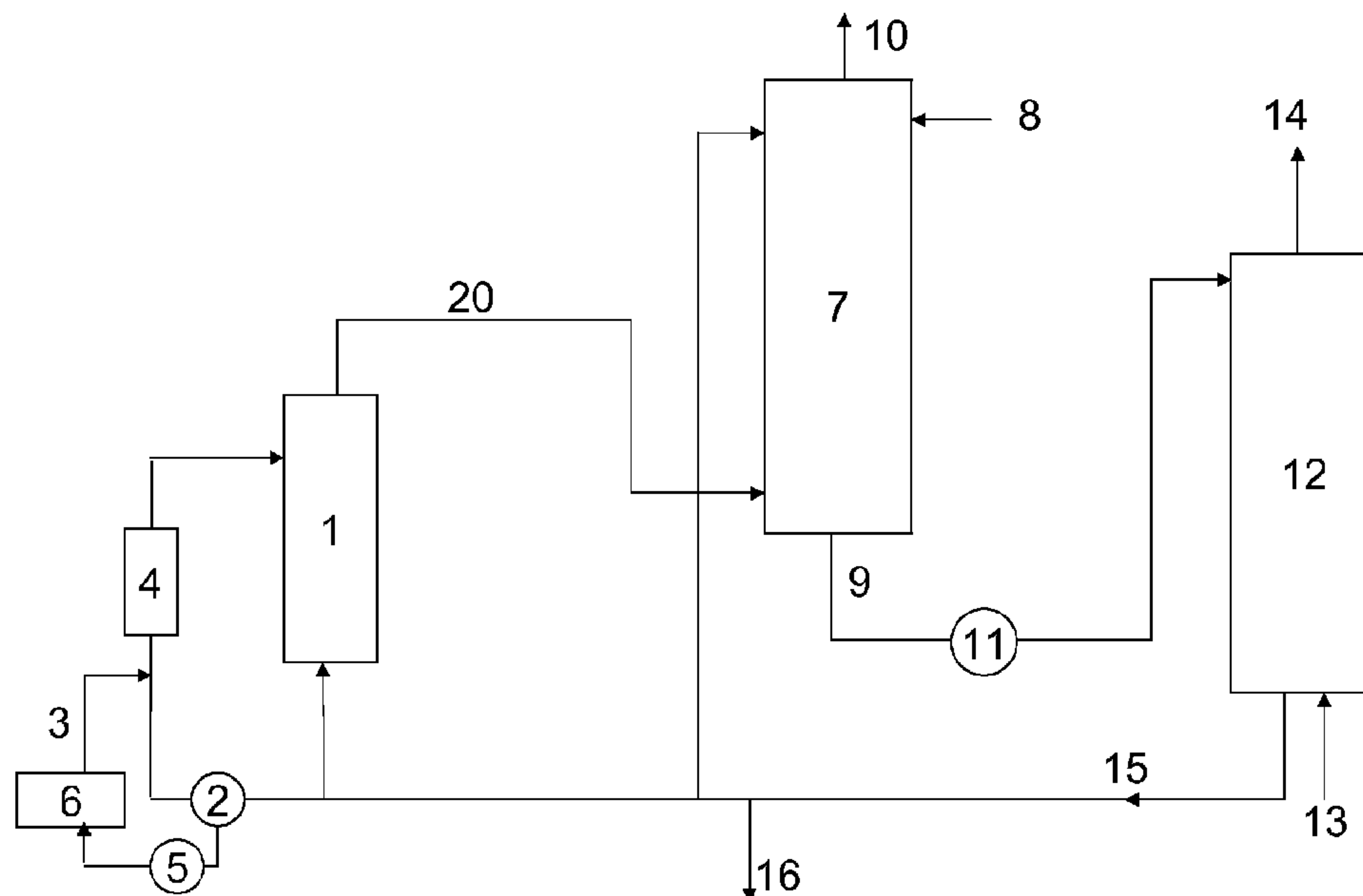




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(54) Title: PROCESS FOR THE PRODUCTION OF CHLORINE DIOXIDE



(57) Abrégé/Abstract:

Process for the continuous production of chlorine dioxide comprising generating chlorine dioxide in an aqueous reaction medium in a reaction vessel (1) maintained at sub-atmospheric pressure, bringing gaseous chlorine dioxide from said reaction vessel to an absorption tower (7) and contacting it therein with a flow of water to form an aqueous solution containing chlorine dioxide, bringing said aqueous solution containing chlorine dioxide to a stripper (12), blowing a gas through said aqueous solution of chlorine dioxide in the stripper to strip off from 10 to 100% of the chlorine dioxide entering the stripper and form a gaseous chlorine dioxide product.

