used
Na_2CO_3	Convert	Made	11.37	1.21	0	
Na_2CO_3	Product	Used	11.37	1.21		
$NaHCO_3$	Product	Made	22.74	1.91	1.91	Made
MeOH	Recycled	Recycled	25.00	0.80		1

*All mass is calculated at dry weight for 100% material.

*Methanol consumption through loss in H_2O during distillation is an estimate.

[00166] Table 6 illustrates the amount of CO_2 captured by NaOCl based on 1 kg of CO_2 captured in the 1-Loop Process*.

Table 6

Compound	Made/Used	Moles	Kg	Total (Kg)	Net Made/Used
CO_2	Used CAPTURED	22.72	1.00	1.00	Used (CAPTURED)
NaOCl	Used	22.72	1.69	1.69	Used
H_2O	Used	22.72	0.41	0.41	Used
HOCl	Made	22.72	1.19	1.19	Made
$NaHCO_3$	Made	22.72	1.91	1.91	Made

[00167] Table 7 illustrates the amount of SO_2 captured by NaOCl based on 1 kg of SO_2 captured in the 1-Loop Process*.

Table 7

Compound	Made/Used	Moles	Kg	Total (Kg)	Net Made/Used
SO_2	Used CAPTURED	15.61	1.00	1.00	Used (CAPTURED)
NaOCl	Used	15.61	1.16	1.16	Used
H_2O	Used	15.61	0.28	0.28	Used
NaCl	Made	15.61	0.91	0.91	Made
H_2SO_4	Made	15.61	1.53	1.53	Made

*All mass is calculated at dry weight for 100% material.

[00168] Table 8 illustrates the amount of NO_x captured by NaOCl based on 1 kg of 95% NO / 5% NO_2 treated by the abatement process in the 1-Loop Process.*

Table 8

Compound	Made/Used	Moles	Kg	Total (Kg)	Net Made/Used
NOx	Used	31.44	1.00	0.90	Used (CAPTURED)
NOx	Untreated	3.14	0.10		Untreated
$NaNO_3$	Made	28.24	2.40	2.40	Made
$NaNO_2$	Made	28.30	1.95	1.95	Made
H_2O	Used	14.43	0.26	0	Made
H_2O	Made	14.43	0.26		
HCl	Made	28.26	1.03	1.03	Made
NaOCl	Used	28.21	2.10	2.21	Used
NaOCl	Used	1.48	0.11		
NaOH	Used	28.26	1.13	1.13	Used

*All mass is calculated at dry weight for 100% material.

[00169] The two equations that describe the removal of NOx from exhaust gas collectively in a ratio assumed to be cumulative treats approximately 90% of the available NOx. If 99+% NOx removal is required, the NOx processes based on ClO_2 is required.

[00170] Table 9 illustrates the ratio of NOx, SO2 and CO2 in marine exhaust from a 2 cylinder engine burning HFO fuel at 100% engine capacity.

Table 9

Pollutant Species	Emission Factors
Units	g/kWh
Nitrogen oxides (NOx)	19.77 ± 0.28
Carbon dioxide (CO_2)	617 ± 11
Carbon monoxide (CO)	0.29 ± 0.02
Sulfur dioxide (SO_2)	11.53 ± 0.20
Particulate Matter (PM)	2.399 ± 0.052
Elemental Carbon (EC)	0.0069 ± 0.0004
Organic Carbon (OC)	0.22 ± 0.01
Ash	0.098 ± 0.002
Hydrated Sulfate (H_2SO_4.6.5 H_2O)	2.17 ± 0.19

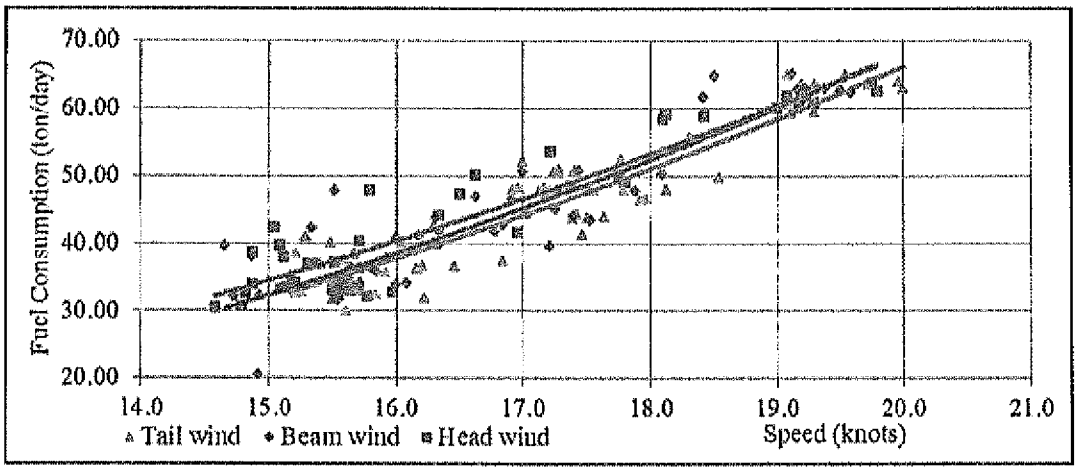
[00171] Table 10 illustrates the physical characteristics of a "typical ship" used in the disclosed calculations

Table 10

- Delivery year:	2008
- Car Capacity:	6500 CEU (Car Equivalent Unit)
- Length overall:	199.99 m
- Breadth:	32.26 m
- Draft (design):	9 m
- Displacement:	32,791.6 ton (loaded at design draft)
- Main Engine:	MAN B&W 7S60ME-C
- Power:	15,820 kW
- Speed (design):	20 knot

[00172] Table 11 illustrates the fuel consumption from an actual vessel used at specified speeds and wind conditions.

Table 11



[00173] Table 12 illustrates the typical NO_x, SO_2 and CO_2 emissions from fuel oil combustion in a two stroke marine engine.

Table 12

Pollutant Species	Emission Factors
Units	g/kWh
Nitrogen oxides (NOx)	19.77 ± 0.28
Carbon dioxide (CO_2)	617 ± 11
Carbon monoxide (CO)	0.29 ± 0.02
Sulfur dioxide (SO_2)	11.53 ± 0.20
Particulate Matter (PM)	2.399 ± 0.052
Elemental Carbon (EC)	0.0069 ± 0.0004
Organic Carbon (OC)	0.22 ± 0.01
Ash	0.098 ± 0.002
Hydrated Sulfate (H_2SO_4.6.5 H_2O)	2.17 ± 0.19

[00174] Table 13 illustrates the amount (kg/hour) for NO_x, SO_2 and CO_2 emissions from a typical ship described above.*

Table 13

- 312.8 Kg of NOx are made per hour
- 9750.0 Kg of CO_2 are made per hour
- 182.0 Kg of SO_2 are made per hour

*The NOx ratio of NO/NO_2 is defined as 95/5.

