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(54) Title: METHOD FOR TREATING WATER AND AQUEOUS SYSTEMS IN PIPELINES WITH CHLORINE DIOXIDE

(54) Bezeichnung : VERFAHREN ZUR BEHANDLUNG VON WASSER UND WÄSSRIGEN SYSTEMEN IN ROHRLEITUNGEN MIT CHLORDIOXID

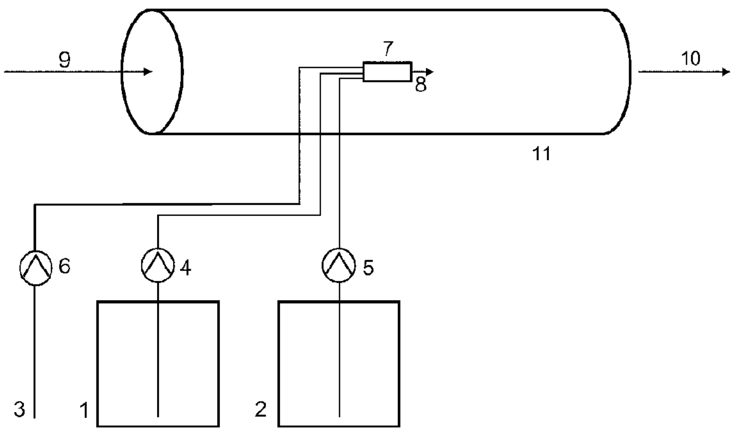

Fig. 1

(57) Abstract: Method for treating water and aqueous systems in pipelines with chlorine dioxide, wherein the reaction space in which the ClO_2 is generated is surrounded completely by the water (9) to be treated, and the reaction space is part of a mobile device (14), which can be introduced and removed again independently of the pressure state in the pipeline (11).

(57) Zusammenfassung: Verfahren zur Behandlung von Wasser und wässrigen Systemen in Rohrleitungen mit Chlordioxid, wobei der Reaktionsraum, in dem das ClO_2 erzeugt, vollständig von dem zu behandelndem Wasser (9) umgeben ist und der Reaktionsraum Bestandteil einer mobilen Vorrichtung (14) ist, die unabhängig vom Druckzustand der Rohrleitung (11) eingebracht und wieder entfernt werden kann.

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Method for treating water and aqueous systems in pipelines with chlorine dioxide

The invention relates to a method of treating water and aqueous systems - hereinafter called the systems to be treated - in pipes with chlorine dioxide (ClO_2).

Chlorine dioxide is used in water treatment and for treating aqueous systems because of its high bactericidal, virucidal and algicidal activity. Aqueous systems are used in a multiplicity of industrial processes such as, for example, in the food industry, in brewing processes, in the drinks industry and in paper making, inter alia, as transport medium, as heating and cooling medium and for washing purposes. The transport of aqueous systems within the industrial processes proceeds principally in pipes. Generally, biological growth in these systems must be restricted by using biocides such as, for example, chlorine dioxide. Owing to the explosive tendency of gaseous chlorine dioxide ($c > 300\ g/m^3$) and chlorine dioxide solutions ($c > 26\ g/l$), chlorine dioxide cannot be stored in compressed form or in solutions of relatively high concentration. Owing to these chemical properties, chlorine dioxide must be produced at the point of use. This is achieved by mixing basic chemicals in special reactors of chlorine dioxide generation systems. The chemical storage vessels, the metering appliances and also the reactor of the chlorine dioxide systems form a locally linked unit of apparatus which is generally erected in rooms accessed by people.

There are a plurality of methods, but principally three underlying methods, for synthesizing ClO_2 which are used commercially for water treatment. These methods use sodium chlorite ($NaClO_2$) as one of the starting materials. The underlying chemistry of the three methods is explained hereinafter. The substances used in these methods are termed starting chemicals, or else reactants.

1. Method using sodium chlorite and strong acid

In the first method, a strong acid is used together with sodium chlorite. The strong acid is usually hydrochloric acid or sulphuric acid. When hydrochloric acid is used the reaction stoichiometry is as follows:

$5\ NaClO_2 + 4\ HCl \rightarrow 4\ ClO_2 + 5\ NaCl + 2\ H_2O$

In addition, chlorine dioxide can be formed with the use of sulphuric acid in accordance with the reaction hereinafter:

$10\ NaClO_2 + 5\ H_2SO_4 \rightarrow 8\ ClO_2 + 5\ Na_2SO_4 + 2\ HCl + 4\ H_2O$

2. Method starting from sodium chlorite and chlorine

This method uses gaseous chlorine together with sodium chlorite. The reaction proceeds in two stages, first with the formation of hydrochloric acid.

$Cl_2 + H_2O \rightarrow HOCl + HCl$

The intermediate, hypochloric acid (HOCl), then reacts with sodium chlorite, forming chlorine dioxide (ClO_2).

$HOCl + HCl + 2\ NaClO_2 \rightarrow 2\ ClO_2 + 2\ NaCl + H_2O$

The stoichiometric reaction from the two equations is

$Cl_2 + 2\ NaClO_2 \rightarrow 2\ ClO_2 + 2\ NaCl$

3. Method starting from sodium chlorite and sodium hypochlorite

In the third method, sodium hypochlorite (NaOCl) is used together with sodium chlorite:

$NaOCl + HCl \rightarrow NaCl + HOCl$

$HCl + HOCl + 2\ NaClO_2 \rightarrow 2\ ClO_2 + 2\ NaCl + H_2O$

The synthesis reactions for generating chlorine dioxide are generally carried out in reactors which are operated either continuously or by the batch method.

Two explosion limits must be taken into account in the generation of chlorine dioxide: more than 6 g of ClO_2/l of solution [contact with air] and more than 26 g of ClO_2/l of solution [autodecomposition of the aqueous solution]. In the case of the chlorine dioxide syntheses carried out by methods 1 to 3, when use is made of starting chemicals which would lead in the reaction space to a concentration of greater than approximately 26 g of ClO_2/l of solution, dilution water is added to the reaction space in order to bring this concentration below that of spontaneous autodecomposition. The chlorine dioxide solution leaving the reaction space which generally contains 20 g of ClO_2/l or less is diluted with a further water stream to concentrations of roughly less than 3 g of ClO_2/l of solution.