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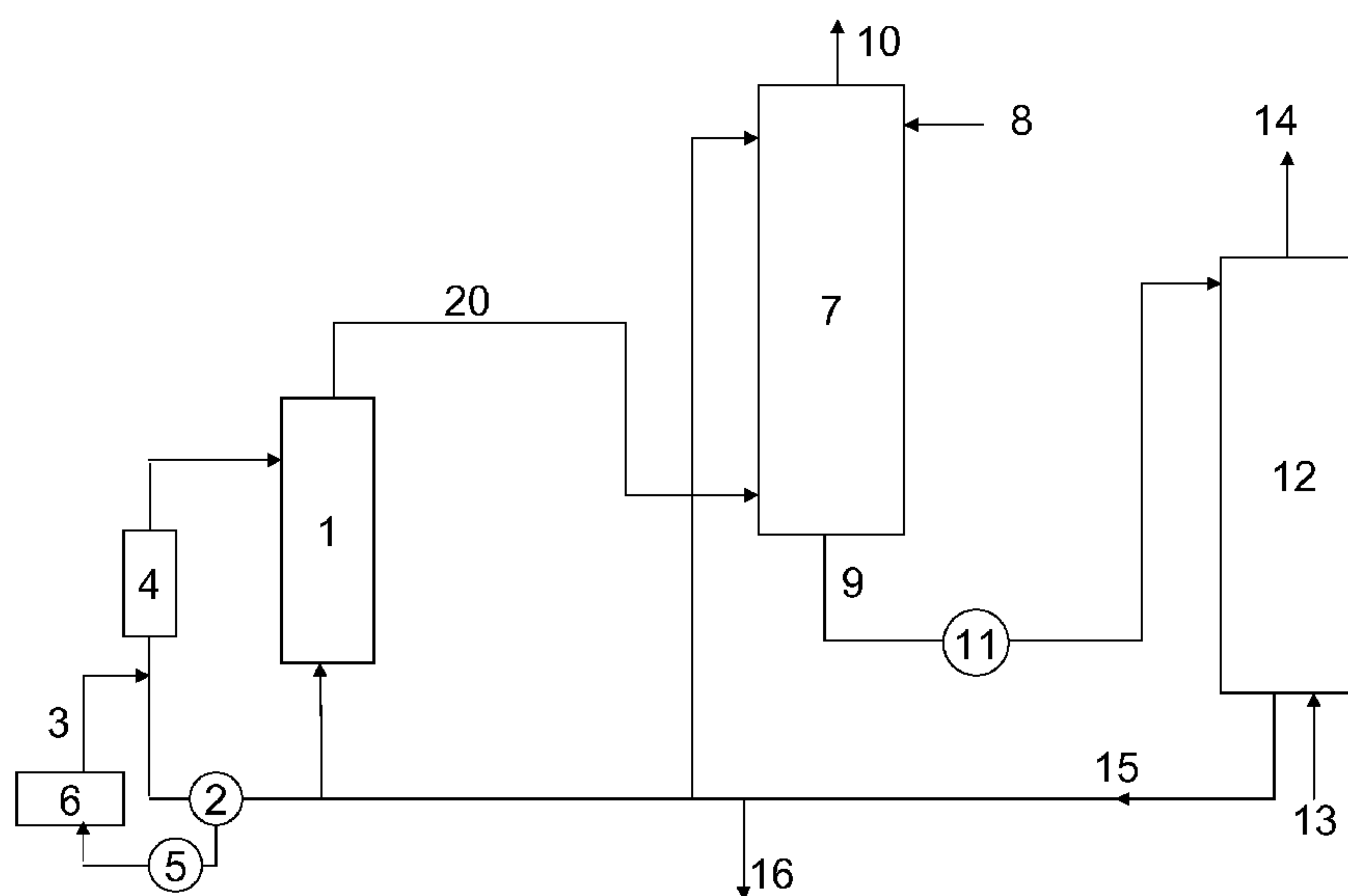


Fig. 1

(57) Abstract: Process for the continuous production of chlorine dioxide comprising generating chlorine dioxide in an aqueous reaction medium in a reaction vessel (1) maintained at sub-atmospheric pressure, bringing gaseous chlorine dioxide from said reaction vessel to an absorption tower (7) and contacting it therein with a flow of water to form an aqueous solution containing chlorine dioxide, bringing said aqueous solution containing chlorine dioxide to a stripper (12), blowing a gas through said aqueous solution of chlorine dioxide in the stripper to strip off from 10 to 100% of the chlorine dioxide entering the stripper and form a gaseous chlorine dioxide product.

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PROCESS FOR THE PRODUCTION OF CHLORINE DIOXIDE

The present invention relates to a process for the production of chlorine dioxide enabling generation of gaseous chlorine dioxide at selected pressure.

There are numerous different processes for chlorine dioxide production. Most large
5 scale processes in commercial use are run at pulp mills and involve continuous reaction of alkali metal chlorate in an acidic reaction medium with a reducing agent such as hydrogen peroxide, methanol, chloride ions or sulfur dioxide to form chlorine dioxide that is withdrawn as a gas from the reaction medium and then absorbed in water. An overview of such processes can be found in "Pulp Bleaching - Principles and Practice", TAPPI PRESS
10 1996, Section II: Raw Materials, Chapter 2: Bleaching Chemicals: Chlorine Dioxide, p. 61-69.

As an example, in one series of processes the reaction medium is maintained under non-crystallising conditions, generally at substantially atmospheric pressure. In most cases depleted reaction medium from a first reaction vessel is brought to a second reaction
15 vessel for further reactions to produce chlorine dioxide. Depleted reaction medium withdrawn from the final reaction vessel, usually referred to as residual acid, contains acid, alkali metal salt of the acid and normally some unreacted alkali metal chlorate. Examples of non-crystallising chlorine dioxide generation processes are described in EP 612686, WO 2006/033609, JP 03-115102 and JP 88-008203.

