APPENDIX No. 1

to the Order dated __________ 2019
No. ______

Safety Guide
in Production, Use, Storage, and Transportation of Chlorine Dioxide in Pipelines at the Ilim Group JSC enterprises

RB-DH-2018

2019

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1 GENERAL PROVISIONS

1.1 This Safety Guide for production and use of chlorine dioxide at the production branches of Ilim Group JSC (hereinafter, the Guide) establishes the requirements aimed at preventing accidents and incidents, as well as cases of industrial injuries at hazardous production facilities (HPF) which handle chlorine dioxide.

1.2 The Guide has been developed in accordance with the federal rules and regulations in the field of industrial safety *Safety Rules for the Production of Chlorine and Chlorine-Containing Media*, regulatory and technical documentation for industrial safety and best practices of the International Paper *Guide for Workshops for the Production of Chlorine Dioxide*.

1.3 The Guide is intended to be applied:

a) in the design, construction, operation, expansion, reconstruction, technical re-equipment, conservation, and liquidation of HPF at the production:

- of aqueous solution of chlorine dioxide;
- using an aqueous solution of chlorine dioxide;

b) during storage of an aqueous solution of chlorine dioxide;

c) when transporting an aqueous solution of chlorine dioxide through pipelines;

d) in the manufacture, installation, commissioning, maintenance and repair of technical devices.

1.4 In order to bring HPF with the circulation of chlorine dioxide into conformity with the requirements of this Guide, the operating organization shall conduct a comprehensive examination of the actual condition of the process facilities, if deviations are found, develop a set of compensatory measures for the further safe operation of such facilities, and arrange introduction of amendments to the documentation or re-development of the documentation.

2. SCOPE OF APPLICATION OF THE GUIDE

2.1 This Guide applies to hazardous production facilities of the Ilim Group JSC branches related to the production of gaseous chlorine dioxide and the consumption of an aqueous solution of chlorine dioxide.

3. BASIC PHYSICAL-CHEMICAL AND SANITARY TOXICOLOGICAL PROPERTIES OF CHLORINE DIOXIDE. SCOPE OF APPLICATION

3.1 Basic physical-chemical properties

Under normal conditions, chlorine dioxide is a greenish yellow gas with an odor resembling that of chlorine mixed with nitrogen oxides.

Chemical formula: ClO_2.

Molecular weight: 67.5 g/mol.

Density: 3.09 kg/m^3 (at plus 11°C).

Boiling point: plus 9.9°C.

Temperature of the onset of exothermic decomposition: plus 39°C. At temperatures above 65°C, gaseous chlorine dioxide decomposes with an explosion.

Explosion limits, % vol.:

- lower: 2.5;
- upper: 100.

Chlorine dioxide can be in three states of aggregation: solid, liquid, and gaseous.

At a temperature of plus 11°C and a pressure of 760 mmHg, chlorine dioxide is liquefied.

At a temperature of minus 59°C and a pressure of 760 mmHg, chlorine dioxide crystallizes to form orange-red crystals.

The density of liquid chlorine dioxide is 1.635 kg/dm^3 (at plus 5°C), the density of solid chlorine dioxide is 1.979 kg/dm^3 (at minus 60°C).

Chlorine dioxide is highly soluble in water. At a temperature of plus 4°C and a pressure of 760 mmHg, 20 volumes of gaseous chlorine dioxide are dissolved in one volume of water.

The boiling, freezing, and melting points for an aqueous solution of chlorine dioxide correspond to the values of these parameters for water.

An aqueous solution of chlorine dioxide is not fire and explosion hazardous.

In pure water, chlorine dioxide is not hydrolyzed. Aqueous solutions of chlorine dioxide with pH ≤ 2 when stored in the dark and at a temperature of less than 5°C are very stable; they slowly decompose in the light. In an alkaline environment, chlorine dioxide hydrolyzes to form chlorite and chlorate, i.e. exhibits the properties of anhydride of chlorous ($HClO_2$) and chloric ($HClO_3$) acids simultaneously.

The oxidative activity of chlorine dioxide is usually compared with the activity of chlorine in its ability to disengage atomic oxygen during a chemical reaction:

$$ClO_2 + 0.5H_2O \longrightarrow HCl + 2.5O$$

One gram of chlorine dioxide in terms of oxidizing ability is equivalent to 2.63 grams of “active chlorine.”

Under the action of active chlorine, many materials suffer corrosion. Titanium, tantalum, lead, some types of plastics, porcelain, glass, and some special alloys are chemically resistant in the medium of chlorine dioxide.

3.2 Basic sanitary-toxicological properties

The odor of chlorine dioxide in the air is felt by the human sense of smell at a concentration of 0.0017% in the air.

Maximum allowable concentration in the air of the working area is 0.1 mg/m^3.

The hazard class in the air of the working area is 1.

Highly toxic substance. In case of acute poisoning, it causes irritation of the ocular mucosa, upper respiratory tract, weakness, dizziness, and vomiting. The consequences of prolonged exposure are conjunctivitis, bronchitis, and pulmonary emphysema.

3.3 Scope of application of an aqueous solution of chlorine dioxide

An aqueous solution of chlorine dioxide is used to bleach sulfite and sulfate pulp and to neutralize drinking and waste water.

Due to the selective ability of chlorine dioxide to destroy lignin and coloring pigments in the fiber, its use for pulp bleaching allows to obtain cellulose with a high degree of whiteness without any noticeable decrease in the mechanical strength of the fiber.

The aqueous solution of chlorine dioxide produced in the workshops of the Ilim Group JSC branches must comply with the requirements of the standards of the branches and contain in:

- Koryazhma, obtained by the Matheson method, “active” chlorine from 14.0 to 17.0 g/dm^3;
- Bratsk, obtained by the Matheson method, “active” chlorine from 12.1 to 26.3 g/dm^3;
- Bratsk, obtained by the integrated method (R6), chlorine dioxide from 9.8 to 10.0 g/dm^3;
- Ust-Ilimsk, obtained by the SVP method, chlorine dioxide from 6.0 to 10.0 g/dm^3.

4 BRIEF DESCRIPTION OF THE PROCESS OF PRODUCING AN AQUEOUS SOLUTION OF CHLORINE DIOXIDE

An aqueous solution of chlorine dioxide at the industrial sites of Ilim Group JSC is obtained using the following methods:

- Matheson method using integrated reactors – a branch in Koryazhma;
- Matheson method with successive reactors – a branch in Bratsk;
- integrated (R6) – a branch in Bratsk;
- SVP – a branch in Ust-Ilimsk.

4.1 Matheson method

The process of producing chlorine dioxide is based on the reduction of sodium chlorate by sulfur dioxide in the presence of sulfuric acid and is described by the overall reaction equation:

$$2NaClO_3 + SO_2 \xrightarrow{H_2SO_4} 2ClO_2 + 2NaHSO_4 \quad (1)$$

The production of chlorine dioxide includes the following stages:

- reception, storage, and supply to the production of chlorate-chloride solution;
- reception, storage, and supply to the production of sulfuric acid;
- reception and supply to the production of sulfur dioxide (sulfurous-acid anhydride);
- obtaining gaseous chlorine dioxide;
- absorption of gaseous chlorine dioxide and storage of an aqueous solution of chlorine dioxide;
- purification of exhaust gas;
- collection and neutralization of the spent solution.

Reception, storage, and supply to the production of chlorate-chloride solution

Chlorate chloride solution that meets the following requirements:

1) provided that the chlorine dioxide production reactors are located one in

another:

- mass concentration of sodium chlorate – from 620 to 650 g/dm^3;
- mass concentration of sodium chloride – from 50.0 to 70.0 g/dm^3;
- mass concentration of chlorine – 0.35 g/dm^3;
- concentration of hydrogen ions (pH) – from 7.8 to 8.0;

2) provided that the chlorine dioxide production reactors are arranged successively:

- mass concentration of sodium chlorate – from 550 to 650 g/dm^3;
- mass concentration of sodium chloride – from 40.0 to 60.0 g/dm^3;
- mass concentration of ammonium ions – 10.0 mg/dm^3, maximum

is supplied through an inter-workshop pipeline from the site of production to storage tanks in which to prevent its crystallization a temperature is maintained from plus 50 to plus 60°C (for the method with reactors located one in another) and from plus 25 to plus 40°C (for the method with successive reactors) using a heat exchanger heated by steam and circulation according to the scheme: tank – pump – heat exchanger – tank.

From storage tanks, the chlorate-chloride solution is pumped through a filter of an environment-resistant material to a pressure tank wherefrom it flows by gravity through a flowmeter to a primary chlorine dioxide reactor through siphons installed below the surface of the liquid phase of the reactor.

The filter is designed to clean the solution from various impurities and suspended particles in order to prevent decomposition of chlorine dioxide, accompanied by “popping” in the primary reactors.

Acceptance, storage, and supply to production of sulfuric acid

Sulfuric acid with a mass fraction of monohydrate from 92.5 to 94.0% and permanganate oxidizability of 5 cm^3 maximum (provided that the chlorine dioxide production reactors are located one in another) and 10 cm^3 maximum (provided that the chlorine dioxide production reactors are arranged successively) is supplied through a filter of an environment-resistant material to a storage tank from a discharge point from railway tanks or from storage tanks wherefrom it is pumped through a stainless steel filter to a pressure tank from which it flows by gravity to primary reactor producing chlorine dioxide through siphons installed below the surface of the liquid phase reactor.

Reception and supply to the production of sulfur dioxide (sulfurous-acid anhydride)

Evaporated sulfurous-acid anhydride of own production or imported, exhaust gases of displacement and blowdown, exhaust gases from safety valves of sulfur dioxide storage tanks with a temperature of 30 to 70°C enter the buffer via an inter-workshop pipeline wherefrom they enter a cone-shaped mixer where they are mixed with air or nitrogen to a volume fraction from 8 to 11%.

From a cone-shaped mixer, the gas-air mixture is supplied through variable area flow meters and diffusers to primary and secondary chlorine dioxide reactors. Diffusers break the gas into tiny bubbles which rising up react with a chlorate-chloride solution forming gaseous chlorine dioxide exiting the upper part of the reactor through a stripping (scrubber) column.

Obtaining gaseous chlorine dioxide

Upon receipt of chlorine dioxide using reactors built into each other, the process occurs simultaneously in the primary and secondary reactors. A chlorate-chloride solution and sulfuric acid are fed into the primary reactor through siphons installed below the surface of the liquid phase, as well as through six diffusers of a 95% mixture of sulfur dioxide with air. After filling the primary reactor and triggering of most of the sodium chlorate (to a mass concentration of 17 to 25 g/dm^3), the reaction solution flows continuously into the secondary reactor where further reduction of sodium chlorate continues to a residual content of 1 to 3 g/dm^3 where the remaining 5% of mixture of sulfur dioxide with air are fed through one diffuser.

When producing chlorine dioxide using successively installed reactors, the main reaction proceeds in a primary reactor in which sulfuric acid and chlorate-chloride solution are continuously fed through siphons installed below the surface of the liquid phase. From a primary reactor, a reaction mixture with a mass concentration of sodium chlorate from 18 to 30 g/dm^3 continuously flows through an overflow pipe into a secondary reactor designed to more fully recover sodium chlorate (to a residual content of 1.0 to 2.5 g/dm^3), in the lower part of which a mixture of sulfur dioxide is supplied with air or nitrogen.

In order to avoid the formation of an explosive mixture of chlorine dioxide and air in the reactor, the volume fraction of sulfur dioxide in the air mixture fed into the reactors is maintained in the range from 8 to 11% (for successively installed reactors) and not more than 9% (for built-in reactors) which provides a volume fraction of chlorine dioxide in air at the outlet of the reactor of 10% maximum.