In order that the prior art methods can be operated with satisfactory results with respect to plant safety, chlorine dioxide yield and time-specific production rate, a variety of processing variations are performed, inter alia,

- Installation and use of metering points on the pipe having systems to be treated for addition of chlorine dioxide generated outside the pipe.
- Use of diluted starting chemicals: respective concentrations of the chlorine dioxide solution produced falling below 26 g/l or 6 g/l.
- Generation of reduced pressure in the reactor by applying a vacuum: reduction of the chlorine dioxide concentration in the gas phase to < 300 g/m³.
- Generation of reactor overpressure, e.g. by using pressure-retention valves at the reactor outlet: prevention of the formation of a gas phase by exceeding the solubility limit of chlorine dioxide; increasing the yield.
- Use of batch methods having long reaction times: increasing the yield when diluted starting chemicals are used.
- Use of superstoichiometric acid amounts in the chlorite/acid method and use of superstoichiometric chlorine amounts in the chlorite/chlorine method: increasing the yield.

Despite the use of these procedures, in the event of incorrect operation of the chlorine dioxide generation systems, e.g. due to loss of dilution water or by failure of the pressure control, spontaneous decomposition (explosion) of chlorine dioxide can occur, or chlorine dioxide may, owing to leakage or breakage of separation surfaces between the chlorine-dioxide-containing solution and the environment, lead to hazards in the surroundings of the generation systems. The use of diluted starting chemicals which lead to chlorine dioxide solutions with a concentration of less than 6 g/l, and therefore the sacrifice of relatively high time-specific generation rates of the chlorine dioxide systems, also cannot exclude the hazard to the surroundings of the generation systems by exceeding the MAK value [maximum workplace concentration] of 0.1 ppm in the event of incorrect operation. In order to minimize these hazards, various measures are implemented at the generation systems themselves, and also at the sites where the chlorine dioxide generation systems are erected, e.g. complex servicing work on the generation systems including regular replacement of the reactors, spatially isolated erection sites for the generation systems, forced aeration and air monitoring of the atmosphere of the erection site by continuous gas analyses.

After production of the chlorine-dioxide-containing solutions, they are transported into the pipes according to the prior art using pressure elevation appliances, in which pipes the systems to be treated are situated. This takes place, for example, via connection ports which are situated in the pipe. The metering line for the chlorine-dioxide-containing solution which extends into the pipe having the systems to be treated can only be worked on after clearance of this pipe. Clearance in this case means depressurizing and emptying the system-bearing pipe. The points for chlorine dioxide addition are frequently in bypass lines which are provided with shutoff elements upstream and downstream of the addition site.

The object is therefore to design the treatment of water and aqueous systems - hereinafter called the systems to be treated - which are situated in pipes with chlorine dioxide so as to be safer and more efficient. Especially, the object is, at a high time-specific generation rate of the chlorine dioxide methods, to minimize the hazard potential of this type of treatment and simultaneously to reduce the expenditure on the safety installations. All necessary process steps should be able to be carried out independently of the pressure state of the pipe which contains the system to be treated.

A safe method for the environment and people should be found with avoidance of the emission of ClO_2 into the environment, in particular into the spaces in which the plant is customarily operated. At the same time the advantages resulting from the use of concentrated starting chemicals such as, e.g., reduced material transport, higher reaction rate, higher yields, lower reactor volume, should be made utilizable and the necessary assembly and maintenance work for chlorine dioxide treatment of systems to be treated in pipes should be able to be carried out independently of the pressure state of the system-bearing pipe.

The invention relates to a method of treating water and aqueous systems in pipes with chlorine dioxide, characterized by the features

1. the reaction space in which the ClO_2 is generated is completely surrounded by the system to be treated,
2. the system surrounding the reaction space is simultaneously the system to be treated,
3. the reaction space is a component of a mobile device and the mobile device can be introduced into the pipe in which the system to be treated is situated and removed again independently of the pressure state of the pipe containing the system to be treated,
4. the reaction space is situated after use of the mobile device in the pipe containing the system to be treated,
5. the ClO_2 generated in the reaction space is delivered to the system to be treated which is situated in the pipe.

Surprisingly, the object was achieved by the measures according to the claims and the description.

Features 1. to 5. are essential to the invention for the present method in a combination thereof which enables safe working by avoiding the escape of ClO_2 into working rooms or the environment and eliminates adverse consequences of explosive decompositions. The reaction space is a component of a mobile device which can be brought into the pipe and removed again independently of the pressure state thereof.

The reaction space in which the ClO_2 is generated is a component of a mobile device and after introduction into the pipe is completely surrounded by water or an aqueous system and this is simultaneously the system to be treated.
Shifting the point of formation of the chlorine dioxide out of spaces accessed by people and the storage site of the starting chemicals significantly increases safety. Leaks up to explosions of the reaction space are virtually neutralized by the large volume of the systems to be treated.
The reaction space can be introduced into a pressurized pipe through which a system to be treated flows, and can be removed from this pipe again without interrupting the transport and therefore the utilization in the pipe of the system to be treated. In addition, the reaction space is preferably in the main pipe of the system to be treated and not in a bypass line to the main line which can be spatially isolated by shutoff elements situated upstream and downstream of the site in the bypass line for feeding chlorine dioxide to the system to be treated.

The advantages of the novel method will be described in more detail hereinafter. Chlorine dioxide can be added to a system to be treated which is situated in a pipe at any position and at any pressure state of the pipe. A leak of the reaction space, in particular of the reactor, which is situated in a pipe can be handled simply and safely in the system to be treated which is flowing past the wall thereof. The chlorine dioxide, in particular, exiting in the event of a leak of the reaction space is diluted to a non-critical concentration and transported away. The same applies to any starting chemicals exiting from the reaction space, in particular the reactor. Since the synthesis of chlorine dioxide from concentrated starting chemicals can proceed without dilution by water, the necessary superstoichiometric yield-increasing excess amounts of acid and/or chlorine can be decreased and additionally there is a significant increase in reaction rate, a high specific generation output of the reaction space results. By reducing the necessary median residence time of the reactants in the reaction space there is the possibility of minimizing the reaction space volume, as a result of which, e.g., the installation of the reaction space, in particular the reactor, into a pipe through which the system to be treated flows becomes possible.