20 In another series of processes the reaction medium is maintained in a single reaction vessel under boiling conditions at subatmospheric pressure, wherein alkali metal salt of the acid is precipitated and withdrawn as a salt cake. Examples of such processes are described in US patents 5091166, 5091167, 5366714 and 5770171, and in WO 2006/062455. Such processes are usually the most efficient ones for large scale
25 production of chlorine dioxide, and are generally referred to as single vessel processes (SVP). Usually methanol or hydrogen peroxide is used as reducing agent, which avoids formation of significant amounts of chlorine as a by-product.

When producing chlorine dioxide from alkali metal chlorate with chloride as a reducing agent, high amounts of chlorine is obtained as a by-product. It has then been
30 disclosed in e.g. US patents 4086329, 5324497 and 2108976 to purify the chlorine dioxide from chlorine by various unit operations, including absorption and stripping.

Chlorine dioxide is normally used as an aqueous solution obtained in the production process, particularly in pulp bleaching. It has also been disclosed to use chlorine dioxide in gas phase, for example for removing lignin from wood chips as described in US
35 patents 6569285 and 6752904, or for treatment of flue gas as described in e.g. US patent 3023076.

WO 2009/010456 discloses a process for producing gaseous chlorine dioxide in a reaction vessel maintained at super-atmospheric pressure by bringing withdrawn gaseous chlorine dioxide to an aqueous absorption medium and withdrawing gaseous chlorine dioxide from the absorption medium.

5 It would be advantageous to be able to provide a process run at sub-atmospheric pressure that is attractive for producing chlorine dioxide to be used in gas phase at selected pressure. Due to stability problems it is difficult to store gaseous chlorine dioxide and those processes in which chlorine dioxide is withdrawn from the reaction medium as a gas are difficult to control sufficiently rapidly to meet variations in the demand, whereby a
10 liquid storage tank is necessary. It would also be advantageous to be able to provide a process to produce gaseous chlorine dioxide at sub-atmospheric pressure having low concentrations of by-products such as chloride, chlorate and sulfate ions.

It is an object of the present invention to provide an efficient process for the production at subatmospheric pressure of chlorine dioxide that is suitable for
15 applications in which gaseous chlorine dioxide is used.

According to the present invention there is provided a very efficient process for producing chlorine dioxide run at sub-atmospheric pressure and it has surprisingly been found that the process may be used to produce gaseous chlorine dioxide of high purity and obtained at a desired pressure, which is otherwise very difficult to achieve.
20 Accordingly, the present invention concerns a process for the continuous production of chlorine dioxide comprising generating chlorine dioxide in an aqueous reaction medium in a reaction vessel maintained at sub-atmospheric pressure, bringing gaseous chlorine dioxide from said reaction vessel to an absorption tower and contacting it therein with a flow of water to form an aqueous solution containing chlorine dioxide, bringing said
25 aqueous solution containing chlorine dioxide to a stripper, blowing a gas through said aqueous solution of chlorine dioxide in the stripper to strip off from 10 to 100% of the chlorine dioxide entering the stripper and form a gaseous chlorine dioxide product.

The present invention also concerns a process for the continuous production of chlorine dioxide comprising generating chlorine dioxide in an aqueous reaction medium
30 in a reaction vessel maintained at sub-atmospheric pressure, bringing gaseous chlorine dioxide from said reaction vessel to an absorption tower and contacting the gaseous chlorine dioxide therein with a flow of water to form an aqueous solution containing chlorine dioxide, bringing said aqueous solution containing chlorine dioxide from the absorption tower to a stripper, wherein the pH of the aqueous solution containing
35 chlorine dioxide is from about 6.5 to 7.8, blowing a gas through said aqueous solution of

2a

chlorine dioxide in the stripper to strip off from 10 to 100% of the chlorine dioxide entering the stripper and form a gaseous chlorine dioxide product obtained from the stripper with a partial pressure of from 0.5 to 20 kPa.

The present invention also concerns a process for the continuous production of chlorine dioxide comprising generating chlorine dioxide in an acidic aqueous reaction medium in a reaction vessel maintained at sub-atmospheric pressure, bringing gaseous chlorine dioxide from said reaction vessel to an absorption tower and contacting the gaseous chlorine dioxide therein with a flow of water to form an aqueous solution containing chlorine dioxide, bringing said aqueous solution containing chlorine dioxide from the absorption tower to a stripper, wherein the pH of the aqueous solution containing chlorine dioxide is from about 6.5 to 7.8, blowing a gas through said aqueous solution of chlorine dioxide in the stripper to strip off from 10 to 100% of the chlorine dioxide entering the stripper and form a gaseous chlorine dioxide product obtained from the stripper with a partial pressure of from 0.5 to 20 kPa, wherein the gaseous chlorine dioxide product has a content of elemental chlorine less than 1 wt%.

The chlorine dioxide may, for example, be generated as described in the earlier mentioned US patents 5091166, 5091167, 5366714 and 5770171, and WO 2006/062455.

