A PROCESS AND AN APPARATUS FOR OBTAINING USEFUL PRODUCTS FROM A SODIUM CHLORIDE-CONTAINING WASTE MATERIAL

Abstract: A process and an apparatus for obtaining caustic soda (87) and hydrochloric acid, preferably in solution (67), or other useful product containing chlorides (243'), such as an anti-icing solution (244'), from a sodium chloride-containing waste material (12,17), typically a tannery waste material, wherein a step is provided of contact, at a predetermined temperature, comprising reactions of the sodium chloride of the saline solution (17), of an amount of a carbonaceous material (18'), of steam (49) and of preferably atmospheric oxygen, from which a gas mixture is obtained (62) that contains hydrogen chloride, preferably subjected to an absorption into water (73) to obtain an aqueous solution (67), and also sodium oxide is obtained stuck on the carbonaceous residue (18'). The step of contact may comprise alternate steps of supplying steam and air. A step is provided of washing the carbonaceous residue (18') preferably in a tubular conveyer apparatus (71) such as a screw conveyer in which water (72) is preferably countercurrently recycled until a caustic soda solution (72) is obtained at a predetermined concentration. The process makes it possible to obtain useful products from saline waste water such as the brine resulting from a preliminary washing of skins and from treatment of fleshings in tanning industry.
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DESCRIPTION

Field of the invention

The present invention relates to a process and to an apparatus for obtaining useful products, based on caustic soda and on hydrochloric acid, from a solution of sodium chloride.

More in detail, the invention relates to a process for recovering caustic soda and hydrochloric acid, or derivatives thereof, from a sodium chloride-containing waste solid, or from a diluted or concentrated waste solution of the tanning industry. In particular, the solution may contain a solid matter including an organic material that is difficult to separate from sodium chloride, as in the case of some waste materials of the tanning process.

The solution treated by the process and by the apparatus may contain other chlorides, sulphates, organic residues, as well as suspended inorganic particulate matter.

Background of the invention

As well known, most caustic soda is industrially produced from sodium chloride, by a process comprising:

- an electrolysis (chlorine-soda process) of an aqueous sodium chloride solution, to obtain an aqueous sodium hydroxide solution as well as gaseous chloride and hydrogen, according to the reaction:

\[ 2 \text{NaCl} + 2 \text{H}_2\text{O} \rightarrow 2 \text{NaOH} + \text{H}_2 + \text{Cl}_2 \]  \[ \text{[a]} \]

In this process chlorine and hydrogen are converted into hydrochloric acid, according to the reaction:

\[ \text{Cl}_2 + \text{H}_2 \rightarrow 2 \text{HCl}. \]  \[ \text{[b]} \]

This electrolytic process has many drawbacks. In fact:

- it requires a large amount of electric energy, which is about one half of the
whole production cost;
— considering the low value of the products, a large scale production should be provided, i.e. large size plants should be built, which means a considerable investment cost;
— expensive purifying operations are required for the brine produced;
— it provides soda containing at most 12% NaOH, along with a large quantity of unreacted sodium chloride, which may be more than 15%. For this reason, in order to obtain commercial soda, water must be evaporated until a concentration of 50% NaOH is attained, and then sodium chloride must be crystallized, which also requires a large amount of energy;
— it has a high environmental impact;
— it involves a health risk for the workers, in particular if mercury cathodes are used;
— the reaction between chloride and hydrogen is strongly exothermic and potentially explosive, in any case treating the gas produced by reaction [a] has a relevant cost.

It is therefore felt the need of a process for making caustic soda and useful hydrochloric acid derivatives that eliminates or at least reduces the above-mentioned drawbacks.

It is also known that many animal derivatives transformation processes provide protein-containing by-products from which salt solutions can be recovered.

This is the case, for instance, of tanning industry: the skins are stored by salt addition in order to prevent the formation and the growth of bacteria, as well as to prevent decomposition reactions. The first tannery operation to be performed is the so-called soaking, which comprises removing surface dirt, and bringing a part of the proteins into sodium chloride solution, in order to restore the original moisture and swell state of the skins.

To this purpose, the skins are washed at room temperature with a large amount of water within special containers, regularly changing the bath water to remove microorganisms, fat matter, hair and the salt that is released by the skin. The waste water that is discharged has normally a high organic load, i.e. a high COD (Chemical Oxygen Demand) and organic nitrogen. Furthermore, it may contain suspended solids and sulphates.
At present, this waste material is treated in depuration plants along with the waste streams produced by subsequent tannery operations. Therefore, the treatment of soaking waste water requires chemical additives and energy, so it has a relevant cost. Furthermore, no potentially useful product can be recovered from it.

Besides skin soaking waste water, waste liquids are obtained in the tanning industry when removing flesh residues from skins, which comprise a semisolid waste known as fleshings, which is rich in proteins as well as in sodium chloride, still due the skin preservation treatment.

Fleshings treatment processes are known for recovering fat and proteins. While fat and proteins are advantageously used, for example, in zootechny, in agriculture or in the production of gelatine, the sodium chloride-containing residue is currently disposed as such, since it contains organic impurities that cannot be separated from sodium chloride by industrially profitable methods.

A process is known to obtain hydrochloric acid from sodium chloride, clay and a carbonaceous binder, as described in US0740903. A mixture of these three components is heated in an oven until a porous coke is formed. Afterwards, a steam stream is caused to pass through the porous coke, thus obtaining hydrochloric acid. The carbonaceous material may be asphalt, pitch, an acid waste water, etc. US0740903 does not deal with the production of sodium hydroxide.

In WO2009/141672 a process is described for making hydrochloric acid and caustic soda starting from sodium chloride, in which steam is caused to bubble through a mass of sodium chloride that is maintained within a reactor at a temperature higher than its melting temperature, in particular at a temperature set between 800 and 950°C, thus causing a reaction in which sodium chloride and water are changed into hydrochloric acid and sodium hydroxide. Hydrochloric acid is withdrawn from the reactor as a gas and is collected outside of the reactor. The mixture of sodium hydroxide product and of unreacted sodium chloride, which is left within the reactor, is cooled down to a temperature lower than the hardening temperature of sodium chloride, such that it hardens and allows the separation of sodium hydroxide in the molten state.

In FR 992928 a hydrochloric acid synthesis process is described which starts from gaseous chlorine or from a chlorine-containing gas, in the presence
of coal. The coal may be present as a reducing body, i.e. in order to cause a chlorine reduction reaction to form a chloride, and as a porous material to retain the product hydrochloric acid, from which it is separated by cooling. With respect to other chlorine reduction processes involving the presence of coal, which were known at the date of filing of FR992928, the porous carbon makes it possible to produce pure and concentrated hydrochloric acid, which prevent wasting an excess amount of coal, it makes it possible to reduce the reaction temperature, which allows a safer process, and to limit the concentration of residual chloride in the acid product. FR992928 does not provide indications about how to treat sodium chloride, as a solid or in solution, to obtain hydrochloric acid and caustic soda at a predetermined concentration.

The need is therefore felt of a process for treating a waste water that contains an important amount of sodium chloride resulting from animal derivative processing, in particular a tannery waste water, and for recovering products that may be useful, in particular, in the tanning industry.

The need is also felt of a process for treating a waste water containing sodium chloride at a concentration of a few percentage units, typically a concentration of about 3%, and for recovering products that may be useful, for instance, in the field of tanning industry.

In fact, as well known, in the tanning industry a so called oxidative depilation process of the skins is carried out, in which caustic soda is used.

Therefore the need is also felt of such a treatment process of a sodium chloride solution containing other pollutants to be removed, such as organic residues, inorganic solid particulate, and other dissolved salts like sulphates.

Summary of the invention

It is therefore a feature of the present invention to provide a process for obtaining caustic soda and possibly other hydrochloric acid based useful products from a sodium chloride-containing waste material, at an investment, operation and maintenance cost lower than in the prior art processes.

It is a particular feature of the invention to provide such a process for treating an aqueous sodium chloride-containing waste solution, in particular a diluted solution, obtaining caustic soda at a predetermined concentration.
It is another particular feature of the invention to provide such a process for treating a solid sodium chloride-containing waste which allows obtaining caustic soda at a predetermined concentration.

It is a particular feature of the invention to provide such a process that reduces production energy costs, and in particular which does not involve relevant power consumption.

It is another particular feature of the present invention to provide such a process that makes it possible to obtain caustic soda at a predetermined concentration without requiring any evaporation step.

It is also particular feature of the invention to provide such a process for treating sodium chloride solutions, i.e. brines that contain determined amounts of organic impurities, without subsequently requiring expensive purification treatments.

It is also a feature of the invention to provide such a process suitable for treating a waste water containing process organic residues besides sodium chloride, to obtain hydrochloric acid and caustic soda, in particular suitable for treating a liquid and/or a substantially solid waste of the tanning industry, such as a waste water resulting from soaking the skins in order to remove the sodium chloride used as a preservative agent for the skins, or for treating a waste water that contains fleshing residues.

It is also particular feature of the invention to provide such a process for treating sodium chloride solutions that contain a determined amount of inorganic impurities, in particular sulphate impurities.

It is a further particular feature of the invention to provide such a process for disposing a saline waste water in which useful products are obtained for the skin treatment industry, more in particular, for tanning industry.

It is also a feature of the present invention to provide an apparatus for carrying out such a process.

According to an aspect of the invention, the above objects are achieved by a process for obtaining sodium hydroxide and a chloride-containing useful product, comprising the steps of:

— prearranging a source of sodium chloride;
— prearranging an amount of a carbonaceous material at a reaction temperature;
— prearranging an amount of a carbonaceous material;
— prearranging a source of steam;
— prearranging a source of water;
— contacting the sodium chloride with the amount of a carbonaceous material at a predetermined reaction temperature, obtaining a reaction mixture;
— bringing the steam into contact with the reaction mixture such that the steam, the carbonaceous material, and the sodium chloride interacts forming:
  — hydrogen chloride and carbon dioxide as a gas mixture in a reaction gas;
  — a residue fraction of the carbonaceous material; and
  — sodium oxide (Na$_2$O) stuck to the residue fraction of the carbonaceous material,
wherein the reaction temperature is higher than 400°C;
— washing the residue fraction of the carbonaceous material with said water, until a washed carbonaceous residue and an aqueous sodium hydroxide solution are obtained;
— separating the carbonaceous residue from the aqueous sodium hydroxide solution, and concentrating the aqueous sodium hydroxide solution until it reaches a predetermined concentration.
During the step of contacting, sodium oxide is formed sticking to the residue fraction of the carbonaceous material. By washing the carbonaceous material with water, the sodium oxide turns into sodium hydroxide dissolved in the washing water.

The method makes it possible to obtain a caustic soda that has a desired concentration, as well as a hydrochloric acid-containing gas mixture that can be used to obtain a wide range of useful products, as described hereinafter. Due to the concentration step, the process takes place without releasing waste water, since the washing water is completely used for making the solution of sodium hydroxide, i.e. caustic soda, at the desired concentration. Furthermore, the process makes it possible to use all the carbonaceous material, without producing carbonaceous by-products.
In particular, the reaction temperature is set between 400°C and 600°C. More in particular, the reaction temperature is set between 500°C and 600°C. Preferably, the reaction temperature is about 550°C.

The steam may have a pressure set between 1.0 and 1.5 absolute bar, and may be a dry saturated steam or a superheated steam with a determined superheat, for example a superheat set between 3 and 10°C, in particular between 4 and 8°C, more in particular, about 5°C.

The source of sodium chloride may be an aqueous sodium chloride solution, in particular a brine.

In particular the aqueous sodium chloride solution is a liquid effluent of an industrial processes, in particular a brine resulting from a process of preliminary washing of skins that contain sodium chloride as a preservative agent, and/or from a separation step of sodium chloride from tannery fleshings. Therefore, the process according to the invention avoids the disposal of solid and liquid waste material from the skin preliminary treatment to a waste treatment plant, which reduces chemical additives consumption and saves energy, and also remarkably reduces biological risk. In particular, the organic part of the aqueous sodium chloride solution contains fleshing residues, i.e. mainly collagen which, as well known, is a protein comprising carbon atoms, as well as nitrogen, hydrogen and oxygen atoms, which at the reaction temperature forms a carbon deposit that provides the reaction with further carbon atoms, further improving the energy balance.

The process according to the invention also allows recovering from such waste water useful products, i.e. hydrochloric acid, which have a wide industrial use, along with caustic soda. In particular, the caustic soda obtained can be used in an oxidative depilation treatment for removing animal hair from the skins, or for other factory uses or in any case in the field of tanning industry.

In particular, the step of bringing steam into contact with the reaction mixture comprises the steps of:
— supplying the steam and reaction of the steam with the carbon of the carbonaceous material, thus producing carbon monoxide and hydrogen;
wherein the supplying of the steam is carried out by supplying oxygen, in particular as the oxygen contained in an air flow, wherein the oxygen reacts:
— with hydrogen, thus producing a reaction heat;
— with the carbon monoxide and with sodium chloride, thus producing sodium oxide and gaseous carbonyl chloride;
— reaction of gaseous carbonyl chloride with water, thus producing hydrogen chloride.

In particular, the water, with which carbonyl chloride reacts, is present as steam within the container.

More in detail, in the step of contacting, the carbonaceous material reacts with steam to form carbon monoxide and hydrogen, according to the reaction:

\[ \text{C(s)} + \text{H}_2\text{O(g)} \rightarrow \text{CO(g)} + \text{H}_2(g) \]  \hspace{1cm} \text{[II]}

and hydrogen is subjected to an exothermic combustion reaction:

\[ \text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{H}_2\text{O(g)} + \Delta' \]  \hspace{1cm} \text{[III]}

wherein the reaction heat \( \Delta' \) is useful for maintaining the reaction temperature.

Carbon monoxide, in the presence of oxygen, in particular of atmospheric oxygen, combines with the sodium chloride of the saline solution forming solid sodium oxide and gaseous carbonyl chloride according to the reaction:

\[ \text{CO(g)} + 2\text{NaCl} + \frac{1}{2} \text{O}_2(g) \rightarrow \text{Na}_2\text{O(s)} + \text{COCl}_2(g) + \Delta'' \]  \hspace{1cm} \text{[IV]}

which also occurs with a release of a reaction heat \( \Delta'' \) that serves for maintaining the reaction temperature.

Reactions [III] and [IV] have oxygen among the reagents. In the reaction environment, an amount of atmospheric oxygen may be present, i.e. an amount of oxygen associated with air that accompanies the material fed to the reactor, or associated with air that leaks into the reactor due to a slight underpressure that is established within the reactor. Oxygen may also be fed to the reactor by a feed means, for example by a feed means of the type that is described more in detail hereinafter, with reference to a reactor according to a particular exemplary embodiment of the invention. The feed means is provided with a shut-off means such as a shut-off valve which allow an air or oxygen inlet only if the steam inlet is blocked, in order to prevent the formation of an explosive mixture within the reactor.

Sodium oxide remains on the surface of the carbonaceous material, whereas carbonyl chloride reacts in a substantially instantaneous way with steam, according to the reaction:
\[ \text{COCl}_2(g) + \text{H}_2\text{O}(g) \rightarrow 2\text{HCl}(g) + \text{CO}_2(g) \quad [V] \]

and forms a reaction gas mixture in which hydrogen chloride is present along with carbon dioxide.

Therefore, the carbonaceous material, which may advantageously be a coke, serves both as a reagent, to provide the carbon atoms required for forming the compounds of interest and sodium chloride, via the intermediate products CO and COCl\(_2\), and as a fuel, to provide the heat required by the whole process. For this reason, and more in general due to the presence of exothermic reactions, the energy production costs are extremely low, with respect to the electrolytic processes.

Advantageously, the steps of supplying the steam stream and oxygen take place in turn, more in particular, they are consecutive with respect to each other. This way, explosive mixtures of hydrogen and oxygen cannot form in the reaction environment.

In an operation mode of the method according to the invention, the step of supplying oxygen starts when the reaction temperature achieves a predetermined minimum value and stops when the reaction temperature achieves a predetermined maximum value, whereas the step of supplying the steam stream starts when the reaction temperature achieves the predetermined maximum value and stops when the reaction temperature achieves the predetermined maximum value. This way, a control step of the reaction temperature is carried out within a predetermined temperature range, substantially set between the maximum value and the minimum value, since the temperature decreases as long as the steam is supplied, due mainly to a heat exchange with the superheated steam, which is colder than the carbonaceous material, while the temperature increases as long as oxygen is supplied, due mainly to the reaction heat \( \Delta' \) of reaction [II].

According to a particular operation mode of the method, the solution of sodium chloride may be supplied continuously, i.e. it may be supplied both when supplying oxygen and when supplying steam, in alternative the solution of sodium chloride may be supplied only when supplying steam or only when supplying oxygen, preferably only when supplying steam.
In another operation mode of the method according to the invention, the steps of supplying the steam stream and of supplying the oxygen take place in turn with respect to each other according to a predetermined time program, and the sodium chloride solution starts to be supplied into the container when the reaction temperature achieves a predetermined maximum value and stops to be supplied when the reaction temperature achieves a predetermined minimum value. This way, a step of controlling the reaction temperature within a predetermined temperature range is carried out, substantially set between the maximum value and the minimum value, since the temperature decreases as long as the aqueous sodium chloride solution is fed, due mainly to the evaporation of water from the solution, while the temperature increases when this solution is not being fed, during the step of oxygen supplying, due to the reaction heat $\Delta'$ of reaction [II].

Caustic soda, during the step of washing, is directly produced at a predetermined concentration, typically at a concentration of 50%, without requiring any evaporation step, which strongly reduces energy consumption.