The process of reducing sodium chlorate with sulfur dioxide is exothermic. When 1 kg of chlorine dioxide is formed, up to 800 kcal of heat is released. In order to avoid thermal decomposition of chlorine dioxide and to suppress side reactions of the reduction of sodium chlorate leading to the formation of free chlorine, the temperature of the reaction mass in the reactors is maintained in the range from plus 32 to plus 38°C. When the temperature rises above the regulated value, the valves on the supply lines of all reagents are closed and the valve on the supply line of compressed air to the reactor opens to dilute the chlorine dioxide in the gas mixture to its content below the explosive limit.

Heat is removed by river water supplied to both tank jackets and submerged coil coolers located radially in the primary reactor.

A mixture of chlorine dioxide and chlorine in air or nitrogen formed in the primary and secondary reactors is suctioned off under vacuum to the absorption unit.

Absorption of gaseous chlorine dioxide and storage of an aqueous solution of chlorine dioxide

The gas mixture of chlorine dioxide and chlorine with air (nitrogen) from the stripping (scrubber) column under the influence of rarefaction enters the absorption column which is irrigated with cooled filtered or river water with a temperature from plus 4 to plus 9°C.

Due to the different water solubility of chlorine dioxide and chlorine in the absorption column, chlorine dioxide is mainly absorbed from the gas mixture, and chlorine is partially absorbed.

The resulting aqueous solution of chlorine dioxide is drained by gravity into a storage tank wherefrom it is pumped through inter-workshop pipelines to consumer shops.

Purification of exhaust gas

Abgases containing chlorine and a small amount of chlorine dioxide enter from the absorption column under vacuum to the primary sanitary column irrigated by river water, and then into the secondary column filled with Pall or Raschig rings for irrigation of which the sodium hydroxide solution is pumped from the circulation tank. Sanitary columns operate under rarefaction from minus 1.5 to minus 3.9 kPa.

The sodium hypochlorite solution formed in the circulation tank is periodically pumped to the sharpening unit by a pump.

The air cleared of chlorine after sanitary columns is ejected by an ejector using a fan into the atmosphere through a diffusion pipe.

The rarefaction in the gas cleaning system created by the fans prevents the release of gaseous substances into the air of industrial premises.

Collection and neutralization of the spent solution

The spent reaction solution with a mass concentration of sodium chlorate of 3 g/dm^3 maximum flows from the primary and secondary reactors by gravity into the stripper (stripping column) where chlorine dioxide and chlorine are blown out therefrom using compressed air.

The air mixture with a small content of chlorine dioxide and chlorine from the stripper (stripping column) is fed for further purification to the absorption column, and the spent solution containing sulfuric acid and residual concentrations of "active chlorine" is drained by gravity into the storage tank. Subsequently, after dilution with water or, in case of necessity of neutralization by electro-alkali liquors, it is fed through an industrial sewage system to the neutralizers at the biological treatment plant of industrial waste water of the enterprise and can be used, if necessary, in the process.

4.2 Integrated method (R6)

The process of producing chlorine dioxide is based on the reduction of sodium chlorate in the presence of hydrochloric acid with the participation of sodium chloride in a complex (integrated) plant supplied by Aker Solutions which includes three main process sections where two intermediate products are produced:

- sodium chlorate ($NaClO_3$) by electrolysis;
- hydrochloric acid (HCl) by burning gaseous hydrogen and chlorine and further absorption of hydrogen chloride vapors in demineralized water, and the final product:

- aqueous solution of chlorine dioxide (ClO_2).

The process of producing chlorine dioxide is described by the overall reaction equation:

$$NaClO_3 + 2.32HCl \rightarrow 0.92ClO_2 + 0.7Cl_2 + NaCl + 1.16H_2O \quad (2)$$

The production of chlorine dioxide includes the following stages:

- preparation of a solution of “strong” chlorate;
- feeding to the production of hydrochloric acid;
- obtaining gaseous chlorine dioxide;
- absorption of gaseous chlorine dioxide and storage of an aqueous solution of chlorine dioxide;
- purification of exhaust gas.

Preparation of a solution of “strong” chlorate

A solution of “strong” chlorate obtained by electrolysis and satisfying the following requirements:

- mass concentration of sodium chlorate – from 480 to 500 g/dm^3;
- mass concentration of sodium chloride – from 100 to 120 g/dm^3;
- mass concentration of sodium dichromate – from 3.5 to 4.5 g/dm^3;
- solid inclusions – absent,

enters the feed tank from which passing through a filter of environment-resistant material and a cooler with a temperature of 25°C maximum, is fed into the chlorine dioxide generator. The cooler is a plate heat exchanger cooled by water with a temperature of 7°C maximum.

Filtration of the solution from various impurities, suspended particles, mainly from iron oxides, is carried out through ceramic tubular filter elements and allows to minimize the risk of decomposition of chlorine dioxide in the generator.

Periodic filter cleaning is carried out by forced supply of demineralized (desalted) water from the pipes to the annulus, i.e. by “water hammer.”

Feeding to the production of hydrochloric acid

Hydrochloric acid of own production with a mass fraction of hydrogen chloride from 31 to 33% is fed to the 1st (70%) and 2nd (30%) sections of the chlorine dioxide generator by the pump from the storage tank through polypropylene cartridge filters. Subsequently, the acid consumption is maintained in proportion to the consumption of “strong” chlorate.

Obtaining gaseous chlorine dioxide

The process of producing gaseous chlorine dioxide is carried out in a generator which is a horizontal cylindrical apparatus divided into nine sections some of which (3, 5, 7, 8, and 9th) are equipped with heating tube bundles for supplying low pressure steam.

“Strong” sodium chlorate is fed into the chlorine dioxide generator in excess relative to hydrochloric acid in order to spend its maximum possible amount. During the reaction, the concentrations of acid and sodium chlorate decrease, and its speed slows down; in order to compensate this, the temperature of the solution is gradually increased with the help of heaters along the generator axis from 25°C (at the input) to 85°C (at the output). Operation at low temperatures leads to incomplete consumption of hydrochloric acid.

Hydrochloric acid is evenly distributed over the first two sections of the chlorine dioxide generator in order to prevent the reaction from proceeding too quickly. The high temperature of the supplied “strong” chlorate and the high reaction rate can lead to the decomposition of gaseous chlorine dioxide in the generator.

To mix the reaction mass in order to increase the reaction efficiency and improve heat transfer between the solution and the heaters, air is supplied to all sections of the generator by bubbling through the solution. The air supply also ensures the maintenance of the volume fraction of chlorine dioxide in the gas phase of the generator of 10% maximum. For periodic cleaning of bubblers from crystalline deposits, demineralized water is used.

When the temperature of the solution in the first section of the generator rises above 35°C, the supply of hydrochloric acid ceases and the generator is rapidly cooled down by demineralized water.

A pressure relief device, an exhaust pipe, is installed in the upper part of the generator which opens when the pressure in the generator rises above 1.25 kPa.

The solution containing unreacted chlorate and sodium chloride and hydrochloric acid is removed from the generator and, after evaporation of excess water in the evaporator of “weak” chlorate, is returned to the electrolytic unit for producing sodium chlorate. Condensate generated in the evaporator and chlorine dioxide generator is collected in the condensate tank.

Absorption of gaseous chlorine dioxide and storage of an aqueous solution of chlorine dioxide

The gas mixture of chlorine dioxide, chlorine, water steam, and air released from the generator is fed through a “weak” chlorine centrifugal gas blower to a packed column (absorber) irrigated with cooled filtered water with a temperature of plus 7°C maximum, installed on the chlorine dioxide solution collector. As it moves, the chlorine dioxide gas upstream is absorbed by the downward flow of water to form an aqueous solution that is drained into the chlorine dioxide collector. The temperature of the solution in the collector does not exceed plus 12°C.

Subject to the norms of the technological regime, the temperature of gaseous chlorine dioxide entering the absorber should be from plus 55 to plus 60°C, and the temperature of the gas phase and solution in the chlorine dioxide collector should be plus 40°C. When the temperature rises above 75°C, isolation valves for supplying hydrochloric acid to the generator are closed; when the temperature rises above 80°C, the control valves for supplying a solution of “strong” chlorate and low pressure steam to the generator are closed, and the valves are opened on the emergency spray line of demineralized water to cool down the gas phase in generator.

From the collector, an aqueous solution of chlorine dioxide is pumped to storage tanks equipped with floating roofs from which it is pumped through inter-workshop pipelines to the softwood pulp bleaching workshop. The presence of a floating roof consisting of interconnected segments and supported by pontoons minimizes the accumulation of gaseous chlorine dioxide in the gas space of the tanks. Along with the floating roof, there is also a fixed one. To prevent the accumulation of chlorine or chlorine dioxide, the gas space above the floating roof is continuously blown with air which is then discharged to the hypochlorite tower.

Purification of exhaust gas

Gas vents generated in the feed tank of “strong” chlorate, the intermediate tank of the chlorate solution, the storage tank of hydrochloric acid, and the storage tanks of the aqueous solution of chlorine dioxide are fed with the aim of purification from chlorine into the packed column (“hypochlorite tower” with an integrated collector) irrigated with an aqueous solution of caustic soda with mass fraction of 18%.

Gas vents enter the “hypochlorite tower” directly under the nozzles and are released to the atmosphere by a fan through the top choke. A solution of caustic soda is introduced into the upper part of the “hypochlorite tower” through a liquid distributor and flows down towards the upward gas flow.

Throughout the entire absorption system, a small rarefaction is maintained by a fan which prevents the release of gaseous substances into the air of industrial premises.

After cooling in the refrigerator to a temperature of 35°C maximum, the resulting solution of sodium hypochlorite is pumped through an inter-workshop pipeline to the installation of sharpening.

4.3 SVP method

The process of producing chlorine dioxide is based on the interaction of solutions of chlorate and sodium chloride with sulfuric acid and is described by the following reaction equations:

$$NaClO_3 + NaCl + H_2SO_4 \rightarrow ClO_2 + \tfrac{1}{2}Cl_2 + Na_2SO_4 + H_2O \ (3)$$
$$NaClO_3 + 5NaCl + 3H_2SO_4 \rightarrow 3Cl_2 + 3Na_2SO_4 + 3H_2O \ (4).$$

The production of chlorine dioxide includes the following stages:

- reception, storage, and submission to the production of sodium chloride solution;
- reception, storage, and supply to the production of sodium chlorate solution;
- reception, storage, and supply to the production of sulfuric acid;
- obtaining gaseous chlorine dioxide;
- absorption of gaseous chlorine dioxide and storage of an aqueous solution of chlorine dioxide;
- recuperation of sodium sulfate.

Reception, storage, and submission to the production of sodium chloride solution

A sodium chloride solution of own production with a mass concentration from 285 to 310 g/dm^3 is supplied from the warehouse through an inter-workshop pipeline to a receiving tank from which it is fed through a cartridge filter made of a synthetic mesh to a chlorine dioxide reactor.

Reception, storage, and supply to the production of sodium chlorate solution

A sodium chlorate solution delivered from the Bratsk branch with a mass concentration from 680 to 750 g/dm^3 is supplied from the warehouse through an inter-workshop pipeline to a receiving tank from which it is fed by gravity to the chlorine dioxide reactor through a cartridge filter made of a synthetic mesh.

Acceptance, storage, and supply to production of sulfuric acid

Sulfuric acid with a mass fraction of monohydrate from 92.5 to 94.0% is supplied through a filter from a discharge point from railway tanks or from warehouse storage tanks through an inter-workshop pipeline to a receiving tank from which it is fed by gravity through a filter made of an environment-resistant material to the chlorine dioxide reactor. Immediately before being fed to the reactor, the sulfuric acid is diluted with filtered water to a mass fraction of monohydrate from 62 to 65%.