In addition, from the safety aspect, there is an improvement of the ratio between the amount of chlorine dioxide permanently present during synthesis in the reaction space and the amount of system to be treated.

Shifting the point of production of the chlorine dioxide out of the spaces accessed by people and the storage site of the starting chemicals significantly increases safety. Reaction space leaks up to reaction space explosions are virtually neutralized by the large volume of system to be treated relative to the amount of chlorine dioxide which is present in the reaction space. Preferably the site of addition of the chlorine dioxide to the system to be treated is not situated in a bypass line to the main line of the system to be treated which can be spatially isolated by shutoff elements situated upstream and downstream of the site of addition situated in the bypass line, but directly in the main line. By this means incorrect addition of chlorine dioxide into a space having restricted volume and without replacement of the system to be treated (space isolated by shutoff elements) and the resultant hazards are safely prevented. The high flexibility of the method according to the invention significantly expands the fields of application of chlorine dioxide treatment and, in addition to the hazard potential due to the starting chemicals and the chlorine dioxide simultaneously reduces the industrial expenditure for treatment of systems to be treated in pipes.

The features 1. to 5. are essential to the invention for the present method in a combination thereof which, in addition to the flexibility of the biocide treatment method, also permits safe working, even with the use of concentrated starting chemicals, by avoiding the escape of ClO_2 into working rooms or the environment and eliminates the adverse consequences of explosive decompositions.

The reaction space in which the ClO_2 is generated is completely surrounded by the systems to be treated and the system to be treated which surrounds the reaction space is simultaneously the system to be treated.

The use of a reactor as reaction space is preferred.

According to process steps 3. and 4. the reaction space is a component of a mobile device which preferably consists of a piston-like tube in which the reaction space is situated, and wherein this mobile device has a reaction space outlet and feed lines for the reactants and optionally dilution water. The mobile device, preferably the piston-like tube, with the reaction space is conducted and moved into a guide channel, preferably a cylindrical outer tube, which tube, which is shut off by a shutoff element from the pipe having the system to be treated, has access to the pipe having the system to be treated. After introduction of the mobile device, preferably the piston-like tube having the reaction space into the guide channel, preferably the cylindrical outer tube, the shutoff element can be opened and the mobile device, preferably the piston-like tube having the reaction space can be introduced into the pipe having the system to be treated. Preferably, the feed lines for the reactants and optionally dilution water are conducted from the top into the mobile device and the reaction space. Likewise, for example, structures are possible in which the feed lines are conducted outside the reaction space, preferably reactor, to the inlet of the reaction space, such as, e.g., from the side or from the bottom.

It is possible, in process step 5., to deliver the ClO_2 which is formed into the system which is to be treated without diversions or other additional lines directly from the reaction space in which the ClO_2 is formed since the outlet is situated directly at the end of the reaction space, preferably the reactor, and therefore likewise is surrounded by the system to be treated. Preferably, the reaction space is situated in the main pipe of the system to be treated and not in a bypass line to the main line which can be spatially isolated by means of shutoff elements situated upstream and downstream of the site lying in the bypass line for feeding chlorine dioxide to the system to be treated. This measure is the preferred variant of the method.

The renewal rate of the system to be treated at the outlet of the reaction space, preferably the reactor outlet, is affected by the mass flow rate of the system to be treated and the geometrical ratios in the pipe. If the reaction space outlet is situated, for example at the effluent side of the system to be treated at the reaction space, vortices generating reduced pressure form, which vortices accelerate the distribution of the chlorine dioxide generated in the system to be treated.

The reaction space, preferably the reactor, is preferably operated without a pressure control appliance. Via a free outlet at the end of the reaction space, preferably the reactor, it is ensured that the pressure in the reaction space can only increase up to the value which is exerted on the reaction space by the surrounding system to be treated.

The concentration of the chlorine dioxide formed in the reaction space, preferably in the reactor, can be set, in combination with pressure and temperature of the surrounding system to be treated, in such a manner that the solubility limit of chlorine dioxide in the system to be treated is not exceeded. As a result, the formation of a 2-phase system due to a forming chlorine dioxide gas phase can be prevented.

The pressure ratios for a reactor used in a pipe can be affected, for example by shutoff elements integrated into the pipe. Furthermore, fittings situated in the pipe can modify the turbulence of the flow of the system to be treated and thereby the distribution of the added chlorine dioxide in the system to be treated.

If the system to be treated at the outlet of the reaction space, preferably the reactor, is renewed at a corresponding rate, the concentration of the chlorine dioxide solution leaving the reaction space, preferably reactor, can be abruptly shifted to a milligram range.

In principle, all chemical methods of producing ClO_2 in the reaction space can be employed, in particular the methods 1. to 3. described at the outset, or else starting from chlorate.

Preference in this invention is given to the hydrochloric acid-chlorite method (1.). In this method the starting chemicals (reactants) of alkali metal chlorite salt, preferably sodium chlorite, can be present in aqueous solutions of 3.5% to 40%. The acid is preferably hydrochloric acid in a concentration of 3.5% to 42%.

In the particularly preferred embodiment of the invention, use is made of concentrated starting chemicals and the hydrochloric acid chlorite method (1.) is employed. The concentration of the hydrochloric acid is then about 33-42% and that of the sodium chlorite solution is about 25-40%. The starting chemicals are not diluted before or in the reaction space, preferably the reactor.

The starting chemicals (reactants), in particular acid and chlorite, are passed into the reaction space as aqueous solution, as described above, separately by inherent pressure of the solutions or using pumps, and brought to reaction.

In the preferred procedure, the reactants are used as concentrated solutions and the use of dilution water is dispensed with, and so the chlorine dioxide concentration at the end of the reaction space, preferably at the reactor outlet, or the outlet line, is set to greater than 80 g/l of solution. Alternatively, dilution water can be used in order to set the chlorine dioxide concentration at the end of the reaction space, preferably at the reactor outlet, or at the outlet line, between greater than 3 g/l of solution, preferably greater than 26 g/l of solution, and, particularly preferably, greater than 80 g/l of solution.