The chlorine dioxide is preferably generated by reducing chlorate ions by means of a chemical reducing agent. Any known reducing agent may be used alone or in mixtures, such as at least one of chloride ions, sulfur dioxide, methanol and hydrogen peroxide, of which methanol and hydrogen peroxide, alone or in mixture with one or more other reducing agents, are particularly preferred.

The pressure and the temperature are preferably set so to evaporate water from the reaction medium to dilute the chlorine dioxide formed and withdrawn from the reaction medium and brought from the reaction vessel. Preferably the reaction medium is maintained

at a temperature from about 15 to about 100°C, most preferably from about 30 to about 85°C. Suitably the reaction medium is maintained at an absolute pressure from about 8 to about 80 kPa, preferably from about 8 to about 55 kPa, most preferably from about 10 to about 50 kPa. Preferably the reaction medium is maintained at its boiling point at the
5 prevailing pressure.

As the evaporation of water from the reaction medium normally consumes more energy than generated in the process, this is preferably balanced by supplying heat to the reaction medium, for example by circulating reaction medium through a heater in a circulation conduit. Any kind of heater may be used, such as heat exchangers heated by
10 steam or any other hot fluid medium.

Any alkali metal chlorate may be used, such as chlorate of sodium, potassium or mixtures thereof. Normally sodium is preferred. It is also possible to feed the alkali metal chlorate as a pre-mixed solution with the hydrogen peroxide. The concentration of alkali metal chlorate maintained in the reaction medium may vary within wide limits, for example
15 from about 0.25 moles/dm³ up to saturation, preferably from about 1.5 moles/dm³ up to saturation, most preferably from about 2.5 moles/dm³ up to saturation.

The aqueous reaction medium in the reaction vessel is preferably acidic, for example having an acidity from about 0.5 to about 12 N or from about 1 to about 10 N, most preferably from about 1.5 to about 7 N. The acidity may be provided by feeding any
20 suitable acid, preferably a mineral acid. Examples of acids include sulfuric acid, hydrochloric acid, phosphoric acid and chloric acid, of which sulfuric acid is particularly preferred.

If sulfuric acid is used, it is preferably fed at a concentration from about 30 to about 98 wt%, most preferably from about 60 to about 85wt%. Sulfuric acid of low concentration is
25 easier to mix with the reaction medium, but a high concentration gives the advantage of utilisation of the heat of dilution and not needing to evaporate a lot of water. The amount fed is preferably balanced to the amount of chlorate fed in order to arrive at a steady state concentration in the generator suitable for the reducing agent chosen.

If hydrogen peroxide is used as reducing agent, it is preferably fed in an amount
30 from about 0.5 to about 2 moles per mole alkali metal chlorate fed, most preferably from about 0.5 to about 1 mole per mole alkali metal chlorate fed, particularly most preferably from about 0.5 to about 0.6 moles per mole alkali metal chlorate fed.

If methanol is used as reducing agent, it is preferably fed in an amount from about 0.2 to about 1 moles per mole alkali metal chlorate fed, most preferably from about 0.2 to
35 about 0.8 mole per mole alkali metal chlorate fed, particularly most preferably from about 0.2 to about 0.4 moles per mole alkali metal chlorate fed.

It is preferred to operate the process under conditions to obtain precipitation of solid alkali metal sulfate in the reaction medium. Depending on the acidity of the reaction medium, substantially neutral sulfate or acidic sesquisulfate may form. However, it is also possible to operate the process under such conditions that no formation of solid alkali metal sulfate
5 occurs.

At least some of the alkali metal sulfate formed is normally withdrawn, preferably as a solid salt cake which may be removed on a conventional filter, and may in some cases be used as a by-product. However, it is also possible to electrochemically acidify some of the alkali metal sulfate and recycle it to the reaction medium to replace some of the sulfuric acid
10 feed. Such electrochemical acidification is described in e.g. US patents 4129484, 5478446, 5487881, 5858322 and 632269.

Gaseous chlorine dioxide gas is withdrawn from the reaction medium, preferably together with evaporated water and optionally other gaseous components formed or added, such as oxygen in case hydrogen peroxide is used as reducing agent. The
15 concentration of chlorine dioxide in the withdrawn gas is preferably maintained at a partial pressure from about 1 to about 30 kPa or from about 5 to about 10 kPa. The total pressure is also made up from the amount of water vapor and soluble and insoluble gases.

High system utilisation may, depending on the reaction vessel design, result in a
20 co-transportation of reaction medium as aerosols, thereby bringing electrolytic components to the absorption tower together with the chlorine dioxide. Such component, for example sodium chlorate or sodium sulfate, may in the present invention be separated from the final gaseous chlorine dioxide product.

The gaseous chlorine dioxide withdrawn from the reaction medium is brought to
25 an absorption tower where it is contacted with a flow of water to form an aqueous solution containing chlorine dioxide. By the term "absorption tower", as used herein, is meant any column or tower or the like where gas is contacted with a liquid flow to absorb water soluble compounds therein. Gas and liquid preferably flow counter-currently. Inside the absorption tower devices such as plates or packing elements are preferably placed to
30 provide interfacial surfaces where the mass transfer between the gas and the liquid can take place. Any conventional packing elements and plates can be used such as Raschig rings, Berl saddles, Intalox saddles, sieve plates and bubble cap plates.