Obtaining gaseous chlorine dioxide

The process of producing chlorine dioxide in the reactor occurs when the reaction mixture is boiled under vacuum (absolute pressure from 30 to 33 kPa) and a temperature from plus 70 to plus 78°C. The heat necessary for conducting the process is supplied to the reaction mass during its circulation through a shell-and-tube heat exchanger heated by steam. The temperature in the reactor is measured at three points: at the inlet to the heat exchanger, at its outlet, and at the outlet of the gas-vapor mixture from the reactor. When the temperature rises to 78°C, the supply of sulfuric acid and solutions of chlorate and sodium chloride to the reactor stops at the outlet of the gas-vapor mixture from the reactor. When the temperature rises to 85°C, the vapor supply to the shell-and-tube heat exchanger stops, and the valves on the emergency water supply line open to suppress the reaction in the reactor.

The water supplied to the reactor with the initial solutions and resulting from chemical reactions evaporates during the boiling of the reaction mixture, and the resulting water vapor is removed with gaseous products through the gas duct, thereby reducing the concentration of explosive chlorine dioxide in the gas phase. For the same purpose, compressed process air is supplied to the upper part of the reactor.

The resulting gas-vapor mixture is transported through the gas duct by a vapor-jet vacuum pump to the absorption stage through a shell-and-tube heat exchanger where it is cooled to a temperature of +25...+45°C and water vapor is condensed.

Absorption of gaseous chlorine dioxide and storage of an aqueous solution of chlorine dioxide

A cooled mixture of chlorine dioxide with chlorine and noncondensed water vapor enter the lower part of the chlorine dioxide absorber the nozzle of which (Raschig ring) is constantly irrigated with cold filtered water with a temperature from +5 to +10°C. Due to the higher in comparison with chlorine solubility of chlorine dioxide in water, in the absorber an aqueous solution of chlorine dioxide is, mainly formed which is pumped to the storage tank. The absorber is under vacuum due to the constant pumping of the unabsorbed gas-vapor mixture therefrom with a vapor-jet steam vacuum pump, which prevents the release of gaseous substances into the air of industrial premises.

The gas-vapor mixture after the vapor-jet vacuum pump passes the refrigerator where it is cooled with circulating water and enters the lower part of the chlorine absorber the nozzle of which (Raschig rings) is also constantly irrigated with cold filtered water. The resulting chlorine solution with a small content of chlorine dioxide flows from the absorber into the chlorine water tank.

Unabsorbed gases enter the treatment package consisting of a sanitary column, exhauster, circulation tank, and circulation pump. The sanitary column is continuously irrigated with a solution of caustic soda with a mass concentration from 48 to 52 g/dm^3 supplied from the circulation tank. The resulting sodium hypochlorite solution flows by gravity into the circulation tank.

When saturated with chlorine, the solution spent to a residual alkalinity of 5 g/dm^3 is pumped to a sodium hypochlorite preparation plant for further strengthening.

After chlorine air purification in the sanitary column using a fan, the ejector releases the air into the atmosphere through a diffusion pipe.

An aqueous solution of chlorine dioxide with a mass concentration of chlorine dioxide of 6 to 10 g/dm^3 and chlorine of 3.5 g/dm^3 maximum is accumulated in storage tanks from which it is pumped through inter-workshop pipelines to bleaching shops of the enterprise.

Gas vents generated in the storage tanks of an aqueous solution of chlorine dioxide are sent for use and treatment to the reactor and the sanitary column.

Recuperation of sodium sulfate

As a result of chemical reactions taking place in the reactor, in addition to gaseous products, sodium sulfate is generated (volume fraction of 15%, maximum) which crystallizes as it is accumulated in the reaction mixture. In order to recuperate it, the reaction mixture is pumped to a vacuum filter where the precipitate is separated from the mother solution, washed with hot water and then blown with compressed hot air to the filter scraper wherefrom it falls by gravity into the pipeline and is washed off by the flow of black liquor coming from the evaporation shop in a tank of a suspension of sodium sulfate in black liquor. The suspension generated in the tank is pumped through the inter-workshop pipeline to the evaporation shop of the enterprise.

5 BRIEF DESCRIPTION OF THE PROCESS OF USING AN AQUEOUS SOLUTION OF CHLORINE DIOXIDE

5.1 USE OF AN AQUEOUS SOLUTION OF CHLORINE DIOXIDE IN BLEACHING SHOPS

Aqueous solution of chlorine dioxide is one of the chemicals used in bleaching shops to remove coloring agents and lignin from the fibers that are left after digestion and give the cellulose the required degree of whiteness. A feature of bleaching cellulose using chlorine dioxide is its selective effect (oxidation) on lignin without significant destruction of fiber.

The supply of an aqueous solution of chlorine dioxide to bleaching shops from the plants for its production is performed continuously through inter-shop pipelines laid along above-ground trestles and equipped with heat tracers or through pipelines laid inside industrial buildings to service storage tanks installed at the elevation of 0.00 m.

Service storage tanks are equipped with level sensors, an audible warning that sounds when the upper fill level is reached, and an interlock that closes the valve on the chlorine dioxide solution supply line when the maximum fill level is reached.

From service storage tanks, an aqueous solution of chlorine dioxide is continuously pumped to the appropriate bleaching stages in the pulp mixers with the solution. From the mixers, the pulp treated with an aqueous solution of chlorine dioxide is sent to the absorption column of the bleaching tower where it pushed up and then overflows to the outside part of the tower.

The consumption rate of an aqueous solution of chlorine dioxide supplied to each stage of bleaching is controlled by circuits.

5.2 USE OF AN AQUEOUS SOLUTION OF CHLORINE DIOXIDE ON FILTER-RESISTANT CONSTRUCTIONS

One of the chemicals used in water treatment plants for disinfecting river water is an aqueous solution of chlorine dioxide.

The supply of an aqueous solution of chlorine dioxide to the water treatment shop from the plants for its production is carried out continuously through one of two inter-workshop pipelines (working and standby) laid along the above-ground trestle and equipped with heat tracers in service storage tanks installed at the elevation of 0.00 m.

Service storage tanks are equipped with level sensors, an audible warning that sounds when the upper fill level is reached, and an interlock that closes the valve on the chlorine dioxide solution supply line when the maximum fill level is reached.

From service storage tanks, an aqueous solution of chlorine dioxide is continuously pumped to the filters of water treatment plants for the purification and disinfection of drinking and filtered water.

6. BASIC PHYSICAL-CHEMICAL PROPERTIES OF SUBSTANCES USED IN THE PRODUCTION OF CHLORINE DIOXIDE AND REQUIREMENTS THERETO

It is necessary to conduct regular incoming inspection of chemicals used in the production of chlorine dioxide observing the frequency and list of indicators required for analysis specified in the technology regulations.

6.1 Chlorine-chloride solution (sodium chlorate solution, “strong” chlorate)

Molecular weight: 106.421 g/mol.

Under normal conditions, it is a clear, odorless liquid.

Chemical formula: $NaClO_3$.

Upon obtaining of chlorine dioxide, a sodium chlorate-chloride solution containing $NaClO_3$ is used – from 55 to 65% of the mass.

The specific gravity of the solution under normal conditions is from 1,329 to 1,400 kg/m^3 depending on the mass content of sodium chlorate.

Solubility 100.5 g in 100 g of water at 25°C (for sodium chlorate).

Boiling point: decomposes.

Not flammable, not explosive liquid. When dried, the chlorine-chloride solution can explode in a mixture with combustible substances, decompose with an explosion in case of heating, impact, and friction, and form chlorine dioxide (explosive and highly toxic substance of hazard class 1) when mixed with concentrated mineral acids.

The maximum allowable concentration in the air of the working area is 5.0 mg/m^3 (for sodium chlorate).

The hazard class in the air of the working area is 3.

When entering the human body, a toxic substance causes vomiting, gastrointestinal upsets, and kidney damage, acts on the skin. The lethal dose when taken orally is 5 g of sodium chlorate ($NaClO_3$). Sodium chlorate is a blood poison.

6.2 Sodium chloride solution

Molecular weight – 58.5 g/mol.

Under normal conditions, it is a clear, odorless liquid.

Chemical formula: NaCl.

To produce chlorine dioxide, a solution of sodium chloride is used with a mass concentration of 285 to 310 g/dm^3.

The specific gravity of the solution under normal conditions is from 1.180 (for 283.2 g/dm^3) to 1.197 (for 311.2 g/dm^3) g/dm^3 depending on the mass content of sodium chloride.

Solubility – 35.9 g in 100 g of water at 21°C.

Boiling point – 107°C.

Not flammable, not explosive liquid.

Maximum allowable concentration in the air of the working area is 5.0 mg/m^3.

The hazard class in the air of the working area is 3.

Toxic substance. Acts on skin, causes irritation.

6.3 Sulfur dioxide

Molecular weight – 64.066 g/mol.

Under normal conditions, it is a colorless gas with a characteristic pungent odor (the smell of a burning match).

Chemical formula – SO_2.

The specific gravity under normal conditions is 2.926 kg/m^3.

Liquefies under pressure at room temperature.

Dissolves in water with the formation of unstable sulfurous acid (H_2SO_3), also dissolves in ethanol and sulfuric acid. Solubility decreases with increasing temperature.

Solubility – 11.5 g in 100 g of water at 20°C.

Boiling point – minus 10.08°C.

Melting point – minus 72.7°C.

Not flammable gas.

Maximum allowable concentration in the air of the working area is 10.0 mg/m^3.

The hazard class in the air of the working area is 3.

Maximum allowable concentration in the atmospheric air of populated areas:

- maximum one-time – 0.5 mg/m^3,
- daily average – 0.05 mg/m^3.

Toxic substance. Irritates the upper respiratory tract, in case of more severe poisoning (concentration up to 60 mg/m^3) affects the deep airways, mucous membranes, and causes pneumonic fever and pulmonary edema. Irritates skin and causes eyes burns with penetration into the cornea.

6.4 Sulfuric acid

Molecular weight – 98.0 g/mol.

Under normal conditions, concentrated sulfuric acid (mass fraction of monohydrate 92.5–94.0%) is a heavy oily liquid without color and odor, with an acidic “copper” taste.

Chemical formula: H_2SO_4.

The specific gravity under normal conditions is 1.8365 g/cm^3.

Boiling point: plus 332.4°C (for 98% sulfuric acid).

Melting temperature: plus 10.3°C.

Solubility: miscible with water in all ratios.

The dissolution of sulfuric acid in water is accompanied by the release of a large amount of heat.

Noncombustible liquid.

The maximum permissible concentration of sulfuric acid aerosol in the air of the working area is 1.0 mg/m^3.

The hazard class in the air of the working area is 2.

Very caustic substance. If the vapors are inhaled, they irritate the upper respiratory tract, cause a runny nose, cough, respiratory difficulty, and laryngospasm. In case of contact with skin, causes severe burns, with eyes – loss of vision.

Maximum allowable concentration in the atmospheric air of populated areas:

- maximum one-time – 0.3 mg/m^3,
- daily average – 0.1 mg/m^3.

6.5 Hydrochloric acid

Hydrochloric acid is a solution of hydrogen chloride (HCl) in water. The maximum concentration of hydrochloric acid at 20°C is 38% by weight.

Molecular weight – 36.46 g/mol.

Under normal conditions, hydrochloric acid is a colorless, transparent, corrosive liquid, “fuming” in the air. Technical hydrochloric acid is yellowish due to impurities of iron, chlorine, etc.).

The specific gravity under normal conditions (38% acid) is 1.189 g/cm^3.

Chemical formula: HCl.

Boiling point: plus 48.0°C (for 38% sulfuric acid).

Melting point: minus 26.0°C.