The residue fraction of carbonaceous material, which is available substantially at the reaction temperature after taking part in the step of contact and reaction, typically incandescent coke at the reaction temperature, bears the sodium oxide Na$_2$O solid produced by exchange reaction [IV].

In particular, sodium oxide Na$_2$O is stable at the above-mentioned temperatures, at which the plurality of reactions [II], [III], [IV], [V] may take place in a same reaction environment with an acceptable HCl and Na$_2$O yield. In other words, the decomposition temperature of sodium oxide is higher than the above indicated reaction temperatures.

This way, the residue fraction of the carbonaceous material allows to extract the sodium oxide product from it, and to bring it in an environment suitable for the reaction:

$$\text{Na}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{NaOH},$$  \[VI\]

wherein sodium oxide is converted into sodium hydroxide, i.e. it is converted to a solution of caustic soda, due to the presence of water, at a concentration that is predetermined by fixing the amount of water to be used.
The process is also suitable for treating sodium chloride in a solution different from an aqueous solution, for example in an alcohol solution of an alcohol such as methyl alcohol, ethyl alcohol, a propyl alcohol or still other alcohols, as well as a mixed water-alcohol solution.

A process according to claim 3, where the sodium hydroxide concentration of the solution is higher than 40% by weight, more in particular, it is higher than 45% by weight, even more in particular, it is about 50% by weight.

The chloride-containing useful product may be an aqueous solution of hydrochloric acid. In this case, a first step is advantageously provided of absorbing the gas mixture into an amount of water, in particular into an amount of water that has a predetermined content of minerals, such that an aqueous solution of hydrochloric acid is obtained, in particular a 30% aqueous solution. Hydrochloric acid aqueous solutions are in fact widely used in many industrial files as well as at home.

Advantageously, the gas mixture of the reaction gas is cooled before being brought into contact with the amount of water prepared for absorption. Preferably, a step is provided of recovering the heat released by the reaction gas to a cooling fluid during the cooling.

Said chloride-containing useful product may be an aqueous solution of hydrochloric acid. In this case, advantageously, after the first step of absorption a second step of absorption is provided of the gas as transformed in the first step of absorption, into an amount of a calcium hydroxide suspension, wherein the carbon dioxide interacts with the calcium hydroxide forming a calcium carbonate suspension, according to the reaction

\[ \text{CO}_2 + \text{Ca(OH)}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} \]  \[\text{[XIV]}\]

This way, it is possible to avoid atmospheric emissions of the carbon dioxide produced by the reactions involved in the process, in particular, produced by combustion reactions of carbon or of other fossil fuel used to provide heat to the process and to heat the carbonaceous material up to a suitable temperature.

In an exemplary embodiment, the step of washing the carbonaceous material of the residue fraction, during which the aqueous sodium hydroxide solution is formed, is carried out within a tubular apparatus preferably arranged to carry the carbonaceous material of the residue fraction according to a
conveying direction along the tubular apparatus. Preferably, the step of concentrating the aqueous sodium hydroxide solution comprises a step of feeding a stream of such water into the tubular apparatus, in such a way that this flows along inside the tubular apparatus, wherein a same mass water is repetitively recycled into the tubular apparatus. This way, at each recycle passage the water is enriched in sodium hydroxide, and the solution of sodium hydroxide can be obtained at a predetermined sodium hydroxide concentration, in particular a 50% solution. In particular, the water flows along the tubular apparatus countercurrently with respect to the movement direction of the carbonaceous material of the residue fraction.

In an exemplary embodiment, a step is provided of separating a carbonaceous waste and/or a sodium chloride excess from the sodium hydroxide solution, in particular a step of centrifugal separation. This separation step may be carried out, for instance, by a conventional centrifugal separation device. This makes it possible to obtain a solution of caustic soda that has a purity degree comparable with the commercial purity degree, and in any case it makes it possible to obtain a solution which can be used, for instance, for a preliminary treatment of the skins in the tanning industry, typically for the caustic depilation of the skins.

The carbonaceous waste may be advantageously be subjected to a step of compaction, i.e. of agglomeration, to provide an agglomerated particle material, for example small brick-shaped agglomerations, preferably with the aid of an organic agglutinant such as glucose and/or sucrose and/or dextrose, by a process and an equipment that is well known in the art of agglomerating small-size and irregular particle matter.

Advantageously, a step is provided of recycling the carbonaceous waste, wherein said agglomerated material forms a part of said carbonaceous material that is subjected to said step of contact and reaction.

Preferably, the amount of a carbonaceous material at this predetermined temperature is prepared by a partial combustion of a corresponding amount of a carbonaceous material having a predetermined grain size. This way, it is possible to produce a carbonaceous material that is available for the reaction as an incandescent coal, at a temperature of about 700°C, according to a well-established partial combustion technique in a vertical blast furnace-type oven,
into which warm air is supplied from below and from which, besides the incandescent coal, an exhaust gas i.e. a combustion gas is extracted that contains carbon dioxide and, in a lower amount, carbon monoxide.

The use of an organic agglutinant such as glucose and/or sucrose and/or dextrose for compacting the carbonaceous waste coming from the raw solution of sodium hydroxide makes it possible to obtain solid particles or small brick-shaped agglomerations that have a predetermined porosity, which increases their the surface-volume ratio, in order to assist the reactions that take place in the oven to prepare the carbonaceous material at a predetermined temperature, and in order to assist the reactions that take place during the step of contact with the solution of sodium chloride and with the steam.

Advantageously, the combustion gas is brought into contact with the aqueous solution of sodium chloride along with the incandescent carbonaceous material and the steam. This way, the carbon monoxide contained in the combustion gas interacts with sodium chloride, as well as the carbon monoxide produced by interaction of the carbonaceous material with water does, according to reaction [II].

For example, the amount of a carbonaceous material having a predetermined grain size may comprise coke.

Such amount of a carbonaceous material having a predetermined grain size may even comprise predetermined proportions of the residue fraction of the carbonaceous material that is subjected to the washing step.

In this case, the carbonaceous material, after the washing step, is preferably subjected to drying, in particular, which involves a mass and heat exchange with a preferably countercurrently flowing hot air stream.

Advantageously, the drying hot air, after being used for the drying step, may be joined to the reaction gas and sent to water absorption together with the reaction gas.

Such amount of a carbonaceous material having a predetermined grain size may comprise predetermined proportions of the carbonaceous waste that is separated from the solution of sodium hydroxide, preferably as an agglomerated matter i.e. a compacted matter, as described above.

In particular, the step of bringing into contact is carried out within a vertical container that has a bottom portion arranged to receive a layer i.e. a bed of the
carbonaceous material at the predetermined reaction temperature, and wherein steps are contemporaneously carried out of:

- continuously or intermittently spraying an upper surface of the bed of the carbonaceous material with the aqueous sodium chloride solution, wherein, in particular the step of spraying is preceded by a step of nebulising the aqueous solution;
- causing the steam to pass through the bed of the carbonaceous material;
- feeding the carbonaceous material into the container and removing an amount of the residue fraction of the carbonaceous material from the container, in particular said amount having the same volume as the carbonaceous material fed to the container. This way, the bed of carbonaceous material is continuously renewed during the reaction.

The above described process may be used also for treating solutions of chlorides of other alkali and alkali-earth metals, thus obtaining hydrochloric acid and the corresponding hydroxide as reaction products, provided the formed oxides are stable at the reaction temperature.

A continuous process for treating a sodium chloride-containing solution, in particular a low sodium chloride concentration tannery effluent, in which the sodium chloride concentration may be lower than the 3%, comprises a step of concentrating the sodium chloride contained in the liquid effluent, to obtain a concentrated solution of sodium chloride.

As described, the process also comprises the steps of:

- prearranging a carbonaceous material.
- a step of converting the concentrated solution of sodium chloride into a solution of sodium hydroxide at a predetermined concentration and into a reaction gas that contains hydrogen chloride, carbon dioxide and steam. Such step of conversion comprises:
  - a step of bringing into contact and causing the concentrated solution of sodium chloride to react with the carbonaceous material in the presence of air and of steam, to obtain a raw reaction product that contains sodium oxide Na₂O and a carbonaceous residue;
  - a step of washing the raw reaction product with a water-containing washing liquid, wherein sodium oxide is transformed into sodium hydroxide, and sodium hydroxide forms a heterogeneous mixture
comprising the solution of sodium hydroxide and the carbonaceous residue.

The industrial liquid effluent may contain a sulphate, in this case the process advantageously includes a step of removing the sulphate, comprising a step of bringing the liquid effluent into contact with a precipitating agent containing a salt of a first cation that is adapted to form a first precipitate of a substantially insoluble sulphate salt. For example, the precipitating agent contains barium chloride BaCl₂, whereby the first precipitate contains barium sulphate BaSO₄ in a mixture comprising a chloride solution. The step of bringing into contact and of precipitating may be carried out in a static mixer.

Preferably, the process comprises a step of regenerating the precipitating agent, said step of regeneration comprising steps of:
— dissolving the first precipitate, wherein the first precipitate is treated with a carbonate of a second cation that is adapted to form a second precipitate of a carbonate of the first cation, in particular barium carbonate BaCO₃, and a solution of a sulphate of the second cation. The second cation may be sodium, whereby the carbonate of the second cation is Na₂CO₃, whereby the solution of sulphate contains sodium sulphate Na₂SO₄;
— restoring the precipitating agent by treating the second precipitate with a hydrogen chloride-containing gas, wherein the carbonate of the first cation of the second precipitate is displaced by hydrogen chloride to yield carbon dioxide CO₂, such that a gas stream is formed that contains carbon dioxide. Advantageously, this hydrogen chloride-containing gas comprises at least one part of the reaction gas produced during the step of converting the concentrated sodium chloride solution into a sodium hydroxide solution.

The step of regeneration may also comprise the steps of:
— reaction of the solution of sulphate with a first alkaline hydroxide of a third cation to form a third precipitate of a sulphate of the third ion and to form a solution of a second hydroxide of the second ion. For example, the first alkaline hydroxide is calcium hydroxide Ca(OH)₂, whereby the third precipitate contains calcium sulphate CaSO₄ and the second hydroxide contains sodium hydroxide NaOH.
— absorption and reaction of a first carbon dioxide-containing gas into/with the solution of the second hydroxide, to form a solution of a carbonate of the
second cation, in particular a solution of sodium carbonate \( \text{Na}_2\text{C}_0\text{3} \).

The solution of the carbonate of the second cation is used for treating the first precipitate in the step of dissolving.

Advantageously, the first carbon dioxide-containing gas comprises at least one own portion selected from the group consisting of:
— a portion of the reaction gas produced in the conversion step;
— a portion of the carbon dioxide-containing gas stream formed in the step of restoring the precipitating agent.

In particular, a step is provided of treating the third precipitate with a predetermined amount of an additive adapted to turn the third precipitate into a further useful product. Preferably, this additive is ammonium sulphate \((\text{NH}_4\text{)}_2\text{SO}_4\), whereby the further useful product is an aqueous solution containing a soluble complex of formula \((\text{NH}_4\text{)}_2\text{SO}_4-\text{CaSO}_4-\text{H}_2\text{O}\), which can work as a fertiliser.

Advantageously, the washing liquid for the raw reaction product washing step comprises an amount of the concentrated sodium chloride solution obtained during the step of concentrating, whereby, by washing the raw reaction product, a crystallization is caused of said sodium chloride of the amount of the concentrated solution, during which a crystalline solid is formed that contains sodium chloride, while an amount of sodium chloride remains in solution at a concentration lower than or equal to a predetermined value, in particular a sodium chloride concentration lower than or equal to 1%.

The step of converting the sodium chloride concentrated solution into caustic soda may also advantageously comprise steps of feeding the substantially solid material to said conversion step, in order to assist the formation of said reaction mixture.

In an advantageous exemplary embodiment, the step of prearranging a carbonaceous material comprises a step of proliferation of an initial amount of an alga, such that a proliferated amount of said alga is obtained that contains the carbonaceous material used for converting sodium chloride in caustic soda. The step of proliferation comprises a step of bringing into contact a second carbon dioxide-containing gas with the initial amount of the alga. Advantageously, the second carbon dioxide-containing gas comprises an amount of the reaction gas.
The step of bringing into contact the second carbon dioxide-containing gas with the initial amount of the alga comprises a step of absorbing the second carbon dioxide-containing gas into an aqueous suspension of the initial amount of the alga before feeding the aqueous suspension of initial amount of the alga to a proliferation reactor. Preferably, during the absorption step, the concentration of the carbon dioxide aqueous suspension is increased until a concentration close to the saturation concentration is achieved.

Alternatively, or in addition, the step of bringing into contact the second carbon dioxide-containing gas with the initial amount of the alga may comprise a step of dosing the second carbon dioxide-containing gas at a plurality of feed points of a tubular proliferation reactor, in order to maintain the concentration of the carbon dioxide at a predetermined value while carbon dioxide is consumed due to the proliferation reaction, preferably the concentration of the carbon dioxide aqueous suspension is increased by such dosed supply up to a value close to the saturation concentration.

Preferably, a step is provided of treating the reaction gas to obtain a further useful product. Such step of treatment comprises a step of bringing into contact the reaction gas with an aqueous liquid, wherein a useful aqueous chloride-containing solution is obtained and a carbon dioxide-containing gas is released. Advantageously, the aqueous liquid is a lime Ca(OH)$_2$ solution or suspension, and the step of obtaining a useful solution comprises a step of converting calcium hydroxide into calcium chloride CaCl$_2$, forming a solution of calcium chloride that has anti-icing properties. Preferably, the step of treating the reaction gas comprises a step of adding and mixing an additive to/in the solution of calcium chloride in order to control the chemical aggressiveness and/or the slipperiness of the calcium chloride solution, typically the additive may be triethanolamine, glycerine, or a combination thereof.

The step of treatment may also comprise a step of cooling and condensation, wherein an amount of condensation water is obtained as well as a mixture of non-condensable gases including hydrogen chloride and carbon dioxide.

In an exemplary embodiment, the step of concentrating comprises:
- a step of reverse osmosis of the liquid effluent to obtain a solution of sodium chloride having a first predetermined concentration, in particular a
concentration of about 15% by weight;
— a subsequent step of evaporating the sodium chloride solution that has said first concentration, the step of evaporating comprising a step of transferring the heat generated in an exothermic step of the process, such that a solution of sodium chloride is obtained that has a second concentration higher than the first concentration. This second concentration is set between 20% and 26%, advantageously it is about 25% by weight.

For example, the evaporation heat for concentrating the solution of sodium chloride may be transferred from the step of cooling and condensing the reaction gas. As an alternative, or in addition, the evaporation heat may come from the step of bringing into contact the mixture of non-condensable gases with the calcium hydroxide to obtain the solution of calcium chloride. As an alternative, or in addition, the evaporation heat may come from the step of absorbing carbon dioxide into the aqueous suspension of the initial amount of the alga. As an alternative, or in addition, the evaporation heat may come from the step of restoring the precipitating agent by treating the second precipitate with a hydrogen chloride-containing gas.

According to a further aspect of the invention, the above-mentioned objects are achieved by an apparatus for carrying out the method described above.

In an exemplary embodiment, the step of bringing said steam into contact with said reaction mixture of the concentrated solution of sodium chloride to form a solution of sodium hydroxide is carried out within a conversion reactor, wherein a treatment chamber is provided that has an inlet section and an outlet section, the conversion reactor comprising:
— a conveying means arranged between the inlet section and the outlet section, said conveying means comprising a conveyor belt that has a hold-up structure in which spaces are defined for retaining a liquid. For example, the hold-up structure may be a porous structure and/or a network or mesh structure.

The conversion reactor also comprises, along the conveyor belt:
— a distribution means for distributing a mixture of the solution of sodium chloride and of the carbonaceous material on the conveyor belt, in order to form a reaction bed of a reaction mixture in the structure of the conveyor belt;
— an air feed means for feeding hot air to the conveyor belt, said feed means preferably arranged laterally of and below the conveyor belt,
— a steam feed means for feeding steam, preferably arranged at an upwards-facing portion of the conveyor belt.

This way, by operating the conveyor belt, the reaction mixture, retained within the spaces of the hold-up structure, reaches and maintains a predetermined reaction temperature, typically a reaction temperature set between 500°C and 600°C, in particular a reaction temperature of about 550°C, and gives rise to chemical reactions by which the reaction gas is produced, while the reaction bed, on the conveyor belt, turns into a reaction residue that comprises a carbonaceous residue associated with sodium oxide Na2O; preferably, the hot air feed means is arranged below the steam feed means.

— a gas extraction means for extracting the reaction gas, which is preferably arranged in an upper portion of the treatment chamber: this way, the hot air and the steam flow through the reaction bed in the conveyor belt, in particular according to the width direction.

— a means for spraying the reaction residue with a washing liquid.

In particular the conversion reactor comprises, at the means for spraying, a steam suction means for sucking the steam that is generated when spraying the reaction residue with the washing liquid.

In particular the steam feed means is in pneumatic communication with the suction means, in such a way that the steam generated when spraying the reaction mixture is distributed.

In particular the conversion reactor comprises one or more dividing wall/s that are arranged transversally with respect to the conveyor belt, and are provided with tight passages for the conveyor belt, the one or more dividing wall/s defining distinct treatment rooms in the treatment chamber. In particular, the dividing walls defining a reaction room or zone wherein the hot air feed means and the steam feed means is arranged, said reaction room tightly separated from a preheating and reaction room where the steam feed means is not present, and from a washing room wherein the spray means is arranged.