[00175] Table 14 illustrates the combined CO_2, SO_2 and NO_x capture based on actual ratios in 2 stroke marine combustion of HFO per hour at 100% engine capacity.*

Table 14

Process Data Table	Compound	Made-Used Per Hour	Kg	Total (Kg)	Net Made/Used Per hour	Notes
5 and 6	CO_2	Used	9750	9750	Used	
7	SO_2	Used	182	182	Used	
8	NOx	Used	281.52	312.8	90% Used	
8	NOx	Untreated	31.28			
5 and 6	H_2O	Used	4192.5	4243.46	Used	1
7	H_2O	Used	50.96			
8	NaOH	Used	353.46	4643.46	Used	2
5 and 6	NaOH	Used	4290			
8	$NaNO_2$	Made	609.96	609.96	Made	
8	$NaNO_3$	Made	750.72	750.72	Made	
5 and 6	$NaHCO_3$	Made	18622.5	18622.5	Made	
8	HCl	Made	322.18	322.18	Made	
7	NaCl	Made	165.62	165.62	Made	

7	H_2SO_4	Made	278.46	278.46	Made	
7	NaOCl	Used	211.12	211.12	Used	2
5 and 6	HOCl	Made	0	487.23	Used	2
8	HOCl	Used	487.23			

1. The H_2O is 90+% recycled. Makeup will come from desalinization plant.

2. The NaOH, NaOCl and HOCl are all generated from NaCl carried on ship or captured from the seawater.

[00176] Table 14 reports data used to adjust the ratios of NOx, CO_2 and SO_2 reported in the Tables to the actual chemical ratios shown for exhaust in the typical ship used in this report when operating at 100% engine capacity. However, the accumulated mass balance is hypothetical because the ratio of these compounds will vary with different fuels and engine operation.

[00177] The following data refers to the energy required in the electrochemical process necessary to generate NaOH and NaOCl and HOCl required to treat 100% of the CO_2, 90% of the NOx and 100% of the SO_2. This calculation assumes there is no SO_2 pre-scrubber. All of the three chemicals described above are made from NaCl carried on the ship or removed from seawater.

[00178] All other energy for recycling the chemicals through the 1-Loop Process and 2-Loop Process modules are entirely provided from the waste energy generated by the combustion source. The waste heat also contains required energy to generate the electricity necessary for pumps, mixers and other mechanical devices used in the chemical processing, but utilizing that waste heat would require additional equipment. Therefore, it is practical to use a small amount of additional fuel for the generation of this electrical energy.

[00179] The ideal energy required to generate 1Kg of NaOH, and all required NaOCl plus HOCl from saturated NaCl solution is 0.911 kWh. If seawater is used as the source for NaCl the electrical energy consumption will be greater. Table 15 illustrates the energy in various fuel oils*.

Table 15

Grade	Heating Value (*Btu/US gal*)	Comments
Fuel Oil No. 1	132900 - 137000	Small Space Heaters
Fuel Oil No. 2	137000 - 141800	Residential Heating
Fuel Oil No. 4	143100 - 148100	Industrial Burners
Fuel Oil No. 5 (Light)	146800 - 150000	Preheating In General Required
Fuel Oil No.5 (Heavy)	149400 - 152000	Heating Required
Fuel Oil No. 6	151300 - 155900	Bunker C

*1 kWh = 3412 BTU

[00180] Pursuant to Tables 12 and 15, only 95.77 gallons of Fuel Oil No. 5 (Heavy) are required to treat all of the CO_2, 90% of the NOx and all of the SO_2 generated per hour of 100% engine capacity by the typical ship described in Tables 10 and 11.

[00181] While the inventive features have been particularly shown and described with reference to preferred embodiments thereof, it will be understood by those in the art that the foregoing and other changes can be made therein without departing from the sprit and the scope of the disclosure. Likewise, the various diagrams may depict an example architectural or other configuration for the disclosure, which is done to aid in understanding the features and functionality that can be included in the disclosure. The disclosure is not restricted to the illustrated example architectures or configurations, but can be implemented using a variety of alternative architectures and configurations. Additionally, although the disclosure is described above in terms of various exemplary embodiments and implementations, it should be understood

that the various features and functionality described in one or more of the individual embodiments are not limited in their applicability to the particular embodiment with which they are described. They instead can be applied alone or in some combination, to one or more of the other embodiments of the disclosure, whether or not such embodiments are described, and whether or not such features are presented as being a part of a described embodiment. Thus, the breadth and scope of the disclosure should not be limited by any of the above-described exemplary embodiments.

What is claimed is:

1. A method of chemically sequestering sulfur dioxide (SO_2), nitrogen oxide (NO), nitrogen dioxide (NO_2) and carbon dioxide (CO_2) by a loop sequence, comprising:

a) providing a mixture of SO_2, NO, NO_2, CO_2, sodium hypochlorite (NaOCl) sodium hydroxide (NaOH) and water (H_2O) in the one or more second reaction chambers;

b) reacting SO_2 with NaOCl and H_2O to generate sodium chloride (NaCl) and sulfuric acid (H_2SO_4) in the mixture;

c) reacting NO and NO_2 with NaOCl and H_2O to generate sodium nitrate ($NaNO_3$) and hydrochloric acid (HCl) in the mixture;

d) reacting CO_2 with NaOCl and H_2O to generate hypochlorous acid (HOCl) and sodium bicarbonate ($NaHCO_3$) in the mixture;

e) reacting NO and NO_2 with NaOH and NaOCl to generate sodium nitrite ($NaNO_2$) and H_2O in the mixture;

f) reacting CO_2 with NaOH to provide $NaHCO_3$ in the mixture;

g) adding an alcohol solvent to the mixture, forcing the generated NaCl $NaHCO_3$ and Na_2SO_4 to precipitate, and removing the precipitate from the mixture;

h) removing the alcohol solvent from the mixture;

i) adding a dialkyl ketone solvent to the mixture, forcing the generated $NaNO_2$, $NaNO_3$ to precipitate, and removing the precipitate from the mixture;

j) removing the dialkyl ketone solvent from the mixture;

k) optionally adding NaOCl, NaOH and/or H_2O to the mixture; and

l) adding SO_2, NO, NO_2 and CO_2 to the mixture in the one or more second reaction chambers and reacting the mixture according to step b to complete the loop sequence.

2. The method of claim 1, wherein the alcohol solvent is methanol or tert-butanol; and the dialkyl ketone solvent is acetone.

3. The method of claim 1, wherein the mixture in the one or more reaction chambers is in an aqueous solution, an aqueous mist, or a gas phase.

4. The method of claim 1, wherein NaOCl, NaOH and H_2O are introduced into the one or more reaction chambers as an aqueous solution or an aqueous mist.