The device for carrying out the method according to the invention comprises essentially suitable devices and apparatuses. The device typically includes one or more tanks for the starting chemicals (reactants), in particular an acid storage tank and a chlorite storage tank, wherein an aqueous acid solution is stored in the acid storage tank and a solution of an alkali metal salt of a chlorite ion is stored in the chlorite storage tank. Apparatuses are provided which not only can feed the suitable components into the storage tanks but can also take off solutions. Preferably, these apparatuses include pumps and feed lines which are sufficient to ensure the flow rates of the starting chemicals (reactants), in particular of aqueous acid solutions and solutions of alkali metal salts of a chlorite ion, and also of dilution water rate. Specialists in the field can readily determine suitable sizes for the relevant storage tanks, feed lines and pumps in order to achieve the required feed rates of reactant solutions (i.e., e.g. aqueous acid solutions, solutions of an alkali metal salt of a chlorite ion).

Preferably, the device has embodiments having at least two pumps for two starting chemicals (reactants), but in particular one for the solution of the alkali metal salt of a chlorite ion and the other for the aqueous acid solution.

The device further comprises an apparatus for mixing the solution of the starting chemicals (reactants), in particular the solution which contains the alkali metal salt of a chlorite ion and the aqueous acid solution, in order to provide an aqueous reaction solution of the starting chemicals (reactants). Any apparatus which mixes the abovementioned solutions adequately can be used, including conventional T pieces or other connection elements which combine two streams or three streams to form one combined stream, throttle lines and/or a stirred tank. The aqueous reaction solution can then be fed after mixing into the reaction space. Preferably, the two reactants and the optionally used dilution water are mixed in the reaction space. The mixing operation can be introduced by any appliance, such as baffle plates, injectors or packings, for example, which ensures optimum mixing.

As reaction space, use can be made of any reactor which is able to initiate the reaction between the starting chemicals (reactants), in particular the aqueous acid solution and the alkali metal salt of a chlorite ion, simple tanks, mass-flow or plug-flow reactors and tubular reactors. A tubular reactor is particularly preferred. Usually, a chlorine dioxide generation unit consists of only one tubular reactor, but the generation output of a unit can be increased by the parallel arrangement of a plurality of reactors, for example to form a tube bundle. The reactor can be not only temperature-controlled, but also consist of a good heat-conducting material in order to deliver liberated heat of reaction to the surrounding system to be treated. The material of which the reactor is fabricated consists of materials which exhibit good stability to the respective reaction solutions. In the generation of chlorine dioxide solutions having concentrations of greater than 28 g/l, the reaction material is, for example, titanium, alloy 31, glass or chemistry materials, e.g. polymers, such as, e.g., PVDF or PTFE. When titanium is used as reactor material, the reaction solutions are fed in such a manner that when hydrochloric acid is used, this does not come into contact with the titanium surface without the reaction partner which in this case is an oxidizing agent (e.g. sodium chlorite) being present simultaneously. This procedure prevents titanium corrosion since the corrosion-triggering property of the hydrochloric acid is abolished under oxidizing conditions. This state can be achieved, e.g., by feeding the hydrochloric acid via a plastic line into the centre of the reactor - at the greatest possible distance from the titanium surface - and the oxidizing reaction partner being situated close to the hydrochloric acid feed point. The ClO_2 is conducted away from the reactor by any desired mechanism which is able to remove an aqueous solution from a reactor. Preferably, the reaction is carried out continuously, and ClO_2 is continuously removed from the reactor. After it leaves the reactor, the ClO_2 is metered directly into the system to be treated.

A tubular reactor is preferably used according to the present invention. Generally the tube of the tubular reactor is constructed in such a manner that it has a sufficient length to ensure sufficient residence time in the reactor in order that the components react sufficiently in view of the flow rate of the reaction solution, its concentration of reactants and the temperature of the reaction solution. A particularly preferred reactor which can be used for producing a suitable generator of aqueous chlorine dioxide on site is a tubular reactor which contains one or more tube coils. Specialists in the field are able to vary the size and shape of the reactor as a function of the amount of aqueous chlorine dioxide to be produced, the flow rate and concentration of reactants, the pH of the aqueous reaction solution, the pH of the ClO_2 and the temperature of the reactor. Specialists in the field are likewise able to modify the temperature of the reactor appropriately.

The reaction time in the reaction space can vary. With increasing concentration of the reactants in the reaction space, the optimum of the residence time decreases. If a solution having a chlorine dioxide concentration of 20 g/l is produced, the median reactor residence time is about 60 minutes to 4 minutes, preferably approximately 4 to 6 minutes, in order to achieve a yield of approximately 85%. If the chlorine dioxide concentration according to the particularly preferred embodiment increases to greater than 80 g/l, the median reactor residence time is about 0.1 minute to 1.5 minutes, preferably 0.3 to 0.6 minute, particularly preferably approximately 0.4 minute, for a 95% yield. The minimum of the median residence time can be achieved when the reactants are used as concentrated solutions, dilution water is not used and the necessary stoichiometric excess of acid or chlorine is minimized. If in the method according to the invention the reactor is designed for a certain generation rate, e.g.

10 kg/h, surprisingly this gives the possibility of increasing the amount of chlorine dioxide generated by more than threefold. Although this high flexibility of generation rate is accompanied in the case of relatively large generation rates with a decrease in conversion rate (10 kg/h = 95% yield; 30 kg/h = 80% yield), especially for such applications considerable advantages result in which considerable increases of the standard required rates of chlorine dioxide result temporarily and at low frequency.

The chlorine dioxide solution leaving the reaction space outlet is diluted in such a manner that the renewal rate of the system to be treated at the reaction space outlet is about 0.1 m^3/h to 20 m^3/h per gram and hour of chlorine dioxide generated, preferably 1 m^3/h to 4 m^3/h per gram and hour of chlorine dioxide generated.

The method according to the invention can be carried out, for example, using the devices depicted in Figure 1 and Figures 2a and 2b.

Figure 1 shows an outline structure for carrying out the method having a reaction space in a pipe without the mobile device and without being restricted to certain starting chemicals (reactants) or embodiments. The units having the stated numbers may therefore be used correspondingly generally in their function for all methods having the various possible starting chemicals (reactants) and easily recognizable to those skilled in the art.