Noncombustible liquid.

The maximum permissible concentration of hydrochloric acid vapor in the air of the working area is 5.0 mg/m^3.

The hazard class in the air of the working area is 2.

Highly concentrated hydrochloric acid is a caustic substance, in case of contact with skin it causes severe chemical burns. Eye contact is especially hazardous.

When opening the vessels with concentrated hydrochloric acid, hydrogen chloride vapors attracting air moisture, form fog that irritates human eyes and respiratory tract.

Hydrochloric acid dissolves most metals with the release of hydrogen, except for gold, silver, platinum, tantalum, and niobium, frets steel and other metals with the formation of gaseous hydrogen.

The maximum permissible concentration of hydrochloric acid vapor in atmospheric air is 0.2 mg/m^3.

Lethal toxic dose of hydrochloric acid vapor (LCt_{50}) – 20.0 mg·min/dm^3.

The threshold toxic dose of hydrochloric acid vapor (PCt_{50}) – 2.0 mg min/dm^3.

6.6 Aqueous solution of caustic soda (sodium hydroxide)

Molecular weight – 39.997 g/mol.

Under normal conditions, it is a colorless, odorless solution.

To produce chlorine dioxide, an aqueous solution of sodium hydroxide with a mass concentration of 148 to 240 g/dm^3 is used.

Chemical formula – NaOH.

The specific gravity under normal conditions is from 1.140 to 1.217 g/cm^3 depending on the concentration of the solution.

Boiling point:

– plus 105°C (for 13% solution),

– plus 108.7°C (for 25% solution).

Noncombustible liquid.

The maximum permissible concentration of sodium hydroxide aerosol in the air of the working area is 0.5 mg/m^3.

The hazard class in the air of the working area is 2.

Aqueous solutions of caustic soda have a strong alkaline reaction (pH of 1% solution = 13).

When diluting an aqueous solution of caustic soda, as well as interacting with acids, a large amount of heat is released.

In case of contact with skin, it causes severe chemical and thermochemical burns, hollow long healing ulcers. The higher the concentration and temperature of the solution, the more severe the burns are.

In case of eye contact, it causes burns to ocular mucosa; penetrating deep tissues, can lead to loss of vision.

Alkaline aerosols cause coughing, chest tightness, runny nose, and lacrimation.

6.7 River or filtered water

To cool the reactors and irrigate the absorption columns, river or chilled filtered water supplied from the enterprise networks is used. The water temperature should be within the following limits:

- river water from plus 4 to plus 12°C (for the branch of Ilim Group JSC in Bratsk, the Matheson method);
- chilled filtered water plus 7°C maximum (for the branch of Ilim Group JSC in Bratsk, method R6);
- chilled filtered, drinking water: from plus 4 to plus 9°C (for the branch of Ilim Group JSC in Koryazhma, Matheson method);
- cold filtered water from plus 5 to plus 10°C (for the branch of Ilim Group JSC in Ust-Ilimsk, SVP method).

6.8 Process compressed air

Process compressed air is used for:

- dilution of sulfur dioxide to an explosion-proof volume fraction from 8 to 11% in the gas-air mixture fed to the chlorine dioxide reactors;
- dilution of chlorine dioxide in the gas mixture in the reactors to its content below the explosive limit.

Process compressed air must be previously cleaned of mechanical impurities and dried. The moisture content in the dried air should correspond to a dew point temperature of maximum minus 40°C.

6.9 Compressed nitrogen

Compressed nitrogen can be used for dilution of sulfur dioxide to an explosion-proof volume fraction from 8 to 11% in the gas-air mixture fed to the chlorine dioxide reactors.

6.10 Dry compressed air (for instrumentation)

The air used for instrumentation must first be cleaned of dust, oil and dried from condensed moisture.

The volume fraction of moisture in the dried air should be 0.01% maximum, which should be continuously monitored by an automatic moisture meter with an alarm warning of exceeding the permissible humidity.

7. GENERAL SAFETY RECOMMENDATIONS FOR CHLORINE DIOXIDE PRODUCTION

7.1 The process for the production of chlorine dioxide should be carried out in full compliance with the approved technological regulations. All changes made to the process flow standard, equipment, instrumentation and automation, and other deviations should be recorded in the appropriate section of the technological regulations.

7.2 In the course of production of chlorine dioxide, materials of equipment, pipelines, gaskets and valves, and building structures intended for use in the environment of substances circulating in the production (taking into account the corrosion activity and aggressiveness of the reaction medium) should be used.

7.3 Before putting into operation, all equipment and pipelines designed to work with chlorine dioxide must be free of impurities and washed.

7.4 The placement of process equipment and pipelines should ensure the convenience of performing maintenance, repair and replacement of equipment and its elements as well as the ability to visually monitor the condition of the outer surface of equipment and pipelines.

7.5 The production of chlorine dioxide should be ensured by an uninterrupted supply of mechanically treated water or filtered chilled water, electricity, steam, process compressed air (nitrogen), and compressed air dried for the instrumentation and automation of the required parameters.

7.6 On the valves of the cooling water supply pipelines, there must be signs with the inscription: “DANGER – do not close without informing the technicians” in order to prevent its accidental shutdown.

7.7 On the steam supply valve, steam ejector, when producing chlorine dioxide using the SVP method, signs must be placed with the inscription: “DANGER – do not close without warning the chlorine dioxide workshop operator; strong “popping” is possible” in order to prevent its accidental shutdown.

7.8 Registration plates should be placed on the tanks with specification of the registration number, the name of the medium in the tank with the medium parameters (pressure and temperature) as well as the safety data sheet with the medium characteristics, the list of necessary personal and collective protective equipment as well as the measures of first aid to victims of exposure to the substance.

7.9 Pipelines should be marked with identification painting, warning and marking boards (plates) with the name of the medium being transported, specifying the direction of movement of the medium and the parameters (pressure, temperature) in accordance with the requirements of the applicable RTD. The number of plates should be sufficient to visually identify pipelines at any location. Where pipelines pass through walls and partitions, the information plates should be placed on both sides.

7.10 Plates specifying the item numbers of the equipment in accordance with the flow diagram should be affixed to pipeline valves, pumps, and other equipment.

7.11 The production of chlorine dioxide should be classified as category 1 consumer in terms of electric reliability. All pumping and ventilation equipment and I&C systems directly involved in the continuous process should have a backup power supply ensuring safe shutdown of production.

7.12 The process of producing chlorine dioxide should exclude the possibility of the formation of explosive mixtures in process equipment and utilities, subject to the process flow standard.

In order to increase the explosion safety of the process, the following measures should be provided:

1) filtration of the feedstock (solutions of chlorate and sodium chloride, sulfuric acid, and hydrochloric acid) through a 50 micron bag filter before pumping it into storage tanks when unloading from railway tanks if received from manufacturers or through inter-workshop pipelines from own manufacturing workshops;

2) to produce chlorine dioxide using the Matheson method:

- supply of feedstock (solutions of sodium chlorate and sulfuric acid) into the reactor through 10 micron filters;

- uniform contact of the gas-air mixture (sulfur dioxide with air or nitrogen) with the reaction solution and mixing – supply through diffusers;

- presence of a residual evaporator of sulfur dioxide to prevent leakage of liquid sulfur dioxide into the chlorine dioxide production reactor;

- absence of contact of the chlorate-chloride solution and sulfuric acid with the gas phase of the reactor or the phase interface – their supply to the reactor through siphons;

3) for an integrated method of producing chlorine dioxide (R6):

- supply of feedstock (solutions of chlorate and sodium chloride, hydrochloric acid) into the reactor through 10 micron filters;

- uniform mixing of the reaction mass and maintaining the volume fraction of chlorine dioxide in the gas phase of 10% maximum by bubbling air through a solution in the reactor;

4) to produce chlorine dioxide using the SVP method:

- supply of feedstock (solutions of chlorate and sodium chloride and sulfuric acid) into the reactor through 10 micron filters.

7.13 Used filters for the purification of chlorate-chloride solution and sulfuric acid must be regularly replaced. The degree of filter pollution should be controlled by the pressure drop (or changes in the flow rate of chemicals), and in the absence of instrumentation and control devices that control this parameter, according to the schedule but at least once a month.

7.14 Used filter parts for sodium chlorate solutions must be disposed of correctly by washing them thoroughly with water to remove residual sodium chlorate as they can ignite if dried without washing. Used filters for sodium chlorate should not be stored unwashed because of the risk of ignition.

In order to avoid explosion or accidental formation of gaseous chlorine dioxide, it is forbidden to use acid to clean the filters of sodium chlorate solutions, as well as to store together used filters for sulfuric acid and sodium chlorate solutions.

7.15 In the course of operation, water should not be allowed to enter the sulfuric acid filters as this may result in damage.

7.16 Process systems in which chlorine dioxide is circulated must be tight and exclude the possibility of formation of its hazardous concentrations in the environment in all operating modes.

7.17 Chlorine dioxide reactors should be equipped with safety devices for protection against destruction in case of “collapse.”

7.18 Safety devices installed on equipment in which gaseous chlorine dioxide is formed should have discharge to places where the likelihood of people not participating in the process is minimal, i.e. outside the building or in a well-ventilated chamber of an appropriate design to reduce the likelihood of splashing hazardous solution onto service personnel or the release of gaseous chlorine dioxide.

Access to reactor safety devices during their operation must be restricted. A warning should be placed that access to the reactor safety device is restricted.

7.19 In case of overpressure release from the reactors to the production area, local exhausts (probes) should be installed above the safety devices coupled with a constantly working exhaust ventilation system or have a discharge outside the building to reduce the severity of the consequences of the depressurization of the reactor in case of “collapse” and the release of decomposition products of chlorine dioxide.

7.20 The structure and material design of the safety device must ensure its mechanical resistance to alternating loads and corrosion resistance in the medium of chlorine dioxide under operating conditions throughout the entire service life.

7.21 Equipment and pipelines must be protected against static electricity.

7.22 Membrane safety devices should be installed on nozzles or pipelines directly connected to the vessel in places open and accessible for inspection and installation, and dismantling. Membranes should be placed only in the attachment points intended for them.

7.23 The actuation pressure of the membrane and opening pressure of the safety device, its throughput, are determined by the equipment designer or design organization.

7.24 Volumes and terms of testing safety valves must comply with the requirements of the standards, specifications, and recommendations of the manufacturer.

7.25 At the factory, measures and means should be provided that minimize the possibility of chlorine dioxide entering the air of the working area as well as regular instrumental monitoring of its content in the air of industrial premises.

7.26 In the absence of the possibility of organizing instrumental monitoring of the content of chlorine dioxide in the air of the working area, visual monitoring should be carried out along the route of laying pipelines for supplying its aqueous solution on the trestles by maintenance personnel by walking the entire pipeline route at least once per shift with the obligatory recording of the results in a shift log.

7.27 Premises where the release of chlorine dioxide is possible should be equipped with general exchange and emergency ventilation systems the performance of which should be determined and justified in the design documentation.

7.28 Emissions from emergency ventilation should be directed to an absorption purification system.

7.29 In order to minimize the emission of chlorine dioxide into the environment in case of an emergency depressurization of process equipment and pipelines, the installation of automatic high-speed shut-off and/or blocking-off devices should be provided.

7.30 At the production site, vessels equipment should be provided for emergency emptying of the chlorine dioxide reactor, the capacity of which should be designed to receive products in quantities determined by the conditions for safe shutdown of the process.

7.31 Vessel equipment for draining the contents of reactors should be in constant preparedness and equipped with monitoring and control means.

7.32 In order to avoid explosion in the vessel equipment, for acceptance of the spent solution from the reactor it is required to desorb the solution in the reactor before transferring it to the backup vessel equipment.