5. The method of claim 1, further comprising providing a mixture of SO_2, NO, NO_2 and CO_2 in the one or more reaction chambers, which facilitates a regulated exposure of this mixture as a gas or liquid stream to an aqueous mixture of NaOCl, NaOH and H_2O or a dry powder mixture of NaOCl, and NaOH.

6. The method of claim 1, wherein the one or more reaction chambers causes an interaction between the mixture via a combination of gas/gas interaction, a gas/mist interaction, a gas/liquid interaction, liquid/mist or a liquid/liquid interaction.

7. The method of claim 6, wherein the gas/mist interaction includes interacting SO_2, NO, NO_2, CO_2 gases with NaOCl, NaOH and H_2O droplets using nozzles with or without mechanical droplet shear inducing enhancements.

8. The method of claim 6, wherein the gas/liquid interaction includes interacting SO_2, NO, NO_2, CO_2 gases with NaOCl, NaOH and H_2O solution using a bubble chamber or counter current packed bed scrubber, impingement plate tray tower scrubber or equal.

9. The method of claim 6, wherein the liquid/liquid interaction includes interacting SO_2, NO, NO_2, CO_2 in a solution with NaOCl, NaOH and H_2O in the solution using a static mixer or sonic mixer or equal.

10. The method of claim 1, wherein the optionally added NaOCl and NaOH is produced from electrochemical decomposition of NaCl into NaOH and Cl_2 and a portion of the NaOH and Cl_2 are combined to generate NaOCl, respectively.

11. A method of chemically sequestering carbon dioxide (CO_2) by a loop sequence, comprising:

a) providing a mixture of CO_2, lithium hydroxide (LiOH), sodium hydroxide (NaOH) or potassium hydroxide (KOH) and water (H_2O) in one or more reaction chambers;
b) reacting CO_2 with LiOH to generate lithium carbonate (Li_2CO_3) and water (H_2O) in the mixture;
c) reacting Li_2CO_3 with NaOH or KOH to generate LiOH, and sodium carbonate (Na_2CO_3) or potassium carbonate (K_2CO_3) in the mixture;
d) reacting Na_2CO_3 or K_2CO_3 with CO_2 and H_2O to generate sodium bicarbonate ($NaHCO_3$) or potassium bicarbonate ($KHCO_3$) in the mixture;
e) adding an alcohol solvent to the mixture, forcing the generated $NaHCO_3$ or $KHCO_3$ to precipitate, and removing the precipitated $NaHCO_3$ or $KHCO_3$ from the solution;

f) removing the alcohol solvent from the mixture;

g) optionally adding NaOH or KOH, and/or H_2O to the mixture; and

h) adding CO_2 to the mixture in the one or more reaction chambers and reacting the mixture according to step b to complete the loop sequence.

12. The method of claim 11, wherein the alcohol solvent is tert-butanol or methanol.

13. The method of claim 11, wherein CO_2 is introduced into the one or more reaction chambers as an aqueous solution, an aqueous mist, or a gas phase.

14. The method of claim 11, wherein the LiOH, NaOH or KOH are introduced into the one or more reaction chambers as an aqueous solution, an aqueous mist, or a dry powdered aerosol.

15. The method of claim 11, where CO_2 is providedin the one or more reaction chambers, which facilitates a regulated exposure of CO_2 as a gas or liquid stream to an aqueous mixture of LiOH, NaOH or KOH and H_2O or a dry powder mixture of LiOH, NaOH or KOH.

16. The method of claim 11, wherein the one or more reaction chambers causes an interaction between the mixture via a combination of a gas/mist interaction, or a gas/liquid interaction, or a liquid/liquid interaction or a gas/aerosol powder interaction.

17. The method of claim 16, wherein the gas/mist interaction includes interacting CO_2 gas with LiOH, NaOH or KOH, Na_2CO_3 or K_2CO_3 and H_2O droplets using nozzles with or without mechanical droplet shear inducing enhancements.

18. The method of claim 16, wherein the gas/liquid interaction includes interacting CO_2 gas with LiOH, NaOH or KOH, Na_2CO_3 or K_2CO_3 and H_2O solution using a bubble chamber or counter current packed bed scrubber, impingement plate tray tower scrubber or equal.

19. The method of claim 16, wherein the liquid/liquid interaction includes interacting CO_2 in a solution with LiOH, NaOH or KOH, Na_2CO_3 or K_2CO_3 and H_2O in the solution using a static mixer or sonic mixer or equal.

20. The method of claim 11, wherein the optionally added NaOH or KOH is produced from electrochemical decomposition of NaCl or KCl into NaOH or KOH, respectively.

21. A system for chemically sequestering sulfur dioxide (SO_2), nitrogen oxide (NO), nitrogen dioxide (NO_2) and carbon dioxide (CO_2), comprising:

a) one or more first reaction chambers for quenching/absorbing SO_2, NO, NO_2 and CO_2 with water (H_2O), hypochlorous acid (HOCl) solution or sodium hydroxide (NaOH) solution;

b) an electrochemical generator for reacting sodium chloride (NaCl) or potassium chloride (KCl) and H_2O to generate NaOH or KOH, hydrogen (H_2) and chlorine (Cl_2), wherein NaOH or KOH reacts with Cl_2 to generate sodium hypochlorite (NaOCl) or potassium hypochlorite (KOCl) and H_2O;

c) one or more second reaction chambers for chemically sequestering SO_2, NO, NO_2 and CO_2 by a loop sequence, wherein the generated NaOH or KOH, and NaOCl or KOCl are optionally fed into the one or more second reaction chambers; and

d) one or more third reaction chambers for chemically sequestering carbon dioxide (CO_2) by another loop sequence, wherein the generated NaOH or KOH is optionally fed into the one or more third reaction chambers.

e) an aerosol conveying dry or moist LiOH granules or nano-granules that contact gas phase CO_2 or CO_2 dissolved/suspended in liquid droplets resulting in a reaction. The reaction product and excess reactants are subsequently captured in a mist or liquid that is ultimately recirculated in this process sequence.

f) devices to promote mass transfer of gas phase CO_2, NOx and SO_2 into to liquid phase. For example: droplets containing a reagent formed with or without mechanical/hydraulic shear, sprayed into a gas.