In an embodiment, the absorption tower is specially adapted for processes using chloride ions as reducing agents. Such an absorption tower is described in Barr, A.
35 et al., *The development of an integrated chlorine dioxide process to produce chlorine dioxide solution with low chlorine content*, Appita J., Vol 59, No. 6, (2006) .

The chlorine dioxide concentration in the aqueous solution obtained from the absorption tower is preferably from about 5 to about 18 g/dm³, or from about 8 to about

12 g/ dm³. The temperature is preferably from about 0 to about 35°C, or from about 5 to about 25°C.

The pH of the aqueous solution obtained from the absorption tower can vary within a wide range, partly dependent on the chlorine dioxide concentration, such as from about 0.8 to about 3.2. If methanol is used as reducing agent, the pH is preferably from about 1.0 to about 2.5, while if hydrogen peroxide is used as reducing agent, the pH is preferably from about 2.0 to about 3.2.

In an embodiment of the invention, the aqueous solution in the absorption tower is acidified to suppress the absorption of elemental chlorine and possibly present formic acid by decreasing the chlorine hydrolysis and depressing the deprotonation of formic acid. Elemental chlorine and formic acid are then brought with the off gas from the absorption tower and are thus separated from the chlorine dioxide. The pH in the chlorine dioxide solution is preferably kept as low as possible or at least below pH 2 and most preferably below pH 1.4. Adjustment of pH can be made by any acid, but preferably sulfuric or hydrochloric acid is used.

In an embodiment of the invention, the pH of the aqueous chlorine dioxide solution leaving the absorption tower is increased to from about 6.5 to about 7.8, which decreases the release of volatile by-products from the chlorine dioxide generation process during the following stripping. Adjustment of the pH can be made by any alkali source, but preferably sodium hydroxide is used.

A very high yield of chlorine dioxide with respect to the amount of added chlorate ions may be obtained in the gas stream leaving the stripper. Such a yield may be from 96 % , preferably from 98 % , most preferably from 99 % with respect to the amount of added chlorate ions.

By the above arrangement, it has been found possible to produce chlorine dioxide without employing a liquid storage tank. Such a storage tank is not only an expensive investment, it also takes up a large space, requires extensive safety measures to be taken and chlorine dioxide may be lost due to reactions therein.

Non-absorbed gas departed from the absorption tower, containing for example inert gas, oxygen and water vapor and small amounts of chlorine dioxide, may be used for various purposes like flue gas treatment as described in e.g. US patents 3023076 and 7118720, and in WO 2007/058936. The chlorine dioxide may otherwise be scrubbed off in a scrubber.

The aqueous solution containing chlorine dioxide is brought from the absorption tower to a stripper, wherein from 10 to 100% of the chlorine dioxide is stripped off by blowing a gas through the aqueous chlorine dioxide solution to form a gaseous chlorine dioxide product. By the term "gaseous chlorine dioxide product", as used herein, is meant

the gas leaving the stripper. Apart from chlorine dioxide the gaseous chlorine dioxide product may comprise any non-absorbed part of the gas blown through the aqueous solution in the stripper. Any type of stripper, or stripper column, may be used, for example filler columns and packed columns. Any conventional packing elements may be used, 5 such as structured packing, Raschig rings, Berl saddles, Intalox saddles etc.

The gas used for stripping is preferably an inert gas. Any available inert gas such as nitrogen or oxygen can be used, but for cost reasons it is usually preferred to use air. If the application allows, it may be possible to recover the inert gas and reuse it in the stripper.

10 In an embodiment, part, or all, of the aqueous solution from the stripper may be recirculated to the absorption tower, in order to recover any remaining chlorine dioxide. The recirculation rate of depleted aqueous solution may be from about 0% to about 100%, preferably from about 70% to about 90%. The recirculation rate determines the desired desorption efficiency of the stripper. Preferably from 40 to 95% or from 85% to 15 95%, of the chlorine dioxide entering the stripper may be stripped off.

It is also possible to recirculate the aqueous solution from the stripper to the reaction vessel to convert any remaining chlorate or any other reactants to chlorine dioxide. Such part of the aqueous solution may be from about 10 to about 80 %, preferably from about 10 to about 30 %.

20 In an embodiment of the invention, the aqueous chlorine dioxide solution from the absorption tower may be heated in order to enhance the desorption in the stripper. In a further embodiment, the depleted aqueous solution from the stripper may be cooled before it is recirculated to the absorption tower. This may be done by use of any heating or cooling media available or by use of a heat pump.

25 In an embodiment, the gaseous chlorine dioxide product from the stripper is maintained at a total absolute pressure from about 10 kPa to about 2 MPa, such as from about 95 kPa to about 2 MPa or 105 kPa to 1 MPa.

The gaseous chlorine dioxide product obtained from the stripper may have a partial pressure of chlorine dioxide from about 0.5 kPa to 20 kPa, or from about 4 kPa to 30 about 12 kPa. If the partial pressure of chlorine dioxide is too high the risk for rapid decomposition of chlorine dioxide is imminent.