In Fig. 1, the device for treating water and aqueous systems in pipes with chlorine dioxide consists of two tanks for the starting chemicals (reactants), in particular a chlorite storage tank 1 having feed pump 4 and an acid storage tank 2 having feed pump 5. The water pump 6 is supplied via the water connection 3. All three feed pumps are connected via individual lines to the bottom side of the reaction space, preferably reactor, 7. In the reaction space, preferably reactor, there are situated appliances of the prior art which ensure rapid complete mixing of the components fed in the reaction space. By varying the concentration contents of the reactant solutions or the amount of dilution water used, the concentration of the resultant chlorine dioxide solution is set to greater than 3 g/l, preferably greater than 26 g/l, and particularly preferably to greater than 80 g/l. The preferred variant, however, is to

allow the reactants to react in the reaction space without dilution by water (dilution water feed pump 6 switched off).
At the top, opposite end, of the reaction space, preferably reactor, 7 there is situated the reaction space outlet 8.

A preferred device for the method according to the invention is reproduced in Fig. 2a (maintenance state) and Fig. 2b (operating state). In this case it is essential to the invention that the reaction space, preferably reactor, is situated in a mobile device 14, preferably a piston-like tube 14, and wherein this mobile device possesses a reaction space outlet and feed lines for the reactants and optionally dilution water, and can be slid and moved by the movement device 16, preferably a threaded rod, into the guide channel 13, preferably a cylindrical outer tube 13. In this case the shutoff element 12 is closed and so no system to be treated can penetrate into the interior of the guide channel 13. After the mobile device 14 has been introduced into the guide channel 13 using the movement device 16 (Fig. 2a, maintenance state), the shutoff element 12 can be opened without the system to be treated being able to exit from the guide channel 13. Using the movement device 16, the mobile device 14 and therewith the reaction space, preferably reactor, situated therein, can then be introduced into the system-bearing pipe 11 (Fig. 2b, operating state). The surface between the guide channel 13 and the mobile device 14 is designed in such a manner that it is not permeable to the system to be treated 9. The sealing systems used are either component of the guide channel 13, the mobile device 14, or they are present in both components. In principle, all sealing variants are suitable which prevent the escape of system to be treated 9 from the pipe 11 via the guide channel 13 into the open. Via the feed lines 15 the reactants are transported into the reaction space, preferably reactor. The passages of the feed lines 15 into the reaction space, preferably reactor, are constructed in such a manner that even at relatively high pressures, sealing of these passages is provided.
Preferably, the feed lines 15 are conducted from the top into the mobile device 14 and into the reaction space. Likewise, for example, structures are possible in which the feed lines for the reactants are conducted outside the reaction space, preferably reactor, for entry of the reaction space such as, e.g., from the side or from the bottom. The mobile appliance 14 having the reaction space, preferably reactor, can also be

constructed in such a manner that it is arranged in an additional outer tube. All process modes are possible which prevent escape of the system to be treated from the pipe 11 and simultaneously enable the introduction of the reaction space into this pipe. Preferably, the reaction space, preferably reactor, is a closed space in which the reaction space outlet is situated at the opposite end of the reactant feed line 15. Preferably, the reaction space outlet is formed by bore holes in the reaction space wall and the mobile device 14 is positioned in the pipe 11 in such a manner that the reaction space outlet is situated at the top.
The chlorine dioxide formed can be delivered to the system to be treated 11 via the reaction space outlet. Preferably, the chlorine-dioxide-treated system 10 leaves the pipe section in which the chlorine dioxide solution is added to the system to be treated 9. By varying the reaction space outlet (size, type and number of orifices), position of the reaction space outlet to the direction of flow of the system to be treated, and also by various positioning of the reaction space outlet with respect to the open diameter of the pipe 11, various distribution patterns of the chlorine dioxide generated in the system to be treated 9 can be set in the pipe 11.
In all cases the preferred variant is maximum reduction of the volume of the reaction space, preferably reactor. By using concentrated reactants, in this preferred variant the concentration of the chlorine dioxide solution at the reaction space outlet 8 is set to greater than 80 g/l.
The guide channel 13 is preferably mounted on the system-bearing pipe 11 in a 12 o'clock or 6 o'clock position. Regardless of the site of installation of the guide channel 13, the reaction space, preferably reactor, should preferably be arranged in such a manner that it is situated below relative to the reaction space outlet. The advantage is that gaseous components can leave the reaction space.

The preferred variant comprises allowing the reactants to react in the reaction space without dilution by water (dilution water feed pump 6 switched off). In this case the concentration of the resultant solution at the reaction space outlet 8 can increase to greater than 9 g/l, preferably greater than 26 g/l, and particularly preferably to greater than 80 g/l of chlorine dioxide per litre. In this preferred variant it is advantageous to reduce the reactor volume maximally. Generally, no further appliances are necessary to achieve the renewal rate of the system to be treated 9 at the reaction space outlet 8 in order to shift the concentration of the chlorine dioxide solution after entry into the system to be treated 9 rapidly from preferably greater than 80 g per litre to the milligram region. Likewise, it is generally not difficult to set the pressure of the system to be treated 9 in the pipe 11 in such a manner that the solubility limit of the chlorine dioxide in the aqueous solution in the reaction space, preferably reactor, 7, as shown in Fig. 3, is not exceeded.

Figs. 2a and 2b show an outline structure for carrying out the method according to the invention without being restricted to defined embodiments or starting chemicals (reactants). The units having the specified number are therefore to be employed in their function correspondingly generally for all methods having the various possible starting chemicals (reactants) and may be readily recognized by those skilled in the art.

Legend to Fig. 1, Fig. 2a and Fig. 2b:

1 Chlorite storage tank
2 Acid storage tank
3 Water connection
4 Chlorite feed pump
5 Acid feed pump
6 Dilution water feed pump
7 Reaction space (reactor)
8 Reaction space outlet (reactor outlet)
9 System to be treated
10 Treated system
11 Pipe
12 Shutoff element
13 Guide channel
14 Mobile device
15 Reactant feed lines
16 Movement device

Figure 3 shows the solubility limits of chlorine dioxide in an aqueous solution as a function of pressure and temperature, by way of example for the chlorine dioxide concentrations 70 g/l and 80 g/l.