22. The system of claim 21, wherein chemically sequestering SO_2, NO, NO_2 and CO_2 by a loop sequence comprises:

a) providing a mixture CO_2, lithium hydroxide (LiOH), sodium hydroxide (NaOH) or potassium hydroxide (KOH) and water (H_2O) in one or more reaction chambers;

b) reacting CO_2 with LiOH to generate lithium carbonate (Li_2CO_3) and water (H_2O) in the mixture;

c) reacting Li_2CO_3 with NaOH or KOH to generate LiOH, and sodium carbonate (Na_2CO_3) or potassium carbonate (K_2CO_3) in the mixture;

d) reacting Na_2CO_3 or K_2CO_3 with CO_2 and H_2O to generate sodium bicarbonate ($NaHCO_3$) or potassium bicarbonate ($KHCO_3$) in the mixture;

e) adding an alcohol solvent to the mixture, forcing the generated $NaHCO_3$ or $KHCO_3$ to precipitate, and removing the precipitated $NaHCO_3$ or $KHCO_3$ from the solution;

f) removing the alcohol solvent from the mixture;

g) optionally adding NaOH or KOH, and/or H_2O to the mixture; and

h) adding CO_2 to the mixture in the one or more reaction chambers and reacting the mixture according to step b to complete the loop sequence.

23. The system of claim 21, wherein chemically sequestering carbon dioxide (CO_2) by a loop sequence comprises:

a) providing a mixture CO_2, lithium hydroxide (LiOH), sodium hydroxide (NaOH) or potassium hydroxide (KOH) and water (H_2O) in the one or more third reaction chambers;

b) reacting CO_2 with LiOH to generate lithium carbonate (Li_2CO_3) and water (H_2O) in the mixture;

c) reacting Li_2CO_3 with NaOH or KOH to generate LiOH, and sodium carbonate (Na_2CO_3) or potassium carbonate (K_2CO_3) in the mixture;

d) reacting Na_2CO_3 or K_2CO_3 with CO_2 and H_2O to generate sodium bicarbonate ($NaHCO_3$) or potassium bicarbonate ($KHCO_3$) in the mixture;

e) adding an alcohol solvent to the mixture, forcing the generated $NaHCO_3$ or $KHCO_3$ to precipitate, and removing the precipitated $NaHCO_3$ or $KHCO_3$ from the solution;

f) removing the alcohol solvent from the mixture;

g) optionally adding NaOH or KOH, and/or H_2O to the mixture; and

h) adding CO_2 to the mixture in the one or more third reaction chambers and reacting the mixture according to step b to complete the loop sequence.

FIGURE 1

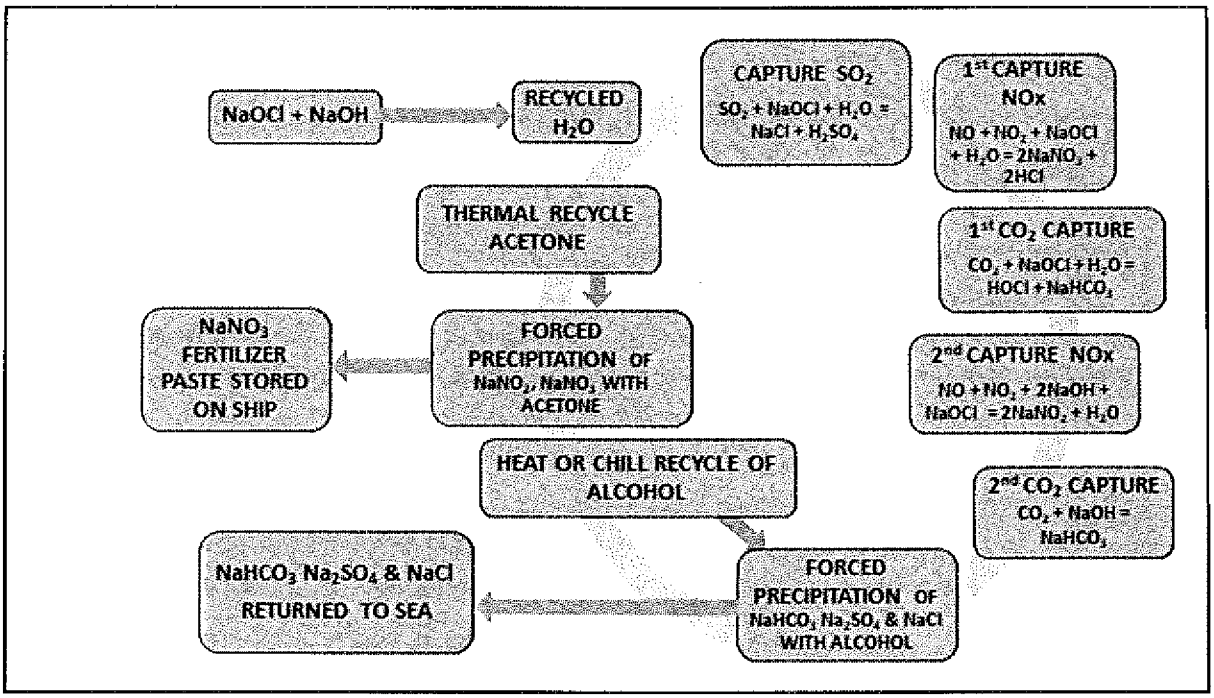

NaOCl + NaOH
RECYCLED H_2O
CAPTURE SO_2
$SO_2 + NaOCl + H_2O = NaCl + H_2SO_4$
1st CAPTURE NOx
$NO + NO_2 + NaOCl + H_2O = 2NaNO_2 + 2HCl$
THERMAL RECYCLE ACETONE
1st CO_2 CAPTURE
$CO_2 + NaOCl + H_2O = HOCl + NaHCO_3$
$NaNO_3$ FERTILIZER PASTE STORED ON SHIP
FORCED PRECIPITATION OF $NaNO_2$, $NaNO_3$ WITH ACETONE
2nd CAPTURE NOx
$NO + NO_2 + 2NaOH + NaOCl = 2NaNO_2 + H_2O$
HEAT OR CHILL RECYCLE OF ALCOHOL
2nd CO_2 CAPTURE
$CO_2 + NaOH = NaHCO_3$
$NaHCO_3$ Na_2SO_4 & NaCl RETURNED TO SEA
FORCED PRECIPITATION OF $NaHCO_3$ Na_2SO_4 & NaCl WITH ALCOHOL

