METHOD FOR PRODUCING AQUEOUS SOLUTION OF CHLORINE DIOXIDE

TECHNICAL FIELD

The invention relates to a method for producing aqueous solution of chlorine dioxide.

BACKGROUND ART

Chlorine dioxide is applied in large quantities for disinfecting water and for bleaching wood pulp, which is an intermediate product of papermaking. Accordingly, there is a number of known methods for producing chlorine dioxide.

A method for producing chlorine dioxide is disclosed in EP 2 069 232 B1. The document specifies a number of different methods for producing a solution of chlorine dioxide. These production methods can be divided into three main groups. According to methods in the first, second, and third groups, chlorine dioxide is produced, respectively, by the oxidation of sodium chlorite, by the reduction of sodium chlorate, and by the disproportionation of chlorous acid produced by the protonation of sodium chlorite.

In the method disclosed in EP 2 069 232 B1, chlorine dioxide is not present in gaseous phase. Instead, the acidic solution with sodium chlorite is in contact with a pore free polymeric membrane through which it diffuses faster than the other components of the solution, from which it may thus be separated. In this case, therefore, separation is performed based solely on different propagation velocities. This solution has the disadvantage that sooner or later the membrane becomes saturated with the components of the solution, and needs to be replaced.

US 8,652,411 B2 a method for generating chlorine dioxide is disclosed according to which chlorine dioxide is expelled from the surface and from inclusions in the crystals of solid sodium chlorite. According to the document, solid sodium chlorite is decomposed applying UV light, which implies that the reaction generating gaseous chlorine dioxide may only take place at surfaces (either at outside surfaces or at such portions of the inclusions that can be irradiated with UV light). A further disadvantage of the method for producing chlorine dioxide according to the document is that it can only be operated intermittently, since the solid material

applied as the starting substance has to be reloaded from time to time. A still further disadvantage of the production method according to the document is that, as the generated chlorine dioxide is highly sensitive to UV light, it may become degraded shortly after its generation. Thereby, due to the degradation of chlorine dioxide, chlorine gas is also generated simultaneously with chlorine dioxide under the effect of UV irradiation, which contaminates the chlorine dioxide produced so far. Solid sodium chlorite is stabilised according to the document by mixing it with alkaline metal hydroxides.

According to US 5,651,996 and US 7,488,457 B2, chlorine dioxide is produced in a reaction of chlorous acid and hypochlorous acid. According to US 5,651,996 an aldehyde is added during the production, while according to US 7,488,457 B2 the solution of chlorous acid is passed through solid calcium hypochlorite. Both methods have the significant common disadvantage that the generated solution becomes contaminated either with a carboxylic acid or with compounds dissolved out from the solid substance.

In the method of WO 2007/064850 A2 gaseous chlorine dioxide is produced in an electrochemical reaction. In the method according to the document it is problematic to manage hydrogen gas that is generated as an explosive by-product. Chlorine dioxide is produced applying a catalyst according to US 2007/231220 A1.

In the article by A. K. Horváth et al.: Kinetics and mechanism of the decomposition of chlorous acid, J. Phys. Chem. A, vol. 107, pp. 6966-6973 (2003), the decomposition process of chlorous acid in a dilute aqueous solution was investigated.

In view of the known solutions, there is a demand for a method for producing chlorine dioxide that allows to prepare aqueous solution of chlorine dioxide from gaseous chlorine dioxide obtained from the decomposition of chlorous acid in a more effective manner than in known solutions, by controlling the concentration of the generated chlorine dioxide gas applying an appropriately chosen control process, preferably preventing the explosive decomposition (puff) of chlorine dioxide.

DESCRIPTION OF THE INVENTION

The primary object of the invention is to provide a method which are free of the disadvantages of prior art solutions to the greatest possible extent.

A further object of the invention is to provide a method for producing chlorine dioxide that allows the generation of aqueous solution of chlorine dioxide applying gaseous chlorine dioxide obtained from the decomposition of chlorous acid in a more effective manner than in known solutions, by controlling the concentration of the generated chlorine dioxide gas applying an appropriately chosen control process, preferably preventing the explosive decomposition of chlorine dioxide.

The objects of the invention can be achieved by the method according to claim 1. Preferred embodiments of the invention are defined in the dependent claims.

In a manner different from US 8,652,411 B2, in the method according to the invention for producing aqueous solution of chlorine dioxide, chlorine dioxide is carried away from a solution by means of a gas flow, preferably air flow.

According to the invention the volume ratio of gaseous chlorine dioxide in the gas space of the starting reactor (the reaction vessel) is controlled applying substances capable of receiving a proton, e.g. alkaline metal hydroxides, along the chemical reactions described herebelow. In contrast to this, according to US 8,652,411 B2 the alkaline metal hydroxides are added to solid starting substances, e.g. in order to stabilise the starting substance. According to US 8,652,411 B2 the generation of chlorine dioxide is controlled by switching on and off an UV light source.

BRIEF DESCRIPTION OF THE DRAWINGS

Preferred embodiments of the invention are described below by way of example with reference to the following drawings, where

Fig. 1 illustrates an arrangement adapted for carrying out an embodiment of the method according to the invention,

Fig. 2 shows a flow chart illustrating an embodiment of an example method,

Fig. 3 shows a flow chart illustrating a further embodiment of an example method ,

Fig. 4 shows a flow chart illustrating a still further embodiment of the method according to the invention, and

Fig. 5 shows a diagram wherein the molar absorptivity of chlorine dioxide is plotted as a function of the wavelength of irradiation.

MODES FOR CARRYING OUT THE INVENTION

The method according to the invention is adapted for producing an aqueous solution of chlorine dioxide. In the course of method according to the invention gaseous chlorine dioxide is produced and the chlorine dioxide gas is carried away by means of a gas flow. Furthermore, in the method according to the invention, in the course of producing the chlorine dioxide gas, the chlorine dioxide gas is generated from a reaction of chlorous acid in a starting solution comprised in a starting reactor, in the course of carrying away the chlorine dioxide gas by means of the gas flow, the chlorine dioxide gas is carried from the starting reactor into an aqueous solution comprised in an end product reactor by means of the gas flow, and the volume ratio of the chlorine dioxide is controlled in the gas space of the starting reactor by modifying the velocity of the gas flow and/or by adding a substance capable of receiving a proton.

In contrast to the method disclosed in US 8,652,411 B2, in the method according to the invention chlorine dioxide gas is generated in solution (i.e., as described above, in the starting solution which is preferably an aqueous solution), and therefore chlorine dioxide is generated in the entire volume of the starting substances held in the starting reactor, contrary to the process described in US 8,652,411 B2 wherein chlorine dioxide is generated on the surface of the starting solid substance. Thereby, the chlorine dioxide yield of the inventive method may significantly exceed the yield of the method disclosed in US 8,652,411 B2.

Furthermore, in contrast to the method described in US 8,652,411 B2, according to the inventive method chlorine dioxide is produced from a reaction of chlorous acid in a manner described below. The method according to the invention is also different from the method disclosed in US 8,652,411 B2 in that gaseous chlorine dioxide is carried from the starting reactor into the end product reactor applying a gas flow, preferably air flow, and it is introduced into the aqueous solution held therein to produce an aqueous solution of chlorine dioxide.

