

Best available ClO_2 technologies for the pulp industry

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Best available ClO₂ technologies for the pulp industry

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Abstract

Eka Engineering is an engineering and contracting division within Nouryon Pulp and Performance Chemicals that specializes in the design and supply of chlorine dioxide (ClO₂) plants and equipment to the pulp and chemical industries.

Eka Engineering has developed a number of different process technologies, for safe and efficient ClO₂ generation that makes the division a world-leading supplier of chlorine dioxide plants.

ClO₂ is an oxidizer commercially used for bleaching pulp since the mid-1940s. ClO₂ is the most cost-effective bleaching agent of pulp, achieving high brightness while maintaining high strength.

ClO₂ is produced on site by reducing sodium chlorate (NaClO₃) in an acidic solution, either under vacuum (SVP processes) or atmospheric conditions (HP-A process). Different by-products are generated by varying the type of reducing agent and acid.

In this paper we will focus on the HP-A, the SVP-LITE and the SVP-SCW processes which are the most common ClO₂ processes used nowadays.

Also, we will briefly discuss about ClO₂ decompositions and other application for ClO₂.

(Abstract in Japanese)

1. Introduction

Eka Engineering is an engineering and contracting division within Nouryon Pulp and Performance Chemicals that specializes in the design and supply of chlorine dioxide (ClO₂) plants and equipment to the pulp and chemical industries. Eka Engineering has designed, built, re-built, handled spare parts and operated chlorine dioxide systems for pulp bleaching for over 40 years.

As an international leader in ClO₂ technology, Eka Engineering can supply all the ClO₂ processes to match the client requirements, from the design and procurement of the process equipment to a complete turnkey installation or rebuild of existing plants.

Eka Engineering also offers service, support, spare parts and equipment for the large-scale production and application of both vacuum and atmospheric processes.

A list with the orders during the last years is shown below:

Year	Pulp mill	Capacity	Process	Note
2019	Bracell SP, Bracell mill, Brazil	2 x 60 ton ClO ₂ /day	SVP-LITE/SCW	New plants in parallel (ongoing)
2019	Klabin, Ortigueira mill, Brazil	75 ton ClO ₂ /day	SVP-SCW	Debottlenecking (ongoing)
2019	Arauco, Horcones mill, Chile	51 ton ClO ₂ /day	SVP-SCW	New plant (ongoing)
2018	Sappi, Stanger mill, South Africa	4 ton ClO ₂ /day	HP-A	New plant
2017	Sappi, Ngodwana mill, South Africa	8 ton ClO ₂ /day	HP-A	Capacity increase
2017	Sappi, Saiccor mill, South Africa	30 ton ClO ₂ /day	HP-A	Conversion of Mathieson process
2016	SCA, Östrand mill, Sweden	26 ton ClO ₂ /day	SVP-LITE	New plant
2016	Stora Enso, Skoghall mill, Sweden	15 ton ClO ₂ /day	HP-A	New plant
2015	Fibriä, Tres Lagoas mill, Brazil	60 ton ClO ₂ /day	SVP-SCW	New plant
2015	Södra Cell, Värö mill, Sweden	35 ton ClO ₂ /day	SVP-LITE	New plant
2015	Metsä Fibre, Äänekoski mill, Finland	65 ton ClO ₂ /day	SVP-SCW	New plant

2. ClO₂ generation process

ClO₂ is an oxidizer commercially used for bleaching pulp since the mid-1940s and it can also be used to reduce NO_x compounds in flue gas.

ClO₂ is produced on site by reducing sodium chlorate (NaClO₃) in an acidic solution, either under vacuum (SVP processes) or atmospheric conditions (HP-A process). Different by-products are produced by varying the type of reducing agent and acid.

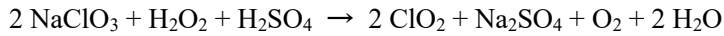
The most common ClO₂ processes used nowadays are the HP-A, the SVP-LITE and the SVP-SCW.

2.1 HP-A Process

HP-A process

The HP-A process benefits are: (a) low investment, (b) ease of operation and (c) gives the possibility to upgrade atmospheric installations (Mathieson process).

In the HP-A process, sodium chlorate (NaClO_3) reacts with hydrogen peroxide (H_2O_2) in the presence of sulphuric acid (H_2SO_4) to form chlorine dioxide (ClO_2) and a spent acid stream containing sulphuric acid and sodium sulphate. Oxygen (O_2) and water are generated as by-products of the reaction.