If it is impossible to desorb the solution in the reactor, it must be diluted strongly with water before being transferred to the vessel equipment.

7.33 It is forbidden to drain the “active” solution from the chlorine dioxide reactor into the sewage collector in order to avoid explosion.

It is forbidden to simultaneously drain chemical reagents into a common sewage collector.

7.34 It is forbidden to store materials containing sulfides in the premises of the chlorine dioxide production, in order to avoid emissions of hydrogen sulfide.

It is necessary to isolate the following materials from each other during storage, in the supply, filtration, sampling, and sewage systems:

- 92.5–94.0% sulfuric acid should not be in contact with solutions of sodium chlorate, hydrogen peroxide, a solution containing sulfide, and caustic soda;
- sodium chlorate solution should not come into contact with acid, wood, cardboard, cellulose, leather, oils and other organic substances, and hydrogen peroxide. It is forbidden to use tools and equipment with wooden handles.

7.35 At each process stage that discharges industrial wastewater, regular monitoring of its quality should be carried out in accordance with the requirements of the technological regulation and the monitoring schedule.

7.36 The pipe part of heat exchangers, evaporators, and condensers operating in a chlorine dioxide environment should be made of seamless pipes. The material of the casing and tube side should correspond to the type and parameters of the working environment.

7.37 Tubular or plate heat exchangers should be located on the pressure side of the pump; a temperature regulator should be provided for in order to avoid overheating and ignition of sodium chlorate.

Pumps for pumping aggressive and caustic products must be equipped with pans or trays of corrosion-resisting materials, except for glandless pumps with a magnetic coupling or the availability of a common spill collection system.

7.38 Sampling should be carried out using flowing samplers the design of which eliminates the ingress of aggressive media into the production premises.

7.39 In production premises and open areas for work with sodium chlorate solutions or a solution from a chlorine dioxide reactor, scaffolding and ladders of aluminum or fiberglass should be used. The use of wooden scaffolding or ladders is prohibited.

7.40 A stock of primary fire-extinguishing equipment should be arranged in the production premises.

7.41 In order to provide timely and high-quality first aid to victims of industrial incidents, a medical kit must be completed with the necessary means for the first aid provision.

7.42 Production facilities should be equipped with safety showers at all process check points. A safety shower and potentially hazardous equipment should be located on the same level and in close proximity.

7.43 Production premises should be equipped with two different types of communication for the operational communication of maintenance personnel and the transmission of information according to the localization and emergency response plan (LERP).

7.44 At the production site, LERP should be developed and regularly reviewed in accordance with the requirements of regulatory documents.

LERP, as well as changes thereto, should be read and studied by production personnel against signatures in the acknowledgement list. LERP knowledge shall be checked by the commission upon admission of personnel to independent work and at the next knowledge assessment.

Workplaces should be completed with work instructions and LERP.

7.45 In case of an emergency, maintenance personnel must act in accordance with the LERP.

7.46 The following persons are allowed to service the equipment of installations:

a) those who have reached the age of 18 years, without medical contraindications;

b) those who have passed briefing and industrial training, knowledge assessment by the qualification commission (to be confirmed annually) and received admission to work independently.

7.47 Maintenance personnel must know:

a) the distinguishing features and potential hazards of substances circulating in the production of an aqueous solution of chlorine dioxide, in particular: sulfur dioxide, chlorine dioxide, chlorine, sodium chlorate, sodium chloride, sodium hypochlorite, sulfuric and hydrochloric acids, and aqueous sodium hydroxide solution;

b) potential emergency situations, methods for their localization and consequences elimination;

c) escape routes in case of emergencies. In case of an emergency with a chlorine dioxide reactor, it is necessary to move from it towards the exit from the building while remaining, if possible, under the shelter of equipment or walls;

d) the used protection methods and personal protective equipment;

e) methods of provision of first aid to victims of exposure to hazardous substances circulating in the workplace and hazardous production factors.

7.48 Emergency exits should be marked in all premises. If necessary, pointing signs indicating the path to the emergency exit should be placed in accessible places.

7.49 In all premises there should be provided emergency lighting designed according to group 1 of power supply – from three independent power sources (UPS should be used as the third one providing maintenance of emergency lighting up to two hours).

7.50 Temporary, untrained visitors may be admitted to the production premises only accompanied by trained personnel while they should be informed of the presence of hazards and trained to act in case of an emergency.

7.51 All works with chlorine dioxide, sulfur dioxide, sulfuric and hydrochloric acids, sodium chlorate solutions, and other caustic and toxic substances must be carried out with the use of protective clothing and personal protective equipment (PPE) against chemical factors that can impact the skin, eyes, and respiratory system. Works without using protective clothing and personal protective equipment established by the standards are not allowed.

7.52 Personal protective equipment for maintenance personnel should be provided in accordance with the approved Intersectoral rules for providing workers with protective clothing, protective footwear and other personal protective equipment approved by order of the Ministry of Health and Social Development of the Russian Federation.

7.53 PPE used when working with sodium chlorate solutions should not include leather gloves or leather shoes.

7.54 Each employee must personally check the availability and serviceability of personal protective equipment before the shift begins.

7.55 To protect respiratory system against chlorine dioxide and chlorine, it is permissible to use filtering PPE for respiratory system, but only if the concentration of chlorine in the air is within the range of possible measurements of the signaling device but does not exceed 0.5% by volume. In case of a higher chlorine concentration, it is required to use insulating PPE for respiratory system and suits insulating from chemical factors.

7.56 All works related to connecting equipment and supplying chlorine dioxide, removing plugs from vessel equipment and pipelines are gas hazardous and should be carried out if there are work permits for hazardous works and respiratory system PPE for workers.

7.57 The number and location of personal protective equipment is determined by the number of staff and LERP.

7.58 In order to eliminate the consequences of accidents and to evacuate the maintenance personnel in case of accident occurrence at the production site, the necessary stock of technical means and personal protective equipment should be available in accordance with the list of equipment with emergency means of HPF related to the production, storage, and use of chlorine dioxide.

7.59 Eating and smoking are prohibited at the workplace. Eating is allowed only in a room specially equipped for this purpose. Before eating, it is necessary to put off contaminated clothing and wash hands with soap. Smoking is allowed only in specially designated areas.

7.60 When working with sodium chlorate solution, the use of organic oils and lubricants as well as the use of protective creams for hands and face is prohibited. Any leaks of sodium chlorate solution must be washed off immediately preventing its drying and crystallization as crystalline sodium chlorate can ignite from friction. It is forbidden to approach the fire and hot objects, smoke in work clothes contaminated with sodium chlorate, and go home in work protective clothes or take it home as dried sodium chlorate may ignite. If sodium chlorate is spilled on clothing, it must be changed and put at the wash, and if it is not possible to wash it, soak it in water and leave until washing.

7.61 In processes in which, when deviating from predetermined process conditions, chlorine dioxide may enter the inert medium supply line (nitrogen and other media), a check valve or another device is installed on the latter preventing the flow of chlorine dioxide into the inert medium supply line.

7.62 The subdivision manager is responsible for all aspects of inspections of chlorine dioxide reactors. They are obliged to personally be engaged in inspection, reporting and subsequent analysis as well as the supervision required for quick and effective taking measures.

8. GENERAL SAFETY RECOMMENDATIONS FOR STORAGE OF AN AQUEOUS SOLUTION OF CHLORINE DIOXIDE AND RAW MATERIALS FOR ITS PRODUCTION

8.1 The total storage volume and the optimal volume of unit storage tanks for an aqueous solution of chlorine dioxide and initial chemicals for its production should be determined by the project based on the needs of production and the conditions for eliminating the potential hazard of personal injury.

8.2 Aqueous solutions of chlorine dioxide and the chemicals used to produce it should be stored in vessel equipment made of materials intended for use in the medium of circulating substances, taking into account the corrosivity and aggressiveness of the reaction media.

8.3 Storage tanks for all chemicals, mechanically treated and filtered water and related equipment should be located in places protected against traffic flow.

8.4 It is necessary to use flange covers for vessel equipment handling chemicals contact with which may result in loss of vision, as well as to prescribe the mandatory wearing of safety glasses.

8.5 Availability of backup vessel equipment is mandatory which should ensure the discharge of chemicals from the emergency tank into the backup one.

8.6 For storage tanks for sulfuric and hydrochloric acids and solutions of sodium chlorate, it is required to have a pan or storage tank in the industrial sewage system that may contain the entire volume of the spillage in case of complete destruction of the tank.

8.7 The system of emergency absorption of acid and alkali should be provided with a stock of neutralizing agents sufficient to contain the emergency.

8.8 Pans for vessel equipment should be tight and made of materials intended for use in the medium of circulating substances (taking into account the corrosivity and aggressiveness of the reaction media). The height of the pan should be 0.2 m above the level of the estimated volume of spilled liquid. Pans should be constantly inspected and released from precipitation (when installing storage tanks outdoors) and other objects.

8.9 When operating vessel equipment with sulfuric and hydrochloric acids, aqueous solutions of caustic soda and sodium chlorate, the possibility of ingress of substances that can cause an increase in temperature, pressure or form fire hazardous mixtures must be excluded. The following reaction must be excluded:

- sulfuric acid with water, metal powders, carbides, salts of nitric, chloric, picric acids, and combustible materials;
- hydrochloric acid with metals, oxidizing agents, especially with nitric acid and salts of perchloric acid; and
- sodium chlorate solution with combustibles, acids, and sulfur.

8.10 When storing an aqueous solution of chlorine dioxide in order to prevent its decomposition or gas formation, exposure to the following factors and reaction with the following substances should be excluded:

- heat sources, direct sunlight, sparks, and open flame;
- with metal salts, reducing agents, oxidizing agents, acids, combustible materials, and organic products.

8.11 Manhole covers of storage tanks for an aqueous solution of chlorine dioxide shall be equipped with means for collecting evolved gases (air vents, hydraulic locks, etc.), which should be directed to the absorption purification system.

8.12 Storage tanks for an aqueous solution of chlorine dioxide should be equipped with floating roofs consisting of interconnected segments supported by pontoons to reduce the accumulation of gases in the free space of the tank. The air supplied to the gas space above the floating roof should be directed to the absorption purification system.

8.13 To prevent crystallization of sodium chlorate solutions in storage tanks, it is necessary to maintain its temperature in the range from 25 to 40°C.

8.14 In order to avoid overfilling of the vessel equipment, it is necessary to observe the filling coefficients established for specific substances.

8.15 Storage tanks for all chemicals and mechanically purified or filtered water should be equipped with level measuring and control systems with automatic actuation of sound and light signals in the control room and at the site upon reaching the maximum rate of filling and emptying of the tank, as well as equipped with devices preventing supply of the product into the tank when reaching the maximum level of its filling.

9. GENERAL SAFETY RECOMMENDATIONS FOR TRANSPORTATION OF AN AQUEOUS SOLUTION OF CHLORINE DIOXIDE

9.1 Transportation of an aqueous solution of chlorine dioxide is carried out through inter-workshop pipelines.

9.2 Pipelines should be made of materials resistant to chlorine dioxide and should ensure reliable operation in the working temperature and pressure range.

9.3 When laying pipelines of an aqueous solution of chlorine dioxide, seamless titanium pipes joined by welding should be used. Flange joints should be located in the places of valves installation and equipment connection, as well as in areas where, according to operating conditions, periodic disassembly is required for pipelines cleaning and repairing. The number of flanges should be minimal.

9.4 Protective casings should be installed on all flanged joints, except for the pipelines for the supply of sodium chlorate solutions.

9.5 To fasten the flange joints to the pipelines for the supply of aqueous solutions of chlorine dioxide and sodium chlorate, bolts with a coating of zinc or teflon (sermagard) should be used. The use of stainless steel bolts is not allowed.