Since according to EP 2 069 232 B1 chlorine dioxide gas only appears in a dissolved form in the solution, according to this known method no protection is necessary to prevent the fast decomposition of chlorine dioxide. According to the method disclosed in EP 2 069 232 B1, resulting also from the fact that chlorine dioxide only appears in dissolved form, the yield of the method is significantly lower than the yield achievable utilising the method according to the invention, as due to the easy solubility of chlorine dioxide it may be expelled in a far less effective manner applying diffusion than with the application of external energy, i.e. utilising an air stream.

Since chlorine dioxide is present in the gas space of the starting reactor in a gaseous form, in course of the method it is preferred to make efforts to prevent the so-called explosive decomposition (puff) of chlorine dioxide in the gas space. The explosive decomposition of chlorine dioxide, which causes rapid volume expansion, typically occurs above a chlorine dioxide concentration of 25 V/V% (volume percent). To provide that the method according to the invention is carried out in a continuous and safe manner, the volume ratio of chlorine dioxide in the gas space of the starting reactor is controlled. According to the invention, the control may be performed by modifying the velocity of the gas flow and/or by the addition of a substance capable of receiving a proton. In the embodiments described below a combination of both of these provisions is applied.

A reactor arrangement adapted for carrying out the method according to the invention – i.e., for producing an aqueous solution of chlorine dioxide – is shown in Fig. 1.

Due to its small size, the chlorine dioxide gas molecule is capable of easily diffusing through seals made from various plastic and silicone materials, and therefore the reactors applied in the arrangements are preferably either made from tinted glass, or the inner wall of the reactors has glass coating. The pipes through which the gas is carried from one reactor to the other are preferably also made from a glass material. At the various joint locations, polished elements fitting to each other are preferably applied in order to prevent chlorine dioxide from escaping. Since chlorine dioxide is sensitive to light, all components applied in the reactor arrangement are preferably made from tinted glass.

In the method according to the invention, the chlorine dioxide gas is generated from the decomposition of chlorous acid according to the following reaction equation:

$$5\ HClO_2 \rightarrow 4\ ClO_2 + Cl^- + 2\ H_2O + H^+$$

Chlorous acid ($HClO_2$) is preferably yielded from the reaction of sodium chlorite and sulfuric acid according to the following equation (the reaction also produces sodium sulfate (Na_2SO_4)):

$$2\ NaClO_2 + H_2SO_4 = 2\ HClO_2 + Na_2SO_4$$

As an end product, the reaction generating chlorine dioxide also produces sodium chloride (NaCl) and sodium chlorate ($NaClO_3$):

$$5\ HClO_2 = 4\ ClO_2 + HCl + 2\ H_2O$$

$$4\ HClO_2 = 2\ ClO_2 + HCl + HClO_3 + H_2O$$

In the above reactions hydrochloric acid (HCl) and $HClO_3$ (chloric acid) are produced according to two limiting stoichiometries, and then hydrochloric acid and chloric acid react with the starting substance sodium chlorite, producing sodium chloride and sodium chlorate in addition to chlorous acid.

$$NaClO_2 + HCl = HClO_2 + NaCl$$

$$NaClO_2 + HClO_3 = HClO_2 + NaClO_3$$

Hydrochloric acid and chloric acid play a role also in the case wherein a substance capable of receiving a proton, by way of example, NaOH, is added to the starting solution in order to control chlorine dioxide generation. In this reaction, in addition to water, sodium chloride and sodium chlorate are also produced as by-products.

$$HCl + NaOH = NaCl + H_2O$$

$$HClO_3 + NaOH = NaClO_3 + H_2O$$

The starting solution in which gaseous chlorine dioxide is continuously generated is stirred continuously.

According to the following reaction equation:

$$5\ HClO_2 \rightarrow 4\ ClO_2 + Cl^- + 2\ H_2O + H^+$$

in case of a 100% yield, 0.8 mol (90.44 g) of chlorine dioxide is generated from 1 mol of sodium chlorite (53.96 g), while 0.2 mol (19.6 g) of sulfuric acid is consumed. This means that, based on the above stoichiometry, 596 g of chlorine dioxide can be produced from 1000 g of pure sodium chlorite (i.e. of 80% m/m

sodium chlorite that is available commercially). The reaction describing the decomposition of chlorous acid has another boundary stoichiometry as follows:

$$4\ HClO_2 \rightarrow 2\ ClO_2 + Cl^- + ClO_3^- + H_2O + 2H^+.$$

It is shown that in this case half of the amount of the consumed sodium chlorite is converted into chlorine dioxide. Using the figures of the above example, this means that 372 g of chlorine dioxide can be generated from 1 kg of pure sodium chlorite applying the stoichiometry specified by the equation of the example. In a reactor operated discontinuously, 372–596 g of chlorine dioxide can be produced from 1 kg of pure sodium chlorite, the exact value can be adjusted by the modification of the conditions of the experiment. The achievable yield of chlorine dioxide also depends on the amount of losses due to the imperfect joints of the reactor. Applying appropriately chosen joints, this loss can be minimized.

In the following, the components of the reactor arrangement shown in Fig. 1, adapted for carrying out the method according to the invention are described. The reactor arrangement according to Fig. 1 comprises a starting reactor 100, an end product reactor 200 and an auxiliary reactor 300, comprising, respectively, solutions 110, 210, and 310 as illustrated in the figure. First, the components connected to the reactor 100 are described.

The arrangement according to Fig. 1 comprises a filter 25, with the application of which mechanical contaminants (by way of example, dust) can be removed from the air introduced into the reactors. The filter 25 may preferably be applied also for filtering out chemical substances. By including an appropriately selected filter insert in the filter 25, the removal of carbon dioxide from the air introduced through the stub shown at the top portion of the filter 25 may be provided for. At more downstream locations of the pipe system, where chlorine dioxide is already found, the carbon dioxide content of the air cannot be removed by forming carbonate ions, because for such removal an alkaline surface is applied (the chlorine dioxide coming in contact with the alkaline surface would disproportionate into chlorite and chlorate ions).

From the filter 25 air is carried into an air pump 24. The air pump 24 may be applied for providing the flow of filtered air. The air pump preferably provides a

constant flow velocity, and has controllable throughput. In case the velocity of the air flow introduced into the reactor 100 falls below a specific value (referenced with C' in Figs. 3 and 4) the volume ratio of chlorine dioxide in the air space of the reactor 100 could reach 25 V/V%, which would cause the rapid, spontaneous decomposition (explosive decomposition) of the gas into chlorine gas and oxygen. Accordingly, by keeping the flow velocity at an appropriate value, the explosive decomposition of the generated chlorine dioxide gas can be prevented (the corresponding process control principles are described in relation to Figs. 2 to 4 herebelow). In addition to controlling the concentration of chlorine dioxide in the gas space, the air flow driven by the air pump 24 has another function, namely, that, being carried through the solution 110 (which is preferably stirred continuously) it assists in expelling the generated chlorine dioxide gas from the solution 110 (the so-called mother alkaline). Air flow velocity may be measured applying a flow sensor 28, and thereby the throughput of the air pump 24 may be controlled applying the flow sensor 28.

The air flow is introduced into the reactor 100 by means of a pipe 26. By mounting a jet dispenser at the end of the pipe 26 that extends into the reactor 100 the efficiency of removing the chlorine dioxide gas from the reactor 100 may be improved. The pipe end extending into the reactor 100 is situated under a liquid level of the solution 110.