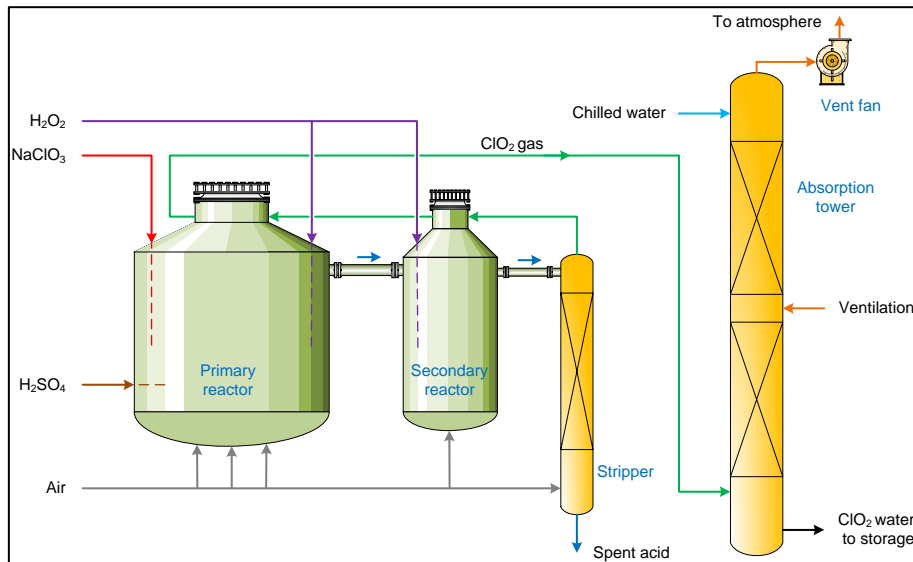


Typical chemical feed consumption and products for the HP-A process are presented in the tables below:

Feed chemical	Expected consumption
Sodium chlorate	1,65 ton NaClO_3 (100%) / ton ClO_2
Sulphuric acid	2,20 ton H_2SO_4 (100%) / ton ClO_2
Hydrogen peroxide	0,30 ton H_2O_2 (100%) / ton ClO_2

Product / Main by-product	Expected production
Chlorine dioxide solution	8 g ClO_2 /l
Spent acid	5 ton spent acid / ton ClO_2

The figure below shows a simplified HP-A process flow diagram:



(1) Primary reactor

Sodium chlorate, sulphuric acid, and hydrogen peroxide are all fed into the primary reactor. Air nozzles diffuse an air flow through the reactor solution. The reactor solution temperature is controlled via a cooling

coil and the reactor pressure is kept slightly negative. The ClO₂ gas generated in this reactor is collected in a gas header and sent to the absorption tower. Approximately 90-95% of the chlorine dioxide is produced in the primary reactor. The reactor solution overflows by level difference into the secondary reactor.

(2) Secondary reactor

Hydrogen peroxide is fed into the secondary reactor to increase the overall chlorate yield in the process. Air is introduced in the same manner as in the primary reactor. Temperature and pressure are likewise controlled. The ClO₂ gas generated in this reactor is also collected in the gas header to the absorption tower. The reactor solution overflows by level difference into the Stripper.

(3) Air blower system

The purpose of the air blower is to (a) mix the reactor solution in both reactors, (b) strip the chlorine dioxide out of the reactor solution and (c) dilute the ClO₂ in the gas stream to the absorption tower for a safe operation.

(4) Stripper and spent acid tank

Spent acid overflows from secondary reactor into the stripper. Air from the blower flows counter-current to the spent acid to strip out any residual chlorine dioxide. The off-gas from the stripper is combined with the off-gas from the secondary reactor. The stripped spent acid flows by gravity to the spent acid tank.

In the spent acid tank additional ClO₂ stripping takes place. ClO₂ gas collected from this tank is directed to the middle of the absorption tower through the ventilation system.

(5) Absorption tower

The purpose of the ClO₂ absorption tower is to absorb chlorine dioxide gas into chilled water to form a ClO₂ solution that can be safely stored and then used in the bleaching plant. The chlorine dioxide, oxygen, air, and water vapor collected in the gas header enters the absorption tower and flows up the column. Chilled water is added to the top of the absorption tower and flows down the column. As the water and gas pass each other, the ClO₂ is absorbed into the water to form the ClO₂ water. The ClO₂ water is pumped to the storage tanks.

