

## Chlorine dioxide technologies - Best available techniques (BAT) for ClO<sub>2</sub> production

### SVP-LITE®

Our large-scale, single-vessel processes (SVP) generate chlorine dioxide in a vacuum environment and produce a solid salt cake by-product. SVP-Lite systems use methanol as a reducing agent.

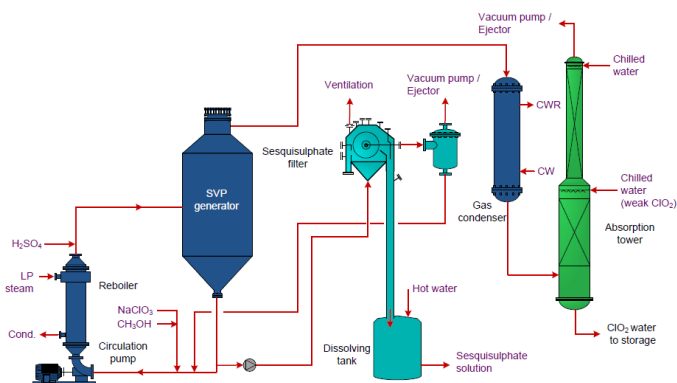
#### Reaction chemistry

Our SVP-LITE process generates chlorine dioxide (ClO<sub>2</sub>) by reducing sodium chlorate (NaClO<sub>3</sub>) using methanol (CH<sub>3</sub>OH or MeOH) in a sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) solution, according to the following reaction:



The by-product of this reaction is an acidic salt cake, sodium sesquisulfate Na<sub>3</sub>H(SO<sub>4</sub>)<sub>2</sub> that is approximately 18 - 25 wt.% sulfuric acid. By recovering the sulfuric acid from the sodium sesquisulfate salt, acid feed requirements and salt cake volume can be reduced by approximately 17% and 25%, respectively. Recovering this acid is the function of the salt-cake wash (SCW).

#### Overview of the SVP-LITE process



#### Benefits of SVP-LITE

The SVP-LITE process is an ideal choice for pulp mills that want to:

- Eliminate chlorine in the chlorine dioxide water in order to produce real ECF pulp
- Have low salt cake make-up requirements
- Economically expand the capacity of existing SVP (R3) plants
- Eliminate chlorine water or sodium hypochlorite use

It is possible to convert any SVP process to another with only minor equipment changes.

The key feature of the SVP-LITE process is the circulation of the main reactor vessel, which is kept under vacuum:

1. Reactants (chlorate, methanol and sulfuric acid) are fed to the reactor system where they react to form chlorine dioxide and a salt cake by-product precipitates
2. Steam is added to the reboiler to evaporate water from the generator solution
3. Gas leaving the generator is a mixture of chlorine dioxide and water vapor, which is absorbed into water in the absorption tower
4. The absorption tower tail gas is further scrubbed to avoid emissions
5. A side stream of the reactor solution is fed to the filter, which removes the salt cake by-product
6. The reactor solution is returned to the reactor
7. Chlorine dioxide water from the absorption tower is transferred to storage tanks
8. An emergency stop interlock system is in place that will shutdown the process should pressure, temperature or flow parameters operate out of range



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### SVP-SCW

The SVP-SCW (salk cake wash) process is an add-on option to the SVP-LITE process.

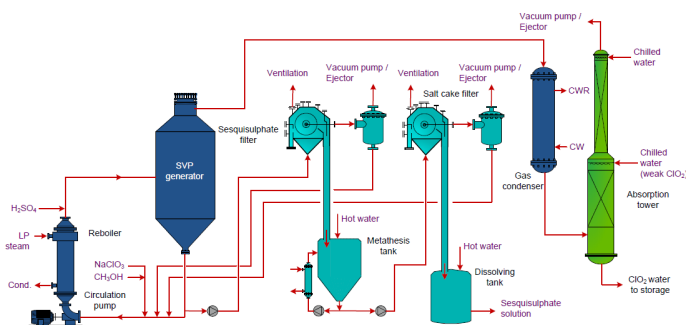
#### Reaction chemistry

Our SVP-SCW process generates chlorine dioxide (ClO<sub>2</sub>) by reducing sodium chlorate (NaClO<sub>3</sub>) using methanol (CH<sub>3</sub>OH or MeOH) in a sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) solution, according to the following reaction:



The byproduct of this reaction is an acidic salt cake, sodium sesquisulfate Na<sub>3</sub>H(SO<sub>4</sub>)<sub>2</sub>, that is approximately 18 - 25 wt.% sulfuric acid. By recovering the sulfuric acid from the sodium sesquisulfate salt, acid feed requirements and salt cake volume can be reduced by approximately 17% and 25%, respectively. Recovering this acid is the function of the salt cake wash (SCW).