In the arrangement according to Fig. 1, a container 20 comprising sulfuric acid ((H_2SO_4) solution (preferably having a concentration of 50%) is connected to the reactor 100 through a pipe. The container 20 may e.g. be made from plastic or glass. If, as in the experimental arrangement shown in Fig. 1, the air space (gas space) of the reactor 100 and the container 20 are at equal pressure due to the connection shown in the figure, and if the reactor is made from glass, then, in order to prevent chlorine dioxide loss, it is expedient to make also the container 20 from glass. The substance (sulfuric acid) held in the container 20 is – in the above mentioned 50% dilution – strongly corrosive. Since in case of the potential explosive decomposition of chlorine dioxide the disruption of the container 20 presents the greatest danger, it is preferred to arrange the container 20 at the largest possible distance from the reactor 100. In case the air space of the

container 20 is separated from the air space of the reactor 100, the container 20 may be made from plastic up to the inlet tap 22. The tap 22 is preferably made from glass.

In the arrangement illustrated in Fig. 1, a container 12 is also connected to the reactor 100, the container 12 comprising the other starting substance required for producing chlorine dioxide in addition to sulfuric acid, namely, saturated sodium chlorite ($NaClO_2$) solution. By way of example, also the container 12 may be at equal pressure with the reactor 100, in which case the wall of the container 12 is preferably made from glass. The sodium chlorite solution itself that is held in the container 12 does not react with a plastic-walled container, and, therefore, by the separation of air spaces applied also in the case illustrated in Fig. 1, it may not be necessary to utilise a glass-walled container. The substance (sodium chlorite) may slowly decompose under the effect of light, and thus the container wall is preferably not transparent.

Since 100% pure sodium chlorite is explosive, it is typically made commercially available in a concentration of 80 weight%. In that case the substance is diluted with sodium carbonate (Na_2CO_3), as well as, by way of example, with sodium chloride (NaCl). Applying ion chromatography measurements the exact concentration values of specific components can be determined. The diluents present in 20 weight% in the commercially available substance are not required to be removed prior to chlorine dioxide generation, i.e. before adding the substance to the solution 110. The presence of sodium carbonate is even preferable because it adjusts the pH of the solution in the container 12 to slightly alkaline. This is preferred because thereby the disproportionation of sodium chlorite may be prevented in the container 12. Due to the pH of the solution it would be problematic if the container 12 and the solution 110 had a common air space and thus the generated chlorine dioxide gas, coming into contact with the alkaline solution, could disproportionate, producing chlorite and chlorate. For the above reasons it is expedient to separate the air spaces of the reactor 100 and the container 12. The other diluent is sodium chloride. As pointed out in the above cited article (A. K. Horváth et al.: Kinetics and mechanism of the decomposition of chlorous acid, J. Phys. Chem. A, vol. 107, pp. 6966-6973 (2003)), the

decomposition process of chlorous acid is shifted by the presence of the chloride ion in a direction where a greater amount of chlorine dioxide is produced for unit mass of the starting substance, and thereby the presence of the chloride ion is advantageous for the purposes of the method according to the invention. For the optimisation of the reaction process it is required that the exact composition of the sodium chlorite substance is known.

In the reactor arrangement illustrated in Fig. 1, a container 16, implemented exemplary as a syringe, and comprising a material capable of receiving a proton, is connected to the reactor 100. Since the concentrated alkaline solution is capable of dissolving glass, the container 16 is expediently not made from glass. Instead, an alkali-resistant polymer is preferably applied. Expediently, the tap 18 arranged between the container 16 and the reactor 100 is also made from plastic to prevent it from getting damaged by the alkaline solution in contact with it and to ensure that it does not get stuck. Our experience indicates that in case polished glass comes into contact with a concentrated alkaline solution the glass tap gets damaged and becomes inoperable. The section of the pipe that extends from the tap 18 to the reactor 100 is expediently made from glass. As the container 16 typically holds a highly concentrated alkaline solution, it may be expedient to connect a pipe immediately downstream of the tap 18, the other end of which pipe being connected to a tank holding high-purity water. This may become necessary in order to wash through the pipe connecting the container 16 and the reactor 100 after using the container 16 to avoid damage to the pipe or the obstruction thereof by deposits that may crystallise from the alkaline solution. The alkaline solution may be any suitable substance as the reaction may be stopped, if necessary, applying any kind of alkaline solution.

As described above, the chlorine dioxide-producing reaction between sodium chlorite and sulfuric acid takes place in the solution 110 comprised in the reactor 100. The solution 110 is stirred continuously applying a – preferably teflon-coated – magnetic stirrer 30, the chlorine dioxide generated therein being removed by carrying through it the gas flow – as described above, expediently air flow – introduced through pipe 26. As the reaction proceeds, the following ions are accumulated in the solution: sulfate, chloride, sodium, and hydrogen ions. In

addition to these ions, chlorate ions may also form in the solution, but their quantity may be reduced by appropriately chosen reaction conditions. In case the reaction is stopped or moderated applying the container 16, the quantity of chlorate ions increases in the solution 110.

It is important to note that in case of an alkaline solution, or, during the rinsing of the pipe connecting the container 16 and the reactor 100, water is introduced into the solution 110, then the temperature of the solution increases due to the heat generated during the neutralisation reaction or the dilution process. Preferably, the level of the solution 110 may never be lower than the height at which the end of the pipe 26 is situated. A minimum height difference is expediently established between the liquid level and the end point of the pipe 26 in order to provide for the removal of the chlorine dioxide from the solution 110. This height difference may vary depending on the size of the reactor. The liquid level of the solution 110 cannot be higher than the level at which the end points of the pipes introducing the reagents and the alkaline solution are situated. This requirement may be incorporated in the parameter E, to be introduced below, that corresponds to the maximum level of the solution 110.

In the reactor arrangement illustrated in Fig. 1 a tap 10 adapted for removing the solution 110 is connected to the reactor 100. The tap 10 is expediently rather made from plastic, and not from metal. Though it cannot be stored in a metal container, the corrosive solution may be stored in a container made from plastic. In case the pH of the solution 110 (the mother alkaline) is set to near neutral (pH = 5-8) then it can be boiled off applying a base when being removed from the reactor 11, thus significantly reducing its volume.

Taking into account the most advantageous of the above mentioned stoichiometries for the reaction leading to the generation of chlorine dioxide, then, applying 1 kg of 80% m/m sodium chlorite (800 g $NaClO_2$, ~150g NaCl, ~50 g Na_2CO_3) and 451 g of 96% m/m sulfuric acid (433 g H_2SO_4, 18.5 g H_2O) the following substances are produced as the end products of the reaction: 476 g of chlorine dioxide (ClO_2), 21 g of carbon dioxide (CO_2) (these two end products leave the reactor 100 in a gaseous state), 253 g of sodium chloride (NaCl), 628 g of sodium sulfate (Na_2SO_4). Taking into account the other, less favourable

boundary stoichiometry of the reaction, the quantities of the end products are as follows (the quantities of the starting substances are the same): 298 g of chlorine dioxide (ClO_2), 21 g of carbon dioxide (CO_2) (these two end products leave the reactor 100 in a gaseous state), 253 g of sodium chloride (NaCl), 627 g of sodium sulfate (Na_2SO_4), and 187 g of chloric acid ($HClO_3$). These exemplary values are intended for illustrating the range in which the composition of the end product may vary.