A desired pressure may be achieved by maintaining the bottom of the absorption tower at a height relative a pump bringing the aqueous chlorine dioxide to the stripper, 35 thus forming a stand pipe. By this arrangement, it is possible to control the pressure of the formed gaseous chlorine dioxide in the stripper. When gaseous chlorine dioxide is used e.g. for flue gas treatment, the chlorine dioxide is preferably contained in a gas

having a pressure above atmospheric in order to be able to be led to the flue gas. Thus, the pressure can be increased by increasing the selected height between the pump and the bottom of the absorption tower. Such a height may be from 5 m, or 10, or 15 m up to 50 m, depending on the pressure desired. However, if no such pressure control is applied, it is also possible to maintain the pressure below atmospheric, if this is preferred in the process. A stand pipe may similarly be formed by selecting the height of the bottom of the reaction vessel in relation to the pump. The desired pressure may also be achieved by using a pressure control valve after the stripper, allowing a pump to increase the pressure of the gaseous chlorine dioxide. Such a pressure control valve is needed both on the gas outlet and the residual solution. Hence, the stripper may be situated on the ground floor.

In an embodiment the process is operated so the gaseous chlorine dioxide product has a content of elemental chlorine less than about 1 wt %, more preferably less than 0.2 wt % of the total active chlorine.

In an embodiment the process is operated so the gaseous chlorine dioxide product may be essentially free from electrolytic impurities as chlorate and sulfate when leaving the stripper, or may have a content of chlorate and sulfate less than 0.1 mg sodium chlorate or sodium sulfate per normal cubic meter dry gas, respectively

In an embodiment the process is operated so the gaseous chlorine dioxide product leaving the stripper has a content of formic acid less than about 100 mg formic acid per normal cubic meter dry gas, or more preferably less than 1 mg formic acid per normal cubic meter dry gas.

Due to the absorbing, gases not soluble in water are not obtained in the aqueous solution containing chlorine dioxide. The stripping further increases the purity of the gaseous chlorine dioxide product. As a result, the gaseous chlorine dioxide product has a high purity in respect of raw materials and unwanted by-products which can be carried out together with the gas stream from the reaction vessel.

In an embodiment of the invention, an aqueous chlorine dioxide product is obtained by bringing the gaseous chlorine dioxide product to another absorption tower to form an aqueous chlorine dioxide product of the above mentioned high purity. Conditions for the absorption tower may be as described above.

In case of interruption of the chlorine dioxide generation, the demand for gaseous chlorine dioxide may still be satisfied for some time by blowing inert gas through the aqueous chlorine dioxide solution and thereby stripping off chlorine dioxide.

An embodiment of the invention will now be described in connection with the appended Figure showing a schematic flow diagram thereof. The invention is, however, not limited to the embodiment shown.

Referring to the Figure, an SVP[®] process for the production of a gaseous chlorine dioxide product according to the invention is schematically shown. A reaction vessel 1 holds a reaction medium under subatmospheric pressure. The reaction medium is circulated by a pump 2 through a circulation conduit 3 and a heater 4 (commonly called “reboiler”) and back to the reaction vessel 1 at a rate sufficient for keeping the temperature of the reaction medium at the boiling point. A sodium chlorate, sulfuric acid and a reducing agent such as methanol or hydrogen peroxide, are fed to the reaction vessel and reacted to form chlorine dioxide, sodium sulfate and, in case hydrogen peroxide is used, oxygen. Chlorine dioxide is withdrawn as a gas 20 together with evaporated water and optionally oxygen and is brought to an absorption tower 7. Sodium sulfate precipitates as a substantially neutral or acidic salt, depending on the acidity of the reaction medium. By a pump 5, reaction medium is circulated through a filter 6 to separate and withdraw the solid sodium sulfate.

In the absorption tower 7 the gaseous chlorine dioxide is contacted with a flow of water 8 to form an aqueous solution containing chlorine dioxide 9. Any non absorbed gas 10 will exit at the top of the absorption tower 7. The aqueous chlorine dioxide departs from the absorption tower 7 and is led by a pump 11 to a stripper 12. A gas 13, preferably an inert gas, usually air, is supplied to the bottom of the stripper 12 to strip off at least 10% chlorine dioxide entering the stripper 12 as a gaseous chlorine dioxide product 14 departing from the top of the stripper 12. an aqueous solution 15, in which part of the chlorine dioxide may remain, is withdrawn from the bottom of the stripper 12 and may fully or partially be recirculated to the absorption tower 7 or the reaction vessel 1. A stream purge 16 might be appropriate in order to maintain the water balance, depending on parameters such as the choice of chemistry, the outlet gas pressure and temperature, the choice of operating conditions in the chlorine dioxide generation and the operating conditions in the stripper. Depending on the operating conditions in the stripper, this stream 16 may contain various amounts of chlorine dioxide and should be treated accordingly. There might also be a demand for an aqueous chlorine dioxide solution for other purposes at the same site. It is then possible to use aqueous chlorine dioxide from the absorber 7, for example by taking out a side stream (not shown) departing from stream 9.

If there is an interruption in the generation of chlorine dioxide in the reaction vessel, the gas flow through the stripper may be continued to strip off chlorine dioxide from the stripper.