#### SCW – sulfuric acid recovery



#### Benefits of SVP-SCW

The SVP-SCW process is an ideal choice for pulp mills that want to:

- Reduce their salt cake by-product (approximately 25%)
- Lower their acid consumption (approximately 17%)

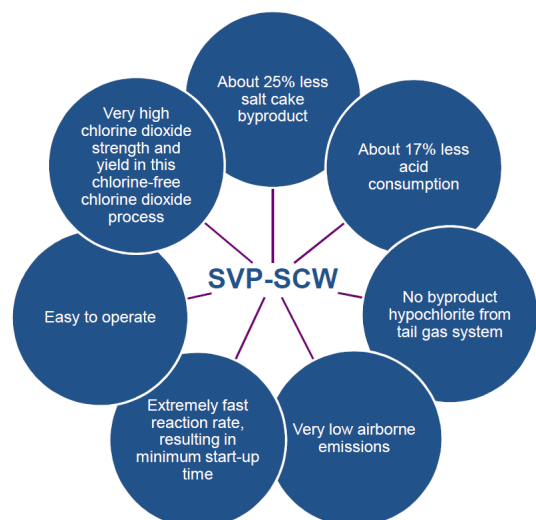
In addition to acid recovery, SVP-SCW features all the same benefits as SVP-LITE. It is possible to convert any SVP process to another with appropriate equipment changes.

To recover the sulfuric acid from the sodium sesquisulfate salt, it is filtered from the generator solution by the first salt cake filter. Then it is transferred to a metathesis tank where it is dissolved in hot water.

The sesquisulfate is converted to sodium sulfate and a weak sulfuric acid solution, according to the following equation:



The slurry from the metathesis tank is pumped to a second salt cake filter where the sodium sulfate is recrystallized and sent to the mill's recovery system or other applications.



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### HP-A®

Our HP-A system features several advantages over earlier atmospheric chlorine dioxide processes, removing the need for historical reducing agents (such as sulfur dioxide, methanol and sodium chloride) and improving the sodium chlorate yield. Thanks to equipment similarities, HP-A is frequently used to upgrade older atmospheric installations.

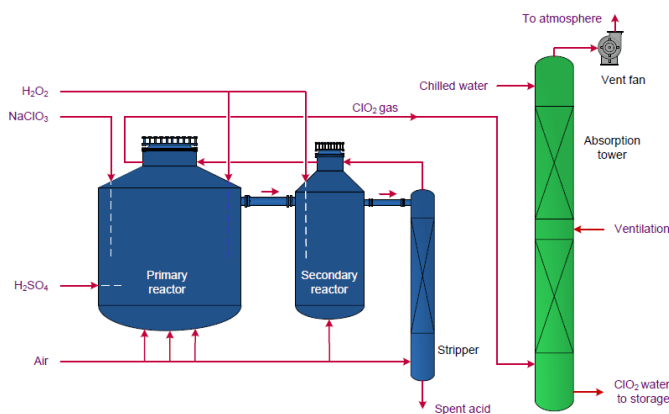
### Reaction chemistry

Our HP-A process produces chlorine dioxide (ClO<sub>2</sub>) by reducing sodium chlorate (NaClO<sub>3</sub>) with hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) in a sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) solution, according to the following equation:



Byproducts of this reaction are oxygen (O<sub>2</sub>) and spent acid containing sodium sulfate (NaHSO<sub>4</sub>): oxygen is released to the atmosphere and the acidic sodium sulfate is reused in other plant processes. Using hydrogen peroxide as a reducing agent brings a number of advantages, including higher capacity for existing generators, a more user friendly reducing which produces the purest chlorine dioxide available.

### HP-A process overview

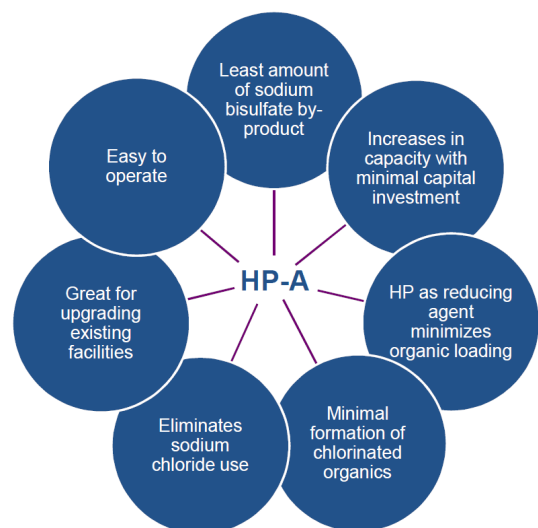


### Benefits of HP-A

The HP-A process is an ideal choice for pulp mills that want to:

- Upgrade existing atmospheric installations
- Increase sodium chlorate yield
- Minimize chlorine by-product production
- Reduce operating complexity