In the reactor arrangement illustrated in Fig. 1 a sensor 23 adapted for measuring the liquid level of the solution 110 for control purposes is connected to the reactor 100. The sensor preferably has teflon/plastic coating to be able to withstand the acidity and oxidising effect of the solution.

For controlling, in the method according to Fig. 2 the absorptivity, while in the method illustrated in Fig. 3 the pressures inside and outside the reactor 100 have to be measured. Thereby, an absorptivity meter and a pressure sensor, collectively represented by a sensor 22, may also be connected to the reactor 100.

Chlorine dioxide gas leaves the reactor 100 through a pipe 28. The pipe 28 is typically bent, the bending angle expediently being over 90°. This configuration is preferred because bending the pipe at an appropriate angle may allow a liquid potentially entering the pipe 28 due to excessive flow velocities to flow back into the reactor 100 without contaminating the end product, i.e. the aqueous solution of chlorine dioxide.

The reactor arrangement of Fig. 1 also comprises reactors 200, 300. In the following, these reactors and the components attached to them are described.

The chlorine dioxide gas purged out from the solution 110 is carried from the reactor 100 to the reactor 200 through the pipe 28. The end of the pipe 28 is submerged in the solution 210 comprised in the reactor 200. By mounting a jet dispenser at the end of the pipe 28 the efficiency of redissolving the chlorine dioxide gas in the aqueous solution may be improved. The application of the jet dispenser may increase the boundary surface between the liquid and the gas, which makes the dissolving of chlorine dioxide more effective.

At the start of the method according to the invention, the reactor 200 is filled with high-purity water. Later in the course of the method according to the invention – which may also be carried out continuously – it is filled with the solution 310 already comprised in the reactor 300. The solutions 210 and 310 are preferably kept in constant motion applying – preferably teflon-coated – magnetic stirrers 30. The finished end product solution – typically, an aqueous solution of chlorine dioxide having a concentration of approximately 0.2-0.4 mol/dm^3 – may be discharged through a tap 34 that is preferably made from glass.

An ampule filling apparatus may expediently be connected directly to the discharge tap 34 of the reactor 200, utilising which apparatus the end product solution may be packaged right after it has reached the required concentration. The concentration values of the aqueous solution of chlorine dioxide filled in the ampules may be recorded applying a spectrophotometer disposed in the reactor 200. Filling the solution in ampules immediately after finishing the process has the advantage that the quality (i.e. concentration) of the end product solution cannot deteriorate. The ampules are preferably made from tinted glass.

A sensor 38 adapted for absorptivity measurement is connected to the reactor 200. The sensor 38 may be utilised in the control. Applying the sensor 38 the concentration of chlorine dioxide in the end product solution 210 may be determined. Thereby, as it is spelled out herebelow in relation to the methods illustrated in Figs. 3 and 4, the quantity of the sulfuric acid and sodium chlorite solution to be introduced into the reactor 100 may be controlled on the basis of the concentration change of the solution 210.

A pH meter 42 applicable for checking the purity of the end product solution 210, i.e. the aqueous solution of chlorine dioxide, by detecting the hydrogen ions resulting from the disproportionation of chlorine gas in case of an accidental chlorine contamination may be connected to the reactor 200. The pH meter 42 may be replaced by an electrode selective to the chloride ion. This should be considered also because the pH meter 42 is capable of detecting the hydrogen ions resulting from the dissolving of carbon dioxide. Thereby, in case the quality of the solution 210 is not affected by dissolved carbon dioxide, it is more expedient to apply a chloride-selective electrode.

In the arrangement shown in Fig. 1 the liquid level of the solution 210 in the reactor 200 is measured utilising a sensor 40. The level of the solution may not be lower than the height at which the end of the pipe 28 is situated.

Through pipe 36 that interconnects the reactors 200, 300 the gas discharging into the gas space of the reactor 200 can be carried into the reactor 300. In a manner described above, as the concentration of chlorine dioxide increases in the end product solution 210, some of the gas starts to remain undissolved in the high-purity water initially comprised in the reactor 200. The undissolved quantity of gas discharges from the reactor 200 through the pipe 36. The gas discharging through the pipe may be dissolved in the reactor 300. The end of the pipe 36 is situated lower inside the reactor 300 than the liquid level of the solution 310. The gas escaping from the solution 310 may preferably be driven into an alkaline solution (for example, NaOH solution) comprised in a container 56 via a pipe 48 connected to the reactor 300, thereby preventing the chlorine dioxide from escaping into the air, as in the alkaline solution comprised in the container 56 chlorine dioxide disproportionates into chlorite and chlorate ions, and the chlorite ions may optionally be reused for producing chlorine dioxide. The container 56 is preferably made from an alkali-resistant polymer material. The concentration of chlorite ions in the solution held in the container 56 may be monitored utilising an absorptivity sensor 58 preferably connected to the container 56.

Initially, the reactor 300 comprises high-purity water that is preferably stirred continuously and is applied for capturing the chlorine dioxide introduced from the reactor 200 to the reactor 300. Thus, the solution comprised in the reactor 300 may preferably be applied to make up for the solution discharged from the reactor 200. The solution 310 may be introduced into the reactor 200 through pipe 44 utilising an expelling means 46 (pump). In the arrangement shown in Fig 1, a container 50 comprising high-purity water is also connected to the reactor 300. The container 50 may be applied for filling the reactor 300 by opening a tap 52. The liquid level of the solution 310 is controlled utilising a liquid level meter 54 connected to the reactor 300.

Thereby, the chlorine dioxide gas driven into the gas space of the end product reactor 200 from the aqueous solution 210 comprised in the end product reactor

200 is carried from the end product reactor into an aqueous solution 310 comprised in an auxiliary reactor 300, and, at the start of the process, the end product reactor 200 is filled with the aqueous solution 210 comprised in the auxiliary reactor 300. Furthermore, in the present embodiment the chlorine dioxide gas discharged into the gas space of the auxiliary reactor 300 from the aqueous solution 310 disposed in the auxiliary reactor 300 is carried into an alkaline solution comprised in an auxiliary container 56.

The high-purity water may be produced from drinking water-quality tap water. The cleaning procedure expediently consists of two phases. In the first phase the water is passed through two ion-exchange resins exchanging respectively anions and cations. The pre-treated water is subsequently passed through a mixed bed column, where the quality of the water is monitored, by way of example, by conductivity measurement. Non-dissociating components and the residue of the resins are removed applying a two-phase distillation process. Both phases of the distillation process are carried out under atmospheric conditions, but during the first phase of distillation decomposition by potassium permanganate is also carried out. In the second phase the distillate resulting from the first phase is further distilled to remove traces of permanganate from the solution.

It is required to remove the gas from the solution 110 and produce the end product (an aqueous solution of chlorine dioxide) in another reactor also because the solution 110 has a low pH (between 0.5 and 1.5), and it also comprises the reagents and reaction products, such as sodium chloride, sodium sulfate, and low quantities of sodium chlorate.