FIGURE 2

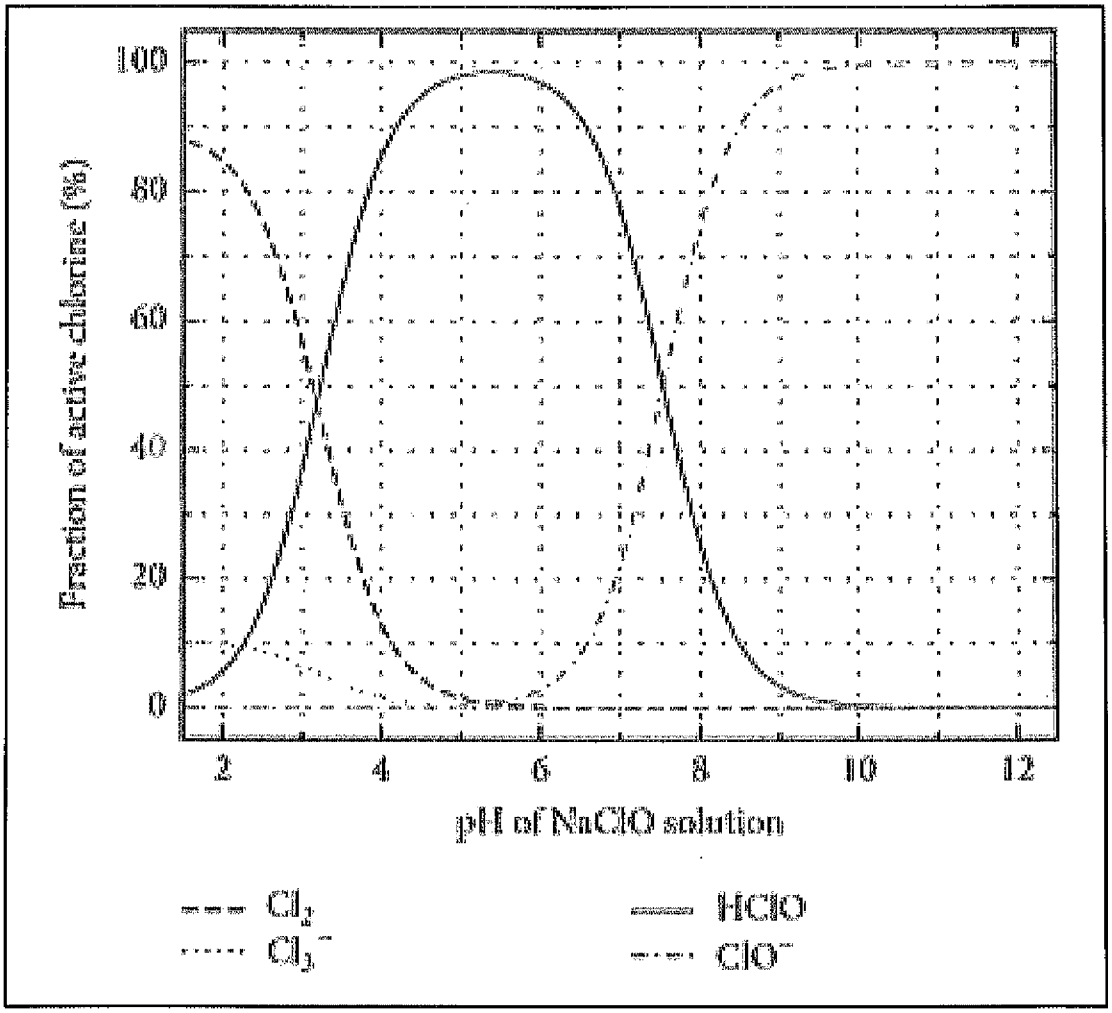

Fraction of active chlorine (%)
100
80
60
40
20
0
2
4
6
8
10
12
pH of NaClO solution
Cl_2
Cl_3^-
HClO
ClO^-