9.6 Chemicals feed pumps should have a drainage valve to remove chemical residues for maintenance purposes. All pumps must have a shut-off valve at the suction and discharge and drainage valve for their proper and safe shut-off.

9.7 Pipelines should be laid above ground on trestles in such a way as to ensure:

- protection against falling objects (hoisting devices and easy detachable sheds above the pipeline are not allowed);
- protection against possible impact by vehicles for which the pipeline is located at a distance from hazardous areas or is separated from them by barriers;
- division into process units and production blocks taking into account the installation and repair works using mechanical means, convenient maintenance, and inspection;
- ability to perform all types of work on monitoring, testing, and diagnosis;
- insulation and protection of pipelines against corrosion and atmospheric and static electricity;
- preventing the formation of ice and other plugs in the pipeline;
- smallest length of pipelines;
- exclusion of sagging and formation of stagnant zones; and
- possibility of homing action of thermal deformations of pipelines and protection against damages. When selecting a pipeline route, it is recommended to provide for the

possibility of self-compensation of temperature deformations due to the route turns;

- possibility of unimpeded movement of hoisting mechanisms, equipment, and fire fighting equipment.
- protection of pipelines against the impact of corrosive and combustible substances. Pipelines must be located at the distance of at least 1 m from pipelines with combustible substances.

9.8 Pipelines should be laid with a slope towards the transmitting and/or receiving tanks in order to ensure the possibility of their emptying by gravity.

9.9 At all drainage valves on chemical supply pipelines that directly vent to the atmosphere, plugs or hoods should be installed to prevent accidental discharge of chemicals.

9.10 Inter-workshop pipelines for transporting an aqueous solution of chlorine dioxide must have chokes with blocks and plugs for their emptying, purging, and crimping.

9.11 It is forbidden to lay pipelines inside administrative, amenity, and utility premises, in the premises of power distribution devices, electrical installations, automation panels, in the premises of transformers, ventilation chambers, heat points, on evacuation routes of personnel (stairwells, corridors, etc.), as well as in transit through premises of any purpose.

9.12 Gaskets for flange joints of pipelines of an aqueous solution of chlorine dioxide shall be made of materials resistant to the action of working media in the operating temperature and pressure range.

9.13 Blocks specially designed for the use in chlorine dioxide should be used on pipelines. Engineering materials of valves should ensure its reliable operation in the operating temperature and pressure range.

9.14 Blocks should be installed in places convenient for maintenance.

9.15 Pipelines conveying an aqueous solution of chlorine dioxide should not be joint to other pipelines (except for heat tracers that are fixed without welding).

9.16 When conveying an aqueous solution of chlorine dioxide through pipelines, the possibility of its freezing in case of the temperature decrease should be excluded, which can be achieved by heating the outer surfaces of the walls of the pipelines with heat tracers or heating electric cables. In this case, the temperature value of the aqueous solution of chlorine dioxide should not exceed the accepted design rate and should be reflected in the technological regulations.

9.17 Pipelines should be marked with identification painting, warning and marking boards (plates) with the name of the medium being transported, specifying the direction of movement of the medium and the parameters (pressure and temperature) in accordance with the requirements of the applicable RTD.

9.18 Before putting into operation, the pipelines of an aqueous solution of chlorine dioxide should be:

- tested for leaks at operating pressure by supplying compressed air (nitrogen) to the pipeline. The pressure drop rate during pneumatic testing of pipelines should not be more than 0.05% per hour. The procedure for checking pipelines for leaks should be regulated.

9.19 Pipeline leak testing should be carried out together with the equipment after installation, repair, and inspection of pipelines, valves, and equipment.

9.20 Volumes and terms of the inspection of pipelines and blocks shall comply with the requirements of the standards, specifications, and recommendations of the manufacturer.

9.21 Before repair, after emptying the pipelines, they should be flushed, purged with compressed air and capped with certified plugs to prevent the possible release of hazardous medium.

10. MONITORING, CONTROL, REGULATION, SIGNALING, AND PROTECTION SYSTEMS

10.1 Systems of monitoring, automatic and remote control, and regulation of processes (hereinafter, the control systems), signaling and emergency protection systems (EPS), as well as communication and emergency warning systems, including those delivered complete with equipment, must meet the requirements of the applicable regulatory and technical documentation and documentation at the enterprise.

10.2 Control systems and EPS should pass comprehensive testing (bringing the settings of software and hardware, communication channels and application programs to the values (state) at which the EPS system can be used in operation).

10.3 Control systems and EPS, as well as communication and emergency warning systems should be located in places convenient and safe for maintenance, excluding vibration, the quantitative characteristics of which exceed the permissible values of vibration indicators for used technical means, contamination with substances circulating in the process, mechanical and other harmful impacts affecting the accuracy, reliability, and speed of the systems. In this case, it is required to provide measures and means for dismantling of systems and their elements without depressurization of equipment and pipelines.

10.4 EPS systems must ensure protection of personnel, process equipment, and the environment in case of an abnormal situation in the production the development of which may lead to an accident. Violation of the control system should not affect the operation of the EPS system.

10.5 EPS systems must use their own sensors. Sensors of control systems can be used for EPS system as additional tools.

10.6 EPS systems should be built on the basis of controllers capable of functioning in a fail-safe structure. In case of failure of the EPS system, the protected process should automatically be transferred to a safe state.

10.7 The response time of EPS systems should be such that the hazardous development of a possible accident is excluded.

10.8 In case of a power outage or cutting off the feed of compressed dried air for feeding the control systems, EPS systems must ensure the transition of the production in a safe state. It is necessary to exclude the possibility of arbitrary shifts in these systems when restoring the supply of electricity or compressed dried air.

10.9 The return of the production equipment to the operational state after the actuation of the EPS system should be carried out by maintenance personnel in accordance with the instructions for launching and shutting down.

10.10 Measurement and regulation of process parameters should be carried out using instrumentation and control devices that are corrosion-resistant in the environment of substances circulating at the production, or protected against their impact (separation devices, pneumatic repeaters, and blowing inert gas).

10.11 The use of faulty instrumentation, as well as instruments not complying with the requirements of the legislation of the Russian Federation on ensuring the measurements uniformity, is not allowed.

10.12 Monitoring, control, and regulation of the processes should be carried out from the operator’s workplace located in the control room and have control duplication using equipment at its location. The need for control duplication using equipment at its location is established by the developer of the design documentation.

10.13 It is not permitted to introduce impulse tubes with chlorine dioxide into the control room.

10.14 Information on the dynamics of process parameters such as pressure, solution level, temperature of the solution, and the gas phase in the chlorine dioxide reactor should be displayed on the control panel. Trends may be displayed on the screen of a local computer (distributed control system or PC) or on pen recorders.

10.15 Monitoring of current indicators of process parameters that determine the potential hazard of the process should be carried out from at least two independent sensors with separate signal sampling points. The list of monitored parameters that determine the potential hazard of the process should be drawn up by the process designer and specified in the design documentation.

10.16 All interlock variables must be calibrated and checked at least once a year.

10.17 The actuating devices of automatic regulators must be tested in conjunction with process valves and utilities.

10.18 Inspection and testing of shut-off valves and control valves should be carried out according to the schedule of major repairs once a year by the mechanical service and the instrumentation and automation service of the enterprise by affiliation.

10.19 The serviceability of emergency safety interlock circuits and alarms, electronic, relay and electrical circuits should be inspected in accordance with the approved schedules and at each process shutdown.

10.20 Production premises in which the process of producing an aqueous solution of chlorine dioxide is carried out and chlorine dioxide, sulfur dioxide, and chlorine may be released must be equipped with automatic continuous gas monitoring and analysis with an alarm system with at least two response levels and signals outputting to the EPS system. All cases of gas contamination should be recorded by devices.

10.21 Production premises in which storage shift tanks for an aqueous solution of chlorine dioxide are installed must be equipped with automatic continuous gas monitoring and analysis devices with an alarm system. All cases of gas contamination should be recorded by devices.

10.22 Installation places and the number of sensors or sampling devices of analyzers should be determined in the design documentation taking into account the requirements of regulatory technical documents on the placement of gas control sensors.

10.23 Light and sound alarms for gas contamination of the air must be provided for:

- at the entrance door – outside to alert the personnel of the hazard;

- inside the premises – in working areas.

10.24 In order to protect maintenance personnel and equipment against possible damage, light and sound alarms of the following process parameters and interlocks should be designed and installed with the aim of safe shutdown of processes for production of an aqueous solution of chlorine dioxide according to the methods of Matheson, R6 and SVP (Tables 1, 2, 3, and 4) and its use in bleaching workshops (Table 5).

10.25 In order to protect maintenance personnel and equipment against possible damage, automatic control systems for the following process parameters for the production of chlorine dioxide according to the Matheson method should be designed and installed, Table 6.

Table 1 Mandatory and recommended alarms and interlocks of the process parameters when producing an aqueous solution of chlorine dioxide according to the Matheson method using integrated reactors

Monitored parameter	Permissible limit of the monitored parameter			
	alarms		interlocks	
	minimum	maximum	minimum	maximum
1	2	3	4	5
Sulfuric acid level in the storage vessel	-	“HIGH” (80%)	-	“HIGH-HIGH” (85%)
Pressure of compressed process air supplied to the chlorine dioxide production installation	“LOW” (4.0 kgf/cm^2)	-	-	-
Pressure of compressed dried air for instrumentation supplied to the chlorine dioxide production installation	“LOW” (4.0 kgf/cm^2)	-	-	-
Pressure of sulfurous-acid anhydride supplied to the mixer	“LOW” (0.8 kgf/cm^2)	-	-	-
Temperature of the gas phase in the reactor	-	“HIGH-HIGH” (38°C)	-	“HIGH-HIGH” (39°C)
Pressure of chilled filtered water fed to the absorption column	“LOW” (0.4 MPa)	-	-	-
Level of an aqueous solution of chlorine dioxide in the storage vessel	-	“HIGH” (80%)	-	-

Continuation of Table 1

1	2	3	4	5
Level of the solution in the circulation tank	“LOW” (20%)	“HIGH” (80%)	-	-
Level of waste solution in the storage tank	“LOW” (20%)	“HIGH” (80%)	-	-
Concentration of chlorine and chlorine dioxide in the air of the working area	-	“HIGH” (0.5 ppm) “ALARM” (0.8 ppm) “HIGH-HIGH” (1.0 ppm)	-	-
Concentration of hydrogen sulfide in the air of the working area	-	“HIGH” (3.0 mg/m^3)	-	-
Volumetric consumption rate of sealing water fed to pumps and compressors	-	-	“LOW” (1.0 kgf/cm^2)	-
Chilled water level in storage tank	“LOW”	-	-	-
Temperature of chilled water fed to the chlorine dioxide production installation	-	“HIGH” (9°C)	-	-
Volumetric consumption rate of an aqueous solution of chlorine dioxide supplied to consumers	“LOW”	-	-	-

Table 2 Mandatory and recommended alarms and interlocks of the process parameters when producing an aqueous solution of chlorine dioxide according to the Matheson method using successively installed reactors

Monitored parameter	Permissible limit of the monitored parameter			
	alarms		interlocks	
	minimum	maximum	minimum	maximum
1	2	3	4	5
Level of chlorate chloride solution or solution of sodium chlorate in a storage vessel	“LOW” (30%) “LOW-LOW” (20%)	“HIGH” (70%) “HIGH-HIGH” (80%)	“LOW-LOW” (20%)	-
Temperature of the sodium chlorate solution in the storage vessel	“LOW” (25°C)	“HIGH” (40°C)	“LOW” (25°C)	“HIGH” (40°C)
Temperature of the sodium chlorate solution after heat exchanger	-	“HIGH” (70°C)	-	-
Sulfuric acid level in the storage tank or pressure tank	“LOW” (30%) “LOW-LOW” (20%)	“HIGH” (70%) “HIGH-HIGH” (80%)	-	“HIGH-HIGH” (90%)
Pressure of the river water supplied to the installation of chlorine dioxide production	“LOW” (3 kgf/cm^2)	“HIGH” (6 kgf/cm^2)	-	-