In an exemplary embodiment, the step of prearranging a carbonaceous material is carried out in an algae proliferation reactor comprising:

— a tubular body having an inlet port for a suspension that contains a lower
algae content and an outlet port for a suspension that contains a higher algae content;
   — an inner reflecting surface;
   — a lighting element arranged within the tubular body,

In particular, the lighting element is a radial emission optical fibre. The proliferation reactor may comprise a light radiation source arranged out of the tubular body, arranged to be functionally connected with the lighting element. The light radiation source may be a conventional light radiation sender device, arranged to convey a light radiation into the optical fibres. As an alternative or, advantageously, in addition, the light radiation source may be also a sunlight receiving device. The sunlight receiving device has a pointing means for pointing the sunlight receiving device according to the direction of the received sun rays.

Preferably, the proliferation reactor comprises an automatic switch device arranged to receive an environmental brightness parameter and to selectively connect the light radiation sender device with the lighting element and/or with the sunlight receiving device, responsive to a current value of the environmental brightness parameter.

In an advantageous exemplary embodiment, the proliferation reactor has a carbon dioxide dosing means comprising a distribution duct configured to be pneumatically connected with a carbon dioxide source, and provided with a plurality of distribution openings for the carbon dioxide.

Preferably, the proliferation reactor comprises an inner longitudinal duct that houses the lighting element and a flow lumen for the dosed carbon dioxide.

The industrial waste material may comprise solid sodium chloride. Even in this case, sodium chloride may come from a by-product of the tanning industry. The above-mentioned objects are then achieved by a continuous process, to obtain from this solid sodium chloride a solution of caustic soda and a chloride-containing useful product, the process comprising the steps of:
   — prearranging the carbonaceous material;
   — forming the reaction mixture of the solid sodium chloride-containing waste with the carbonaceous material;
   — feeding the reaction mixture into a reaction chamber of an oven selected between a rotating oven and a belt oven;
— converting the mixture into a solution of sodium hydroxide that has a predetermined concentration and into a reaction gas that contains hydrogen chloride, carbon dioxide and steam, the step of converting comprising:

— a step of reaction, which is carried out within the reaction chamber of the oven, of the reaction mixture in the presence of air and of steam, to obtain a raw reaction product that contains sodium oxide Na20 and a carbonaceous residue;

— a step of washing the raw reaction product with a water-containing washing liquid, wherein sodium oxide is transformed into sodium hydroxide, and the sodium hydroxide forms a heterogeneous mixture of the solution of sodium hydroxide and of the carbonaceous residue.

Advantageously, the sodium hydroxide concentration of the solution is higher than 40% by weight, in particular it is higher than 45% by weight, more in particular it is about 50% by weight.

The above-mentioned objects are also achieved by an apparatus, which falls within the scope of the invention, which is arranged to make hydrochloric acid and sodium hydroxide through the previously described process.

Hydrochloric acid, as a gas mixture or in aqueous solution at a desired concentration, which is obtained by the previously described process, also falls within the scope of the invention. Sodium hydroxide, i.e. caustic soda, obtained by the previously described process falls within the scope of the invention as well.

Brief description of the drawings

The invention will be now shown with the description of exemplary embodiments of the generator and of the method according to the invention, exemplifying but not limitative, with reference to the attached drawings, in which like reference characters designate the same or similar parts, throughout the figures of which:

— Fig. 1 shows a block diagram of the process according to an exemplary embodiment of the invention;

— Fig. 2 shows a flow chart of the process according to an exemplary embodiment of the invention;
Fig. 3 is a partially cross-sectioned diagrammatical perspective view of a reactor for bringing into contact and causing to react sodium chloride of the aqueous solution with the carbonaceous material and with steam;

Fig. 4 is a sectional diagrammatical longitudinal view of the reactor of Fig. 3;

Fig. 5 is a diagrammatical top plan view of a surface base of a reactor according to another exemplary embodiment of the invention;

Figs. 6 and 7 are diagrammatical perspective views of the device for feeding the carbonaceous material into the reactor of Fig. 3 and 4, at two different steps of the feed cycle of the carbonaceous material;

Figs. 8, 9 and 10 are time diagrams that describe respective operation mode of the reactor of an apparatus according to the invention;

Fig. 11 shows an overall block diagram of the process according to the invention;

Fig. 12 shows a block diagram in which the steps of the process of Fig. 11 are shown as a further exemplary embodiment of the invention;

Fig. 13 shows a block diagram of the steps of solid separation and or sulphates removal of the process of Fig. 11;

Fig. 14 shows a block diagram of the step of converting sodium chloride into caustic soda of the process of Fig. 11, and of a step of preparing a carbonaceous material suitable for this conversion, according to the diagram of Fig. 12;

Fig. 15 shows a block diagram of the step of treating the reaction gas produced in the step of converting sodium chloride;

Fig. 16 shows a block diagram of the step of production / regeneration of a precipitating agent to be used in the step of removing the sulphates of Fig. 11;

Fig. 17 shows a flow chart of the process according to Fig. 12;

Fig. 18 is a diagrammatical longitudinal sectional view of a reactor for bringing into contact and causing the aqueous sodium chloride solution to react with a material based on carbon and with steam;

Fig. 19 is a perspective cross sectional view of the reactor of Fig. 18;
— Figs. 20, 20A and 20B diagrammatically show an algae proliferation device that may be used as the source of carbon for converting the sodium chloride;

— Figs. 21A and 21B show diagrammatical sectional views of a heat exchanger configured for evaporating and preferably for concentrating the fluid of service, and configured to work as a condenser;

— Fig. 22A, 22B and 22C are diagrammatical sectional views of a density-sensitive discharge valve;

— Fig. 23 diagrammatically shows a mixer device to obtain a water suspension of a solid;

— Figs. 24A and 24B show diagrammatical sectional views of an apparatus for absorbing a gas into a liquid, equipped with an heat exchange device similar to the one of the exchanger of Fig. 21 and of Fig. 21B;

— Fig. 25 shows a flow chart of a process, according to the invention, for obtaining caustic soda and a useful product, starting from sodium chloride solid 81.

Description of preferred exemplary embodiments

With reference to the block diagram of Fig. 1, a continuous process is described to obtain hydrochloric acid and sodium hydroxide, in respective aqueous solutions, from a solution of sodium chloride, in particular from a concentrated solution, i.e. a substantially saturated solutions or a brine. In the example of Fig. 1 reference is made to a process for recovering hydrochloric acid and caustic soda from a liquid and/or solid effluent that contains sodium chloride and organic impurities. In an exemplary embodiment, the process comprises a step 100 of preparing a brine, i.e. a saturated solution/suspension of sodium chloride starting from a saline effluent. If necessary, for example in the case of a waste brine from an industrial process, the saturated suspension thus obtained is subjected to a treatment 101 of homogenization of the saturated solution, and preferably to a grinding i.e. to a size reduction of the solid material contained therein, which may comprise organic impurities. This way, the saturated solution may be supplied to a subsequent step 110 of contact and reaction with a carbonaceous material and with steam, as described hereinafter.
In an exemplary embodiment, the process also provides a partial combustion step 130 of a carbonaceous material, preferably of coke or of a material similar to coke, from which an amount of an incandescent carbonaceous material 18' is obtained suitable for the step of reaction 110, and by which a carbon monoxide CO-rich gas 28 is also obtained. Saturated solution 17, incandescent coal 18' and combustion gas 28 produced in step 130 of partial combustion of the coal are brought into contact with one another and with steam in step of contact and reaction 110. In addition to the above listed reactions, a carbonization of possible organic material present in the brine may take place. In the case of waste brine from tanning processes, this may comprise hair, fat matter, protein matter and the like, which are present in the saline effluent.

In step of contact and reaction 110, incandescent coal 18' reacts with steam to yield gaseous carbon monoxide and hydrogen, according to the reaction:

\[ \text{C(s)} + \text{H}_2\text{O(g)} \rightarrow \text{CO(g)} + \text{H}_2(g) \]  \[ \text{[II]} \]

Hydrogen is subjected to an exothermic combustion reaction:

\[ \text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{H}_2\text{O(g)} + \Delta' \]  \[ \text{[III]} \]

that serves to maintain the temperature in the reaction environment.

Carbon monoxide, in the presence of atmospheric oxygen, combines with sodium chloride of the saline effluent, and forms solid sodium oxide along with gaseous carbonyl chloride, according to the reaction:

\[ \text{CO(g)} + 2\text{NaCl} + \frac{1}{2} \text{O}_2(g) \rightarrow \text{Na}_2\text{O(s)} + \text{COCl}_2(g) + \Delta'' \]  \[ \text{[IV]} \]

which is also exothermic. Sodium oxide remains on the surface of coke or of the similar carbonaceous material, while carbonyl chloride reacts substantially immediately with steam, according to the reaction:

\[ \text{COCl}_2(g) + \text{H}_2\text{O(g)} \rightarrow 2\text{HCl(g)} + \text{CO}_2(g) \]  \[ \text{[V]} \]

to form a gas mixture 62 consisting mainly of hydrogen chloride and carbon dioxide.

The coal works then as a reagent to form compounds of interest, through the intermediate CO, and also as a fuel to provide heat to the whole process.
Gas 62 produced during the step of reaction 110 is continuously withdrawn from the reaction environment and is preferably subjected to a cooling step 111, until a temperature is attained that is suitable for being brought into contact with distilled water. This way, a first step of absorption 112 of gas 62 into water is carried out, by which an aqueous solution of hydrochloric acid is obtained.

In an exemplary embodiment, the heat exchanged during the cooling step 111 of gas 62 is used for producing the distilled water that is required to form the solutions of hydrochloric acid and of caustic soda.

In order to prevent any atmospheric release of the carbon dioxide that remains in gas mixture 62 after the first absorption, a step of compression of this gas may be provided, not shown. In alternative, a second step of absorption 113 may be provided, for instance into a calcium hydroxide Ca(OH)2 suspension, from which calcium carbonate is obtained as a reaction product:

$$\text{CO}_2 + \text{Ca(OH)}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$$  \[XIV\]

From the reaction environment is also obtained the incandescent carbonaceous residue 18" that is subjected to a step 121 of washing, preferably with distilled water. This way, the incandescent carbonaceous material 18" is put out, and the sodium oxide deposited on the carbonaceous residue 18" is solubilised, forming a solution of caustic soda. This is carried out according to the reaction:

$$\text{Na}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{NaOH},$$  \[VI\]

Washing step 121 is preferably followed by a drying step 122, in particular using hot air as a heating and drying means. In this case, heating air leaves the environment where the step of drying is performed, taking away compounds similar to those that are present in gas mixture 62. For this reason, expelled heating air may be treated along with gas 62 in the steps of cooling 111 and of absorption 112.

An amount of purified coal is obtained from drying steps 121 and 122, which may be recycled to partial combustion 130.

A solution of caustic soda 72' is obtained from washing step 121, at a concentration that may be predetermined by selecting the amount of water 72 and/or the amount of the water recycled to the washing environment 71. In
particular, it is possible to operate in such a way that a 50% caustic soda solution 72' is obtained, in order to assist the precipitation of sodium chloride. Solution 72' also contains a carbonaceous waste, which may be subjected to a step 140 of solid/liquid separation, such as a filtering step or a centrifugation step. A solid is obtained from step of separation 140 that may be treated in a step of compaction or of agglomeration 150, forming pellets or the like. These may be advantageously recycled to the step of partial combustion 130, without forming dust. The solid-liquid separation step 140 may be a particular centrifugation step from which, besides the carbonaceous waste solid, a solution of caustic soda is obtained at a concentration of about 50%, and a saline suspension is obtained that may be recycled to the step 100 of preparing the saturated solution.

Fig. 2 shows a diagrammatical view of a possible apparatus 10 for carrying out the process for treating a saline effluent that contains organic residues, according to the invention. Apparatus 10 comprises a collection tank 11 of a solution of sodium chloride, typically of solid and/or liquid saline effluent 12 from an industrial process such as a tanning process. Sodium chloride saturation conditions are preferably achieved in tank 11. Collection tank 11 is provided with a water inlet means for controlling the concentration, in order to maintain the saturation conditions. The collection tank may be a vertical underground tank 11, as in the case of Fig. 2, or a container that has a minimum cross section, in order to reduce water evaporation losses, and to maintain the condition of saturation of sodium chloride. Collection tank 11 may also be provided with a deodorization means, not shown, for example a conventional ozone inlet means, to avoid unpleasant odours.

A first pump 14 is provided for transferring the saturated suspension of sodium chloride, i.e. brine 12, from collection tank 11 to a possible fragmenting/mixing equipment 15. In the shown embodiment, this equipment is a vertical tank provided with a stirrer 15', which is arranged to homogenize the size of such a solid as hair, fat matter and other solids that may be present in brine 12. A second pump 16 is provided for transferring the homogenized brine 17 into a reactor 50.

Apparatus 10 also comprises a device 20 for storing carbonaceous material, comprising a tank 21 for a fresh carbonaceous material such as coke,
and possible other collection tanks 22 and 23, which are described hereinafter. The carbonaceous material as coke 18 is transferred, through a conventional solid conveying means, from device 20 into a blast furnace-type vertical oven 25, loaded from above. A partial combustion of the coal is carried out within oven 25. Oven 25 is provided with an air inlet means 26 in a lower portion, which preferably comprises a plurality of nozzles, not shown. Air may advantageously be preheated in a recovery heat exchanger 27, where it receives heat from combustion gas 28 produced in oven 25.

Since combustion gas 28 of oven 25 is rich of carbon monoxide, it may be advantageously sent to reactor 50 to react directly with the sodium chloride that is present in the effluent 12, in order to increase the yield of the reaction step, as described hereinafter.

In oven 25, coal 18 moves downwards and is extracted as incandescent coal 18'. A first screw conveyor 29, equipped with an electric motor 29", is arranged to withdraw a predetermined amount of incandescent coal 18' through a first hopper 29' (Figs. 6 and 7), at the bottom of oven 25, and is arranged to convey the incandescent coal into a load device 40. Load device 40, which is shown more in detail in Figs. 6 and 7, comprises a box 41 arranged below the bottom of reactor 50. Box 41 is coupled with a hydraulic cylinder 42 that is arranged to vertically move, within box 41, a support plane 42' for incandescent carbonaceous material 18' that is fed by screw conveyor 29. Piston 42 moves alternatively downwards and upwards, which allows loading incandescent coke 18' at constant time intervals. In other words, coke 18' is loaded into reactor 50 at a prefixed average load rate. Load device 40 is also partially shown in Figs. 3 and 4.

With reference to Figs. 3 and 4, a possible reactor 50 is now described to carry out step of reaction 110. It comprises a lower cylindrical portion 52 having a high diameter-to-height ratio. A surface base 52' of reactor 50 is arranged to receive upon itself a bed, i.e. a layer 53 of incandescent coal 18' from load device 40. A surface base 52' comprises a preferably radial inlet port 54' and a preferably radial discharge outlet port 54" for incandescent coal 18' of bed 53, where two ports 54' and 54" are arranged at an angle a with respect to each other (see also Fig. 5). Reactor 50 comprises a device 51 for handling and homogenizing bed 53. In an exemplary embodiment shown in Figs. 3 and 4,
handling and homogenization device 51 is rotatably arranged about an axis 50' of cylindrical portion 52 of reactor 50. Device 51 is provided with a plurality of blades 51', and with an actuating means, not shown, arranged to cause a rotation in a direction 55" such that each blade 55', during the rotation, passes at first above inlet port 54' and only afterwards passes above outlet port 54", sweeping an obtuse angle β, supplementary of angle a formed between inlet ports and outlet port 54' and 54" (Fig. 5). The rotation of handling and homogenization device 51 may be continuous, or intermittent, as described hereinafter.

Handling and homogenization device 51 is therefore suitable for distributing and levelling incandescent coal 18' of bed 53, and at the same time for causing incandescent coal 18' to advance from inlet port 54' to outlet port 54". This way, handling and homogenization device 51 makes it possible to discharge a residue fraction 18" of incandescent coal 18', and also to renew bed 53. The bed renewal is carried out in a time that depends upon the frequency of feeding piston 42 and upon the speed of handling and homogenization device 51. In other words, handling and homogenization device 51 is adapted to uniformly lay the coke and to progressively drag it to the discharge mouth (see also Fig. 5). This way, a steady reaction bed 53 is formed upon the bottom of the reactor, comprising the carbonaceous material, in particular incandescent coke 18'.

Figures 3 and 4 show a possible exemplary embodiment in which handling and homogenization device 51 comprises two blades 5V, which have a rake or comb-like structure, equipped with an upper portion comprising a horizontal connection rod 59 and a plurality of teeth 51", which in the shown example are vertical and parallel to one another.

The number of blades 51' of teeth 51", as well as the width and therefore the distance between teeth 51" are features selected to optimize the combined effects of levelling, mixing and dragging incandescent coal 18' of layer 53.

In a possible exemplary embodiment, shown in the top plan view of Fig. 5, eight blades 51' are provided which are keyed on a shaft 56, and are arranged at 45° with respect to one another. In other words, four diametrically-arranged rake or comb-like structures are provided. Reactor 50, according to this exemplary embodiment, advantageously comprises a means for actuating the
rotation of device 51, and also a means for actuating hydraulic cylinder 42 (Figs. 6 and 7), such that a renewal cycle of bed 53 is established. This way, a charge of incandescent carbonaceous material 18 is lifted and supplied to reactor 50 through inlet port 54'. Afterwards, device 51 is operated so that the charge is consecutively swept by two blades 51', and so that a corresponding amount of coal leaves reactor 50 through discharge opening 54". The cycle is then repeated.