FIGURE 3A

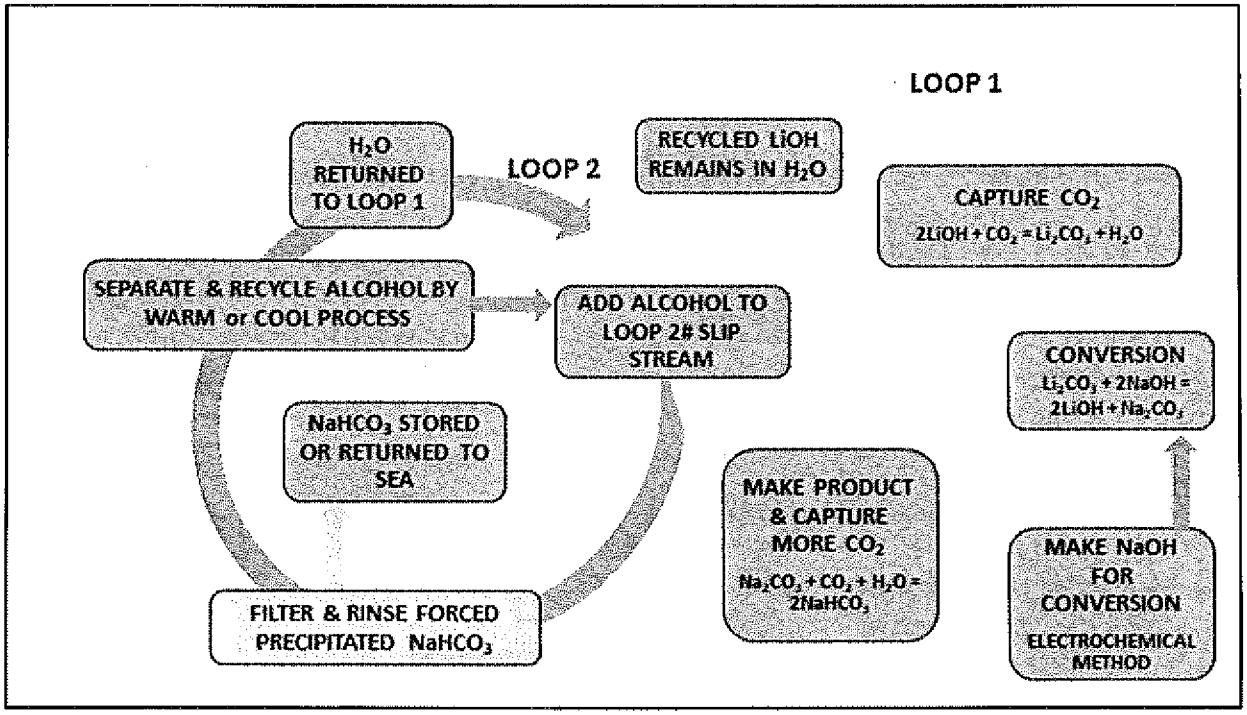


FIGURE 3B

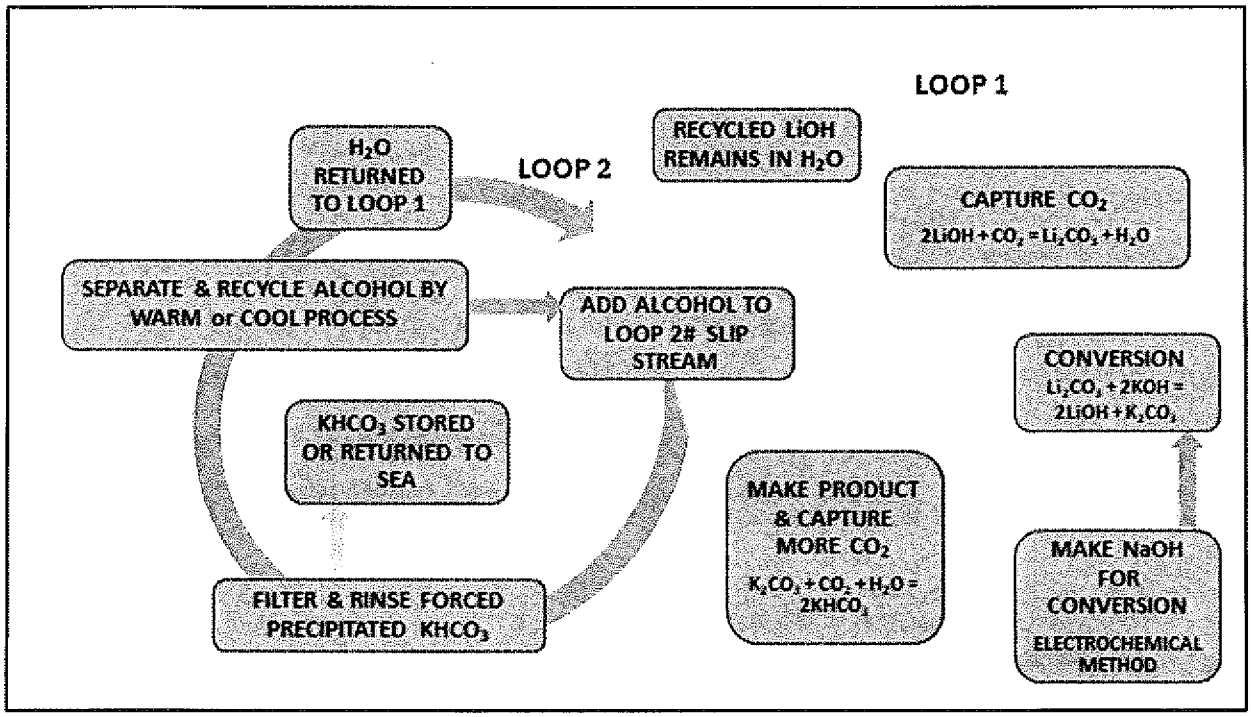


FIGURE 4A

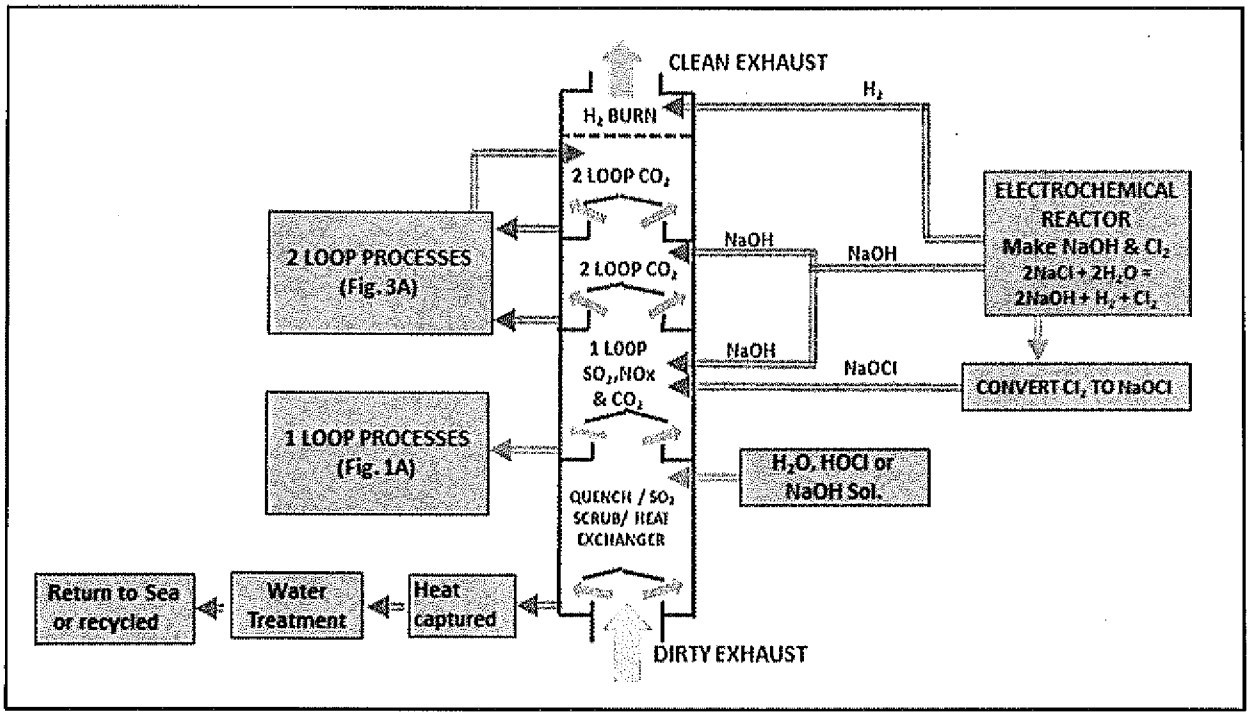


FIGURE 4B

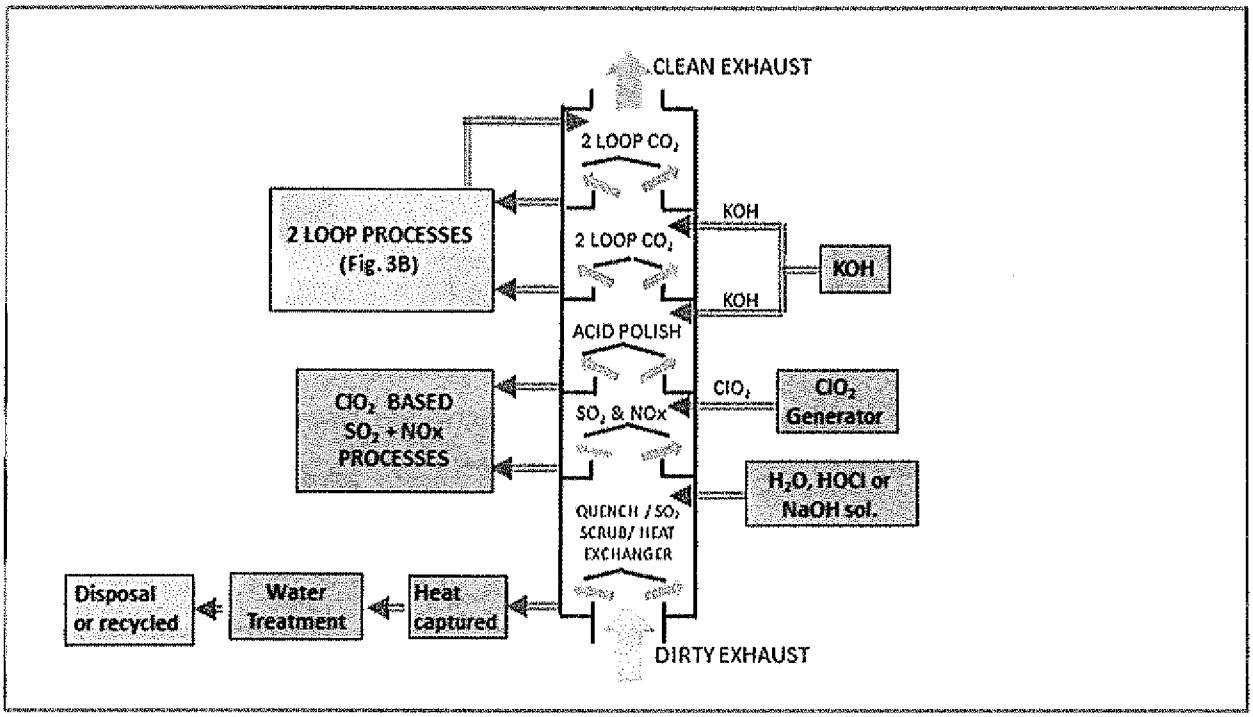


FIGURE 5

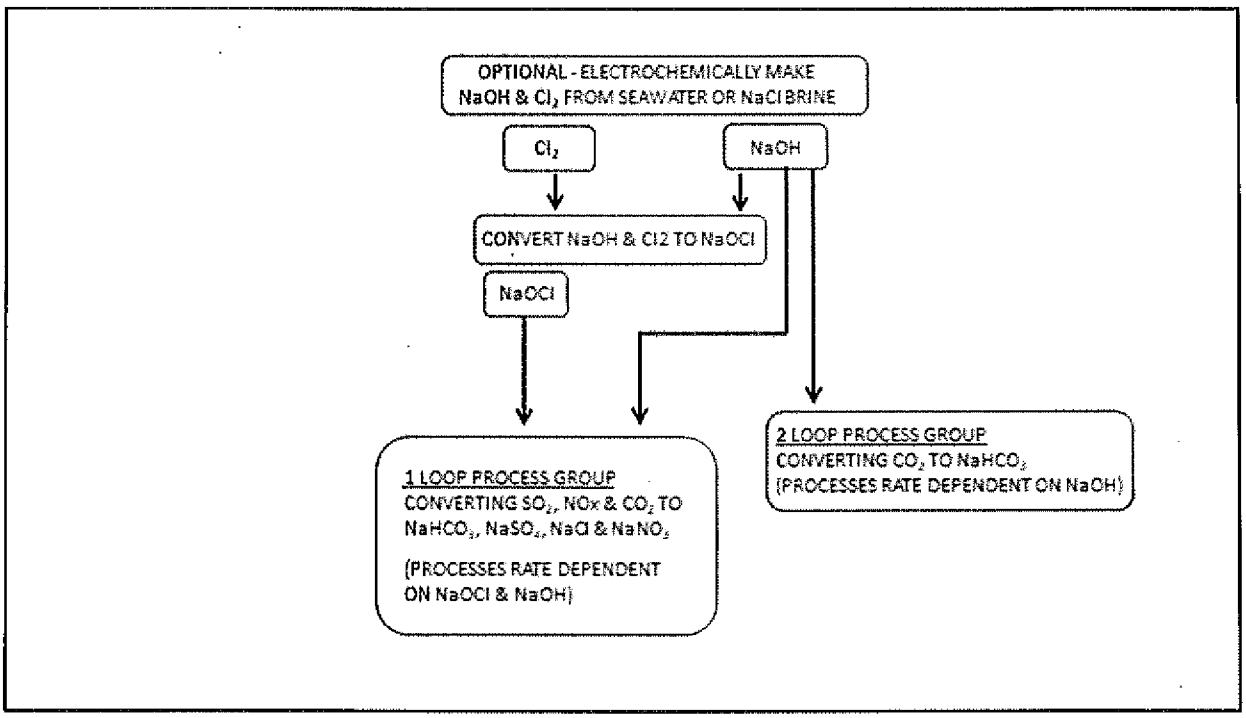

OPTIONAL - ELECTROCHEMICALLY MAKE
NaOH & Cl2 FROM SEAWATER OR NaCl BRINE
Cl2
NaOH
CONVERT NaOH & Cl2 TO NaOCl
NaOCl
1 LOOP PROCESS GROUP
CONVERTING SO2, NOx & CO2 TO
NaHCO3, NaSO4, NaCl & NaNO3
(PROCESSES RATE DEPENDENT
ON NaOCl & NaOH)
2 LOOP PROCESS GROUP
CONVERTING CO2 TO NaHCO3
(PROCESSES RATE DEPENDENT ON NaOH)