As an example of operating conditions when producing chlorine dioxide from sodium chlorate, sulfuric acid and hydrogen peroxide at a pressure of 25 kPa, the aqueous reaction medium in the reaction vessel 1 may contain about 150 g/ dm³ NaClO₃

and about 340 g/ dm³ H₂SO₄, while the gas leaving the reaction vessel may contain about 15-60% v/v of ClO₂. The aqueous solution containing chlorine dioxide obtained in the absorption tower 7 may then have a temperature of about 10°C and contain about 10 g/ dm³ ClO₂.

- 5 The partial pressure of the gaseous chlorine dioxide product obtained from the stripper 10 may be about 6 kPa and the total pressure of the gas stream leaving the stripper may be 105 kPa absolute.

Example: Chlorine dioxide was produced by reduction of chlorate in an SVP[®] process reactor operated at 25.5 kPa and 75 °C. Gas comprising chlorine dioxide was led from the reactor to an absorption tower, where it was contacted with a flow of water to form an aqueous solution containing chlorine dioxide. The aqueous solution containing chlorine dioxide obtained had a temperature of about 12°C and contained about 8-9 g/dm³ ClO₂. The aqueous solution was then led to a stripper, where gaseous chlorine dioxide was stripped off, having a partial pressure of about 6 kPa and a total absolute pressure of 25 kPa. A set of experiment was carried out using a pilot scale stripper column, 4.5 m height, with random packing in two 1.5 m beds. In the referred experiments, chlorine dioxide solution containing 8-9 g/dm³ ClO₂ was fed to the top of the column which was operated in single-pass mode. At the same time air was sucked through the column to facilitate the stripping. Samples were withdrawn from the liquid before and after passing the column and analyzed for ClO₂ content. Process data and analytical results are given in Table 1 below. As can be clearly seen from the results, gaseous chlorine dioxide was stripped off in the stripper column. Depending on the parameters selected at stripping, more or less gaseous chlorine dioxide may be stripped off.

25

Table 1

Exp.	Temp- erature	Pressure	Liquid flow	Air flow	Air/liq. Flow	ClO ₂ conc. in	ClO ₂ conc. out
	°C	kPa	m ³ /h	Nm ³ /h	Nm ³ /m ³	g/dm ³	g/dm ³
1	12	25	2	3	1,5	8,50	5,87
2			3	3	1	8,71	6,49
3			3	3	1	8,60	6,72
4			3	4	1,33	8,56	6,21

CLAIMS:

1. Process for the continuous production of chlorine dioxide comprising:
 - generating chlorine dioxide in an aqueous reaction medium in a reaction vessel maintained at sub-atmospheric pressure,
 - bringing gaseous chlorine dioxide from said reaction vessel to an absorption tower and contacting the gaseous chlorine dioxide therein with a flow of water to form an aqueous solution containing chlorine dioxide,
 - bringing said aqueous solution containing chlorine dioxide from the absorption tower to a stripper, wherein the pH of the aqueous solution containing chlorine dioxide is from about 6.5 to about 7.8, and
 - blowing a gas through said aqueous solution of chlorine dioxide in the stripper to strip off from 10 to 100% of the chlorine dioxide entering the stripper and form a gaseous chlorine dioxide product obtained from the stripper with a partial pressure of from 0.5 to 20 kPa.
2. Process as claimed in claim 1, wherein the chlorine dioxide is generated by reducing chlorate ions by means of a chemical reducing agent.
3. Process as claimed in claim 2, wherein said chemical reducing agent is at least one of methanol and hydrogen peroxide.
4. Process as claimed in any one of claims 1 to 3, wherein from 40 to 95% of the chlorine dioxide entering the stripper is stripped off.
5. Process as claimed in any one of claims 1 to 4, wherein from 85 to 95% of the chlorine dioxide entering the stripper is stripped off.
6. Process as claimed in any one of claims 1 to 5, wherein said reaction medium is maintained at an absolute pressure from about 8 to about 80 kPa.

7. Process as claimed in any one of claims 1 to 6, wherein said reaction medium is maintained at its boiling point at the prevailing pressure.
8. Process as claimed in any one of claims 1 to 7, wherein the temperature of the aqueous solution containing chlorine dioxide is from about 0 to about 35°C.
9. Process as claimed in any one of claims 1 to 8, wherein a total yield of chlorine dioxide leaving the stripper is from about 96% with respect to added chlorate ions.
10. Process as claimed in any one of claims 1 to 9, wherein said gaseous chlorine dioxide product is maintained at a total absolute pressure from about 10 kPa to about 2 MPa.
11. Process as claimed in any one of claims 1 to 10, wherein said gaseous chlorine dioxide product is maintained at a total absolute pressure from about 105 kPa to about 1 MPa.
12. Process as claimed in any one of claims 1 to 11, wherein the aqueous solution from the stripper containing remaining chlorine dioxide is at least partly recirculated to said absorption tower, or to said reaction vessel.
13. Process as claimed in any one of claims 1 to 12, wherein the gas blown through the aqueous solution of chlorine dioxide in the stripper is an inert gas.
14. Process as claimed in claim 14, wherein said inert gas is air.
15. Process as claimed in any one of claims 3 to 14, wherein the chemical reducing agent is hydrogen peroxide which is fed to the aqueous reaction medium in an amount from about 0.5 to about 2 moles per mole of fed alkali metal chlorate.
16. Process as claimed in any one of claims 3 to 14, wherein the chemical reducing agent is methanol which is fed to the aqueous reaction medium in an amount from about 0.2 to about 1 moles per mole of fed alkali metal chlorate.
17. Process as claimed in any one of claims 1 to 16, wherein the aqueous solution in the absorption tower is acidified.