Still with reference to Figs. 3 and 4, reactor 50 is also provided with a distribution means 60 of the suspension, i.e. of brine, 17 along with possible solid impurities of treatable grain size, on bed 53 of incandescent coal 18'. Distribution means 60 are configured for uniformly and preferably finely distributing brine 12 on bed 53, thus preventing any blocking. Furthermore, distribution means 60 may comprise a conventional centrifugal turbine 61, which is arranged at axis 50' of reactor 50, and is equipped with suitable feed means 61'. This way, brine 17 is preferably distributed as a very thin rain or as a mist 19. In the shown exemplary embodiment, reactor 50 has a frusto-conical upper portion that assists the distribution of brine 17 on bed 53 of incandescent coal 18', and, furthermore, aerodynamically assists the extraction of the gas from reactor 50.

Reactor 50 may also be provided with a steam inlet and distribution means 49 on bed 53, preferably associated with a system for generating a dry saturated steam or a superheated steam that has a determined superheat, not shown. For example, the steam generation steam may be a steam generator arranged to generate a dry saturated steam or a superheated steam that has a determined superheat, which may be set between 3 and 10°C, in particular between 4 and 8°C, more in particular, about 5°C, and preferably at a pressure set between 1 and 1.5 absolute bar.

Reactor 50 has an air inlet and distribution means 49' on bed 53.

In the shown exemplary embodiment, the steam inlet and distribution means and/or the air inlet and distribution means comprises a plurality of small holes 57 arranged along a surface base 52' of the reactor (see also Fig. 5).

In bed 53 of incandescent coal 18', due to the feeding, conditions are formed suitable for reactions [II], [III] and [IV], while reaction [V] takes place in the gaseous phase of reactor 50.
Reactor 50 may also be, furthermore, provided with a temperature control means, that is arranged to maintain a temperature between 400°C and 600°C in reactor 50. This way, the carbonization can be carried out without destroying the coal residue that is directly involved in the reaction. In particular, the temperature control means is adapted to maintain the temperature of the reaction bed between 500°C and 600°C, more in particular, about 550°C. The reaction temperature control means may comprise a means, not shown, for adjusting the flowrate of the saline solution and/or of the steam, and/or of the oxygen or air. In particular, the adjustment means comprises a shut-off valve, not represented, i.e. an ON/OFF valve, for starting/Stopping the flow of saline solution and/or of steam, and/or of air to reactor 50, and also comprises a means for opening/closing the shut-off valves. The means for opening/closing the valves comprises a program means that causes the valves to open/close according to a time programme and/or according to value of a process variable, in particular according to a temperature of reactor 50.

Figs. 8, 9 and 10 are time diagrams that describe respective operation modes of reactor 50 of apparatus 10. In these diagrams, the states of presence/absence of a feeding of saline solution, of a feeding of steam and of a feeding of air are shown as a presence/absence of a full line at each abscissa time. A qualitative trend of a temperature reactor 50 is also shown.

With reference to Fig. 8, a first operation mode of reactor 50 is described in which cycles 93 are carried out, each of them schematically comprising:

- a step 91, in which the saline solution is supplied along with the steam, while no air feed is present: in these conditions, the temperature T of reaction bed 53 decreases down to a predetermined minimum value T', by conveying sensible heat and latent heat from incandescent carbonaceous material 18' to solution 17 and to the steam that has been fed: during this step, water-gas formation reaction [II] takes place mainly, which produces carbon monoxide and hydrogen;

- a step 92, in which air is supplied while no saline solution and steam is fed: in these conditions, temperature T of bed 53 increases up to a predetermined maximum value T", due in particular to exothermic reaction [III].
With reference to Fig. 9, a second operation mode of reactor 50 is described, in which reactor 50 is steadily supplied with the saline solution at a flowrate lower than the flowrate of the first operation mode, and in which cycles 96 are carried out, each of them schematically comprising:

- a step 94, in which steam is fed in the absence of any air feed, and the same transformations occur as in above step 91;
- a step 95, in which air is supplied absence of any steam feed: in these conditions temperature T of bed 53 increases up to a predetermined maximum value T\(^*\), due exothermic reactions [III] and [IV].

With reference to Fig. 10, a third operation mode of reactor 50 is described, in which steam and air are fed to the reactor one after the other, according to a determined time sequence 97/98, i.e. according to a predetermined time program. The feeding of sodium chloride solution is started or stopped according to whether the temperature of reactor 50 has attained a predetermined maximum value T\(^*\) or a predetermined minimum value T, and steps of feeding 97 and of absence of feeding 98 of sodium chloride solution alternate each other, and form working cycles 99.

In all the above preferred operation, steam and air are fed in distinct steps, to prevent the formation of explosive mixtures of hydrogen and oxygen.

In an exemplary embodiment, an auxiliary heating means may be provided, not shown, that is arranged to transfer heat or other external form of energy to the reaction mixture, such that the reaction temperature is always maintained within the above mentioned range.

Reactor 50 may also have a gas outlet port 48 for gas mixture 62 produced by the reactions, which mainly comprises hydrogen chloride and carbon dioxide. In an exemplary embodiment, outlet port 48 is associated with an axial hole arranged at axis 50'.

Still with reference to Fig. 2, a heat exchanger 63 may be arranged along a line 63' for conveying gas mixture 62 into a first bubbling or absorption tank 64, in which line 63' forms a submerged feed duct. First absorption tank 64 has a vent line 63'' which forms a submerged feed duct of a second bubbling tank 64', and, in turn, into a third absorption tank 64''. Like first absorption tank 64, second and third absorption tanks 64' are provided with a water supply means 73, in particular with a demineralised water supply means. In absorption tanks
64,64' gas 63' is absorbed into water, and an aqueous solution 67 of hydrochloric acid is obtained. HCl aqueous solution 67 is withdrawn from the bottom portion of absorption tanks 64,64' by a third pump 66, for transferring solution 67 into a hydrochloric acid storage device, for example into a tank 67'.

Gas 62" at the outlet of the series of absorption tanks 64,64', as transformed in said first step of absorption, may pass through a further absorption tank 68 that is provided with a feed means 70 of a calcium hydroxide aqueous solution. Reaction [XIV] occurs in absorption tank 68, from which calcium carbonate is obtained that forms a thick suspension or a slurry 69. Slurry 69 is sent to a storage device by a fourth pump 65'. The vent duct of absorption tank 68 is connected to a fan 79, for example to a lobe compressor, which ensures the gas suction throughout apparatus 10.

A tubular apparatus 71 may be arranged under reactor 50, equipped with a feed means 71' arranged to receive residue fraction 18" of carbonaceous material discharged by reactor 50 through discharge opening 54". Feed means 71' may comprise a second feed hopper 71'. Tubular apparatus 71 is adapted to move carbonaceous material 18" in a predetermined direction, substantially maintaining the reaction temperature. To this purpose, tubular apparatus 71, according to an exemplary embodiment of Fig. 2, is provided with screw drag means 71". In other words, the tubular apparatus has the shape of a second screw conveyor 71. Apparatus 10 may also comprise a tank or preferably a plurality of tanks 78, which are arranged parallel to one another, and are provided with water supply means, in particular they are provided with distilled or demineralised water supply means. A means is also provided for conveying this water from tanks 78 into screw conveyor 71, which may comprise a fifth pump 80. In a shown exemplary embodiment, this conveying means is configured to form a flow of distilled water within screw conveyor 71, preferably countercurrently with respect to the direction of the carbonaceous material of residue fraction 18" in screw conveyor 71. The water, due to the contact with the sodium oxide Na₂O of the coal, causes reaction [VI] to occur, which yields sodium hydroxide NaOH. The conveying means may also advantageously be configured for repetitively recycling the distilled water to screw conveyor 71, so that at each recycle passage the distilled water become richer in the sodium hydroxide solute. This way, it is possible to obtain a solution 72' that has a
predetermined sodium hydroxide concentration, in particular a concentration of 50%, such that the excess sodium chloride crystallizes, and only about 1% of sodium chloride remains in solution. Tanks 78 are connected to exit apertures of second screw conveyor 71, in such a way that at least one of tanks 78 receives, in a continuous operation, sodium hydroxide solution 72′ formed by causing water to flow along inside screw conveyor 71.

Tanks 78 may be associated with a means for conveying sodium hydroxide solution 72′, for example a sixth pump 81, to a conventional centrifugal separation device 82, that is arranged to separate a solution of pure caustic soda 87, i.e. at a concentration of about 50%, from solid residues, as described hereinafter.

Centrifugal separation device 82 may be a centrifugal type decanter, and may be configured to separate two solid phases 83,84 that have different specific weights, in this case sodium chloride 83 and carbonaceous residue 84. In this case, a means is provided for conveying sodium chloride 83 into collection tank 11, where sodium chloride 83 is mixed with sodium chloride solution 12 when entering into apparatus 10. A means is also provided for conveying coal residue 84 to a compaction device 85, which is arranged to agglomerate carbonaceous waste 84 to form pellets 86 or similar agglomerates. Preferably, the carbonaceous waste is compacted with a conventional organic agglutinant 89, in particular glucose, sucrose or dextrose. This way, the carbonaceous waste can be fed into oven 25 along with coke 18. To this purpose, a means 86′ is provided for conveying pellets 86 into tank 22. Tank 22, as well as tanks 21 and 23, has a discharge means to oven 25. A means is also provided for conveying centrifuged pure caustic soda 87 into a storage tank 88.

A third screw conveyor 74 may be also provided arranged to receive washed coal from second screw conveyor 71. Third screw conveyor 74 has a feed means 75 for a heating fluid, which may be for example hot air. In the exemplary embodiment of Fig. 2, feed means 75 is arranged to form a co-current flow of the coal and of hot air within third screw conveyor 74. A conveying means is associated to third screw conveyor 74, for transferring coal 74′, depurated from the sodium oxide and then dried, into tank 23 of storage device 20 of carbonaceous material 20. The conveying means may comprise, for instance, a fourth screw conveyor 76. Preferably, a proportioning device is
provided, not shown, for withdrawing coke 18, carbonaceous waste pellets 86' and washed and dried coal 74' from tanks 21, 22 and 23, respectively, and for feeding predetermined proportions of these materials to second screw conveyor 71 and to third screw conveyor 74.

A means may also be provided for conveying heating air 77 from the outlet of third screw conveyor 74 to the system of absorption tanks 64,64',68.

With reference to the block diagrams of Figs. 11-16, and to the flow-sheet of Fig. 17, a continuous process is described for treating an industrial liquid effluent 201 that contains sodium chloride NaCl, for example an effluent of tanning industry, and for obtaining caustic soda 236" and a useful product 243' that contains chlorides.

In this case, the effluent 201 may possibly contain other chlorides, sulphates, organic residues, as well as suspended inorganic particulate matter.

For a solution 201 that contains suspended solids, the process according to the invention advantageously comprises a step 210 of removing substantially solid pollutants 222"",222'". The expression "solid" refers to both organic solids 222" and inorganic solids 222'". In the case of an effluent 201 of tanning industry, organic solid 222" may result from fleshings and from other material coming from an animal tissue. Still in the case of an effluent 201 of tanning industry, inorganic solid 222'" may comprise heavy metals compounds such as chromium compounds, in particular salt and hydroxides.

In an exemplary embodiment, solid removal step 210 comprises a preliminary step 221 of correcting the pH to a basic value (Figs. 12 and 13), preferably to a value set between 8 and 10, in particular to a value about 9. This serves to assist the separation process. pH Correction step 221 provides a pH correction additive 202, which may be an acid or basic substance, according to whether the pH of solution 201 to be treated is higher or lower than a determined pH value. For example, correction additive 202 may be hydrochloric acid or sodium hydroxide, respectively. pH Correction step 221 also comprises a subsequent step of mixing effluent 201 with additive 202. In an advantageous exemplary embodiment, this mixing may be carried out in a static mixer 321 (Fig. 17). A step is advantageously provided of adjusting the flowrate of correction additive 202 responsive to the pH value of the effluent at the inlet or at the outlet of static mixer 321 or of an equivalent device.
The alkalinized effluent 221' (Figs. 12 and 13) is subjected to a step 222 of separation of solids 222",222"", from which a clarified effluent 222' is obtained.

If both organic residues and inorganic particulate are present, solid separation step 222 is advantageously carried out in one or more apparatuses 322 (Fig. 17). Each apparatus 322 is configured to separate three streams, clarified solution 222', organic material 222" and inorganic solid 222"". The number of apparatus depends upon the flowrate of solution 201 to be treated. In particular, this apparatus may be a centrifugal separation device 322 known as Tricanter. The organic material is discharged as a solid suspension 222", while the inorganic solids are discharged as a wet panel 222"". Organic material 222" is advantageously used along with the carbon-containing raw material in the subsequent step of sodium chloride conversion, as described hereinafter. Inorganic solids 222"" may be sent to a user out of the process, or sent to disposal.

For a sulphate-containing solution 201, the process according to the invention comprises advantageously a sulphate removal step 220 (Fig. 11). The sulphates may be removed by a precipitation step 224 (Figs. 12 and 13), typically treating solution 222' with a precipitating agent 258'. Precipitating agent 258' may be a salt of an anion adapted to form with sulphate ion SO₄²⁻ a not much soluble or a fully insoluble salt. This salt advantageously comprises a cation that is compatible with the effluent treatment, and/or a cation already present in effluent 201, typically chloride ion Cl⁻. In particular, precipitating agent 258' contains barium chloride BaCl₂, preferably in the form of an aqueous solution, such that barium sulphate BaSO₄ is formed as a precipitate in a mixture 224' comprising the chloride solution and a precipitate of barium sulphate, according to the reaction:

\[ \text{Na}_2\text{SO}_4 + \text{BaCl}_2 \rightarrow 2\text{NaCl} + \text{BaSO}_4. \]  

Precipitating agent 258' is preferably subjected to a regeneration step 270, wherein another useful product may be formed, for instance a solution 263' that contains sulphates (Fig. 11).

In an exemplary embodiment, sulphate removal step 220 comprises a preliminary step 223 of correcting the pH to an acid value (Figs. 12 and 13). Preferably the pH is corrected to a value set between 3 and 5, in particular to a
value about 4. This serves to assist the precipitation of the sulphates, for example of barium sulphate. pH Correction step 223 provides a further pH correction additive 203, comprising an acid substance, for example hydrochloric acid. pH Correction step 223 also comprises a step of mixing clarified effluent 222' with the pH correction additive 203, from which an acidified effluent 223' is obtained. In an advantageous exemplary embodiment, this mixing may be carried out in a static mixer 323 (Fig. 17). A step is advantageously provided of adjusting the flowrate of correction additive 203 according to the pH value of the effluent at the inlet or at the outlet of static mixer 323 or of an equivalent device.

Obviously, if solid removal step 210 is not performed, effluent 201 may be subjected directly to sulphate removal step 224.

Also sulphate precipitation step 224 may be carried in a static mixer 324, in which acidified solution 223' is brought into contact with a solution 258' of the precipitating agent, for example barium chloride, forming mixture 224'.

Mixture 224', along with precipitated sulphates, is subjected to a step 225 of separating solid sulphates 225'' from a substantially sulphates-free solution 225', which contains chlorides (Figs. 12 and 13). If hydrochloric acid is used as pH correction agent 202,203, solution 225' has a sodium chloride concentration higher than the corresponding concentration in the solution or in effluent 201. The treated solution may change from a sodium chloride concentration of a few percentage decimals, for example a concentration of about 0.5%, to a concentration of about 1 - 2%, typically about 1.3%. Such solution will be indicated hereinafter as middle concentration solution. Solid separation step 225 is carried out in at least one apparatus 325, preferably in at least one centrifuge 325 (Fig. 17). The sulphates, discharged as wet panel 225'' by centrifuge/s 325, are subjected to regeneration step 270, as described hereinafter.

Chloride middle concentration solution 225' may be used as a refrigerant means in subsequent steps of the process that take place with a production of heat, as described hereinafter.

The process according to the invention comprises a step 230 of concentrating the solution i.e. the effluent to be treated. Concentration step 230 may treat the inlet solution 201 or, if organic and/or inorganic solid removal step 222",222'" is performed, clarified solution 222' or, if the sulphates removal step
is performed, sulphate-substantially free solution 225' (Figs. 11 and 12). From concentration step 230 a solution 231' is obtained, hereinafter indicated as chloride high concentration solution or brine, and an amount of water 230' separated from the brine is also obtained. The quality of brine 231' and of separated water 230 depends upon the technology used.

In an exemplary embodiment, concentration step 230 comprises a step of reverse osmosis 228 (Fig. 17) of solution 201', or 222', or 225'. In this case, solution 231' may have a concentration of about 15% by weight. This concentration value is substantially the maximum that can be attained with the presently available reverse osmosis technology, i.e. with the presently known membrane devices 328.

In an exemplary embodiment, concentration step 230 also comprises a subsequent step 229 (Fig. 17) of evaporating solution 201', or 222', or 225'. Advantageously, evaporating step 229 comprises a step of transferring an amount of heat from process exothermic operations to this solution. For instance, with reference to Fig. 17, the concentration step is carried out in the apparatus 341,343,345,358, as described more in detail hereinafter. Evaporation step 229 further increases the concentration of high concentration solution 231'. In particular, a sodium chloride solution 231'' can be obtained from evaporation step 229 at a concentration between 20% and 26%. Advantageously, the concentration is about 25%.