In the gas space of the reactor 100 the concentration of chlorine dioxide is preferably not greater than 20 V/V%, since above a concentration of 25-30 V/V% gaseous chlorine dioxide undergoes rapid decomposition according to the following reaction equation:

$$2\ ClO_2 \rightarrow Cl_2 + 2\ O_2.$$

As it is shown in the equation, the decomposition of chlorine dioxide involves a 1.5 times expansion, which may rupture the reactor 100. The decomposition does not cause an explosion. The greatest danger would be posed by damage to the

container 20 in which the sulfuric acid reagent is stored. The chlorine gas accidentally generated by the decomposition reaction must be removed before chlorine dioxide generation is restarted, as it could contaminate the chlorine dioxide that is redissolved in the reactor 200. The decomposition of chlorine dioxide is prevented in the methods illustrated in Figs. 2 to 4 in two ways:

1. Keeping the flow velocity at an appropriate value.
2. In case the inlet velocity of chlorine dioxide is too high, then some – preferably concentrated – substance capable of receiving a proton, e.g. an alkaline solution (either sodium hydroxide, calcium hydroxide, or potassium hydroxide) is introduced into the solution 110 from the container 16, thereby increasing the pH of the reaction mixture. Due to the reduced hydrogen ion concentration the speed at which chlorine dioxide is generated decreases, and furthermore, a portion of dissolved gas disproportionates into chlorite and chlorate ions affected by alkaline solution.

In the following, three alternatives applicable for controlling the process of the method according to the invention are described in relation to Figs. 2 to 4. Applying the control scheme illustrated in Figs. 2 to 4, in some methods for producing an aqueous solution of chlorine dioxide the production process may be controlled, stopped and restarted.

Fig. 2 illustrates a method, in which the reactor arrangement is controlled by the monitoring of four parameters. The monitored parameters are the following:

- the concentration of chlorine dioxide in the gas space of the reactor 100; this parameter is indicated by x in Fig. 2 and is measured in the arrangement according to Fig. 1 by means of the sensor 22;
- air flow velocity in pipe 26; this parameter is indicated by y in Fig. 2 and is measured in the arrangement of Fig. 1 applying the flow meter 28;
- the liquid level of the solution 110; this parameter is indicated by z in Fig. 2 and is measured utilising the liquid level meter 23; and
- a switch position (f), adjusting of which the reactor 100 may be stopped in a pre-planned manner.

In the method illustrated in Fig. 2, therefore, the concentration of chlorine dioxide gas measured in the gas space of the starting reactor 100 is applied for controlling

the volume ratio of chlorine dioxide gas in the gas space of the starting reactor 100. Furthermore, in the present method the concentration of chlorine dioxide is determined by means of a spectrophotometer measurement at a predetermined wavelength in the gas space of the starting reactor 100, based on the wavelength dependence of the molar absorptivity of chlorine dioxide. The velocity of the gas flow and the liquid level of the starting solution 110 are also applied for controlling the volume ratio of chlorine dioxide gas in the gas space of the starting reactor 100.

The concentration value x may e.g. be measured applying a single-wavelength spectrophotometer. A diagram wherein the molar absorptivity of chlorine dioxide is plotted as a function of wavelength is shown in Fig. 5. The spectrum shown in Fig. 5 may be directly applied for determining the concentration of chlorine dioxide dissolved in water, but it may also be utilised for determining the quantity of chlorine dioxide in the gas space, since its distribution coefficient between air and water is known. In case of a potential complete shutdown – wherein chlorine dioxide generation is stopped by adding a substance capable of receiving a proton – it is not required to clean the reactor 100 as the chlorine dioxide generation process is not hindered by the generated chlorate ions. By adjusting the pH of the solution 110 to an appropriate value, e.g. by the addition of sulfuric acid from the container 20, the chlorine dioxide gas generation process may be continued.

In the present method the reaction applied for generating chlorine dioxide is controlled based on the concentration of chlorine dioxide in the gas space, as well as on flow velocity. The method illustrated by the flowchart shown in Fig. 2 is started at the place labelled Start. As a recurring first step of the method the respective values of the four parameters x, y, z, and f are read in. The parameter f represents the position of a two-position toggle switch. By toggling the switch from 0 to 1 the reaction may be stopped during the process as described below.

In the methods illustrated in Figs. 2, 3 and serving explanation purposes, the reactor 300 (shown in Fig. 1) is not utilised, or it is not even connected to the reactor 200.

After reading in the monitored parameters, the parameter x, i.e. the concentration of the chlorine dioxide in the gas space of the reactor 100 is investigated. In the figures, letters A and B represent, respectively, a predetermined lower and upper limit value of the concentration of chlorine dioxide. First, the condition $x \leq A$ is investigated whether it is true or not. If the condition is true, i.e. the concentration x has fallen below the predetermined lower limit value, the condition $y \leq C$ is tested (C is a predetermined lower limit of air flow velocity, D is the upper limit thereof). In case y has not yet fallen below the lower limit, i.e. the air flow velocity can still be lowered, then y is lowered and the first step (i.e., reading in the four monitored parameters) is performed again. In this part of the method the concentration of chlorine dioxide does not reach the predetermined lower limit, this is compensated for in the present method by, if possible, reducing the air flow velocity, i.e. the chlorine dioxide gas is purged out from the solution 110 more slowly in order to keep the concentration of the gas in the gas space between the predetermined limits A and B.

If $x \leq A$ and the flow velocity cannot be reduced further, i.e. $y \leq C$ is true, then it is tested if the liquid level of the solution 110 exceeds the predetermined upper limit E. If it does exceed the limit, the tap 10 is opened and a predetermined quantity of the solution 110 is discharged. In the extreme case of $y \leq C$ (the flow velocity is too low), therefore, the level of the solution 110 is tested, and in case the level of the solution 110 is too high simultaneously with the concentration being too low, a predetermined amount of the solution 110 is discharged. Subsequently, control is returned to the initial step, and the values of the parameters x, y, z, and f are read in.

In case it is found that the condition $z \geq E$ does not hold, i.e., the liquid level of the solution 110 does not exceed the predetermined upper limit E (and also x is below the predetermined upper limit), then it depends on the value of f whether the reaction is stopped by opening the tap 18, or – by opening the taps 14 and 22 – certain amounts of the starting substances are added to the solution 110 attempting to increase the value of x. After the specific amounts of reagents have been added, control is returned to the initial step of the present method, i.e. the four parameter values to be tested are read in.

Once these four parameters have been read in, and in case the condition $x \leq A$ does not hold then the condition $x \leq B$ is tested, i.e. it is examined whether the concentration x is lower than the upper limit B. Since in this branch of the process the value of x is greater than A, in case the condition $x \leq B$ holds, the reaction is proceeding correctly, the value of x is set between the two limit values A and B.

If the condition $x \leq B$ does not hold, i.e. the concentration is higher than the desired upper limit, the concentration of the chlorine dioxide gas is approaching the critical threshold value corresponding to explosive decomposition, and thereby the value of x should be returned between A and B. At this point the condition $y \geq D$ is tested, i.e. it is examined whether air flow velocity has reached the predetermined upper limit. If not, then the concentration of chlorine dioxide in the gas space may be reduced by increasing the velocity of the air flow. In case, therefore, the condition $y \geq D$ does not hold, the value of y is increased, and then control is returned to the initial step, i.e. the four parameters to be tested are read in.

