18.3 Pulp Bleaching, ClO$_2$ Technology & Related Challenges

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Pulp Bleaching, ClO$_2$ Technology and Related Challenges

Preface

In the highly competitive global Pulp and Paper industry the safe, reliable and efficient generation, storage and application of chlorine dioxide (ClO$_2$) is one of several processes critical to sustainable management of bleached pulp production.

Introduction

Chlorine dioxide (ClO$_2$) is a strong and selective gas phase oxidizer discovered in the early 1800's and first used as a bleaching agent over a century later in the textile industry during the 1920's. [26] Early applications for pulp bleaching dates back to the 1940's. Due to ClO$_2$'s oxidizing performance characteristics for producing brighter, stronger pulp, industry use continued to increase into the 1960's and 70's. [1-5, 10, 30-46]

During the 1990's local and federal environmental regulations further pushed the Canadian and US industries towards ECF pulp production, 100% ClO$_2$ substitution. Over the past century driven by environmental, quality, cost and competitive considerations ClO$_2$ has emerged as the globally dominant pulp bleaching agent. The benefits of ClO$_2$ bleaching outweigh the associated challenges. [12, 30-46] However, to remain competitive the challenges associated with ClO$_2$ demand significant industry investment and attention, particularly within aging North American (NA) facilities.

In pulp mills ClO$_2$ must be produced on site at the point of application which introduces a host of considerations. Safety is paramount within any modern industry and Under the US Code of Federal Regulations (29 CFR 1910.119), ClO$_2$ is designated as a highly hazardous chemical, thus demanding site and organizational focus on Process Safety Management (PSM[6]) programs. [6, 8, 9, 13, 62] Furthermore, production of ClO$_2$ also represents the highest annual chemical cost within operating bleach plants.

Ongoing Industry Challenges Specific to ClO$_2$:

➢ Regulatory compliance: Safety, environmental stewardship and process reliability
➢ Feed chemical acquisition, storage and delivery (NaClO$_3$, Acid and Reducing Agent)
➢ Utility requirements: chilled water, process waters, HP/ LP steam, power
➢ Process technology: ClO$_2$ plant, equipment, operations and area maintenance
➢ ClO$_2$ solution storage, delivery and efficient bleach plant application

For Canadian and US facilities, successfully addressing these challenges remain prerequisites to sustainable bleached pulp production and global competitiveness.

ClO$_2$ Background

ClO$_2$ is always generated as a gas and requires the reduction of sodium chlorate (NaClO$_3$) or sodium chlorite (NaClO$_2$) in the presence of a proton donor. All ClO$_2$ generating processes, regardless of scale, involve reactions with sodium chlorate. Global production of sodium chlorate is estimated at over 3 million metric tons annually with a flat to modest growth projection. Over 90% of this total global volume is consumed by pulp bleaching for ClO$_2$ production. The balance is used in manufacture of chlorates/perchlorates, intermediates in reaction synthesis, fireworks, solid rocket fuel, oxygen candles, agriculture, mining and sodium chlorite production for small scale ClO$_2$ applications. [11, 47-64]

Annual global production of ClO_2 for pulp bleaching is estimated at 1.65 to 1.7 million metric tons requiring approximately 2.8 million metric tons of sodium chlorate. Thus, bleached pulp consumes over 98% of all ClO_2 produced on the planet. However, like other oxidizers, ClO_2 is also an excellent biocidal agent, enjoying expanding applications as a primary water treatment disinfectant and broad-spectrum micro-biocide. In fact, ClO_2 increasingly may be recognized as the "Ideal Biocide" with expanding and valuable use patterns within food preservation, processing, health care, and industrial sectors applied directly as a gas or in solution. [26, 47-61, 64]

ClO_2 Utilization

Within the Pulp and Paper industry early production of ClO_2 relied on atmospheric process such as Mathieson, Hooker R-2, and Solvay which utilized sulfur dioxide (SO_2), methanol (CH_3OH) and salt (NaCl) respectively as reaction reducing agents. [10] Most atmospheric processes operating around the world today remain limited to less than 20 metric tons per day (mTPD) of ClO_2 production and rely on H_2O_2 as the reducing agent. A typical atmospheric process flow diagram is presented in Figure 3.