The process according to the invention comprises a step 240 of conversion of the sodium chloride that is contained in effluent 231' and that is treated as described above, into caustic soda 236'', i.e. into a solution of sodium hydroxide NaOH at a predetermined concentration (Fig. 11). As already mentioned, in the step of conversion 240 a reaction gas 233" is obtained that contains hydrogen chloride HCl, carbon dioxide CO₂ and steam (Figs. 12 and 17). Reaction gas 233" is an intermediate product of the process shown in Figs. 12 and 17.

As shown in detail in Figs. 12 and 14, step 240 of sodium chloride conversion comprises a step 233 of treating saline solution 231' by contact and reaction with a carbonaceous material 246' in the presence of air and of steam. In treatment 233, a raw reaction product 233' is obtained that contains sodium oxide Na₂O and a carbonaceous residue. Sodium chloride conversion step 240
also comprises a step 234 of washing sodium oxide 233' in water or in an aqueous solution 237'. During washing step 234, sodium oxide is transformed into sodium hydroxide, which forms caustic soda 235'. Other steps of process 240 of conversion to caustic soda will be described more in detail hereinafter.

Sodium chloride conversion step 240 advantageously comprises a step 232 of mixing and homogenising effluent 231', treated as above described, with carbonaceous material 246'. Mixing step 232 is advantageously associated with a step of grinding possible previously formed solid material. Homogenisation step 232 produces a substantially homogeneous mixture 232' of the saline solution and of the carbonaceous material.

More in detail, in contact and reaction step 233, the carbonaceous material of mixture 232' reacts with steam to give carbon monoxide CO and gaseous hydrogen $\text{H}_2$, according to the reaction:

$$\text{C(s)} + \text{H}_2\text{O(g)} \rightarrow \text{CO(g)} + \text{H}_2(g) \quad \text{[II].}$$

Hydrogen gives rise to an exothermic combustion reaction:

$$\text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{H}_2\text{O(g)} + \text{H}_2(g) \quad \text{[III]},$$

which serves to maintain the temperature in the reaction environment.

Carbon monoxide, in the presence of atmospheric oxygen, combines with sodium chloride of the effluent, forming solid sodium oxide $\text{Na}_2\text{O}$ and gaseous carbonyl chloride $\text{COCl}_2$, according to the reaction:

$$\text{CO(g)} + 2\text{NaCl} + \frac{1}{2}\text{O}_2(g) \rightarrow \text{Na}_2\text{O(s)} + \text{COCl}_2(g) + \Delta'' \quad \text{[IV]},$$

which is also exothermic. Sodium oxide remains partially stuck on the carbonaceous material surface. Carbonyl chloride reacts substantially immediately with steam, according to the reaction:

$$\text{COCl}_2(g) + \text{H}_2\text{O(g)} \rightarrow 2\text{HCl(g)} + \text{CO}_2(g) \quad \text{[V]},$$

forming the gas mixture 233" that substantially consists of hydrogen chloride and carbon dioxide.

Therefore, the carbonaceous material serves not only as a reagent to obtain compounds of interest, through the intermediate CO, but also as a fuel for providing the heat required by the whole process.
The heat exchanged during step 241 of cooling gas 233" may be used, for example, for further concentrating middle concentration solution 225' or high concentration solution 231', as mentioned above, and described more in detail hereinafter.

From the reaction environment raw reaction product 233' is also obtained, which contains sodium oxide and the carbonaceous residue. Raw product 233' is subjected to washing step 234, which is carried out with a washing liquid 237', to dissolve the sodium oxide deposited on the solid carbonaceous material residue. Washing liquid 237' may be distilled water, or a process aqueous solution. Washing liquid 237" is taken from a feeding system comprising a tank 338 and a pump 339 (Fig. 17). This way, a solution of caustic soda is obtained, according to the reaction:

$$Na_2O + H_2O \rightarrow 2NaOH.$$  \[VI\]

Advantageously, washing liquid 237" comprises an amount 231" of chloride high concentration solution 231', which is delivered during effluent concentration step 230, in particular during reverse osmosis step 228 (Figs. 12, 14 and 17). This way, a substantially quantitative sodium chloride crystallization takes place, in which only about 1% of sodium chloride remains in solution. Crystallized sodium chloride (Fig. 17) is separated together with the carbon residue in solid/liquid separation step 235, and is recycled to homogenisation step 232. Solid-liquid separation step 235 may comprise a step of centrifugation that is carried out in a conventional centrifuge 335 (Fig. 17), from which a carbonaceous panel 235", and caustic soda 235' are obtained.

A heterogeneous mixture 234' of a sodium hydroxide solution and of a carbonaceous residue is then obtained from step washing 234. A solid/liquid separation step 235 is therefore provided in which carbonaceous residue 235" is separated from caustic soda 235', at a NaOH concentration that depends upon the amount of water that is recycled to the washing environment. In particular, it is possible to operate in such a way that caustic soda 235' is obtained at a concentration of about 50%. The residual solid may be recycled to mixing step 232 (Figs. 12 and 14).

With reference to Figs. 18 and 19, a reactor 333 is described, according to an exemplary embodiment of the invention, for converting sodium chloride of
saline solution 232' into a solution 235' of sodium hydroxide, i.e. into caustic soda. In particular, reactor 333 may serve for performing both contact and reaction step 233 and washing step 234 (Figs. 12 and 14).

Reactor 333 comprises an elongated reaction chamber 500, in particular a chamber that has a substantially rectangular cross section, which extends longitudinally from a first end portion 500' to a second end portion 500". The inner faces of the walls of this chamber comprise a material resistant to chlorides at a temperature of about 500-550°C. In particular, this material may be titanium, or a titanium alloy.

Reactor 333 (Fig. 18) also comprises a conveying means 501 for conveying a product from end portion 500' to end portion 500". In an exemplary embodiment, conveying means 501 comprise a conveyor belt 502 arranged along elongated reaction chamber 500. In an exemplary embodiment, conveyor belt 502 is operated by a couple of rollers 503' and 503" arranged at end portions 500' and 500". In this exemplary embodiment, rollers 503', 503" have normally a rotation sense such that an upwards-exposed portion 502' of the tape moves from roller 503' towards roller 503", whereas a downwards-facing portion 502" of the tape moves from roller 502" towards roller 503'. Advantageously, downwards-facing portion 502" of conveyor belt 502 is located within reaction chamber 500. With this arrangement, during the return path of conveyor belt 502 from end portion 500" to end portion 500', conveyor belt 502 is heated/is maintained at a temperature close to the reaction temperature. This way, an amount of the reaction heat received by the material of conveyor belt 502 is recovered for heating the reaction mixture 232" that is put upon/within conveyor belt 502 in a feed zone 510 of oven 333.

Conveying means 501 has a structure adapted to retain mixture 232' while the latter is carried between end portion 501' and end portion 501", and while it is transformed according to reactions [II] and [IV] to form reaction mixture 232". For instance, in the exemplary embodiment of Fig. 18, conveying means 501 may comprise a conveyor belt 502 that has a porous or network or mesh structure, in which spaces are defined of a size suitable for retaining reaction mixture 232". This way, the conveyor belt and reaction mixture 232" may form a reaction bed 507 longitudinally movable within oven 333.
In an advantageous exemplary embodiment, conveying means 501, for example conveyor belt 502, is made of a heat-conductive material, such that a uniform temperature is obtained throughout reaction bed 507.

For example, the heat-conductive material comprises a Nickel alloy such as a Hastelloy, which also provides a suitable chemical resistance.

A duct 504 is arranged along reactor or oven 333 which is in pneumatic communication with reaction chamber 500. This way, it is possible to suck the reaction gas produced during the operation of oven 333 by a suction means 347, which is described hereinafter (Fig. 17). In an exemplary embodiment of Figs. 18 and 19, suction duct or collector 504 is longitudinally arranged in an upper portion of oven 333. In an exemplary embodiment, collector 504 comprises a first portion and a second portion 504', 504" that extend along oven 333 and that are joined to each other by a connection member 504" arranged at one end portion 500" of reaction chamber 500. For example, the connection member comprises a 180° elbow. Portion 504' is pneumatically connected or can be pneumatically connected with suction device 347, whereas other portion 504" is in pneumatic connection with reaction chamber 500 through duct elements 508 (Fig. 19). In the example shown, first portion and second portion 504', 504" have axes arranged substantially in a same vertical plane, i.e. first and second duct portion 504', 504" are substantially arranged above each other.

Duct 504, or a connection duct to communicate with suction means 347, is provided with a heat exchange means 505 for heating a fluid exploiting a heat amount released by the reaction gas. The heat exchange means flows along duct 504 during the operation of oven 333. Advantageously, the heat exchange means may comprise at least one jacket 505 that is formed along the outer surface of duct 504, and that has respective input and outlet ports, not shown, for a fluid to be heated. Heat exchange means 505 are preferably arranged downstream of pneumatic connections 508 of duct 504 with chamber 500. For example, in a represented exemplary embodiment, the heat exchange means is arranged along second portion 504" of duct 504.

Duct 504, or a duct of connection to suction means 347, has a means 506 for controlling the temperature of the reaction gas which flows along duct 504 during the operation of oven 333. Advantageously, temperature control means 506 may comprise (Fig. 19) a device 506' for causing an at least partial post-
combustion of the reaction gas and/or may comprise a device 506" for supplying a gas colder than the combustion gas, for example air. In particular, device 506" may be an outer air suction device. Temperature control means 506 advantageously comprises at least one temperature sensor, not shown, and an actuation means, not shown, for selectively operating devices 506',506" according to whether the temperature of the reaction gas is lower or higher than a predetermined value. Temperature control means 506 is preferably arranged downstream of the pneumatic connection members of duct 504 with chamber 500. For instance, in a represented exemplary embodiment, temperature control means 506 is arranged along second portion 504" of duct 504.

From another point of view, duct 504, or a connection duct to communicate with suction means 347, has gas mixture post-combustion means 506', which are preferably actuated responsive to a temperature threshold of a temperature measured in the reaction gas. Advantageously, the temperature threshold is selected as a temperature limit above which the concentration of carbon monoxide in the gas is negligible, i.e. it is lower than a predetermined safety value. Carbon monoxide, besides being harmful to health if the reaction gas is emitted to environment, is not allowed in some uses for which the gas is intended, in particular it is not allowed in some steps of the preparation of a carbonaceous material for converting sodium chloride into sodium hydroxide, as described hereinafter.

Fig. 18 also shows a support structure 509' of reactor 333.

As mentioned above, reactor 333 has feed zone 510 at end portion 500' of reaction chamber 500. Feed portion 510 comprises, within reaction chamber 500, a distribution means 511 of mixed saline solution 232'. Distribution means 511 is adapted to lay mixed solution 232' onto conveyor belt 502, in order to spray reaction bed 507 formed in conveyor belt 502. In an advantageous exemplary embodiment, the distribution means comprises a conventional turbine distribution means arranged to form a uniform and preferably thin dispersion of the mixed saline solution. This way, brine 232' can be distributed as a very thin rain or as a mist 512.

Oven 333 comprises then a preheating and carbonization zone 520, which follows and is preferably adjacent to feed zone 510, with respect to the conveying direction of the conveyor belt. Preheating and carbonization zone
520 has a hot air feed means, which comprises at least one hot air feeding ducts 521 arranged in its lower part. Moreover, preheating and carbonization zone 520 is in pneumatic communication with duct 504 through passageways 522. By operating the conveying means, in particular conveyor belt 502, mixed saline solution 232' distributed on conveyor belt 502 reaches preheating and carbonization zone 520, where it is subjected to an initial heating by contact with the hot air supplied through feed means 521, and causes reactions [II]-[V] to occur forming a gas that contains hydrogen chloride, carbon dioxide, carbon monoxide, hydrogen, oxygen and steam. This reaction gas is sucked through passageways 522.

Furthermore, reactor 333 comprises a reaction zone 530 which also is equipped with a hot air feed means, as well as with a steam feed means. The feed means comprises hot air feeding ducts 531 and steam feeding ducts 531. In an exemplary embodiment, the feeding ducts extend along reaction chamber 500 up to reaction zone 530. Hot air longitudinal ducts 531 extend also along preheating and carbonization zone 520. In an advantageous exemplary embodiment, longitudinal ducts 531,532 are arranged along vertical side walls of reaction chamber 500. Ducts 531,532 also comprise passage ports 531',532', to the portions of reaction chamber 500 that correspond to zones 520,530 of reactor 333. Preferably, the steam passage ports are substantially aligned at the same height of upwards-facing portion 502' of conveyor belt 502. In an advantageous exemplary embodiment, the hot air passage ports, in reaction zone 530, are substantially aligned under the steam passage ports. The passage openings for outlet of the reaction gas are preferably aligned along a longitudinal upper central axis of chamber 500. This way, hot air and steam entering through side passage ports cross and interact with reaction bed 507 throughout its width.

The hot air passage ports of zones 520,530 are preferably in pneumatic connection with heat exchange means 505 of duct 504. For example, connection tubes 535 may be provided with at least one external jacket 505. This way, it is possible to exploit a part of the sensible heat of gas 233" for heating the air used by the process.

In an exemplary embodiment, reactor 333 comprises a steam suction means for sucking the steam generated in a washing chamber 540 due to the
contact of the washing aqueous solution with reaction bed 507. In particular, the suction means comprises at least one suction duct 533, which is preferably longitudinally arranged in an upper portion of washing chamber 540. The steam feeding channels 532 may be pneumatically connected with suction duct or with ducts 533, for example through a conveying system that comprises connection ducts 534.

Steam feed means 532 may be associated with a dry saturated or superheated steam generation system, not shown. For example the steam generation steam may be a steam generator arranged to produce a dry saturated steam, or a superheated steam with a determined superheat. The superheat is set, for example, between 3°C and 10°C, in particular it is set between 4°C and 8°C. More in particular, the superheat is about 5°C. Preferably, the pressure is set between 1.0 and 1.5 absolute bar.

When moving along zones 520 and 530, sodium chloride of reaction bed 507 is progressively changed into sodium oxide according to reaction [IV].

In an advantageous exemplary embodiment, reactor 333 comprises also a washing zone 540, where the sodium oxide is brought into contact with an amount of a washing liquid 237", for instance water or an aqueous solution, which is suitable for causing reaction [VI] to form sodium hydroxide as an aqueous solution, preferably at a concentration about 50%. This aqueous solution is normally accompanied by a carbonaceous residue, and forms along with it a mixture 234’ (Figs. 12 and 14), which is collected in a tank 334 located underneath washing zone 540 of reactor 333. Tank 334 has preferably an inclined lower wall 434, in order to assist mixture 234’ to flow out by gravity. The amount of washing liquid 237" is supplied into washing zone 540 through a spray means that comprises a plurality of supply nozzles 542, which are fed by a collector 541 and are preferably arranged to uniformly lay the washing liquid in reaction bed 507, i.e. in conveyor belt 502.

Dividing walls, not represented, are preferably provided between preheating and carbonization zone 520 and reaction zone 530 and/or between reaction zone 530 and washing zone 540. In particular, both dividing walls 529 and dividing walls 539 are provided, which are arranged transversally with respect to conveyor belt 502, in order to separate reaction zone 530 from adjacent zones 520,540, forming corresponding distinct treatment rooms within
treatment chamber 500. Dividing walls 529 and/or 539 comprise passage openings, not represented, for conveyor belt 502. These passage openings preferably have a sealing element, not shown, that is arranged to provide a seal about conveyor belt 502 during the movement of conveyor belt 502 in the operating conditions of reaction chamber 500 of oven 333. In particular, the sealing element comprises a seal made of graphite, preferably a highly pure degree graphite, in particular a graphite having a purity degree of 99.8%.

Due to the preheating that takes place in zone 520, and to steam and of air fed into zone 530, conditions are created in bed 507 that allow reactions [II], [IV]. Reactions [III] and [V], instead, mainly occur in the gaseous phase that is present within reactor 333, above reaction bed 507.

Reactor 333 may be also be provided with a temperature control means, that is arranged to maintain a temperature set between 400°C and 600°C in bed 434, in order to perform the carbonization step without destroying the carbonaceous residue obtained, which is directly involved to the reaction. In particular, the temperature control means is adapted to maintain the temperature in the reaction bed between 500°C and 600°C, more in particular, to maintain a temperature of about 550°C. The reaction temperature control means may comprise a means, not shown, for adjusting the flowrate of the saline solution and/or of the steam, and/or of the oxygen or air. The adjustment means may comprise valves, not shown, for starting/stopping the flow of saline solution and/or of steam, and/or of air into reactor 333, and may also comprise a means for opening/closing these valves. The means for opening/closing the valves may comprise a program means that opens and the closes the valves according to the value of a process variable, in particular according to a temperature within reactor 333.

Caustic soda 235° discharged as a liquid phase in separation step 235 (Figs. 12 and 14) is sent to a storage device 336 (Fig. 17). Advantageously, a step 236 is provided of measuring the concentration of delivered sodium hydroxide solution 235°, and of conveying solution 235° (Figs. 12 and 14) to a destination selected between an out-of-specification product tank and a final product storage tank 338 (Fig. 17), according to whether the measured sodium hydroxide concentration is lower than a reference concentration value, or not, respectively. In an exemplary embodiment, the storage device of the out-of-
specification product may comprise a tank 337 from which the solution of hydroxide is taken for washing step 234. In particular, the reference concentration value may be about 50% by weight.

This way, it is possible to repetitively recycle the sodium hydroxide solution between tank 337 and reactor 333, such that the solution become richer in dissolved sodium hydroxide at each recycle passage, until the desired or reference concentration value is achieved.