Continuation of Table 2

1	2	3	4	5
Pressure of compressed process air supplied to the chlorine dioxide production installation	“LOW” (4.0 kgf/cm^2)	“HIGH” (6.0 kgf/cm^2)	“LOW” (3.5 kgf/cm^2)	-
Pressure of compressed dried air for instrumentation supplied to the chlorine dioxide production installation	“LOW” (4.0 kgf/cm^2)	“HIGH” (8.0 kgf/cm^2)	“LOW” (3.5 kgf/cm^2)	-
Pressure of nitrogen supplied to the installation of chlorine dioxide production	“LOW” (4.0 kgf/cm^2)	-	-	-
Pressure of compressed process air (nitrogen) fed to the mixer	“LOW” (0.8 kgf/cm^2)		“LOW-LOW” (0.7 kgf/cm^2)	-
Pressure drop across the filters of sodium chlorate solution	-	“HIGH” (1.0 kgf/cm^2)	-	-
Pressure drop across sulfuric acid filters	-	“HIGH” (1.0 kgf/cm^2)	-	-
Pressure drop across river water filters	-	“HIGH” (0.6 kgf/cm^2)	-	-
Mass fraction of sulfuric acid monohydrate fed to chlorine dioxide reactors	“LOW” (1,436 g/dm^3)	-	-	-
Temperature of sulfurous anhydride supplied to the chlorine dioxide production installation	“LOW” (30°C)	“HIGH” (70°C)	-	-
Temperature of water in the sulfur dioxide anhydride residual evaporator	“LOW” (45°C)	“HIGH” (95°C)	-	-

Continuation of Table 2

1	2	3	4	5
Temperature of sulfurous anhydride after residual evaporator	“LOW” (30°C)	-	-	-
Pressure of sulfurous-acid anhydride supplied to the mixer	“LOW” (1.5 kgf/cm^2)	“HIGH” (3.5 kgf/cm^2)	-	-
Volume fraction of sulfur dioxide in the gas-air mixture fed to the primary reactor	“LOW” (6%)	“HIGH” (11.5%)	-	“HIGH” (12.0%)
Volumetric consumption rate of the gas-air mixture fed to the primary reactor	“LOW” (0.83 nm^3/min)	-	-	-
Rarefactions in primary reactors	-	“HIGH” (minus 0.6 kPa) “HIGH-HIGH” (minus 0.5 kPa)	-	“HIGH” (minus 0.2 kPa)
Temperature of the liquid phase in the primary reactor	“LOW” (30°C)	“HIGH” (40°C) “HIGH-HIGH” (42°C)	-	“HIGH-HIGH” (42°C)
Temperature of the gas phase in the reactor	-	“HIGH” (40°C) “HIGH-HIGH” (42°C)	-	“HIGH-HIGH” (42°C)

Continuation of Table 2

1	2	3	4	5
Volumetric consumption rate of river water fed to absorption columns	“LOW” (16 m^3/h)	-	-	-
Volumetric consumption rate of river water fed to sanitary columns	“LOW” (6 or 18 m^3/h depending on the column)	-	-	-
Total volumetric consumption rate of river water and chlorine water fed to the absorption and sanitary columns	“LOW” (16 m^3/h)	-	-	-
Water level in the sanitary column	“LOW” (30%)	“HIGH” (50%)	“LOW” (30%)	-
Level of an aqueous solution of chlorine dioxide in the tank Storage	“LOW” (30%) “LOW-LOW” (20%)	“HIGH” (70%) “HIGH-HIGH” (80%)	-	“HIGH-HIGH” (90%)
Gas-air rarefaction in the tank of storage of an aqueous solution of chlorine dioxide	“LOW” (minus 0.3 kPa) “LOW-LOW” (minus 0.5 kPa)	“HIGH-HIGH” (0.2 kPa)	-	-

Continuation of Table 2

1	2	3	4	5
Level of the solution in the circulation tank	“LOW” (20%)	“HIGH” (80%)	-	-
Level of waste solution in the storage tank	“LOW” (30%) “LOW-LOW” (20%)	“HIGH” (70%) “HIGH-HIGH” (80%)	“LOW-LOW” (20%)	-
Air-gas rarefaction in the tank of storage of waste solution	“LOW” (minus 1.5 kPa)	-	-	-
Concentration of sulfurous anhydride in the air of the working area	-	“HIGH” (10 mg/m^3) “HIGH-HIGH” (50 mg/m^3)	-	“HIGH-HIGH” (50 mg/m^3)
Concentration of chlorine and chlorine dioxide in the air of the working area	-	“HIGH” (0.1 mg/m^3) “HIGH-HIGH” (0.5 mg/m^3)	-	“HIGH-HIGH” (0.5 mg/m^3)
Volumetric consumption rate of sealing water fed to pumps and compressors	“LOW” (1 kgf/cm^2)	-	-	-

Table 3 Mandatory and recommended alarms and interlocks of the process parameters when producing an aqueous solution of chlorine dioxide according to the R6 method

Monitored parameter	Permissible limit of the monitored parameter			
	alarms		interlocks	
	minimum	maximum	minimum	maximum
1	2	3	4	5
Pressure drop across filters of “strong” sodium chlorate solution	-	“HIGH” (160 kPa)	-	-
Level of “strong” sodium chlorate solution in the feed tank	“LOW” (30%) “LOW-LOW” (5%)	-	“LOW-LOW” (5%)	-
Temperature of the gas phase in the 1st section of the reactor	-	“HIGH” (30°C) “HIGH-HIGH” (35°C)	-	“HIGH-HIGH” (35°C)
Temperature of the gas phase in the 3rd section of the reactor	-	“HIGH” (40°C) “HIGH-HIGH” (45°C)	-	-

Continuation of Table 3

1	2	3	4	5
Temperature of the gas phase on the line: exiting the generator – entering the absorber	-	“HIGH” (70°C) “HIGH-HIGH” (75°C) “ABNORMALLY HIGH” (80°C)	-	“HIGH-HIGH” (75°C) “ABNORMALLY HIGH” (80°C)
Consumption rate of air fed for dilution in the generator	“LOW” (260 kg/h)	-	“LOW” (260 kg/h)	-
Pressure of air fed for dilution in the generator	“LOW” (60 kPa)	-	“LOW” (50 kPa)	-
Pressure in generator	“LOW-LOW” (50 kPa)	-	“LOW-LOW” (50 kPa)	-
Hydrochloric acid consumption rate in the generator	-	“HIGH” (3.1 m^3/h)	-	“HIGH” (3.1 m^3/h)
Water consumption rate for compressor hydraulic lock	“LOW” (3 m^3/h)	-	“LOW” (3 m^3/h)	-

Continuation of Table 3

1	2	3	4	5
Compressor separator water level	-	“HIGH”	-	“HIGH”
Compressor engine operation	Status signaling		-	-
Consumption rate of chilled filtered water in chlorine dioxide absorber	“LOW” (20 m^3/h)	-	“LOW” (20 m^3/h)	-
Vapor-gas phase pressure at the inlet to the absorber	“LOW-LOW” (minus 3.0 kPa)	“HIGH-HIGH” (minus 0.25 kPa)	-	“HIGH-HIGH” (minus 0.25 kPa)
Solution level in the chlorine dioxide absorber collector	“LOW” (20%) “LOW-LOW” (10%)	“HIGH” (80%)	“LOW-LOW” (10%)	-
Temperature of vapor-gas phase / solution in the chlorine dioxide absorber collector	-	“HIGH” (70°C) “HIGH-HIGH” (75°C) “ABNORMALLY HIGH” (80°C)	-	“HIGH-HIGH” (75°C) “ABNORMALLY HIGH” (80°C)

Continuation of Table 3

1	2	3	4	5
Temperature of the “weak” chlorine gas-blower bearing	-	“HIGH” (100°C) “HIGH-HIGH” (110°C)	-	“HIGH-HIGH” (110°C)
Pressure of “weak” chlorine at the outlet of the gas blower	“LOW” (20 kPa) “LOW-LOW” (14 kPa)	-	“LOW-LOW” (14 kPa)	-
Pressure of compressed air fed to the “weak” chlorine gas-blower seal	“LOW” (10 kPa) “LOW-LOW” (8 kPa)	-	“LOW-LOW” (8 kPa)	-
Operation of the “weak” chlorine gas-blower engine	Status signaling		-	-
Solution level in sodium hypochlorite tower	“LOW” (60%) “LOW-LOW” (50%)	-	“LOW” (60%) “LOW-LOW” (50%)	-

Continuation of Table 3

1	2	3	4	5
Redox potential in sodium hypochlorite tower	-	“HIGH” (550 mV)	-	“HIGH” (550 mV)
Pressure of sodium hypochlorite circulating at the inlet to the tower	“LOW” (minus 3 kPa)	-	-	-
Consumption rate of solution circulating at the inlet to the sodium hypochlorite tower	“LOW” (20 m^3/h)	-	“LOW” (20 m^3/h)	-
Level of an aqueous solution of chlorine dioxide in the storage tank	“LOW-LOW” (10%)	“HIGH-HIGH” (90%)	“HIGH-HIGH” (90%)	-
Level of demineralized water in the tank	“LOW” (75%) “LOW-LOW” (5%)	-	“LOW” (75%) “LOW-LOW” (5%)	-
Level of chilled filtered water in the tank	“LOW” (85%) “LOW-LOW” (5%)	-	“LOW-LOW” (5%)	-

Continuation of Table 3

1	2	3	4	5
Demineralized water pressure in the feed pipe	“LOW” (350 kPa)	-	“LOW” (350 kPa)	-
Volumetric consumption rate of an aqueous solution of chlorine dioxide in the pipeline of supply to the bleaching workshop	“LOW” (26.4 m^3/h) “LOW-LOW” (2.0 m^3/h)	-	“LOW” (26.4 m^3/h) “LOW-LOW” (2.0 m^3/h)	-
Pressure of nitrogen supplied to the chlorine dioxide production installation	“LOW” (180 kPa) “LOW-LOW” (50 kPa)	-	“LOW” (180 kPa) “LOW-LOW” (50 kPa)	-
Pressure of compressed dried air for instrumentation supplied to the chlorine dioxide production installation	“LOW” (500 kPa)	-	“LOW” (500 kPa)	-
Operation of the “sodium hypochlorite fan”	Status signaling		-	-

Continuation of Table 3

1	2	3	4	5
Concentration of chlorine in the air of the working area	-	“HIGH” (0.9 mg/m^3) “HIGH-HIGH” (1.0 mg/m^3)	-	“HIGH-HIGH” (1.0 mg/m^3)
Concentration of chlorine dioxide in the air of the working area		“HIGH” (0.09 mg/m^3) “HIGH-HIGH” (0.1 mg/m^3)	-	“HIGH-HIGH” (0.1 mg/m^3)

Table 4 Mandatory and recommended alarms and interlocks of the process parameters when producing an aqueous solution of chlorine dioxide according to the SVP method