If y has already reached the predetermined upper limit, that is, the condition $y \geq D$ holds, then the air flow velocity cannot be increased further, implying that other means have to be applied to attempt to reduce the concentration x. In this case, an amount of the substance capable of receiving a proton (stored in the container 16) is added to the solution utilising the tap 18, which preferably reduces the value of x, as well as the speed at which chlorine dioxide is being generated. After introducing the substance, the liquid level in the reactor 100 is tested, and in case the condition $z \geq E$ does not hold, then – returning to the initial step – the four parameters are read in to make sure that the addition of the substance has had the desired result with respect to the value of x. In case $z \geq E$ is true, i.e. the liquid level is too high in the reactor 100, then an amount of solution 110 is discharged utilising the tap 10, and subsequently control is returned to the initial step involving the reading-in of the four parameters.

In the method detailed above it may become difficult to determine the concentration of chlorine dioxide in the air space of the reactor 100 if the measurement wavelength cannot be guaranteed to be kept constant with an

appropriately low margin of error. A change in wavelength during the course of the method may result in an error in determining the concentration value.

In the method illustrated in Fig. 3 the errors resulting from inaccurate concentration values cannot occur because in this method the concentration of chlorine dioxide measured in the gas space (the parameter x) is not utilised for process control. In the present method, process control is performed monitoring the following parameters:

- the concentration of chlorine dioxide in the aqueous solution thereof; identified in Fig. 3 by the reference c_n, and measured inside the reactor 200 comprising the aqueous solution of chlorine dioxide (the target value of the parameter is referenced by $c_{solution}$);
- the air flow velocity (similar to the method according to Fig. 2); this parameter is identified by the reference y also in Fig. 3;
- the liquid level of the solution 110; in a manner similar to the method shown in Fig. 2 this parameter is referenced by z;
- the switch position identified by the reference f also in Fig. 2, which may be applied for the planned shutdown of the reactor;
- the ratio of the pressure measured inside the reactor 100 and the ambient pressure measured outside it, identified in Fig. 3 by the reference p^*.

In the method illustrated in Fig. 3, therefore, the solution concentration of chlorine dioxide measured in the aqueous solution of chlorine dioxide is applied for controlling the volume ratio of chlorine dioxide gas in the gas space of the starting reactor 100. Furthermore, in the present method the volume ratio of chlorine dioxide gas in the gas space of the starting reactor 100 is controlled further utilising the pressure measured in the gas space of the starting reactor 110, the ambient pressure measured outside the starting reactor 100, the liquid level of the starting solution 110, and the value of the solution concentration measured a measurement cycle earlier.

Thus, in the present method it is not sufficient to measure the value c_n, but also the concentration value measured in the previous measurement cycle has to be stored (the value measured in the current cycle is referenced in Fig. 4 by c_2, the value recorded in the previous cycle is referenced by c_1, the difference of the two

values is $\Delta c = c_2 - c_1$). According to the above, therefore, the concentration data recorded in the n-1-th cycle have to be utilised in the n-th control cycle. In the present method the reactors 100 and 200 are controlled simultaneously, the concentration of chlorine dioxide being measured in dissolved phase. This concentration value can be determined with very high accuracy (1-2%).

In contrast to the method according to Fig. 2, in the present method the values of the parameters listed above are read in in the initial step of the process. After the parameters have been read in, the first test to be performed is checking if p*, the ratio of inside and outside pressure values, is greater than a predefined maximum value P (checking if the condition $p^* \leq P$ holds). In case the pressure ratio is greater than the predefined threshold value, then the tap 18 is opened to release some of the substance stored in the container 16, and then it is tested whether the level of the solution 110 exceeds the predefined upper limit value E. If the level is below the limit, the parameters are read in again, i.e. the effect of the release by opening the tap 18 of the substance held in the container 16 on the parameters is checked. In case the level of the solution 110 exceeds the predefined maximum level E, then an amount of the solution 110 is discharged by opening the tap 10, and control is returned to the initial step, i.e. the parameters to be tested are read in.

If the condition $p^* \leq P$ is true, that is, the pressure ratio is below the predefined maximum value, then the condition y ≤, C' is tested, i.e. it is checked if the air flow velocity is below a predefined threshold C'. The value C' corresponds to such a low flow velocity below which the reactor must be shut down. If the condition $y \leq C'$ holds, then the process is stopped by opening the tap 18.

If the condition $y \leq C'$ does not hold, then the condition $y \leq C$ is tested. In this condition and also in another one below, C and D, respectively, are predetermined lower and upper limits of air flow velocity. If the condition $y \leq C$ holds, i.e. y is above a critical lower limit C' but below the predetermined minimum value, then y is increased, and, returning to the initial step, the parameters to be tested are read in. If, however, $y \leq C$ does not hold, then the condition $y \geq D$ is tested, i.e. it is checked whether the flow velocity exceeds the upper limit value. In case $y \geq D$, then the value of y is decreased, and control is returned to the initial step of

reading in data. In these two steps it is attempted to return the value of y in between the predetermined limits.

If the condition $y \geq D$ does not hold, i.e. the value of y is in between the predetermined limits (as indicated by the relation shown in the flowchart), then it is tested whether the value of the concentration, i.e., c_2, exceeds a predetermined value $c_{solution}$. In case the condition $c_2 \geq c_{solution}$ holds, that is, the currently measured concentration rises above the predetermined target concentration value, then the finished end product solution 210 is discharged and the reactor 200 is filled up with water. If the measured concentration has not yet exceeded the predetermined limit value $c_{solution}$, then concentration change is compared with the value recorded in the previous measurement cycle, thus, it is examined if the difference $\Delta c = c_2 - c_1$ has a positive value, i.e. whether the concentration has risen since the previous measurement. In case the condition $\Delta c \geq 0$ holds, it is checked if the difference is above a predetermined (target) value G, i.e. if the condition $\Delta c \geq G$ holds. If the increase in concentration is above G, then control is returned to the previous step, and the parameters to be tested are read in again. In this case, the concentration of the end product is increasing as expected. According to the present method, therefore, certain parameters are measured in the reactor 200, while others, such as the level of the starting solution 110, are measured in the reactor 100.

If the condition $\Delta c \geq G$ does not hold, then it is checked whether the level of the solution 110 is above the predetermined value E. If yes, then a specific amount of the solution 110 is discharged by opening the tap 10, and, returning to the initial step, the parameters to be tested are read in again. In case the level of the solution 110 does not reach the predetermined value E, then the taps 14, 22 are opened so as to introduce an amount of the starting substances into the reactor 100, and then, returning to the initial step, the parameters are read in again. In the discharge case, the level of the solution 110 exceeded E in spite that the expected increase of the concentration $c_{solution}$ did not happen, i.e. the chlorine dioxide generation process in the solution 110 was not going as expected. Hence by discharging an amount of the solution 110 an attempt is made to achieve a more favourable chlorine dioxide generation rate in the solution 110. If the level of the

solution 110 is not yet too high, i.e. it does not exceed the value E, then an attempt is made to provide that the rate of increase of the concentration $c_{solution}$ can reach a desired value.