During the late 1960's and early 1970's proprietary R^{13} and SVP^{14} series vacuum technology was introduced for ClO_2 production. [8, 10] Figures 2 and 4 provide basic flow diagrams of a vacuum process. Vacuum technology soon began displacing atmospheric processes, offering expanded production capacities, higher product concentrations and lower operating costs with improved safety and environmental emissions features. Further driven by 1998 promulgation of the US EPA^5 technology based ELG^{12} regulations for the pulp, paper, and paperboard category (referred to as the "Cluster Rule") and Canadian Environmental Protection Act, ClO_2 vacuum technology quickly became the dominant process applied in the industry. [13, 62]

Currently over 80 vacuum plants are operating under evergreen technology license agreements in NA producing more than 2,500 mTPD ClO_2. All but one of these NA plants have been in operation for 20 to 50 years.

Over recent decades ClO_2 has emerged globally as the most cost-effective and environmentally compatible bleaching agent for producing the highest quality pulp. [1-5, 30-46] Since the mid-1990's design improvements to the ClO_2 vacuum process have been ongoing in the areas of safety, control and operating efficiencies. However, the fundamental process equipment, materials of construction and reaction chemistry implemented in NA have remained the dominant and "Best Available Technique" for ClO_2 production within the global bleached pulp sector. In the last decade numerous ClO_2 vacuum plants with capacities ranging from 45 to 100 mTPD have either been commissioned or are currently in various stages of construction in South America, Europe and Asia.

Reliable availability, efficient chemical conversion and safe operational practices specific to ClO_2 production, storage and application, more than ever, are key enablers to achieving a sustainable competitive advantage in the global bleached pulp market.

ClO_2 Vacuum Technology

By far the dominant chemistry for ClO_2 production involves the reduction of sodium chlorate [$NaClO_3$] with methanol [CH_3OH] in a strong sulfuric acid [H_2SO_4] aqueous solution. This chemistry generates ClO_2, byproduct sodium sesquisulfate [$Na_3H(SO_4)_2$] (saltcake) and formic acid [$HCOOH$] per the following reaction:

$$12\ NaClO_3 + 8\ H_2SO_4 + 3\ CH_3OH \rightarrow 12\ ClO_2 + 3\ HCOOH + 9\ H_2O + 4\ Na_3H(SO_4)_2$$
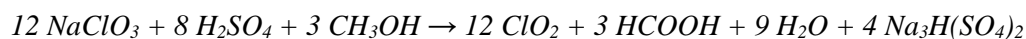
ClO₂ Reactor/ Generator

The reaction components are fed to a classic "Crystallizer" loop that incorporates a cone bottom vessel, axial flow pump and a shell and tube steam heat exchanger. [14] This classic design has been specifically adapted to continuously generate ClO₂ gas under vacuum (110 to 150 mmHg absolute) at boiling temperatures (150 to 175° F) while crystallizing and removing saltcake. [14] The loop serves as a CSTR[1] yet functions as PFR[2] simulating a "Batch Reactor" thus simultaneously facilitating the ClO₂ gas producing reaction, vaporization of excess water (H_2O), and the crystallization and subsequent removal of by-product $Na_3H(SO_4)_2$**.** [14, 17] The reaction liquor or "generator liquor" in this loop, at any given time, is a boiling transient slurry of product ClO₂ gas, reactants $NaClO_3$, CH_3OH, and H_2SO_4, by-products H_2O, $Na_3H(SO_4)_2$ and $HCOOH$. The composition of this generator liquor is an important process control variable for the system. Routine manual liquor samples (recommended every 2 hours) are required for titrimetric determination of H_2SO_4 and $NaClO_3$ concentrations and visual determination of solid salt cake content. These data are critical to operational feedback control of feed chemical flow rates and optimal batch reaction simulation. Generator liquor is an extremely corrosive, erosive and abrasive, near boiling, solution which emits ClO₂ gas when removed from the process. As a result, personnel must exercise extreme caution and use appropriate personal protective equipment (PPE[26]) when conducting routine sample collection and analysis. Chemistry in the reaction loop, for several reasons, is critical to establishment of a "steady-state" reaction; typical generator liquor concentration control parameters are:

> ➢ $NaClO_3$ 200gpl ± 20gpl
> ➢ H_2SO_4 400gpl ± 20gpl
> ➢ $Na_3H(SO_4)_2$ 25 to 30 %ASV

Titanium, grade 2 and/ or grade 7, is the exclusive material of construction used in all areas of process that contact generator liquor and through the gas phase area of the Generator to the exit of the gas cooler/ generator condenser. Given generator liquor composition, cost and availability, titanium remains the most practical material of specification for this area of the ClO₂ vacuum process.