The process according to the invention comprises a step 250 of treating the reaction gas 233 produced during contact and reaction step 233, by which useful products are obtained. With reference to Figs. 12 and 15, reaction gas 233" is continuously withdrawn from the reaction environment and is preferably subjected to a cooling and condensation step 241. From cooling and condensation step 241 a stream of condensation water 241', and a mixture of non-condensable gases 241", containing hydrogen chloride and carbon dioxide, are obtained. In cooling step 241, gas 233" is brought to a temperature preferably close to room temperature.

As described, step 241 of cooling and condensing reaction gas 233" may be carried out by transferring heat (Fig. 17) to an amount 225" of middle concentration solution 225' that is formed in the sulphate removal step 224 and in the subsequent centrifugation step 225, or to an amount 225" of the solution treated in concentration step 231. By this heat transfer, the amount 225" is heated and preferably partially evaporated, increasing its own concentration up to a predetermined value, and forming a very high concentration solution 225"'. For example, the final concentration of the sodium chloride solution may attain values set between 20% and 26%, in particular about 25%. Very high concentration solution 225"' may be advantageously mixed with the high concentration solution before contact and reaction step 233.

Cooling and concentration step 241 may be carried out in a heat exchanger 341, as shown in Fig. 21. In an exemplary embodiment, as shown, exchanger 341 has at least two chambers 442,448. A service chamber 442 comprises an upper half-chamber 442' and a lower half-chamber 442". Upper half-chamber 442' has an inlet port 443 for receiving high concentration solution 231' and/or middle concentration solution 225', and has also an outlet port 450 for steam 242" that is formed by evaporating the solution. Upper half-chamber
442' may comprise a cylindrical body and preferably a body that has a cross section that decreases towards the above, for example a frusto-conical body of connection with steam outlet port 450. Lower chamber 442'' has an outlet port 444 for very high concentration solution 225'''. Half-chambers 442' and 442'' are connected through a plurality of tubular heat exchange elements 447 and by at least one tubular element 446 for conveying the solution. Process chamber 448 is arranged to contain tubular heat exchange elements 447, while transfer tubular element 446 is arranged outside of process chamber 448. Process chamber 448 has an inlet port 449 for receiving reaction gas 233'', an outlet 451 to vent the non-condensables and of an outlet port 452 for condensed water.

By feeding the middle and/or high concentration solution 225',231' into service chamber 442 until a liquid head 452 is formed, by partially flooding upper half-chamber 442', and by feeding process chamber 448 with reaction gas 233'', a heat transfer process is established from solution 225',231' to gas 233'' through tubular heat exchange elements 447. This heat exchange process causes gas 233'' to cool down, and also causes an at least partial condensation of the steam contained therein, which leaves process chamber 448 through outlet port 452, while the non-condensables or not condensed gas leaves process chamber 448 through outlet port 451. The heat exchange process also causes a heating and a natural convention motion within tubular elements 446,447, which arises in addition to the passage flow through chamber 448. At liquid head 453, an evaporation takes place of the water of solution 225',231' which, therefore, become more concentrated.

Very high concentration solution 225''' may be automatically discharged from process chamber 448 when a predetermined concentration value is attained. For instance, very high concentration solution 225'''' may be automatically discharged by gravity through a density-sensitive discharge valve 445 arranged at outlet port 444. Density-sensitive discharge valve 445 is arranged to open/remain open when/as long as the density of the solution becomes/remains higher than a value that corresponds to predetermined concentration value. Furthermore, density-sensitive discharge valve 445 is adapted to close/remain closed when/as long as the density of the solution becomes/remains lower than this density value.
With reference to Fig. 18, a density-sensitive discharge valve 445 is described according to an exemplary embodiment. The density-sensitive discharge valve comprises a hollow body 546', integral to a rod 548, which may comprise a screw rod portion. Rod 548 slides between an upper bearing 547 and a lower bearing 551. Bearings 547,551 are held by a plurality of arms 552,553 integral to respective external rings 554,555. The empty spaces between the arms and the rings allow the flow of the liquid contained in the tank where the valve is installed. An upper portion of rod 548 is integral to an integral body 549 that has a mass adapted to balance the buoyancy that rod 548, along with body 549, receives in distilled water (density = 1 g/cm$^3$). A plurality of calibrated discs 550 are integrally connected to rod 548, preferably in a reversible way. By removing the calibrated discs, if valve 445 is immersed in a liquid having a density lower than distilled water, the weight of rod 548 and of body 549 maintains the rod in a low closed position. If the density of the liquid increases, when it reaches the density of distilled water, rod 548 moves to a high opening position, and lets the fluid flow out. The weight and the number of calibrated discs 550 are selected in such a way to set a valve opening density value higher than the density of distilled water, for example an opening density value equal to the density of an aqueous solution of a salt in a standard condition. This way, a valve is obtained that is configured to open when the concentration of a predetermined salt exceeds a predetermined reference value, in determined operating conditions, and to let flow out a solution that has a concentration not lower than this reference value. Valve 445 is preferably made of a material chemically resistant to the substance with which it is brought into contact. In particular, the parts of the valve exposed to the fluid may be made of a Hastelloy.

Step 250 of treating reaction gas 233" comprises therefore a step 243 (Figs. 12 and 15) of contacting an amount 248' of non-condensables 241" with an aqueous liquid 242' to form a useful aqueous chloride-containing solution 243'. In particular, fed aqueous liquid 242' is a lime Ca(OH)$_2$ solution or suspension. Useful solution formation step 243 may comprise a step of converting calcium hydroxide into calcium chloride, according to the reaction:

$$\text{Ca(OH)}_2 + \text{HCl} \rightarrow \text{CaCl}_2 + \text{H}_2\text{O}, \quad [\text{VII}]$$
such that useful aqueous solution 243' also comprises calcium ions. Solution 243' has anti-icing properties, i.e. it is adapted to lower the freezing point of water with which it comes into contact. Therefore, it may be used as a general-purpose anti-icing solution. After the reduction of hydrogen chloride, according to reaction [VII], gas 243" is released containing, carbon dioxide along with moisture and hydrogen chloride traces.

In order to form aqueous liquid 242', it is advantageously provided a step 242 of mixing an amount 204 of lime CaO or Ca(OH)₂. In particular, mixing step 242 may be carried out in a feed tank 342 (Fig. 23) that comprises a mixing chamber 457' and a feed chamber 457" that are in communication with each other via a passage port 457"'. Advantageously, two chambers 457',457" are defined by two containers that can be arranged at a same height, in particular two identical containers. Mixing chamber 457' is provided with inlet ports for receiving solid lime amount 204 and a water amount 441 "", and with a stirrer 457 for dissolving lime into water, which is arranged to form aqueous lime suspension 242'. Suspension or slurry 242' may flow into feed chamber 457" through passage port 457"'. Feed chamber 457" is associated with a pump 459 that has a suction mouth and a delivery mouth in communication, with lower and upper portions of feed chamber 457", respectively, to cause suspension 242' circulate within feed chamber 457".

In an exemplary embodiment, pump 459 (Fig. 17) has the suction mouth also in hydraulic communication with an absorber device 343 where step 243 of forming useful aqueous solution 243' takes place.

Absorber device 343 is now described with reference to Figs. 24A and 24B. It comprises a gas distribution means 455. Gas distribution means 455 may include gas supply nozzles 456 arranged in a lower portion of a process chamber 448. Preferably, gas distribution means 455 comprises microbubble diffusers, for example sintered ceramic or glass disc-shaped diffuser, to ensure a distribution as much uniform as possible on all the surface of absorber 343. This way, supply nozzles 456 are submerged by lime suspension 242' accumulated in process chamber 442 of absorber device 343. By forcing hydrogen chloride-containing gas 248" (Fig. 17) through gas distribution means 455, the gas comes into contact with lime 243 and reaction [VII] takes place. Reaction [VII] is exothermic. Absorber device 343 advantageously contains heat
exchange means 447 for removing the reaction heat that is associated with reaction [VII]. In an exemplary embodiment, absorber device 343 may have a structure similar to exchanger 341 of Fig. 21. More in detail, absorber device 343 has a service chamber 442 arranged to receive a saline solution, comprising an upper half-chamber 442' and a lower half-chamber 442". The saline solution may be, for example, an amount of middle concentration solution 225'. Moreover, a surface heat exchange is provided between half-chambers 442' and 442", for example in the form of tubular elements 447'. This way, as long as reaction [VII] occurs, the reaction heat is transferred to middle concentration solution 225' that partially evaporates and turns into a very high concentration solution, as already described with reference to step 241 of cooling reaction gas 233" and of condensing the water contained therein. In particular, the step of concentrating the saline solution contained in service chamber 441' is carried out continuously, preferably controlling the pH and the level of the saline solution, for example by means of a radar level sensor. The lime slurry inlet flow-rate is adjusted according to the level of the saline solution, at pH of about 12. The slurry causes solution pH to change. When the pH is between 7 and 8, the solution of CaCl₂ is extracted. For higher pH values, the valve is closed, to let the reaction go on. The final CaCl₂ solution is filtered, and solid unreacted Ca(OH)₂ is incorporated in the lime slurry.

Alternatively, the step of concentrating the saline solution may be carried out discontinuously. In this case, two absorber devices 343 are provided arranged in parallel to each other, and in hydraulic communication with the delivery mouth of calcium chloride suspension feed pump 459.

Advantageously, service chamber 442 of absorber device 343 has a density-sensitive discharge valve at an outlet port 444 for discharging the sodium chloride solution. This valve opens only if a predetermined sodium chloride concentration is reached or exceeded. For example, the density-sensitive discharge valve may be a discharge valve similar to valve 445 of Figs. 22A, 22B, 22C, as previously described.

Advantageously, reaction gas treating step 250 comprises a step 244 of adding and mixing additives 205 to calcium chloride solution 243', adapted to reduce the chemical aggressiveness and/or the slipperiness of this solution (Figs. 12 and 15). For instance, a step may be provided of addition of an
ethanolamine, preferably triethanolamine, and/or of glycerine. This way, an improved anti-icing solution 244' is obtained. In an advantageous exemplary embodiment, step 244 of adding and mixing additives is carried out in a static mixer 344 (Fig. 17). It is also provided a step of sending the improved anti-icing solution 244' to a storage device, or to a user device. The storage device of improved anti-icing solution 244' may comprise at least one storage tank 390.

Gas 243", substantially formed by carbon dioxide, may be used for making a carbonaceous material that can be used in contact and reaction step 233. Fig. 12 relates to a step 246 of algae proliferation, in which carbon dioxide-containing gas 243" is fixed by the algae for their proliferation. In particular, carbonic gas 243" is used to saturate an aqueous suspension 245' of an initial amount of an alga through a step 245 of absorbing C0₂ into the suspension itself.

The alga may be any alga adapted to give rise to a proliferation process at a rate that can provide at least an important part of the carbonaceous material required by contact and reaction step 233. In particular, Chlorella Hamburgensis may be used, which is an alga adapted to fix particularly large amounts of carbon dioxide.

Absorption step 245 may be carried out in an absorber device 345 similar to absorber device 343 of Fig. 19, previously described (Fig. 21). In particular, the dissolution heat of hydrogen chloride into water may be transferred to a middle concentration chloride solution through the wall of tubular elements 447. This way, an evaporation step takes place which allows reaching a predetermined concentration value. This value may be, for example, about 25%, which corresponds to a very high concentration solution. Saturation step 245 gives rise to a residue gas stream 245", as well as to a carbon dioxide-saturated algae solution or suspension 245' (Fig. 12).

Advantageously, service chamber 442 of absorber device 345 has a density-sensitive discharge valve at outlet port 444, for discharging the sodium chloride solution only if a predetermined sodium chloride concentration is reached and/or exceeded. For example, the density-sensitive discharge valve may be a discharge valve similar to valve 445 of Figs. 22A, 22B, 22C, previously described.
Gas residue 245" is sucked by a suction system 347 (Fig. 17). At least one amount 247' of it may be reused in the algae proliferation step 246 (Fig. 12). To this purpose, the amount 247" is supplied to proliferation reactor 346, in order to maintain the concentration of CO₂ in the suspension as long as the algae proliferation takes place, as described above. Preferably, the suction system comprises a lobe rotating compressor 347. Another amount 247" may be used for a step of producing sodium carbonate Na₂CO₃, which is useful for precipitating agent regeneration step 270, as described hereinafter.

With reference to Figs. 20, 20A, 20B, an algae proliferation reactor 346 is described comprising a tubular body 601 that has an inlet port 601' for a suspension 245' containing a lower algae content ("initial amount of an alga", Figs. 12 and 13), and has also an outlet port 601" for a suspension 246' containing a higher algae content. Inlet port 601' is in hydraulic communication with a source of a suspension 245' of an initial amount of an alga. Such suspension may contain dissolved carbon dioxide, preferably it contains a concentration of dissolved carbon dioxide close to the saturation concentration. In this case, the source of a suspension 245' of an initial amount of an alga may be a saturation device 345 (Fig. 17), for example of the type shown in Figs. 24A and 24B, previously described.

Tubular body 601 has an inner reflecting surface, in particular an inner mirror-like surface. In tubular body 601, a lighting element is arranged, in particular a radial emission optical fibre 603. This way, a light 610 emitted by lighting element 603 is reflected on the inner surface of tubular element 601, causing a predetermined lighting of suspension 245' within tubular body 601. This lighting is larger than what can be obtained in prior art tubular proliferation reactors, in which a transparent tubular element is used as well as a light source outside of the transparent tubular element. As long as algae suspension 245' advances along inside tubular body 601, photochemical processes take place that cause a proliferation, i.e. a growth of the algae. In other words, the carbon dioxide present in algae suspension 245' in the form of a dissolved gas is fixed by a semisolid suspended material, i.e. by the algae. This semisolid material can be used in step 233 of treating the saline solution 231', previously described. Therefore, tubular reactor 346 makes it possible to produce an amount of algae that is enough, in a time unit, to treat industrial waste water
flowrates by treatment step 231', which also allows reducing the required installation spaces.

Preferably, lighting element 603 is arranged within a transparent duct 602. Proliferation reactor 346 comprises a light radiation source arranged around tubular body 601, functionally connected with lighting element 603. The light radiation source may comprise a conventional light radiation sender device 605, arranged to convey a light radiation into optical fibre 603. The light radiation source may also comprise a sunlight receiving device 604. Preferably, the sunlight receiving device 604 has a pointing means 608 for pointing the sunlight receiving device 604 according to the position of the sun, not shown. For example, pointing means 608 may comprise a conventional sun-tracker device. The light radiation source may also comprise a switch device 606 for selecting a light radiation coming from the light radiation sender device 605 and/or from the sunlight receiving device 604. Preferably, switch device 606 is an automatic switch device, arranged to switch the light radiation source to the sender device 605 or to the sunlight receiving device 604, responsive to the environment or sun lighting. In other words, switch device 606 is arranged to functionally connect the sunlight receiving device 604 when the sun lighting is higher than a predetermined threshold value. Switch device 606 is also arranged to functionally disconnect the sunlight receiving device 604 and to functionally connect the sender device 605 when the sun lighting solar falls below this threshold value. To this purpose, the switch device is connected to a brightness sensor, not shown, which is arranged close to sunlight receiving device 604.

In a preferred exemplary embodiment, proliferation reactor 346 comprises an additional carbon dioxide supply means 607. The supply means comprises a distribution duct 607 arranged to convey the additional carbon dioxide, which is arranged within tubular body 601, along tubular body 601. Distribution duct 607 is in pneumatic communication with a carbon dioxide source, not shown, and is provided with holes 607' that define additional carbon dioxide supply positions. This way, in each section of proliferation reactor 346, i.e. in each section of tubular element 601, the carbon dioxide concentration is maintained at a predetermined value, while carbon dioxide is consumed due to the proliferation reaction, in spite of carbon dioxide consumption which occurs while algae 245' advance along within tubular element 601. This makes it possible to maintain a
proliferation rate along the whole tubular element 601.

Advantageously, as shown in Fig. 20A, proliferation reactor 346 comprises an inner longitudinal duct 602/607 that houses lighting element 603, in particular a radial emission optical fibre 603, and a passage port for additional carbon dioxide. The flow of additional carbon dioxide 247' (Figs. 12 and 13) through holes 607' of duct 602/607 hinders the deposition of scale from suspension 245' onto the surface of duct 602/607, thus maintaining the surface of duct 602/607 transparent to the light emitted by lighting element 603. This reduces the time-dependent loss of efficiency of proliferation reactor 346.

In an advantageous exemplary embodiment, as diagrammatically shown in Fig. 20B, proliferation reactor 346 comprises a plurality of tubular elements arranged above and/or beside one another, which are in communication with one another through elbows or curved pipe elements, such that a compact reactor structure is obtained, i.e. a structure in which a long proliferation path can be housed within a compact element.

In the exemplary embodiment of Figs. 12 and 16, precipitating agent regeneration step 270 comprises a step 251 of converting the not much soluble or fully insoluble sulphate 225" into a compound that can be attacked by hydrogen chloride. In other words, the not much soluble or fully insoluble sulphate 225", which cannot react with hydrogen chloride, is converted into a salt of a cation that may be displaced by a hydrogen chloride treatment, to form i.e. to restore a solution 258' of the salt that is the precipitating agent of the sulphates.