The method according to the invention is described by the example hereinafter without being restricted thereto:

Example 1

The device described in Figs. 2a and 2b is used. The mobile device 14 having the reactor 7 contained therein is situated with shutoff element 12 open in the pipe 11 through which system flows and is thereby in the operating state. The pipe 11 has a diameter of 600 mm and the system to be treated 9 in the pipe 11 is surface water which is fed at a mass flow rate of 1000 m^3/h via pipe 11 to a treatment unit. The pressure in the pipe 11 is 6.2 bar. Via the feed lines 15, 5.9 l of a 25% strength sodium chlorite solution and 5.3 litres of a 32% strength hydrochloric acid solution are fed per hour to the reactor. The reactor has a free volume of 0.075 litre and the residence time of the reaction mixture in the reaction space is 0.4 minute. 11.1 litres of chlorine dioxide solution having a content of 92 g/l are delivered per hour via the reaction space outlet 8 into the system to be treated 9 (surface water) flowing round the reactor 7. This corresponds to a calculated chlorine dioxide concentration of 1 mg/l. At an acid excess of 300%, the chlorine dioxide is generated at a yield of 95%. The content of chlorine dioxide in the system to be treated 9 (surface water) has reduced to a concentration of 0.2 mg/l at the inlet of the water treatment plant which is approximately 1 km away from the chlorine dioxide metering site.

Claims:

1. Method of treating water and aqueous systems in pipes with chlorine dioxide (ClO_2), characterized by the features
   1. the reaction space in which the ClO_2 is generated is completely surrounded by the system to be treated,
   2. the system surrounding the reaction space is simultaneously the system to be treated,
   3. the reaction space is a component of a mobile device and the mobile device can be introduced into the pipe in which the system to be treated is situated and removed again independently of the pressure state of the pipe containing the system to be treated,
   4. the reaction space is situated after use of the mobile device in the pipe containing the system to be treated,
   5. the ClO_2 generated in the reaction space is delivered to the system to be treated which is situated in the pipe.

2. Method according to Claim 1, characterized in that the reaction space is a reactor.

3. Method according to at least one of the preceding claims, characterized in that the reactor is a tubular reactor.

4. Method according to at least one of the preceding claims, characterized in that the reaction time of the reactants in the reaction space varies from 4 to 60 minutes, preferably 4 to 6 minutes, particularly preferably from 0.1 to 1.5 minutes, very particularly preferably 0.3 minute to 0.6 minute.

5. Method according to at least one of the preceding claims, characterized in that the chlorine dioxide is generated from an alkali metal chlorite salt and hydrochloric acid (reactants).

6. Method according to at least one of the preceding claims, characterized in that the chlorine dioxide is generated from sodium chlorite and hydrochloric acid

(reactants).

7. Process according to at least one of the preceding claims, characterized in that the chlorine dioxide is generated from sodium chlorite in an aqueous solution of 3.5% to 40%.

8. Method according to at least one of the preceding claims, characterized in that the chlorine dioxide is generated from hydrochloric acid in a concentration from 3.5% to 42%.

9. Method according to at least one of the preceding claims, characterized in that the chlorine dioxide is generated from sodium chlorite and chlorine (reactants).

10. Method according to at least one of the preceding claims, characterized in that dilution water is used.

11. Method according to at least one of the preceding claims, characterized in that no dilution water is employed.

12. Method according to at least one of the preceding claims, characterized in that the reactor is operated without a pressure control appliance.

13. Method according to at least one of the preceding claims, characterized in that the reactor has a free outlet at the reactor outlet in such a manner that the pressure in the reaction space can only increase to the value which is exerted on the reaction space by the surrounding system.

14. Method according to at least one of the preceding claims, characterized in that the chlorine dioxide solution leaving the reaction space outlet is diluted in such a manner that the renewal rate at the reaction space outlet of the system to be treated is about 0.1 m^3/h to 20 m^3/h per gram and hour of chlorine dioxide generated, preferably 1 m^3/h to 4 m^3/h per gram and hour of chlorine dioxide generated.

15. Method according to at least one of the preceding claims, characterized in that the ClO_2 formed in the reaction space is passed out of the reaction space directly into the system to be treated, the concentrations of the starting chemicals being selected in such a manner that the concentration at the reactor outlet of the chlorine dioxide formed is greater than 3 g/l of solution, preferably greater than 26 g/l of solution, and particularly preferably greater than 80 g/l of solution.

16. Method according to at least one of the preceding claims, characterized by the features
    1. the reaction space in which the ClO_2 is generated is a reactor without a pressure control appliance and equipped with a free outlet and this reactor is completely surrounded by the system to be treated,
    2. the system surrounding the reaction space is simultaneously the system to be treated,
    5. the ClO_2 formed in the reaction space is passed out of the reaction space directly into the system to be treated, the combination of the concentration of starting chemicals and dilution water optionally used being selected in such a manner that the concentration at the reactor outlet of the chlorine dioxide formed is greater than 3 g/l of solution, preferably greater than 26 g/l of solution, and particularly preferably greater than 80 g/l of solution.

17. Method according to one of the preceding claims, characterized by the features
    1. the reaction space in which the ClO_2 is generated is a reactor without a pressure control appliance and equipped with a free outlet and this reactor is completely surrounded by the system to be treated,
    2. the system surrounding the reaction space is simultaneously the system to be treated and this exerts a pressure on the chlorine-dioxide-containing solution in the reaction space of a magnitude such that the solubility limit of chlorine dioxide in water at a given temperature is not exceeded,
    5. the ClO_2 formed in the reaction space is passed out of the reaction space directly into the system to be treated, the combination of the concentrations of the starting chemicals and dilution water optionally used being selected in such

a manner that the concentration at the reactor outlet of the chlorine dioxide formed is greater than 3 g/l of solution, preferably greater than 26 g/l of solution, and particularly preferably greater than 80 g/l of solution.

18. Method according to at least one of the preceding claims, characterized in that concentrated starting chemicals are used and the hydrochloric acid chlorite method (1.) is employed, the concentration of the hydrochloric acid being 33-42% and that of the sodium chlorite solution being 25-40%.

19. Method according to at least one of the preceding claims, characterized in that the mobile device consists of a piston-like tube.