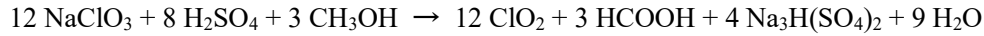
(6) Ventilation

A vent fan creates a slight negative pressure improving the stability of the ClO₂ gas in the process. The fan provides ventilation to the ClO₂ water storage tanks and the spent acid tank preventing ClO₂ gas emissions to the building. The vent gas from the process and tanks ventilation is then released to the atmosphere.

2.2 SVP-LITE process

The SVP-LITE process benefits are: (a) ease of operation, (b) minimal amount of by-product chlorine is formed and (c) the salt cake product is less than with atmospheric process.

In the SVP-LITE process, sodium chlorate (NaClO_3) reacts with methanol (CH_3OH) in sulphuric acid solution (H_2SO_4) to produce chlorine dioxide (ClO_2) and a sodium sesquisulphate solution ($\text{Na}_3\text{H}(\text{SO}_4)_2$).

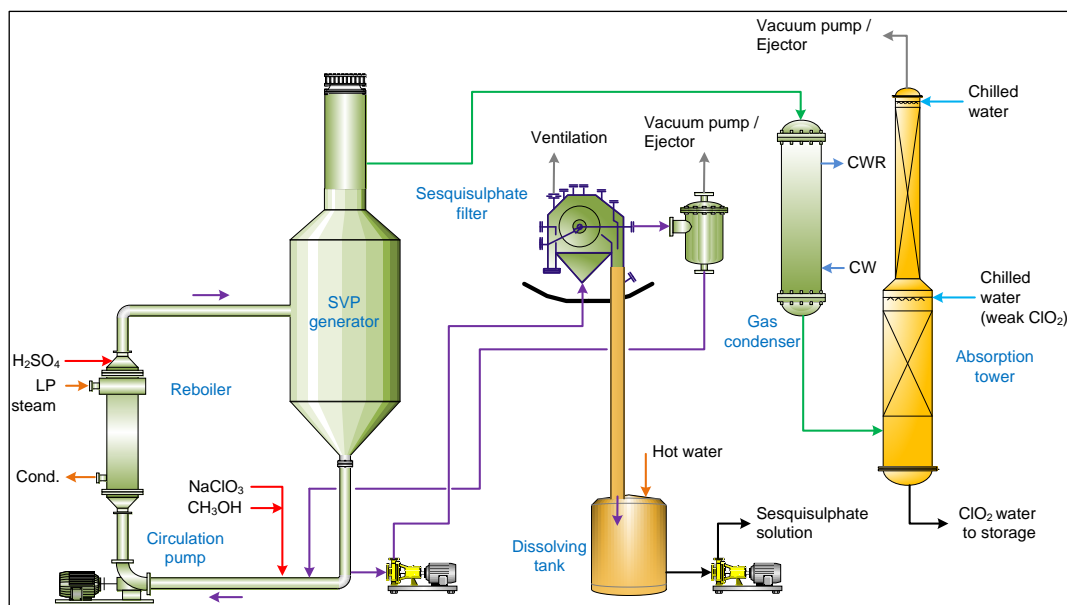


Typical chemical feed consumption and products for the SVP-LITE process are presented in the tables below:

Feed chemical	Expected consumption
Sodium chlorate	1,65 ton NaClO_3 (100%) / ton ClO_2
Sulphuric acid	1 ton H_2SO_4 (100%) / ton ClO_2
Methanol	0,18 ton CH_3OH (100%) / ton ClO_2

Product / Main by-product	Expected production
Chlorine dioxide solution	10 g ClO_2 /l
Sodium sesquisulphate	1,35 ton (100%) / ton ClO_2

The figure below shows a simplified SVP-LITE process flow diagram:



(1) SVP generator system

The heart of the process is an all-titanium generator, a vessel where the reaction takes place. The generator is designed a) to provide the necessary volume to carry out the reaction of the feed chemicals to generate chlorine dioxide, b) to evaporate the water present in the feed chemicals to maintain the level and c) to crystallize the sodium sesquisulphate produced by the reaction. A titanium pump circulates the generator solution through the reboiler. Low pressure steam is fed to the reboiler shell. The vacuum in the system is created by a steam ejector or a vacuum pump.