However, operational caution is required because titanium is quite incompatible with strong acids. [22, 23] Sufficient $NaClO_3$ solution must first be added to the reaction loop to protect the titanium from acid attack prior to addition of H_2SO_4 required for ClO₂ generation. Sodium chlorate is also a very strong oxidizer and once introduced to the reaction loop it forms an oxidative surface layer thus passivating and protecting the titanium alloy from subsequent acid corrosion. Further precautions regarding H_2SO_4 are always required to prevent loss of containment which may result in personnel injury and/ or extensive equipment damage.

ClO₂ Absorber and Scrubbers

Once the product ClO₂ gas exits the generator condenser this high velocity stream enters the lower portion of the absorber. The vessel is a traditional mass transfer, counter-current, packed column that employs chilled water as the gas absorption medium flowing from top to bottom. [14, 18] The ClO₂ gas flows upward as the chilled water flows downward thus forming the ClO₂ solution, which is then transferred from the tower discharge to product storage(s) for subsequent bleach sequence application. The process vacuum is pulled from the top of the absorber and through the entire gas system back to the Generator. The vacuum motive source is created by either a simple titanium steam eductor/ venturi or a liquid ring titanium vacuum pump. [14]

Process gases exiting the ejector or vacuum pump are then directed through a secondary cooler/ condenser which discharges to a chilled water Vent Scrubber. Any weak ClO_2 solution captured by the Vent Scrubber is then directed back to the top of the absorber and becomes part of product solution to storage. The discharge from the Vent Scrubber is typically directed to either a dedicated or a general bleach plant chemical scrubber for ClO_2 destruction. One or more centrifugal vent fans typically provide the motive force necessary to pull the process gases and local vent emissions through both the water scrubber and chemical scrubber.

By design the process takes full advantage of ClO_2's physical properties and extreme hydrophilic nature. ClO_2 gas is unstable; as concentration increases stability decreases. ClO_2 will violently decompose/ explode when the gas concentration nears or reaches approximately 10%, by volume, under STP[3] conditions. [7, 8, 9, 13, 24] However, once dissolved in aqueous solution ClO_2 gas becomes relatively stable at STP[3] conditions. Furthermore, ClO_2's solubility characteristics are inverse; as solution temperature decreases, ClO_2 solubility increases (see Figure 1). Therefore, chilled water is the ideal absorption, transport, storage and application medium for the extremely high ClO_2 concentrations required for efficient pulp bleaching (10 to 12 gpl).

The material of construction for the absorber and all downstream columns is typically hand laid-up fiber reinforced plastic (FRP) with a specified chemical corrosion barrier. Internal trays (distributors, packing supports) are typically made of grade 2 titanium. Packing may be either ceramic or plastic, depending on specific conditions of service. Tower packing type, size and materials are specified based upon packed bed volume relative to anticipated ClO_2 demand and specific mass transfer parameters. [14, 19, 21, 22]