18. Process for the continuous production of chlorine dioxide comprising:

generating chlorine dioxide in an acidic aqueous reaction medium in a reaction vessel maintained at sub-atmospheric pressure,

bringing gaseous chlorine dioxide from said reaction vessel to an absorption tower and contacting the gaseous chlorine dioxide therein with a flow of water to form an aqueous solution containing chlorine dioxide,

bringing said aqueous solution containing chlorine dioxide from the absorption tower to a stripper, wherein the pH of the aqueous solution containing chlorine dioxide is from about 6.5 to about 7.8, and

blowing a gas through said aqueous solution of chlorine dioxide in the stripper to strip off from 10 to 100% of the chlorine dioxide entering the stripper and form a gaseous chlorine dioxide product obtained from the stripper with a partial pressure of from 0.5 to 20 kPa, wherein the gaseous chlorine dioxide product has a content of elemental chlorine less than 1 wt%.

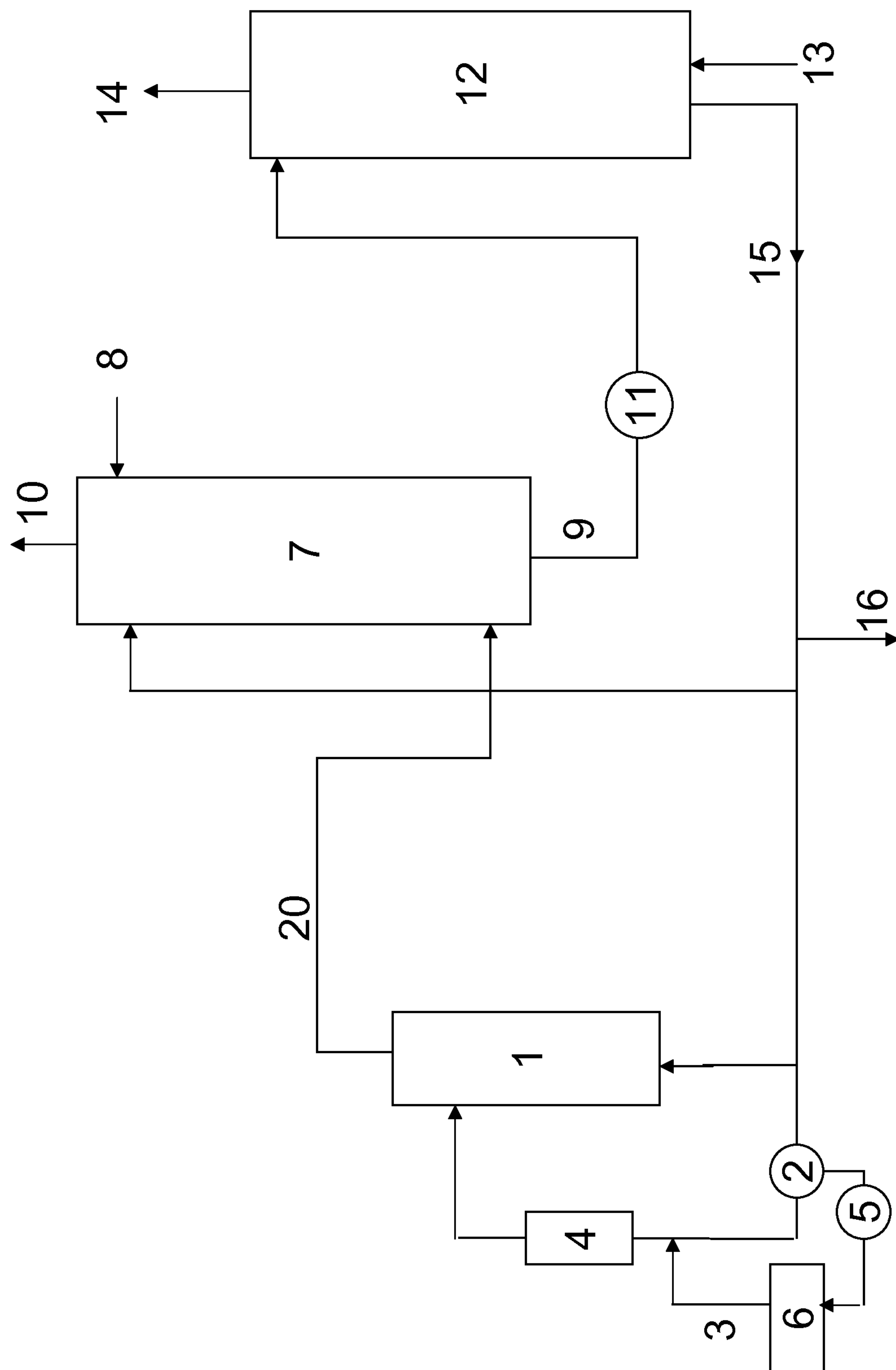


Fig. 1