(2) ClO_2 absorption system

a) The chlorine dioxide, b) formic acid, and c) evaporated water along with d) unreacted methanol are drawn into the gas condenser. In the gas condenser, the water vapor is condensed. The process gases are then drawn into the absorption tower by the vacuum pump or steam ejector.

Chilled water is added to the top of the absorption tower and flows down through the packing. The ClO₂ gas from the gas condenser enters at the bottom of the absorption tower. As the water and gas pass each other, the ClO₂, methanol, and formic acid present in the gas are absorbed into the water to form ClO₂ water. The ClO₂ water is pumped to the storage tanks.

Part of the chilled water used for the absorption is first fed to the back-up scrubber (ventilation system) prior to being used in the absorption tower.

(3) Sesquisulphate filter system

The generator solution is removed from the bottom of the generator circulation pipe and pumped by the filter feed pump to the sesquisulphate filter.

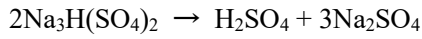
The generator solution flows into the sesquisulphate filter vat and overflows (by gravity) back to the generator circulation pipe. The sesquisulphate filter drum rotates through the vat full of generator solution while vacuum is pulled inside the drum. This vacuum pulls solids onto the face of the drum and the drum rotation carries the cake out of the vat. Wash water is sprayed onto the cake to remove the chemicals (sulphuric acid and sodium chlorate) as air is drawn through the cake, drying the solids. The combined mixture of air and liquid pulled through the cake drains into the center of the drum. This combined stream flows into the sesquisulphate filter separator where the gas (air and traces of ClO₂) and liquid (filtrate: sodium chlorate and sulphuric acid solution) are separated: the gas is drawn out of the sesquisulphate filter separator by the vacuum system and the filtrate drains back to the generator circulation pipe.

After the cake has been washed and dried, it rotates past the blow-off shoe. The blow-off shoe, located inside the filter drum, uses air pressure to blow the cake off the face of the drum and into the sesquisulphate filter chute. The acidic salt cake falls down the chute into the dissolving tank where it is dissolved and pumped to the pulp mill.

2.3 SVP-SCW process

The SVP-SCW process benefits are: (a) ease of operation, (b) minimal amount of by-product chlorine is formed, (c) the salt cake product is less than with atmospheric process and (d) sulphuric acid is recovered and recycled to the generator.

The difference between the SVP-LITE and the SVP-SCW processes is that the acidic sesquisulphate solution is separated in the metathesis tank to a weak acid solution and a neutral sodium sulphate by the following reaction:



The overall reaction of the SVP-SCW process is:

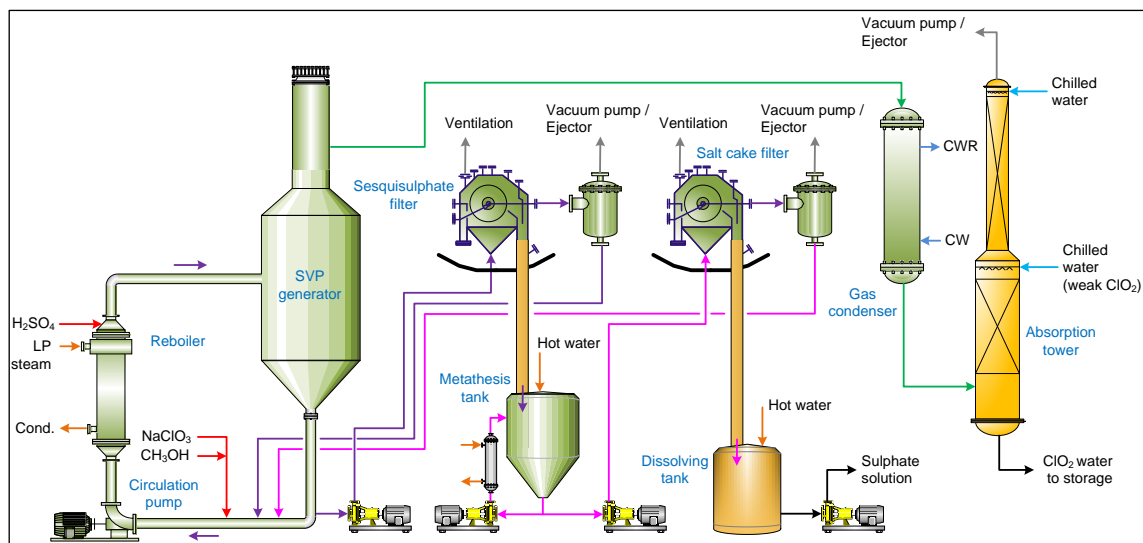


Typical chemical feed consumption and products for the SVP-SCW process are presented in the tables below:

Feed chemical	Expected consumption
Sodium chlorate	1,65 ton NaClO ₃ (100%) / ton ClO ₂
Sulphuric acid	0,80 ton H ₂ SO ₄ (100%) / ton ClO ₂
Methanol	0,18 ton CH ₃ OH (100%) / ton ClO ₂

Product / Main by-product	Expected production
Chlorine dioxide solution	10 g ClO ₂ /l
Sodium sulphate	1,10 ton (100%) / ton ClO ₂

The figure below shows a simplified SVP-SCW process flow diagram:



The metathesis tank and a second filter (salt cake filter) are added in the SVP-SCW process. The acidic sesquisulphate solution is separated in the metathesis tank to form a slurry containing weak acid solution and neutral sodium sulphate. A pump feeds the slurry (from the metathesis tank) to the second filter where the recycled acid is separated from the neutral sodium sulphate. In the salt cake filter the solids (now neutral sodium sulphate) are separated. The filtrate is the valuable weak acid that will be recycled into the generator system. The salt cake filter has the same construction and operation principle as the sesquisulphate filter.

The neutral sodium sulphate crystals fall through the chute into the dissolving tank and is dissolved in hot

water and pumped to the pulp mill.

3. ClO₂ decompositions

ClO₂ decomposition occurs occasionally due to the natural instability of ClO₂ gas. During decomposition, the chlorine dioxide decomposes to form chlorine, oxygen and heat. The decomposition reaction is spontaneous and results in the release of heat and pressure. An increase in generator gas temperature and pressure indicates a ClO₂ decomposition.

Contamination caused by the raw chemicals, utilities or wrong materials in contact with generator solution or ClO₂ gas are a very common cause of decompositions. Bad analysis results, instrumentation problems and foam are also among the more common causes of decompositions. The pictures below show examples of foam and bad quality sulphuric acid and sodium chlorate solution:



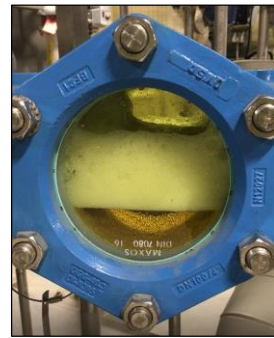
Picture 1



Picture 2



Picture 3



Picture 4

Picture 1: bad quality sodium chlorate solution. Contaminants (iron/organic material) are trapped in the filter element.

Picture 2: bad quality sulphuric acid. Contaminants (iron/organic material) are trapped in the filter elements.

Picture 3: bad quality sulphuric acid samples that were taken before unloading the tanker truck.

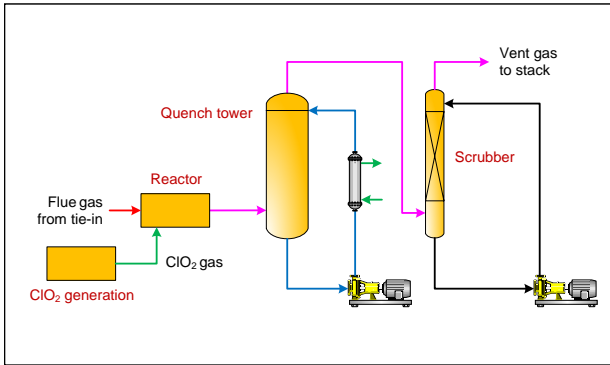
Picture 4: foam in the line between the primary and secondary reactors (HP-A process).

4. Other application for ClO₂

The Application RD&I division within Nouryon Pulp and Performance Chemicals is working on a project focused with assisting heavy polluting industries (waste combustion plants) for cleaner air emissions with the objective to reduce NO_x in flue gases by the use of ClO₂ gas.

The technology has been scaled-up and the full-scale phase is being analyzed.

A simplified process flow diagram and a picture of the 40 ft transportable container of the slip streams trials are shown below:



The transportable container includes the ClO₂ generator and mixing zone, the quench tower, the scrubber, analyzing system for flue gas and instrumentation needed for operation.