At the decision point where the condition $\Delta c \geq 0$ is tested, in case the condition does not hold the parameter f is also tested. If f = 1, i.e. it is desirable to carry out a planned termination of the process, then the tap 18 is opened and such an amount of substance is introduced from the container 16 into the reactor 100 which is sufficient for stopping the chlorine dioxide generation process. In case f = 0, then, depending on the level of the solution 110 measured in the reactor 100, either a specific amount of the solution comprised in the reactor 100 is discharged by opening the tap 10, or – if the level is below E – starting substances are introduced therein by opening the taps 14 and 22. After the discharging or introduction has been performed, control is returned to the initial step, and the parameters to be tested are read in.

The embodiment according to Fig. 4 is different from the method illustrated in Fig. 3 in that a reactor 300 is connected to the reactor 200 in a manner shown in Fig. 1, the reactor 300 being adapted for refilling the contents of the reactor 200. In the embodiment illustrated in Fig. 4, if the chlorine dioxide concentration of the end product solution 210 exceeds a predetermined value $c_{solution}$, then after discharging the end product solution 210 the reactor 200 is filled up from the reactor 300 instead of filling it with water. The reason why the reactor 200 is filled with the solution 310 comprised in the reactor 300 is that it already comprises some chlorine dioxide, and thus chlorine dioxide loss may be reduced. Since gases dissolve much better in cold water, chlorine dioxide loss may be further reduced by cooling the reactor 200. Another possible way of reducing losses is to reduce the target concentration of the end product solution, since that way the amount of chlorine dioxide transferred to the reactor 300, and from there, through pipe 48, into the sodium hydroxide solution, may be reduced.

After filling up the reactor 200 with the solution comprised in the reactor 300, the reactor 300 is filled up with high-purity water, and, returning to the initial step, the parameters to be tested are read in.

The continuous monitoring of the amount of generated gas allows for preventing the so-called explosive decomposition of chlorine dioxide in case the gas flow becomes obstructed for some reason. The controller performs two important functions by monitoring continuously the amount of generated gas: a) if the reactor becomes depleted, the amount of gas being generated to fall below a critical threshold value, then a predetermined amount of starting substances is introduced into the reactor 100 from the containers 12 and 20; b) if the concentration of the gas approaches the limit value where the explosive decomposition of chlorine dioxide would occur, the protection function, described in detail in the first part of the specification, is engaged. The above described controller, therefore, allows for continuous production and production supervision for a prolonged period of time.

According to what has been described in relation to Figs. 3 and 4, the chlorine dioxide production process is stopped or moderated in case the ratio of inside of outside pressure rises above a predetermined value indicating that the gas flow in the reactor arrangement is obstructed. By making the solution more alkaline, the substance capable of receiving a proton applied for stopping or moderating the reaction stabilises the starting substance, and thereby stops the generation of chlorine dioxide (such substances may be by way of example: alkaline metal hydroxides, alkaline earth metal hydroxides, alkaline metal carbonates, alkaline earth metal carbonates, water-mixable organic bases). Substances which will immediately react with the chlorine dioxide, thereby preventing it from explosive decomposition, may also be applied (such as alkaline metal thiosulfates, alkaline metal sulfites, alkaline metal bisulfites). However, the application of the former compound family from the two is more preferable from the aspect that under the given conditions chlorine dioxide disproportionates into chlorite and chlorate, and thereby 50% of the decomposed chlorine dioxide may be recovered when the process is restarted later. In addition to the fact that the whole quantity of chlorine is reduced into chloride by the alkaline metal thiosulfates, alkaline metal sulfites and alkaline metal bisulfites (is rendered incapable of further chlorine dioxide generation), this reaction generates a considerable amount of heat, which may pose mechanical dangers.

Therefore, by way of example, an alkaline metal hydroxide solution is added to the starting solution that, reacting with the chlorine dioxide, reduces the concentration thereof, and also increases the pH of the mother alkaline, which results in a reduced rate of gas generation. The alkaline metal hydroxide (sodium- or potassium hydroxide) solution may be replaced with an alkaline earth metal hydroxide solution (e.g. calcium hydroxide), which stops the reaction along a similar mechanism than the originally suggested alkaline metal hydroxides. In another possible variant of this protection method the alkaline metal hydroxide solution is replaced with an alkaline metal carbonate. In this latter case the mechanism of stopping the reaction is different (see the detailed description below). By reacting with the excess acid in the reactor 100, the carbonate ions increase the pH of the solution, thereby reducing the rate of chlorine dioxide generation. A further advantage of applying carbonate is that carbon dioxide is produced during the reaction with the acid, which, getting discharged from the solution, reduces the chlorine dioxide concentration in the gas space, and thus the danger of explosive decomposition can be avoided. Although the application of the protection method utilising carbonate ions results in a small-scale pressure increase (manageable e.g. by including a pressure relief valve releasing above a predetermined pressure value), it may reduce chlorate formation.

The respective exact effect mechanisms of the so-called “hydroxide protection” and “carbonate protection”, touched upon above, are described in detail below. The hydroxide protection (e.g. utilising a solution of alkaline- or alkaline earth metal hydroxide) functions as follows. The hydroxide ions introduced into the solution react with the substances comprised therein according to the following reaction equations:

$$HClO_2 + OH^- = ClO_2^- + H_2O$$

$$2\ OH^- + 2\ ClO_2 = ClO_3^- + ClO_2^- + H_2O, \text{ and}$$

$$OH^- + H^+ = H_2O$$

Since the reaction takes place in an aqueous solution, the H^+ ions are supplied by the added sulfuric acid, and the hydroxide ions are capable to react with chlorine dioxide. According to the above, therefore, the concentration of hydrogen ions present in the solution, and also the concentration of the chlorous acid responsible

for generating the chlorine dioxide, as well as the amount of ClO_2, is reduced. Due to the reduced amount of hydrogen ions gas generation rate is reduced, and thereby the air introduced into the system can dilute the ClO_2 accumulated in the air space of the reactor, preventing explosive decomposition.

The mechanism of the so-called “carbonate protection” (applying an alkaline- or alkaline earth metal carbonate solution) is the following. The carbonate ions introduced into the solution react with the substances comprised therein according to the following reaction equations:

$$CO_3^{2-} + 2\ H^+ = H_2CO_3$$

the generated carbonic acid is unstable, and reacts as follows:

$$H_2CO_3 = H_2O + CO_2$$

It is apparent, in contrast to the protection method applying hydroxide ions, the carbonate protection does not reduce the quantity of chlorine dioxide in the solution, as it applies a reaction only with the hydrogen ions that increases the pH and reduces the rate of ClO_2 generation. Another significant difference between the two reagents is that the carbon dioxide generated in the course of the carbonate protection process discharges from the solution and dilutes the chlorine dioxide gas accumulated in the reactor space. Thus, it may be capable of preventing explosive decomposition even if the air supply is stopped. This reagent has the further advantage that it does not reduce the amount of chlorine dioxide that has already been generated, and does not produce chlorate ions, the end product that is most difficult to treat.

In case the opening of a tap is indicated in a figure, it is to mean that a specific amount of solution is introduced into the reactor or is discharged therefrom. The specific volume values have to be determined depending on the size of the reactor. The two taps indicated by reference numerals 14 and 22 may be controlled separately by including a pH meter.

The pressure increase caused by the operation of the carbonate protection is much smaller than the increase which would result from explosive decomposition. The protection method applying carbonate has the advantage that the ClO_2 already present in the solution does not disproportionate in case carbonate

introduction is carried on only until pH=6.0, which may be controlled in an automated manner. At this pH value, ClO_2 generation from the decomposition of chlorous acid slows down to a vanishingly slow rate so the reaction virtually stops.