In particular, if precipitating agent 258' is barium chloride, the insoluble salt 225" is barium sulphate. Preferably, the cation that may be displaced by barium is the carbonate ion C0₃⁻. In particular, conversion step 251 is carried out by treating barium sulphate with a sodium carbonate Na₂C0₃ solution 264', and the following conversion reaction:

\[
\text{BaSO}_4 + \text{Na}_2\text{C}0_3 \rightarrow \text{BaC}0_3 + \text{Na}_2\text{SO}_4, \quad \text{[VIII]}
\]

where a heterogeneous mixture 251' is formed of a sodium sulphate solution and of a BaC0₃ solid precipitate. A step 252 is then provided of separating wet solid precipitate 252', in particular barium carbonate, from sodium sulphate solution 252". In an exemplary embodiment, conversion reaction [VIII] may be
carried out in a reactor 351 similar to feed tank 342 of Fig. 23 (Fig. 17). In an exemplary embodiment, solid/liquid separation step 252 comprises a centrifugation step, for example in a conventional centrifuge 352.

It is then provided a step 258 of treating the salt from which the corresponding cation may be displaced, typically as wet precipitate 252', with a hydrogen chloride-containing gas stream. In particular, the hydrogen chloride-containing gas stream comprises an amount 249" of non-condensables released by condensation step 241. The step 258 of treatment with a hydrochloric gas takes place by the reaction:

$$\text{BaCO}_3 + 2\text{HCl} \rightarrow \text{BaCl}_2 + \text{CO}_2 + \text{H}_2\text{O}, \quad [IX]$$

where a barium chloride solution 258' is formed, at a concentration between 20% and 40%. Preferably, barium chloride concentration is set between 25% and 35% by weight, more preferably it is about 30%. In the step 258 of treatment with a hydrochloric gas, a gas stream 258" is released that contains carbon dioxide and steam. Advantageously, before step 258 of treatment with a hydrochloric gas, a step 257 is provided of mixing barium carbonate with water, to obtain a barium carbonate solution 257' at a concentration of about 30%. Barium carbonate may be a raw material, or may be contained in wet precipitate 252' coming from solid/liquid separation step 252. The water for mixing or dissolution step 257 may comprise an amount 249' of condensation water stream 241' obtained from partial condensation 241 of reaction gas 233". In an exemplary embodiment (Fig. 17), mixing step 257 is carried out in a feed tank 357 similar to feed tank 342 of Fig. 23, previously described. In an exemplary embodiment, step 258 of restoring the precipitating agent by a treatment with a hydrochloric gas 249" is carried out in an absorber device 358 similar to absorber device 343 of Figs. 24A and 24B, previously described, in which the reaction heat of reaction [IX] is transferred to a sodium chloride high concentration solution. This way, a very high concentration sodium chloride solution is obtained.

Advantageously, the service chamber of absorber device 358 has a density-sensitive discharge valve at its outlet port, for discharging the sodium chloride solution only if a predetermined sodium chloride concentration is reached and/or exceeded. For example, the density-sensitive discharge valve
may be a discharge valve similar to valve 445 of Figs. 22A, 22B, 22C, previously described.

The precipitating agent, in this case barium chloride solution 258', is used for performing sulphate precipitation step 224, as above described, for example in a static mixer 324 (Fig. 17). Preferably, gas stream 258" is joined with gas 243" formed in chloride solution formation step 243, and/or it may be used in step 245 of absorbing carbon dioxide into aqueous suspension 245' of the initial alga amount.

Precipitating agent regeneration step 270 also comprises a step 261 of formulation of a useful product that contains the sulphate ions obtained in wet solid precipitate separation step 252. In particular, the useful product comprises a sodium sulphate solution 252". The step of formulation of a useful product may include a step 261 of treating sodium sulphate solution 252" with a stream 207 of raw material lime, and may comprise the reaction:

$$\text{Na}_2\text{SO}_4 + \text{Ca(OH)}_2 \rightarrow 2\text{NaOH} + \text{CaSO}_4,$$

in which a heterogeneous mixture 261' is formed of a sodium hydroxide solution and a calcium sulphate CaSO$_4$ solid precipitate. In particular, the sodium hydroxide solution has a concentration set between 15% and 20% by weight, more in particular, the concentration is about 16%. A step 262 is then provided of separating a wet solid precipitate 262', in particular calcium sulphate dihydrate CaSO$_4$$\cdot$$2\text{H}_2\text{O}$, from sodium hydroxide solution 262". In an exemplary embodiment, reaction [X] may be carried out in a reactor 360 similar to feed tank 242' of Fig. 23 (Fig. 17). In an exemplary embodiment, solid/liquid separation step 262 comprises a centrifugation step, for example carried out in a conventional centrifuge 362.

Sulphate ions-containing useful product formulation step 270 may provide a step 263 of treating wet solid precipitate 262', in particular calcium sulphate, with a stream 208 of raw material ammonium sulphate (NH$_4$)$_2$SO$_4$. Calcium sulphate dihydrate CaSO$_4$$\cdot$$2\text{H}_2\text{O}$ dissolves according to the reaction:

$$(\text{NH}_4)_2\text{SO}_4 + \text{CaSO}_4$$2\text{H}_2\text{O} \rightarrow (\text{NH}_4)_2\text{SO}_4$$•$$\text{CaSO}_4$$•$$2\text{H}_2\text{O} \quad [XI]$$
in which an amount of water 230' may be used which comes from concentration step 230. An aqueous solution 263' is then formed, which contains a soluble complex of formula \((\text{NH}_4)_2\text{SO}_4\cdot\text{CaSO}_4\cdot\text{H}_2\text{O}\). Solution 263' may be used as a liquid fertiliser.

In particular, ammonium sulphate amount 208 and lime amount 207 are selected such that predetermined weight ratios are obtained between the amounts of calcium, nitrogen, sulphur, which are elements useful as plant nutrients, and are present in wet solid precipitate 262'.

A step is then provided of sending liquid fertiliser 263' to a storage device 376 (Fig. 17), and/or to a user device, not shown. The storage device of liquid fertiliser 263' may comprise at least one storage tank 376.

Advantageously, a step 265 is provided of absorbing a carbon dioxide-containing gas 266' into sodium hydroxide solution 262" obtained from separation step 262. Typically, gas 266' is absorbed into sodium hydroxide at a concentration of about 16%. This way, a solution of sodium bicarbonate (NaHCO₃) is mainly formed.

\[
\text{NaOH} + \text{CO}_2 \rightarrow \text{NaHCO}_3 ,
\]  
[XII]

Advantageously, the process comprises forming, in absorption step 265, a solution of sodium carbonate Na₂CO₃. This object is difficult to achieve, since sodium bicarbonate is produced according to reaction [XII]. For this reason, a carbon dioxide excess is used, in order to form bicarbonate only. Subsequently, the CO₂ excess is withdrawn by boiling the solution, forming sodium carbonate solution 264', according to reaction [XIII]:

\[
2\text{NaHCO}_3 + \Delta \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2.
\]  
[XIII]

Advantageously, carbon dioxide-containing gas 266' comprises at least one part 247" of gas residue 245" released by absorption step 245. In an exemplary embodiment, step 265 is carried out in at least one absorber tank 365 comprising a gas distribution means 465, which is in pneumatic communication with a delivery mouth of suction device or lobe compressor 347. Distribution means 465 may comprise gas supply nozzles submerged by an amount of soda solution stored within absorber tank 365. By bubbling gas 266',
which contains an excess of carbon dioxide, through the soda contained in absorber tank 365, reaction [XII] takes place, and sodium bicarbonate 265' is formed in the solution. Advantageously, a second absorber tank 366 is also provided equal and parallel arranged to absorber tank 365.

Advantageously, absorber device 365 has a density-sensitive discharge valve at its outlet port, for discharging sodium bicarbonate solution 265' only if a predetermined concentration value is reached and/or exceeded. For example, the density-sensitive discharge valve may be a discharge valve similar to valve 445 of Figs. 22A, 22B, 22C, previously described.

Sodium bicarbonate solution 265' is then transferred from absorber tank 365,366 to a heater tank 367. Heater tank 367 has a heating and temperature maintaining device 467, which is arranged to heat and to maintain solution 265' received from absorber tank 365,366 in boiling conditions. This way, the conditions are created for taking the carbon dioxide excess away from the solution contained in tank 367, and for converting sodium bicarbonate into sodium carbonate, according to reaction [XIII], thus obtaining sodium carbonate solution 264'.

For example, the heating device comprises a heating coil 467 inside or outside of tank 367. Advantageously, the heating/temperature maintaining step is carried out through transferring the heat of reaction of gas 233" to the sodium carbonate solution. In particular, a portion 233''' of reaction gas 233 is caused to flow within heating coil 467 (Fig. 17).

Sodium carbonate solution 264' is preferably used for feeding step 251 of conversion of sulphate 225" into barium carbonate 252'.

With reference to Fig. 25, a process is described, according to another aspect of the invention, for obtaining caustic soda 236" and a useful product 244, starting from solid sodium chloride 281, such as the salt coming from a skin beating operation of the tanning industry, which may contain an organic residue.

Sodium chloride solid 281 is loaded in a feed tank 381 and then is mixed with a carbonaceous material 246' in a mixer 379, for example a screw conveyor mixer. Carbonaceous material 246' may be an alga prepared in a proliferation step 246, for example in a proliferation reactor 346 of the type described with reference to Figs. 20-20B.
In mixer 379 a mixture is formed of sodium chloride 281 and of carbonaceous material 246, which is continuously dosed into a reaction chamber 383' of a conventional rotating oven 383, which is provided with a burner 385. In reaction chamber 383' reactions [II]-[V] take place producing a raw reaction gas 233" that contains hydrogen chloride, carbon dioxide, carbon monoxide, hydrogen, oxygen and steam, and producing a solid raw reaction product 233' that contains sodium oxide and a carbonaceous residue.

An outlet port of reaction chamber 383' is in tight communication with a container or tank 334, in which raw reaction product 233' is washed forming caustic soda 234' and steam 234". The connection mouth of container 334 has a size that allows discharging raw reaction product 233' from reaction chamber 383' of rotating oven 383 to container 334, and at the same time allows the steam 234" which is generated in the container 334 to flow from here to reaction chamber 383'. From the washing step carried out in container 334, a heterogeneous mixture 234' is obtained of a sodium hydroxide solution and of a carbonaceous residue. Heterogeneous mixture 234' is treated in a filter or in a centrifuge 335, similarly to what has been already described with reference to Fig. 17, in order to separate sodium hydroxide solution 235' from a panel that contains carbonaceous residue 235".

Advantageously, a step is provided of measuring the concentration of sodium hydroxide solution 235', by an instrument 238, and a step is provided of conveying solution 235' to a destination selected among container 334, as a recycle stream 239, and/or a tank of an out-of-specification product, not shown, and a final product storage tank 236", according to whether the measured sodium hydroxide concentration measured by means of instrument 238 is lower than a reference concentration value, or not, respectively. The destination may be decided by suitably opening/closing tank 334-side valve 238' or storage-side valve.

This way, it is possible to repetitively recycle the sodium hydroxide solution between tank 337 and reactor 333, such that the solution become richer in dissolved sodium hydroxide at each recycle passage through reactor 333, until the desired or reference concentration value is achieved.

Separated carbonaceous residue 235" may be recycled to feed tank 379 of reaction chamber 383'.
Raw reaction gas 233" is sucked in the head of rotating oven 383 and is preferably conveyed to a post-combustor 384, which also is provided with a burner 386, and in which the carbon monoxide contained in reaction gas 233' is converted into carbon dioxide, such that reaction gas 233" is transformed into a converted reaction gas 283" substantially consisting of hydrogen chloride, carbon dioxide and steam, as in the case of the reaction gas produced in conversion reactor 333 of Fig. 17. Converted reaction gas 283" may be subjected to a cooling step. In particular, the cooling step may comprise a first cooling step, for example in an in-line exchanger 382. The heat exchanged by reaction gas 283" during the first cooling step may be transferred to an air flow 282', thus obtaining a preheated air flow 282" that is supplied to burner 385 of rotating oven 383, and preferably to reaction chamber 383' of rotating oven 383 itself to allow a circulation of the gas stream. The step of cooling the reaction gas may comprise a second cooling and condensation step, according to what has been described with reference to Figs. 12 and 17, for example in a heat exchanger 341 of the type shown in Figs. 21A and 21B. In particular, service side of condenser 341 is supplied with osmotized water, as a cooling liquid.

The water 241" that is obtained from partial condensation of the reaction gas 283", and the non-condensables 241' are preferably used for obtaining a solution of calcium chloride 243' by a step 242 of mixing an amount of lime 204 with water 241", to obtain a lime suspension 242', by a following step of absorption 243 of non-condensables 241' into suspension lime 242, and finally by a step 244 of adding and mixing additives 205, preferably according to the procedure and in the equipment 342,343,344 which have already been described, for instance, with reference to Fig. 17. Still similarly to what has been previously described, carbon dioxide-containing gas 243" is preferably absorbed into a solution of an initial amount of an alga 245' that is fed to algae proliferation reactor 346, for example in an absorber device 345 of the type already described, and the gas residue 247" from absorption step 245 is dosed along proliferation reactor 346. The water steam produced by evaporation of the cooling water or solution used in exchanger 343 and/or in absorber 345 is preferably used as a washing liquid to wash raw reaction product 233' that is discharged from reaction chamber 383' of rotating oven 383 into container 334.

As shown in Fig. 26, instead of a rotating oven 383, for the step of contact
and reaction a conveyor belt reactor 700 may be used consisting of a first part 701 that comprises a reaction chamber 701'. The conveyor belt reactor 700 also comprises a conveyor belt 706 arranged to carry a substantially solid material from a feed zone 710 to an outlet section 711 of reaction chamber 701', and from the outlet section 711 into a tank 702, where guide elements 721 are provided that define a path of said conveyor belt within said tank 702. Conveyor belt reactor 700 is provided with a feed means for feeding a liquid into tank 702 to form a liquid head of this liquid within tank 702. Guide elements 722 are arranged to maintain a portion of the conveyor belt below the liquid head formed within tank 702. Further guide elements 723 define a further path of the conveyor belt that crosses the outlet section 711 of reaction chamber 701 and reaches the inlet section of reaction chamber 701'. A carbonaceous material 379' is fed to the feeding section 710 of reaction chamber 701', and is laid down on conveyor belt 706. Conveyor belt 706 conveys the reaction mixture along and within reaction chamber 701' up to outlet section 711. Conveyor belt 706 is provided with holes and is associated with a steam feed means arranged to transfer steam to reaction mixture 379' on conveyor belt 706 through the holes, not shown, in order to carry out the step contact and reaction according to reactions [II]-[IV], while reaction [V] takes place within the reaction chamber, as in previously described reactors 50 and 133. Reaction mixture 379', at outlet section 710, substantially consists of a carbonaceous residue and of sodium oxide Na₂O stuck on the carbonaceous residue. Conveyor belt 706 is arranged to convey the mixture into the tank, where the washing step is carried out, in which reaction [VI] takes place. In the washing step, a heterogeneous mixture is produced comprising a carbonaceous residue and a sodium hydroxide solution. A means is provided for transferring the heterogeneous mixture to a device 704 for separating the solid carbonaceous residue from the liquid.

The foregoing description of an embodiment of the method and of the apparatus according to the invention, and of the way of using the apparatus, will so fully reveal the invention according to the conceptual point of view, so that others, by applying stream knowledge, will be able to modify and/or adapt in various applications this specific exemplary embodiments without further research and without parting from the invention, and, then it is meant that such adaptations and modifications will have to be considered as equivalent to the
specific embodiments. The means and the materials to realise the different functions described herein could have a different nature without, for this reason, departing from the field of the invention. It is to be understood that the phraseology or terminology that is employed herein is for the purpose of description and not of limitation.
1. A process for obtaining sodium hydroxide and a chloride-containing useful product, comprising the steps of:
   — prearranging (100) a source (12,17,201,231') of sodium chloride;
   — prearranging (260) an amount of a carbonaceous material (18',246');
   — prearranging a source (49) of steam;
   — prearranging a source (72) of water;
   — contacting (110,233) said sodium chloride with said amount of a carbonaceous material (18',246') at a predetermined reaction temperature obtaining a reaction mixture (232');
   — bringing said steam into contact with said reaction mixture (232') such that said steam, said carbonaceous material (18',246') and said sodium chloride of said reaction mixture (232'), at said reaction temperature, interacts forming:
     — hydrogen chloride and carbon dioxide as a gas mixture in a reaction gas (62,233');
     — a residue fraction (18'') of said carbonaceous material; and
     — sodium oxide (Na₂O) stuck to said residue fraction (18'') of said carbonaceous material,
   wherein said reaction temperature is higher than 400°C;
   — washing (121,234) said residue fraction (18'') of said carbonaceous material with said water (237') until a washed carbonaceous residue and an aqueous sodium hydroxide solution are obtained (236');
   — separating said carbonaceous residue from said aqueous sodium hydroxide solution and concentrating said aqueous sodium hydroxide solution until it reaches a predetermined concentration.

2. A process according to claim 1, wherein said reaction temperature (T) is set between 400°C and 600°C, in particular said reaction temperature (T) is set between 500°C and 600°C, more in particular, said reaction temperature (T) is about 550°C.

3. A process according to claim 1, wherein said source (11) of sodium chloride is an aqueous sodium chloride-containing solution (12,27), in
particular a brine.

4. A process according to claim 3, wherein said aqueous solution (12,17) of sodium chloride is an industrial liquid effluent (12,201), in particular selected from the group consisting of:
   — a solution resulting from a process of preliminary washing of skins that contain sodium chloride as a preservative agent, and/or
   — a solution resulting from a separation step of sodium chloride from tannery fleshings.