FIGURE 6

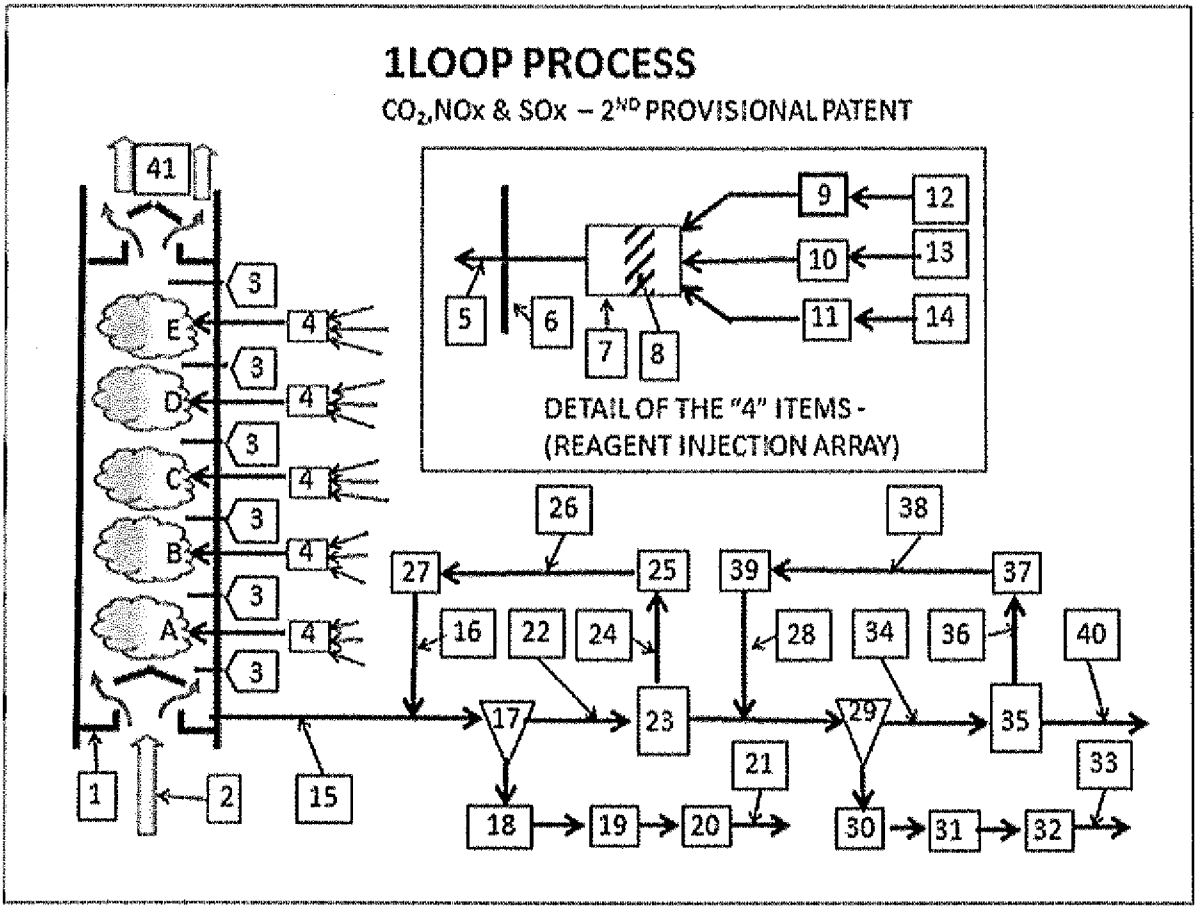
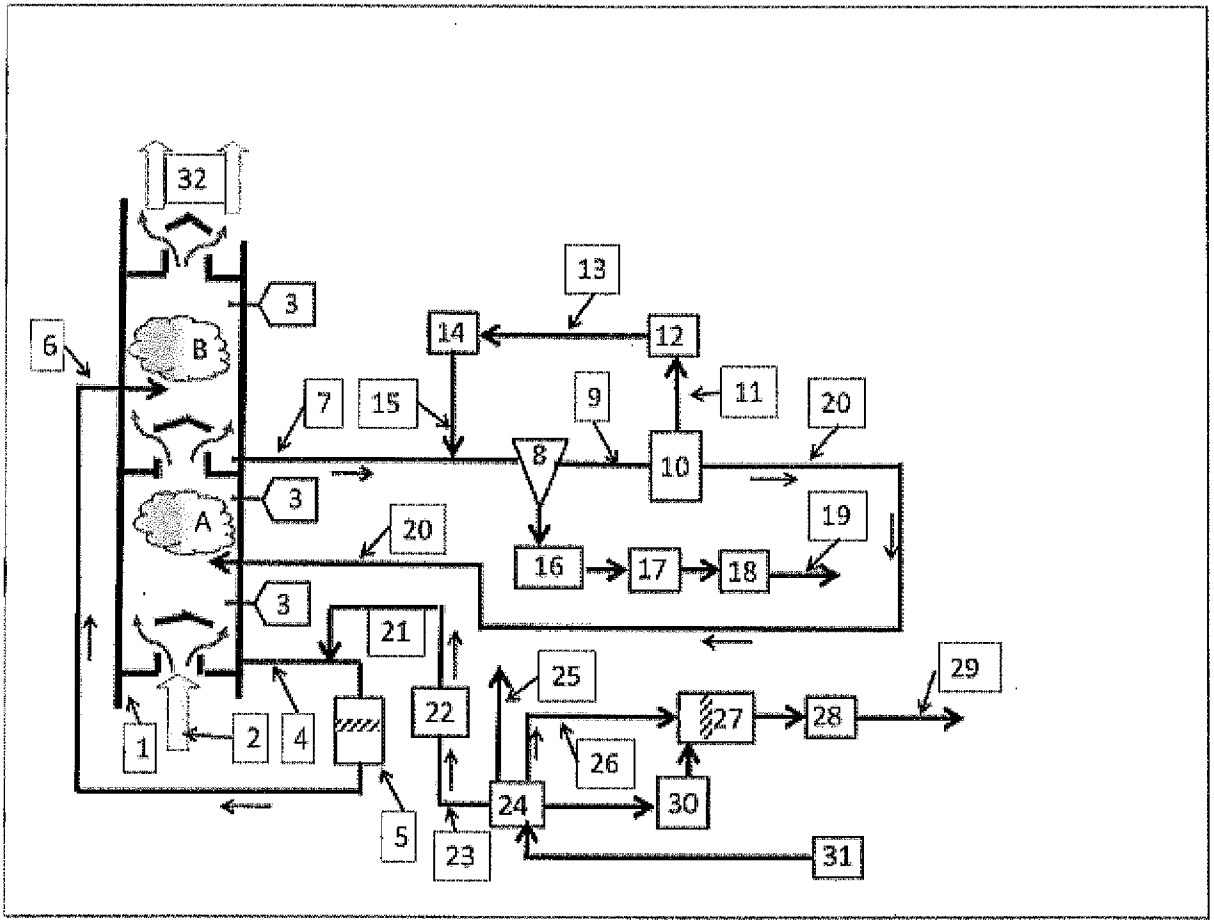

1LOOP PROCESS
CO_2,NOx & SOx – 2ND PROVISIONAL PATENT
DETAIL OF THE "4" ITEMS -
(REAGENT INJECTION ARRAY)
41
3
4
E
D
C
B
A
1
2
15
5
6
7
8
9
10
11
12
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14
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FIGURE 7


32
3
6
B
13
14
12
7
15
9
11
20
8
10
3
A
20
19
16
17
18
3
21
25
29
1
2
4
22
27
28
26
24
30
5
23
31

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 20/15207

A. CLASSIFICATION OF SUBJECT MATTER

IPC - B01D 53/50; B01D 53/56; B01D 53/60 (2020.01)

CPC - B01D 53/60; B01D 53/62; B01D 2251/404; B01D 2257/302

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
See Search History document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
See Search History document

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2010/0254869 A1 (THOMASSEN) 07 October 2010 (07.10.2010), para [0002]; claims 7, 10, 18-9	1-10, 21-23
A	US 5,683,666 A (BERISKO) 04 November 1997 (04.11.1997), abstract; col 6, ln 1-15	1-10, 21-23
A	US 2,461,847 A (SHABICA et al.) 15 February 1949 (15.02.1949), col 2, ln 24-28	1-10
A	US 2005/0160912 A1 (HRYCAK et al.) 28 July 2005 (28.07.2005), abstract; FIG. 1A; paras [0006], [0050]; claim 1	11-20
A	US 2018/0140994 A (KOREA INSTITUTE OF ENERGY RESEARCH) 24 May 2018 (24.05.2018), abstract	11-23
A	GB 532301 A (MCGEORGE et al.) 21 January 1941 (21.01.1941), p. 1, col 2, ln 69-83	11-20

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
06 June 2020	01 JUL 2020
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