Figure 1. ClO_2 Temperature Solubility:
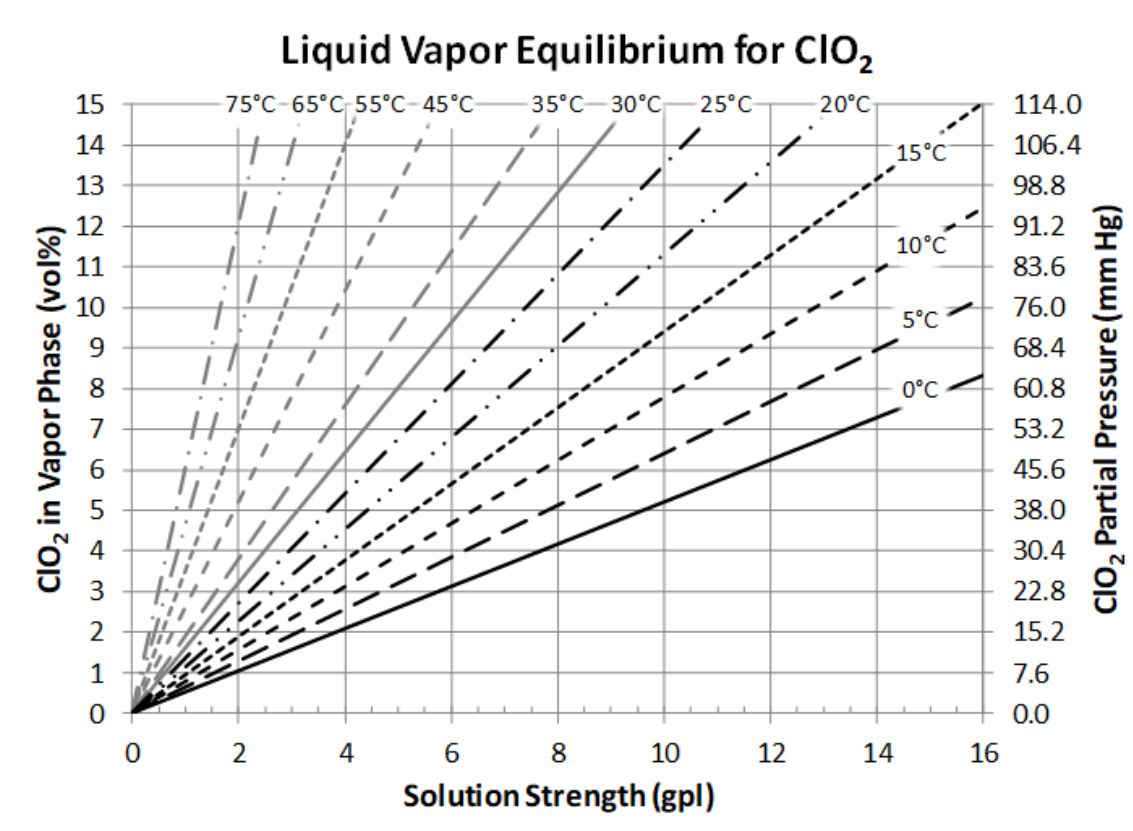
Sesquisulphate Filter

Stoichiometrically the reaction in the generator loop produces approximately 1.3 units of sesquisulfate [$Na_3H(SO_4)_2$] (saltcake) for every unit of ClO_2 generated. This by-product must then be crystallized and continuously removed from the generator liquor (slurry) in proportion to the ClO_2 produced. Maintaining a stable and predictable percentage of this saltcake in the generator liquor is a critical control variable and routinely measured as apparent settled volume (%ASV). Panel operators can also infer relative %ASV by monitoring field instrumentation reporting generator liquor specific gravity and circulation pump motor amps. Obviously, a rise in both remote parameters are indicative of a rise in %ASV.

Focal variables for maintaining consistent saltcake volume in the reaction slurry (25 to 30 % ASV) are generator liquor level, ClO_2 production rate and efficient filter operation. Consistent %ASV in the slurry is important to facilitating a stable "steady-state" reaction and efficient ClO_2 production. However, continuous elevated operation or excursions in %ASV (>40 to 60+%) will result in operational upsets, blockage in slurry transfer lines between the reaction loop and filter, and/ or titanium equipment damage internal to the reaction loop. Failure to control solids in the process will produce extremely negative and undesirable results.

By design the filter system involves pumping a slip-stream slurry from the reaction loop to the surface of a rotating drum with an internal vacuum. The system functions much like a common rotating drum pulp washer. Yet, in functional contrast, the salt cake filter captures, washes and discards solid saltcake from the drum surface while recovering the valuable chemical effluent pulled into the drum interior and returning it to the reaction loop. Therefore, efficient system operation, cake removal and chemical recovery is vital to sustainable reaction conversion efficiencies in the process. Once feed chemicals enter the reaction loop, there are only five ways of possible escape, four of which are extremely undesirable:

> ➤ Loss of containment
> ➤ System decomposition
> ➤ Generator liquor carry-over to the gas absorption train
> ➤ Reaction conversion to ClO_2 gas
> ➤ Inefficient filter operation/ washing and chemical loss with discarded saltcake

The typical saltcake removal system incorporates a rotary drum vacuum filter, motive vacuum source, slip stream transfer lines between the reaction loop and filter, a static gas liquid separator and, ultimately continuous saltcake discharge. [14, 17-21] Material composition of system components contacting the generator liquor and associated gases are minimally grade 2 titanium.