20. Method according to at least one of the preceding claims, characterized in that titanium is used as reactor material, the reaction solutions are fed in such a manner that when hydrochloric acid is used it does not come into contact with the titanium surface without the reaction partner, which in this case is an oxidizing agent such as, e.g., sodium chlorite, being present simultaneously.

21. Method according to at least one of the preceding claims, characterized in that the reaction space is situated in the main pipe of the system to be treated and not in a bypass line to the main line, which can be spatially isolated by shutoff elements situated upstream and downstream of the site in the bypass line for feeding chlorine dioxide to the system to be treated.

22. Method according to at least one of the preceding claims, characterized in that the mobile device can be introduced into the pipe via a feed channel using a movement device, a shutoff element being situated between the feed channel and the pipe.

23. Method according to at least one of the preceding claims, characterized in that the feed channel consists of a cylindrical outer tube and/or the mobile device consists of a piston-like tube.

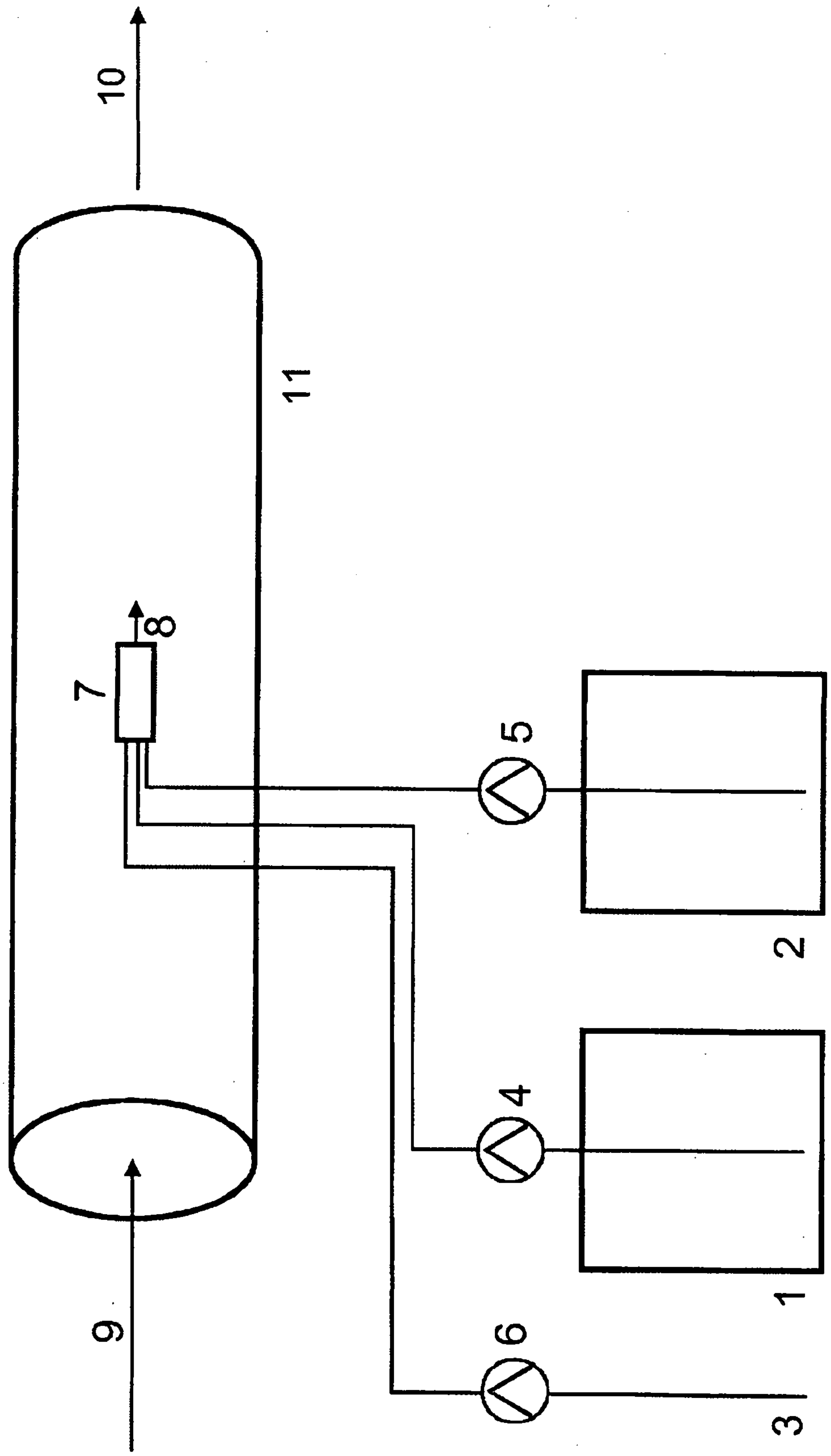

Fig. 1

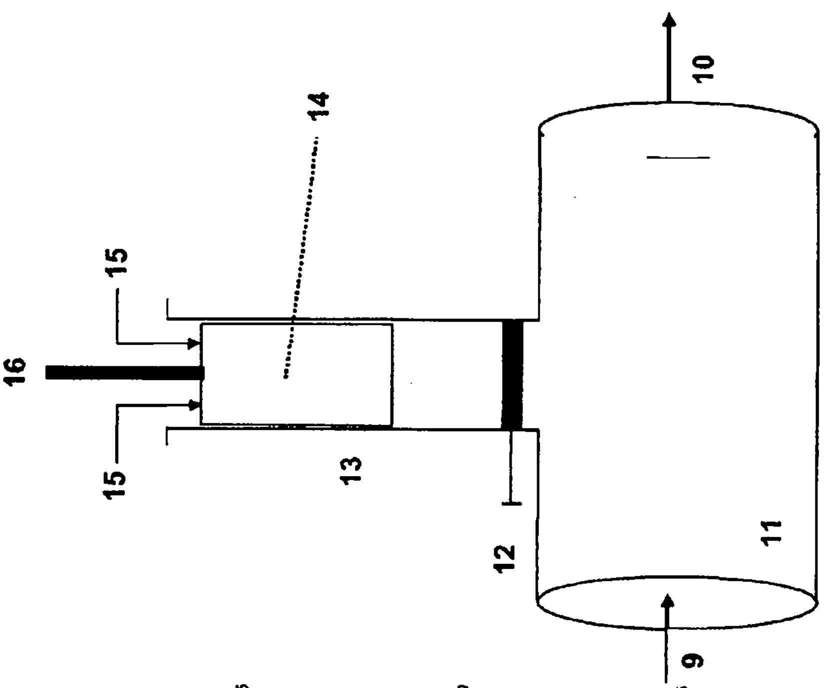

Fig. 2a

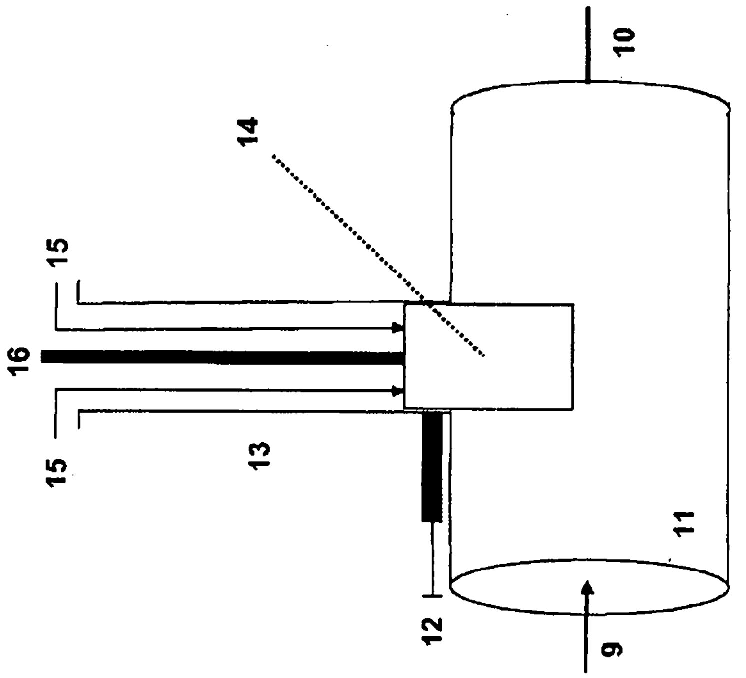

Fig. 2b

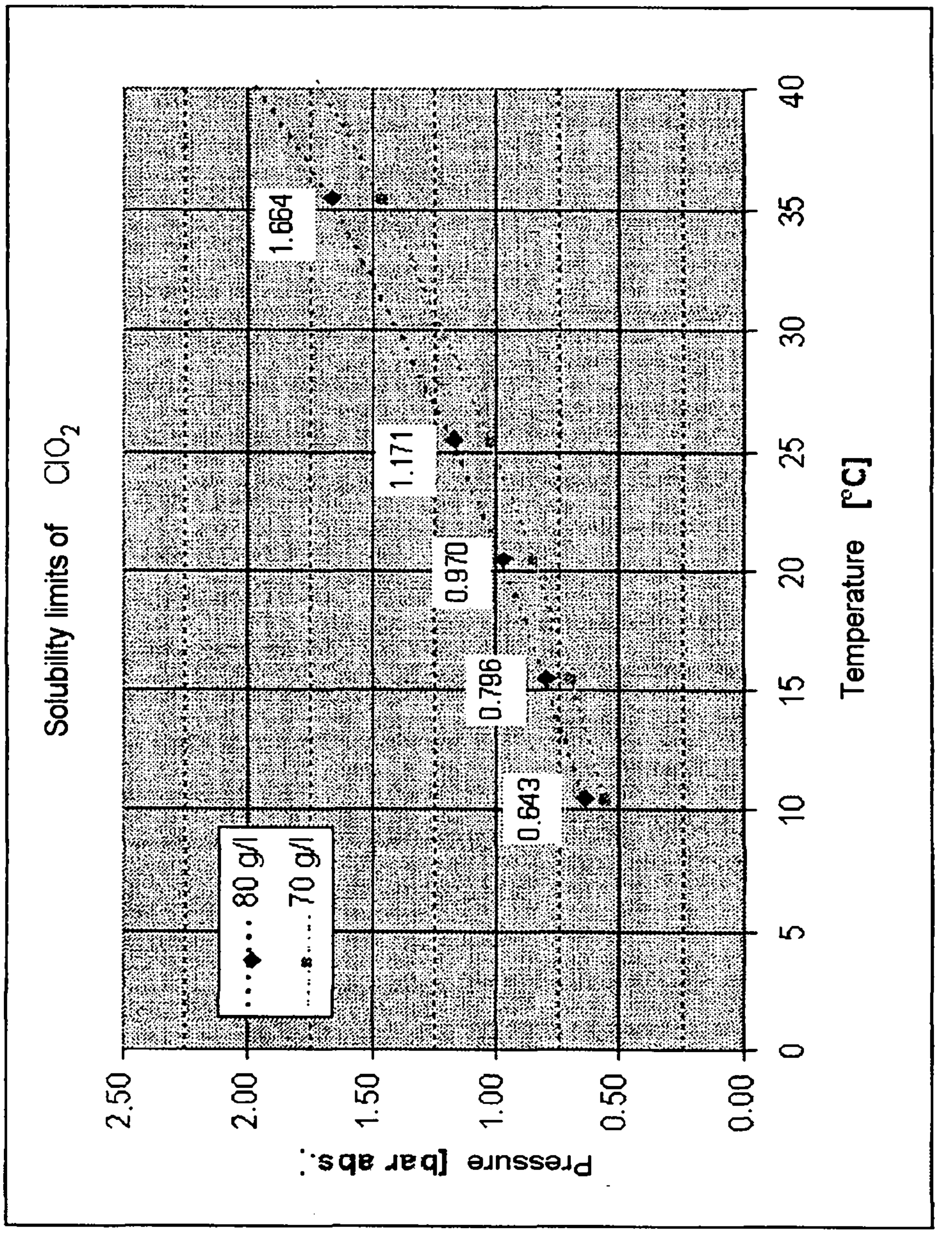
Solubility limits of ClO_2
Pressure [bar abs.]
2.50
2.00
1.50
1.00
0.50
0.00
Temperature [°C]
0
5
10
15
20
25
30
35
40
80 g/l
70 g/l
1.664
1.171
0.970
0.796
0.643

Fig. 3