Monitored parameter	Permissible limit of the monitored parameter			
	alarms		interlocks	
	minimum	maximum	minimum	maximum
1	2	3	4	5
Sodium chlorate solution level in the receiving tank	“LOW” (35%)	“HIGH” (80%)	“LOW” (35%)	“HIGH” (80%)
Sulfuric acid level in the receiving tank	“LOW” (40%)	“HIGH” (80%)	-	“HIGH” (80%)
Sodium chloride solution level in the receiving tank	“LOW” (35%)	“HIGH” (80%)	“LOW” (35%)	“HIGH” (80%)
Volumetric consumption rate of filtered water fed to the reactor	-	“HIGH” (1.5 m^3/h)	-	“HIGH” (1.5 m^3)
Volumetric consumption rate of sodium chlorate solution fed to the reactor	“LOW” 0.5 m^3/h	-	-	-
Volumetric consumption rate of sulfuric acid supplied to the reactor	“LOW” 0.15 m^3/h	-	-	-
Pressure of steam supplied to the heat exchanger for reactor heating	-	“HIGH” (4.4 kgf/cm^2)	-	-
Temperature of the vapor-gas mixture at the outlet of the reactor	-	“HIGH” (78°C)	-	“HIGH” (78°C)

Continuation of Table 4

1	2	3	4	5
Level of the reaction mixture in the reactor	“LOW” (45%)	“HIGH” (80%)	“LOW” (45%)	-
Absolute pressure of vapor-gas mixture in the reactor	-	“HIGH” (67%)	-	“HIGH” (67%)
Absolute pressure of vapor-gas mixture at the outlet of the reactor	-	“HIGH” (84%)	-	“HIGH” (84%)
Volumetric consumption rate of filtered cooling water fed to the chlorine dioxide absorber	“LOW” (15 m^3/h)	-	-	-
Steam pressure fed to the steam jet vacuum pump	“LOW” (7.0 kgf/cm^2)	-	“LOW” (7.0 kgf/cm^2)	-
Level of chlorine dioxide in absorber	-	“HIGH” (80%)	-	“HIGH” (80%)
Volumetric consumption rate of cooling filtered water fed to the chlorine dioxide absorber	“LOW” (15 m^3/h)	-	“LOW” (15 m^3/h)	-
Volumetric consumption rate of cooling filtered water fed to the chlorine absorber	“LOW” (25 m^3/h)	-	“LOW” (25 m^3/h)	-
Level of an aqueous solution of chlorine dioxide in the storage tank	“LOW” (5%)	“HIGH” (80%)	-	“HIGH-HIGH” (80%)
Pressure of compressed dried air for instrumentation supplied to the installation	“LOW” (3.5 kgf/cm^2)	-	“LOW” (3.5 kgf/cm^2)	-

Continuation of Table 4

1	2	3	4	5
Pressure of cooling filtered water supplied to the installation	"LOW" (2.5 kgf/cm^2)	-	"LOW" (2.5 kgf/cm^2)	-
Levels of sodium hypochlorite solution and chlorine water in storage tanks	"LOW" (10%)	"HIGH" (80%)	-	-
Shutdown of a pump pumping an aqueous solution of chlorine dioxide from an absorber into a storage tank	Pump shutdown		Protection against pump shutdown	
Temperature of the compressed process air in the receiver	-	(75°C)	-	-
Concentration of chlorine dioxide in the air of the working area:				
storage compartment	-	"HIGH" 0.1 mg/dm^3	-	-
reactor compartment	-	"HIGH" 1.0 mg/dm^3	-	-
Concentration of hydrogen sulfide in the air of the working area	-	"HIGH" 10.0 mg/dm^3	-	-

Table 5 Mandatory and recommended alarms and interlocks of the process parameters when using an aqueous solution of chlorine dioxide in bleaching and water treatment workshops

Monitored parameter	Permissible limit of the monitored parameter			
	alarms		interlocks	
	minimum	maximum	minimum	maximum
Level of an aqueous solution of chlorine dioxide in a feed storage tank in a bleaching workshop	-	“HIGH” (80%, max)	-	“HIGH” (80%, max)
Level of an aqueous solution of chlorine dioxide in a feed storage tank in a water treatment workshop	-	“HIGH” (80%)	-	“HIGH” (80%)

Table 6 Mandatory and recommended automatic control systems for process parameters when producing an aqueous solution of chlorine dioxide according to the Matheson method

Process parameter	With an integrated secondary reactor	With a remote secondary reactor
1	2	3
Volumetric consumption rate of compressed process air supplied to the mixer	-	+
Pressure of compressed process air supplied to the mixer	+	+
Volumetric consumption rate of sulfurous-acid anhydride supplied to the mixer	+	-
Volumetric consumption rate of the gas-air mixture fed to reactors	+	+
Volume fraction of sulfur dioxide in the gas-air mixture fed to the primary reactor	-	+
Volumetric consumption rate of sulfuric acid supplied to the primary reactor	+	+
Volumetric consumption rate of chlorate-chloride solution (sodium chlorate solution) fed to the primary reactor	+	+
Temperature of the gas phase in the primary reactor by supplying mechanically purified water for cooling (in the jacket of the reactor)	+	-

Continuation of Table 6

1	2	3
Temperature of the liquid phase in the primary reactor by cutting off the supply of air and sulfur dioxide into the mixer	-	+
Temperature of the liquid phase in the secondary reactor	-	+
Volumetric consumption rate of a solution of sodium hydroxide or river water supplied for irrigation of the sanitary column	+	+
Volumetric consumption rate of chilled filtered (river) water fed to the absorption column	+	+
Pressure of chilled filtered water fed to the absorption column	+	-
Level of waste solution in the storage tank	+	-
Pressure of air compressed after water separator	-	+
Temperature of air compressed after water separator	-	+
Volumetric consumption rate of compressed process air supplied to strippers	-	+
Rarefaction of exhaust gas after the absorption column	-	+

Continuation of Table 6

1	2	3
Rarefaction of the gas-air mixture before the sanitary column	-	+
H factor in the neutralizer reactor	-	+
Temperature of the spent solution in the neutralizer reactor	-	+
Rarefaction in the spent solution tank	-	+

10.26 In order to protect maintenance personnel and equipment against possible damage, automatic control systems for the following process parameters for the production of chlorine dioxide according to the R6 method should be designed and installed:

- volumetric consumption rate of a solution of “strong” sodium chlorate fed to the reactor;
- volumetric consumption rate of hydrochloric acid fed to the reactor;
- compressed air pressure on the compressor discharge line;
- pressure of compressed air supplied to the reactor;
- volumetric consumption rate of “weak” chlorine on the line of its recirculation to the reactor;
- temperature of the reaction medium in Sections 3, 5, 7, 8, and 9 of the reactor;
- pressure of compressed dried air for instrumentation and automation fed to the gas blower of “weak” chlorine;
- pressure of “weak” chlorine at the outlet of the gas blower;
- pressure of the gas-air mixture at the inlet to the absorber;
- volumetric consumption rate of chilled filtered water fed to the chlorine dioxide absorber;
- level of an aqueous solution of chlorine dioxide in the collector;
- level of the solution in the evaporator of “weak” chlorate;
- volumetric consumption rate of caustic soda solution fed to the hypochlorite tower;
- volumetric consumption rate of chilled filtered water fed to the hypochlorite tower;
- level in the tank of chilled filtered water;
- level in the condensate tank.

10.27 In order to protect maintenance personnel and equipment against possible damage, automatic control systems for the following process parameters for the production of chlorine dioxide according to the SVP method should be designed and installed:

- volumetric consumption rate of a solution of sodium chlorate fed to the reactor;
- volumetric consumption rate of a solution of sodium chloride fed to the reactor;
- volumetric consumption rate of sulfuric acid supplied to the reactor;
- volumetric consumption rate of filtered water fed to dilute sulfuric acid before feeding it to the reactor;
- mass consumption rate of steam fed to the heat exchanger for heating the reaction mass in the reactor;
- air pressure in the receiver;
- air temperature in the receiver;
- level in the condensate collection tank;
- level of the solution in the chlorine dioxide absorber;
- temperature of the gas mixture after the condenser;
- pressure in the chlorine dioxide absorber;
- volumetric consumption rate of filtered cooling water fed to the chlorine dioxide absorber;
- volumetric consumption rate of filtered cooling water fed to the chlorine absorber;
- level in the tank of storage of an aqueous solution of chlorine dioxide;

- pressure of steam fed to the chlorine dioxide production installation.

10.28 In order to comply with the process flow standard, automatic control systems for the following process parameters should be designed and installed when using an aqueous solution of chlorine dioxide in bleaching shops:

- consumption rate of an aqueous solution of chlorine dioxide fed to the bleaching shop and
- consumption rate of an aqueous solution of chlorine dioxide fed to each stage of bleaching.

11. GENERAL SAFETY REQUIREMENTS FOR THE INSTALLATION, OPERATION, AND REPAIR OF PROCESS EQUIPMENT

11.1. The selection of workshop equipment for the production and use of chlorine dioxide should be carried out in accordance with the technological input data, the production technology regulations, the requirements of regulatory legal acts in the field of industrial safety and Federal Rules and Regulations in the field of industrial safety *Safety Rules for Chemically Hazardous Production Facilities.*

11.2 Operation of the equipment should guarantee the safety of workers both at the stage of installation (dismantling), commissioning, and at its direct operation and maintenance, repair, transportation, and storage.

11.3 The design service life should be established for the used technical devices taking into account the specific conditions of operation which must be specified in the equipment certificates. Also, the requirements for installation, operation, and repair must be established in the manufacturer’s instructions.

11.4 Design and manufacture of the equipment must comply with the requirements of the Technical Regulations of the Customs Union *On Safety of Machinery and Equipment* (TR CU 010/2011), *On Safety of Equipment Working Under Excessive Pressure* (TR CU 032/2013).

11.5 Installation of process equipment, machines, and pipelines should be carried out in accordance with the design documentation, manufacturer’s instructions for installation and operation, Federal Rules and Regulations in the field of industrial safety, and other RTD.

Before the commencement of installation works, a method statement (MS) should be developed by the executor.

Installation works should be carried out in accordance with the safety requirements specified in the MS.

11.6 The procedure for organizing and conducting maintenance and repair of equipment taking into account the specific operating conditions of the equipment is determined by the manufacturer’s instructions (manuals) for repair and maintenance and industry regulations (systems) for maintenance and repair of process equipment.

All types of scheduled repairs should be carried out in accordance with the schedule of preventive maintenance.

Technical devices are subject to repair and maintenance within the time limits stipulated by the schedules approved by the technical manager of the branch.

11.7. Repair of equipment in the conditions of existing production should be carried out in accordance with the requirements of internal regulatory documents on the procedure for the safe conduct of repair works.

Preparation of equipment for repair should be carried out by technological personnel and be handed over to the head of the repair works with a mark in the log or the certificate of delivery of the equipment on the preparatory works and activities carried out with the obligatory execution of a permit to work.

Repair of apparatuses and equipment in existing productions should be carried out with the involvement of a minimum number of repair personnel, observing special safety measures specified in the permit to work.

LIST OF CITED REFERENCES

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2 Federal Rules and Regulations in the field of industrial safety *Safety Rules for Production of Chlorine and Chlorine-Containing Media,* approved by Order of the Federal Service for Environment, Technological and Nuclear Supervision dated November 20, 2013, No. 554.

3 Safety Guide *Recommendations for the Design and Safe Operation of Process Pipelines* approved by Order of the Federal Service for Environment, Technological and Nuclear Supervision dated December 27, 2012, No. 784.

4 GN 2.1.6.3492-17 *Maximum Allowable Concentrations (MAC) of Contaminants in the Air of Urban and Rural Settlements* approved by the Chief State Sanitary Doctor of the Russian Federation Decree dated December 22, 2017, No. 165.

5 GN 2.2.5.3532-18 *Maximum Allowable Concentrations (MAC) of Hazardous Substances in the Air of the Working Area* approved by the Chief State Sanitary Doctor of the Russian Federation Decree dated February 13, 2018, No. 25.

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