In the course of the protection procedure against the explosive decomposition the reaction preferably does not stop, since stopping the reaction is not the primary objective of the protection. These measures are taken in order to keep concentration conditions in the reactor within such limits that the gas is generated in a safe manner, far from concentration values that could lead to explosive decomposition. In case of a critical failure (an air supply stall, or a tap malfunction resulting in a large amount of reagent solution getting introduced into the reactor) the reaction can be stopped by the “hydroxide protection” procedure.

Gas generation takes place in the reactor 100, and the substance capable of receiving a proton is also introduced there. Therefore the protection procedure is performed in the reactor 100. Once the reactor returns within the optimum operation limits, protonation of the chlorite ions can begin by adding an acidic solution, and gaseous chlorine dioxide may be generated again.

Therefore, all such alkaline substances that comprise the hydroxide ion may be applied for control purposes. The general molecular formula of such substances is $B(OH)_x$, and the reaction mechanism is the following:

$$B(OH)_x = B^{x+} + X\ OH^-$$

$$2\ OH^- + 2\ ClO_2 = ClO_3^- + ClO_2^- + H_2O$$

$$OH^- + H^+ = H_2O$$

$$B^{x+} + ClO_3^- = B(ClO_3)_x$$

$$B^{x+} + ClO_2^- = B(ClO_2)_x$$

where B denotes an organic or inorganic cation having a charge x.

All such substances which are capable of receiving a proton may be suitable for moderating the reaction, and thereby for preventing explosive decomposition. Let these substances be denoted by A_nX_y. Of course, other parameters, such as salt formation, the material of the anions and the cations, and the potentially occurring side reactions, have to be taken into account, but the mechanism along which the reaction is moderated is the same for all substances:

$$A_nX_y = nA^{h+} + yK^{t-}$$

$$K^{t-} + tH^+ = H_tK$$

Based on this general mechanism, the salts of all weak acids with strong bases can be suitable for preventing explosive decomposition. (Where A denotes an inorganic or organic cation having a charge h, K denoting an inorganic or organic anion with a charge t.)

In addition to that, explosive decomposition can also be prevented applying water-mixable organic bases, in which case the mechanism is the following:

$$Z + jH^+ = H_jZ^{j+}$$

where Z is an organic base having j electron pairs that can be protonated.

The application of a substance capable of receiving a proton in the control process is preferred also because it increases the pH of the solution 110, and thereby reduces the amount of the generated chlorine dioxide. In case the introduction of the substance is continued until the pH of the solution becomes strongly alkaline (pH>13), the substance will immediately react with a portion of the gaseous chlorine dioxide, thus directly decreasing its concentration. If the explosive decomposition of chlorine dioxide has not occurred, then – after rectifying any errors preventing the continuation of the process – the reactor 100 may be restarted without cleaning by re-acidifying the reaction mixture.

The following considerations have to be borne in mind when storing and transporting the end product solution (the produced aqueous solution of chlorine dioxide):

1. The final solution must be stored in a well sealed glass vessel (metal ions facilitate the decomposition of chlorine dioxide that is capable of permeating through plastic).
2. It may be worth applying a polished glass plug for sealing the storage vessel. The plug should be attached to the container storing the solution applying a plastic ring.
3. Since the agent may undergo photocatalytic degradation, the end product solution should be protected from prolonged exposure to light. Therefore, the outside of the storage vessel should be covered with a plastic or metal coating.

4. To minimise losses, it may be worth storing the finished solution cooled.
5. To reduce chlorine dioxide gas escape upon opening the sealed vessel, it may be expedient to indicate the packaging temperature, since the escape of the gas may be reduced in case the vessel is sealed and opened near the same temperature.

Before filing the gas in bottles, the concentration of the solution should be checked, preferably by a simple absorptivity measurement. Utilising the spectral plot shown in Fig. 5 the concentration of the finished solution may be determined accurately. In addition to that, it may become necessary to check the purity of the solution utilising an electrode selective to the chloride ion. An aqueous solution of chlorine dioxide having the required concentration may then be prepared by simple dilution. During dilution it should be provided that the solution does not come into contact with metals, and using plastic tools should also be avoided.

The invention is, of course, not limited to the preferred embodiments described in details above, but further variants, modifications and developments are possible within the scope of protection determined by the claims.

CLAIMS

1. A method for producing an aqueous solution of chlorine dioxide, comprising the steps of producing chlorine dioxide gas and carrying away the chlorine dioxide gas by means of a gas flow, wherein
   - in the course of producing the chlorine dioxide gas, the chlorine dioxide gas is generated from a reaction of chlorous acid in a starting solution (110) comprised in a starting reactor (100),
   - in the course of carrying away the chlorine dioxide gas by means of the gas flow, the chlorine dioxide gas is carried from the starting reactor (100) into an aqueous solution (210) comprised in an end product reactor (200) by means of the gas flow, and
   - a volume ratio of the chlorine dioxide gas in a gas space of the starting reactor (100) is controlled by modifying a velocity of the gas flow and/or by adding a substance capable of receiving a proton,

   c h a r a c t e r i s e d by

   carrying the chlorine dioxide gas discharged into the gas space of the end product reactor (200) from the aqueous solution (210) comprised in the end product reactor (200) from the end product reactor (200) into an aqueous solution (310) comprised in an auxiliary reactor (300), and, at a starting of the method, the end product reactor (200) is filled with the aqueous solution (210) comprised in the auxiliary reactor (300).

2. The method according to claim 1, characterised by carrying the chlorine dioxide gas discharged into the gas space of the auxiliary reactor (300) from the aqueous solution (310) comprised in the auxiliary reactor (300) into an alkaline solution comprised in an auxiliary container (56).

3. The method according to claim 1, characterised by utilising a gas space concentration of chlorine dioxide gas measured in the gas space of the starting reactor (100) for controlling the volume ratio of chlorine dioxide gas in the gas space of the starting reactor (100).

4. The method according to claim 3, characterised by determining the concentration of chlorine dioxide by means of a spectrophotometer at a

predetermined wavelength in the gas space of the starting reactor (100), based on a wavelength dependence of a molar absorptivity of chlorine dioxide.

5. The method according to claim 3 or claim 4, characterised by further utilising the velocity of the gas flow and a liquid level of the starting solution (110) for controlling the volume ratio of chlorine dioxide gas in the gas space of the starting reactor (100).

6. The method according to claim 1, characterised by utilising a solution concentration of chlorine dioxide measured in an aqueous solution of chlorine dioxide for controlling the volume ratio of chlorine dioxide gas in the gas space of the starting reactor (100).

7. The method according to any of claims 1 to 6, characterised in that the substance capable of receiving a proton is an alkaline metal hydroxide, alkaline earth metal hydroxide, alkaline metal carbonate, or alkaline earth metal carbonate.

8. The method according to any of claims 1 to 7, characterised by producing the chlorous acid from a reaction of sodium chlorite and sulfuric acid.

9. The method according to any of claims 1 to 8, characterised in that the gas flow is air flow.

10. The method according to any of claims 1 to 9, characterised by stirring continuously the starting solution (110) and/or the solution (210) comprised in the end product reactor (200).