5. A process according to claim 3, wherein said step of bringing (110) said steam into contact with said reaction mixture comprises the steps of:
   — supplying (91,94,97) said steam and reaction of said steam with carbon of said carbonaceous material (18'), thus producing carbon monoxide and hydrogen;
   wherein said supplying (91,94,97) of said steam is carried out by supplying (92,95,98) oxygen, in particular the oxygen of an air flow, wherein said oxygen reacts:
   — with said hydrogen, thus producing a reaction heat;
   — with said carbon monoxide and with said sodium chloride, thus producing said sodium oxide and said gaseous carbonyl chloride;
   — reaction of said gaseous carbonyl chloride with water, thus producing said hydrogen chloride,
in particular, said water is present as steam in a reaction environment (50).

6. A process according to claim 5, wherein said steps of supplying said steam and of supplying said oxygen take place in turn, in particular they are consecutive with respect to each other.

7. A process according to claim 5, wherein said step (92,95) of supplying oxygen starts when said reaction temperature achieves a predetermined minimum value (T') and stops when said reaction temperature achieves a predetermined maximum value (T"), whereas said step (91,94) of supplying steam starts when said reaction temperature achieves said predetermined maximum value (T') and stops when said reaction temperature achieves said predetermined maximum value (T").
8. A process according to claim 5, wherein said steps of supplying said steam (97) and said oxygen (98) take place in turn with respect to each other according to a predetermined time program, and said sodium chloride solution starts to be supplied (98') into said reaction environment (50) when said reaction temperature achieves a predetermined maximum value (T') and stops to be supplied (97') when said reaction temperature achieves a predetermined minimum value (T').

9. A process according to claim 3, wherein said sodium hydroxide concentration of said solution (236") is higher than 40% by weight, more in particular, it is higher than 45% by weight, even more in particular, it is about 50% by weight.

10. A process according to claim 3, wherein said chloride-containing useful product is an aqueous solution of hydrochloric acid, and a step is provided (112) of absorbing said gas mixture (62) into an amount of water, such that an aqueous solution (67) of hydrochloric acid is obtained, in particular, said aqueous solution (67) has a concentration of 30% in hydrochloric acid, in particular, said amount of water has a predetermined content of mineral.

11. A process according to claim 9, wherein said step of absorption (112) is a first step of absorption (112), and a second step of absorption (113) is provided in which said gas mixture (62), as transformed in said first step of absorption, (112), is absorbed into an amount of a calcium hydroxide suspension, wherein said carbon dioxide interacts with said calcium hydroxide forming a suspension (69) of calcium carbonate.

12. A process according to claim 3, wherein said step (121) of washing said carbonaceous material (18") of said residue fraction and of forming said aqueous solution (72") of sodium hydroxide is carried out within a tubular apparatus (71) arranged to carry said carbonaceous material (18") of said residue fraction according to a conveying direction along said tubular apparatus (71), and said step of concentrating said aqueous sodium hydroxide solution comprises a step of feeding a stream of said water into said tubular apparatus in such a way that said stream of water flows along inside said tubular apparatus, wherein a same mass of said water is
repetitively recycled into said tubular apparatus (71), such that said water is enriched in said sodium hydroxide at each recycle passage, and said aqueous solution (72') of sodium hydroxide with a predetermined sodium hydroxide concentration is obtained, in particular, said water flowing along said tubular apparatus (71) countercurrently with respect to said movement direction said carbonaceous material (18") of said residue fraction.

13. A process according to claim 3 and 11, wherein said amount of a carbonaceous material (18') at a predetermined temperature is prepared by a partial combustion (130) of a corresponding amount of said carbonaceous material (18,86,74') having a predetermined grain size, in particular selected from the group consisting of:
   — said residue fraction (74') of said carbonaceous material that is subjected to said washing;
   — said carbonaceous waste (86) separated from said solution (72') of sodium hydroxide;
   — coke;
   — a combination thereof.

14. A process according to claim 3, wherein said step of bringing into contact (110) is carried out within a vertical container (50) that has a bottom portion (52) arranged to receive a layer i.e. a bed (53) of said carbonaceous material (18') at said predetermined reaction temperature, and wherein steps are contemporaneously carried out of:
   — spraying an upper surface of said bed (53) of said carbonaceous material (18') with said aqueous solution (17) of sodium chloride;
   — causing said steam to pass through said bed (53) of said carbonaceous material (18');
   — feeding said carbonaceous material (18') into said vertical container (50) and removing an amount of said residue fraction (18") of said carbonaceous material from said vertical container (50), in particular, said step of spraying is preceded by a step of nebulising said aqueous solution (17) of sodium chloride, in particular, said residue fraction (18") of said carbonaceous amount
having the same volume as said carbonaceous material (18') fed to said vertical container (50), such that said bed (53) is continuously renewed during said step of spraying.

15. A process according to claim 3, comprising a step of concentrating (230) of said sodium chloride contained in said liquid effluent (201), obtaining a concentrated solution (231') of sodium chloride.

16. A process according to claim 4, wherein said industrial liquid effluent (201) contains a sulphate, and said process comprises a step (220) of removing said sulphate, comprising a step (224) of bringing said liquid effluent (222') into contact with a precipitating agent (258') containing a salt of a first cation that is adapted to form a first precipitate of a substantially insoluble sulphate salt, in particular, said precipitating agent (258') containing barium chloride BaCl$_2$, whereby said first precipitate contains barium sulphate BaSO$_4$ in a mixture (224') comprising a chloride solution.

17. A process according to claim 16, comprising a step (270) of regeneration of said precipitating agent (258'), said step (270) of regeneration comprising steps of:
   — dissolving (251) said first precipitate (225''), wherein said first precipitate (225'') is treated with a carbonate of a second cation (255',265') adapted to form a second precipitate (252') of a carbonate of said first cation, and a solution (252'') of a sulphate of said second cation;
   — restoring (58) said precipitating agent (258') by treating said second precipitate (252') with a hydrogen chloride HCl-containing gas (249''), in particular consisting of at least of one amount of said reaction gas (233'') produced in said step of bringing said steam into contact with said reaction mixture, wherein said carbonate of said first cation of said second precipitate (252') is displaced by said hydrogen chloride to give carbon dioxide CO$_2$, such that a gas stream (258'') is formed that contains carbon dioxide,

In particular, said carbonate of said second cation (255',265') comprises sodium carbonate Na$_2$CO$_3$, whereby said solution (252'') of sulphate
contains sodium sulphate \( \text{Na}_2\text{SO}_4 \). 

18. A process according to claim 17, wherein said step (270) of regenerating also comprises steps of:
   — reaction (261) of said solution (252") of sulphate with a first alkaline hydroxide (207) of a third cation, to form a third precipitate (262') of a sulphate of said third ion and to form a solution (262") of a second hydroxide of said second ion;
   — absorption and reaction (265) of a first carbon dioxide-containing gas (266') into/with said solution (262") of said second hydroxide, to form a solution (265') of a carbonate of said second cation, in particular a solution of sodium carbonate \( \text{Na}_2\text{CO}_3 \); wherein said solution (265') of said carbonate of said second cation is used for treating said first precipitate (225") in said step of dissolving (251), in particular, said first alkaline hydroxide is calcium hydroxide \( \text{Ca(OH)}_2 \), whereby said third precipitate (262') contains calcium sulphate \( \text{CaSO}_4 \) and said second hydroxide contains sodium hydroxide \( \text{NaOH} \).

19. A process according to claim 18, wherein said first carbon dioxide-containing gas (266') comprises at least one own portion selected from the group consisting of:
   — a portion of said reaction gas (233") produced in said step of bringing said steam into contact with said reaction mixture;
   — a portion of said carbon dioxide-containing gas stream (258") formed in said step of restoring (258) said precipitating agent.

20. A process according to claim 18 wherein a step is provided (263) of treating said third precipitate (262') with a predetermined amount of an additive (208) adapted to turn said third precipitate (262') into a further useful product (263'), in particular, said additive (208) is ammonium sulphate \( \left(\text{NH}_4\right)_2\text{SO}_4 \) and said further useful product is an aqueous solution (263'), containing a soluble complex of formula \( \left(\text{NH}_4\right)_2\text{SO}_4\cdot\text{CaSO}_4\cdot\text{H}_2\text{O} \), which can work as a fertiliser.

21. A process according to claim 15, wherein said washing liquid (237") comprises an amount (231") of said sodium chloride concentrated solution (231') obtained during said step (230) of concentrating, whereby said step
(234) of washing causes a crystallization of said sodium chloride of said amount (231") of said concentrated solution (231'), during which a crystalline solid is formed that contains sodium chloride, while an amount of sodium chloride remains in solution at a concentration lower than or equal to a predetermined value, in particular lower than or equal to 1%.

22. A process according to claim 20, comprising also a step of feeding said substantially solid material (235") to said step (240) of contact of said steam with said reaction mixture, in order to assist the formation of said reaction mixture.

23. A process according to claim 1, wherein said step (260) of prearranging a carbonaceous material (246') comprises a proliferation step (246) of an initial amount of an alga (245'), such that a proliferated amount of said alga (246') is obtained that contains said carbonaceous material, said proliferation step (246) comprising a step of bringing into contact a second carbon dioxide-containing gas (243",247") with said initial amount of an alga (245'), in particular said second gas consisting of an amount (243",247") of said reaction gas (233"), said step of bringing into contact comprising a step selected from the group consisting of:

- absorption (245) of said second carbon dioxide-containing gas (243") into an aqueous suspension (245') of said initial amount of an alga before feeding said aqueous suspension (245') of said initial amount of an alga to a proliferation reactor (346),
- in particular, said absorption increasing the concentration of carbon dioxide in said aqueous suspension (245') up to a value of substantial saturation;
- dosing said second carbon dioxide-containing gas (247') at a plurality of feed points of a tubular proliferation reactor (601), in order to maintain the concentration of said carbon dioxide at a predetermined value while carbon dioxide is consumed due to the proliferation reaction, in particular to maintain a value of substantial saturation,
- a combination of said absorption and of said dosage.

24. A process according to claim 23, wherein said step proliferation (346) of an alga comprises the steps of:
— introducing (601') a suspension (246') that contains a lower alga content into a container (601) provided with an inner reflecting surface;
— internally lighting (603) said tubular body (601), in particular by means of optical fibres, for example optical fibres supplied by sunlight
— supplying carbon dioxide into said container;
— extracting (601") a suspension (245") that contains a higher content of said alga.

25. A process according to claim 1, wherein a step is provided (250) of treating said reaction gas (233"), said step (250) of treating comprising a step selected from the group consisting of:
— a step (243) of bringing said reaction gas (241") into contact with an aqueous liquid (242"), wherein a useful aqueous chloride-containing solution (243') is obtained and a carbon dioxide-containing gas (243") is released,
— a step (241) of cooling and condensation, wherein an amount of condensation water (241') is obtained along with a mixture of non-condensables (241") including hydrogen chloride and carbon dioxide,
— a combination thereof.

26. A process according to claim 25, wherein said aqueous liquid (242") fed is a lime solution or suspension Ca(OH)2 and said step (243) of obtaining a useful solution comprises a step of converting the calcium hydroxide into calcium chloride CaCl2, forming a calcium chloride solution that has anti-icing properties,
in particular, said step (250) of treating said reaction gas comprises a step (244) of adding and mixing an additive (2205) to/in said solution of calcium chloride (243') in order to control the chemical aggressiveness and/or the slipperiness of said solution of calcium chloride,
in particular, said additive is selected among triethanolamine; glycerine; a combination of triethanolamine and glycerine.

27. A process according to claim 15, wherein said step of concentrating (230) comprises:
— a step of reverse osmosis (228) of said liquid effluent (225') to obtain a
solution (231') of sodium chloride having a first concentration, in particular a concentration of about 15% by weight;
— a subsequent step (229) of evaporating said solution (231') of sodium chloride at said first concentration, said step of evaporating comprising a step of transferring the heat generated in an exothermic step selected from the group consisting of:
— said step (241) of cooling and condensation of said reaction gas (233');
— said step (243) of bringing said mixture of non-condensables (241") into contact with said aqueous liquid (242');
— said step (245) of absorbing a carbon dioxide-containing gas (243") into said aqueous suspension (245') of said initial amount of an alga;
— said step (258) of restoring said precipitating agent (258') by treating said second precipitate (252') with a hydrogen chloride-containing gas (249'');
— a combination of the above exothermic steps (241,243,245,258), such that a solution (231'') of sodium chloride is obtained that has a second predetermined concentration higher than said first concentration, set between 20% and 26%, in particular said second concentration is about 25% by weight.

28. A conversion reactor (333) for converting a solution (231') of sodium chloride and a carbonaceous material (246') into a solution (236'') of sodium hydroxide that has a predetermined concentration, and into a reaction gas (233'') that contains hydrogen chloride, carbon dioxide and steam, wherein a treatment chamber (500) is provided that has an inlet section (500') and an outlet section (500''), said conversion reactor (333) comprising:
— a conveying means (501) arranged between said inlet section (500') and said outlet section (500''), said conveying means comprising a conveyor belt (502), said conveyor belt (502) having a hold-up structure wherein spaces are defined for retaining a liquid, in particular said hold-up structure selected between a porous structure and a network or mesh structure,
said conversion reactor (333) also comprising, along said conveyor belt (502):

— a distribution means (511) of a mixture (232’) of said sodium chloride solution (231’) and of said carbonaceous material (246’) on said conveyor (502), in order to form a reaction bed of a reaction mixture (232’);

— an air feed means (521,531,531’) for feeding hot air to said conveyor belt (502), in particular said feed means arranged laterally of and below said conveyor belt (502),

— a steam feed means (532,532’) for feeding steam, in particular arranged at an upwards-facing portion (502’) of said conveyor belt (502),

so that, by operating said conveyor belt (502), the reaction mixture (232’), retained within said spaces of said hold-up structure, reaches and maintains a predetermined reaction temperature, in particular a reaction temperature set between 500°C and 600°C, more in particular, a reaction temperature of about 550°C, and gives rise to chemical reactions by which said reaction gas (233’) is produced while said reaction bed, on said conveyor belt (502), turns into a reaction residue that comprises a carbonaceous residue associated with sodium oxide Na₂O,

in particular, said hot air feed means is arranged below said steam feed means,

— a gas extraction means for extracting said reaction gas, in particular said gas extraction means arranged in an upper portion of said treatment chamber (500), so that said hot air and said steam flow through said reaction bed in said conveyor belt (502),

— a spray means for spraying (541,542) said reaction residue with a washing liquid (237’).

29. A conversion reactor (333) according to claim 28, comprising, at said spray means (541,542), a steam suction means for sucking (533) the steam generated when spraying said reaction residue with said washing liquid (237’).
30. A conversion reactor (333) according to claim 29, wherein said feed means (532,532') of steam is in pneumatic communication with said suction means (533), in order to distribute said steam generated when spraying said reaction mixture (232').

31. A conversion reactor (333) according to claim 29, comprising one or more dividing wall/s (529,539) that are arranged transversally with respect to said conveyor belt (502) and are provided with tight passages for said conveyor belt (502), said one or more dividing wall/s defining distinct treatment rooms (510,520,530,540) in said treatment chamber (500), in particular, said dividing walls defining a reaction room or zone (530) in which said hot air feed means (521,531,531') and said steam feed means (532,532') are arranged, said reaction room tightly separated from
— a preheating and reaction room in which said steam feed means (532,532') are not present, and
— a washing room (540) in which said spray means (541,542) are arranged.

32. A continuous process according to claim 1, for treating an industrial waste (281) that contains sodium chloride solid and for obtaining a solution of caustic soda (236") and a containing-chloride useful product (243'), said process comprising the steps of:
— prearranging (260) said carbonaceous material (246');
— forming said reaction mixture (379') of said solid sodium chloride-containing industrial waste (281) and of said carbonaceous material (246');
— feeding (279) said reaction mixture (379') into a reaction chamber (383',701') of an oven selected between a rotating oven (383) and a belt oven (700);
— converting (283) said mixture (379') into a solution (236") of sodium hydroxide that has a predetermined concentration and into a reaction gas (283") containing hydrogen chloride, carbon dioxide and steam, said step of converting comprising:
— a step (284) of reaction, which is carried out within said reaction
chamber (383',701'), of said reaction mixture (379') in the presence of air and of steam (234''), to obtain a raw reaction product (233') that contains sodium oxide Na₂O and a carbonaceous residue;

— a step (234) of washing said raw reaction product (233') with a water-containing washing liquid (237'), wherein said sodium oxide is transformed into sodium hydroxide, and said sodium hydroxide form a heterogeneous mixture (234') of said solution (236'') of sodium hydroxide and of said carbonaceous residue (235'').
Fig. 13

WASTE
\( \rightarrow 201 \)

NaOH / HCl
\( \rightarrow 202 \)

INORG. SOLIDS
\( \rightarrow 222'' \)

ORGANIC MAT.
\( \rightarrow 222'' \)

pH CONTROL
\( \rightarrow 221 \)

SOLID / LIQUID SEPARATION
\( \rightarrow 222' \)

\((\text{NaCl, NaSO}_4)\)

HCl
\( \rightarrow 203 \)

pH CONTROL
\( \rightarrow 223 \)

SULPHATE PRECIP.
\( (\text{reaction [II]}\) \)
\( \rightarrow 224' \)

SOLID / LIQUID SEPARATION
\( \rightarrow 225' \)

SULPHATES (sol.)
\( (\text{BaSO}_4(s)) \)

\((\text{NaCl 1-2\\%})\)

SOLUTION
\( \rightarrow 225'' \)