1. In the HP-A process, reactants (sodium chlorate, hydrogen peroxide and sulfuric acid) are fed to a reactor system, consisting of the primary and secondary generators, and a stripper unit.
2. Heat used to balance the reaction derives from the dilution of the sulfuric acid
3. Large quantities of air are introduced into the generator for mixing and keeping the ClO<sub>2</sub> concentration (in the gas phase) within the safe operating range
4. Liquor from the second generator overflows to a stripper and remaining ClO<sub>2</sub> is removed before the spent acid solution is discharged from the system
5. Liquor from the primary generator overflows into the secondary generator where the ClO<sub>2</sub> reduction process continues
6. Gas is transferred from the reactors and strippers to the absorption tower where chlorine dioxide gas is absorbed, then transferred to storage tanks
7. Tail gas exiting the absorption tower is further scrubbed to avoid emissions
8. An emergency stop interlock system is in place that will shutdown the process should pressure, temperature or flow parameters operate out of range



## Chlorine dioxide technologies - Best available techniques (BAT) for ClO<sub>2</sub> production

### SVP-HP

The SVP-HP process is based exclusively on use of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) for the reduction of sodium chlorate (NaClO<sub>3</sub>).

#### Process chemistry

Our SVP-HP process generates chlorine dioxide (ClO<sub>2</sub>) by reducing sodium chlorate (NaClO<sub>3</sub>) with hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) in a sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) solution, according to the following equation:



Depending on the acidity of the process solution, the byproduct salt is either sodium sulfate (as in the formula) or sodium sesquisulfate. The byproduct oxygen is released to the atmosphere or applied elsewhere in the bleaching process or effluent treatment process.

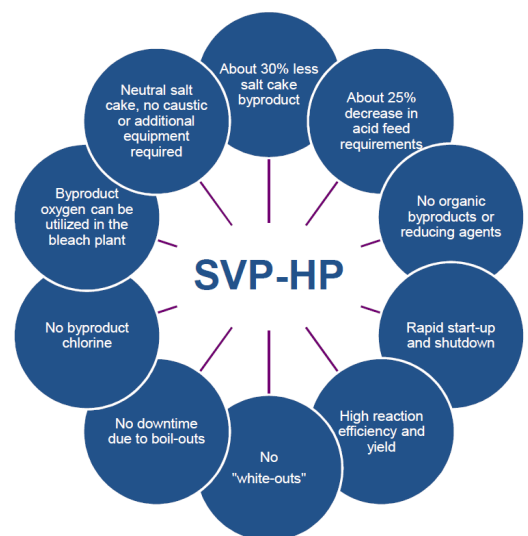
The reaction chemistry can be much faster when using hydrogen peroxide and dependent on the chosen chemistry; low acidity or high acidity. Talk to a Nouryon expert to find out the best solution for your plant

#### SVP-HP Benefits

The SVP-HP process is an ideal choice for pulp mills that want to:

- Reduce their salt cake by-product (approximately 30%)
- Produce a sodium bi-sulfate cake by-product
- Lower their acid feed requirements (approximately 25%)
- Eliminate dangerous and US PSM regulated methanol from the site
- Reduce organic loading to effluent treatment system
- An emergency stop interlock system is in place that will shutdown the process should pressure, temperature or flow parameters operate out of range

In addition to these improvements, SVP-HP delivers the same benefits as SVP-LITE: The first SVP-HP plants were started up in 1993. It is possible to convert any SVP process to another with only minor equipment changes.



## Typical chemical consumption for Eka® ClO<sub>2</sub> generators

Process	SVP-LITE	SVP-SCW	SVP-HP	HP-A
<b>Component</b>				
<b>Product</b>				
ClO <sub>2</sub>	1.0	1.0	1.0	1.0
ClO <sub>2</sub> water	100	100	100	100
<b>Raw material</b>				
NaClO <sub>3</sub>	1.65	1.65	1.65	1.65
H <sub>2</sub> SO <sub>4</sub>	1.0	0.8	0.8	2.1
H <sub>2</sub> O <sub>2</sub> (red. agent)	-	-	0,31	0,29
MeOH	0.18	0.18	-	-
Steam	4.2	5.5	6.0	-
<b>Residual</b>				
Spent acid	-	-	-	3.5
Na <sub>3</sub> H(SO <sub>4</sub> ) <sub>2</sub> (aq)	5.4	-	3.8	-
Na <sub>2</sub> SO <sub>4</sub> (aq)	-	4.6	-	-
O <sub>2</sub>	-	-	0.27	0.26

Units media produced/consumed per unit ClO<sub>2</sub> produced

### Get in touch!

For more information about our technologies,  
please contact our engineering experts:  
[bleaching\\_experts@nouryon.com](mailto:bleaching_experts@nouryon.com)