Efficient filter system operation requires routine manual inspection and local adjustment of fluid transfer, drum vacuum, cake pick-up and washing parameters by operators. Safely conducting such routine activities demands knowledgeable and experienced attention including, but not limited to, use of appropriate PPE[26] and functional verification of all system incorporated safety features. Sesquisulphate solution is a hot (150 to 170 °F) highly corrosive and abrasive slurry having a dry cake acid composition between 20 and 30% by weight. Therefore, saltcake solution, like generator liquor, when contacted has the potential to result in chemical and/ or thermal dermal degradation.
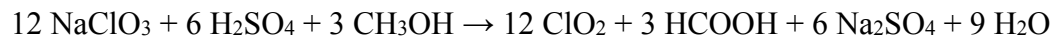
Most vacuum plants placed into service over the past decade or those currently under construction further incorporate a secondary sodium sulfate (Na_2SO_4) washing and filtration system to enhance overall process efficiency, figure 5. Such secondary systems use the solubility characteristics of the H_2SO_4 / Na_2SO_4 / H_2O system to separate H_2SO_4 from the discharged sesquisulphate stream in a metathesis tank while re-crystallizing a neutral Na_2SO_4 saltcake from this weak acid slurry. [14, 17-21] The neutral saltcake is then removed from this slurry by a second rotary drum vacuum filter for sodium/ sulfur makeup in the recovery cycle. System advantages include, recovery of weak acid for pH control and/ or supplemental generator

acid feed, reduction in caustic (NaOH) use associated with sesquisulphate neutralization and improved $NaClO_3$ recovery and ultimately optimum chemical conversion efficiency in the ClO_2 reaction loop.

Stoichiometric representation of a secondary sodium sulfate filter system:

$$2Na_3H(SO_4)_2 \rightarrow H_2SO_4 + 3Na_2SO_4$$
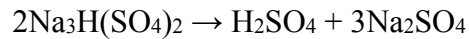
Overall process stoichiometry, with secondary filter washing:

$$12\ NaClO_3 + 6\ H_2SO_4 + 3\ CH_3OH \rightarrow 12\ ClO_2 + 3\ HCOOH + 6\ Na_2SO_4 + 9\ H_2O$$

Chemicals and Safety:

When working with chemicals, particularly oxidizers, the risk to personal safety increases significantly as concentrations and volumes increase. All bleach plant personnel should remain fully aware of the hazardous risks associated with all the ClO_2 process feed, product and intermediate chemicals. Personal safety begins with sound knowledge of all chemical SDS's[10], specifically as they may relate to exposure, reactivity, chemical compatibility, physical properties, temperatures, pressures, volumes, condition of state (gas, liquid and/or solid) and situational process circumstances. Hydrogen peroxide (H_2O_2) and chlorine dioxide (ClO_2) are excellent oxidizers used in various stages of pulp bleaching. [4, 5, 30-46]

However, both are stored and applied at concentrations and volumes that pose risk to health and safety. A simple comparison between pulp bleaching and broad-spectrum disinfection applications for both H_2O_2 and ClO_2 serves to illustrate the significance of concentration to personal exposure, health and safety. In pulp bleaching H_2O_2 solution is typically received and stored at 50% concentration in volumes exceeding 10 metric tons thus avoiding threshold limit values (TLV's) which would define it as a highly hazardous chemical under 29 CFR 1910.119. While ClO_2 is produced on site in concentrations of 8 to 12 grams per liter (gpl), or 8 to 12 thousand parts per million (ppm) and stored in volumes typically exceeding 20 metric tons as a dissolved gas in solution. Obviously, given the constraints associated with ClO_2 for pulp bleaching use classification as a "Highly Hazardous Chemical" is unavoidable within the industry. [3, 13]

In contrast, as a disinfectant/ anti-microbial H_2O_2 is sold commercially for topical application in one-liter volumes or less at 3% concentration. While per EPA[5] guidelines, ClO_2 volumes applied for disinfection of potable water range from hundreds to thousands of pounds per day at concentrations up to 0.8 ppm or 0.0008 gpl. [12, 64] Depending on concentration, volume, temperature, and pressure all chemicals stored and used in a pulp mill present a risk to health and personal safety.

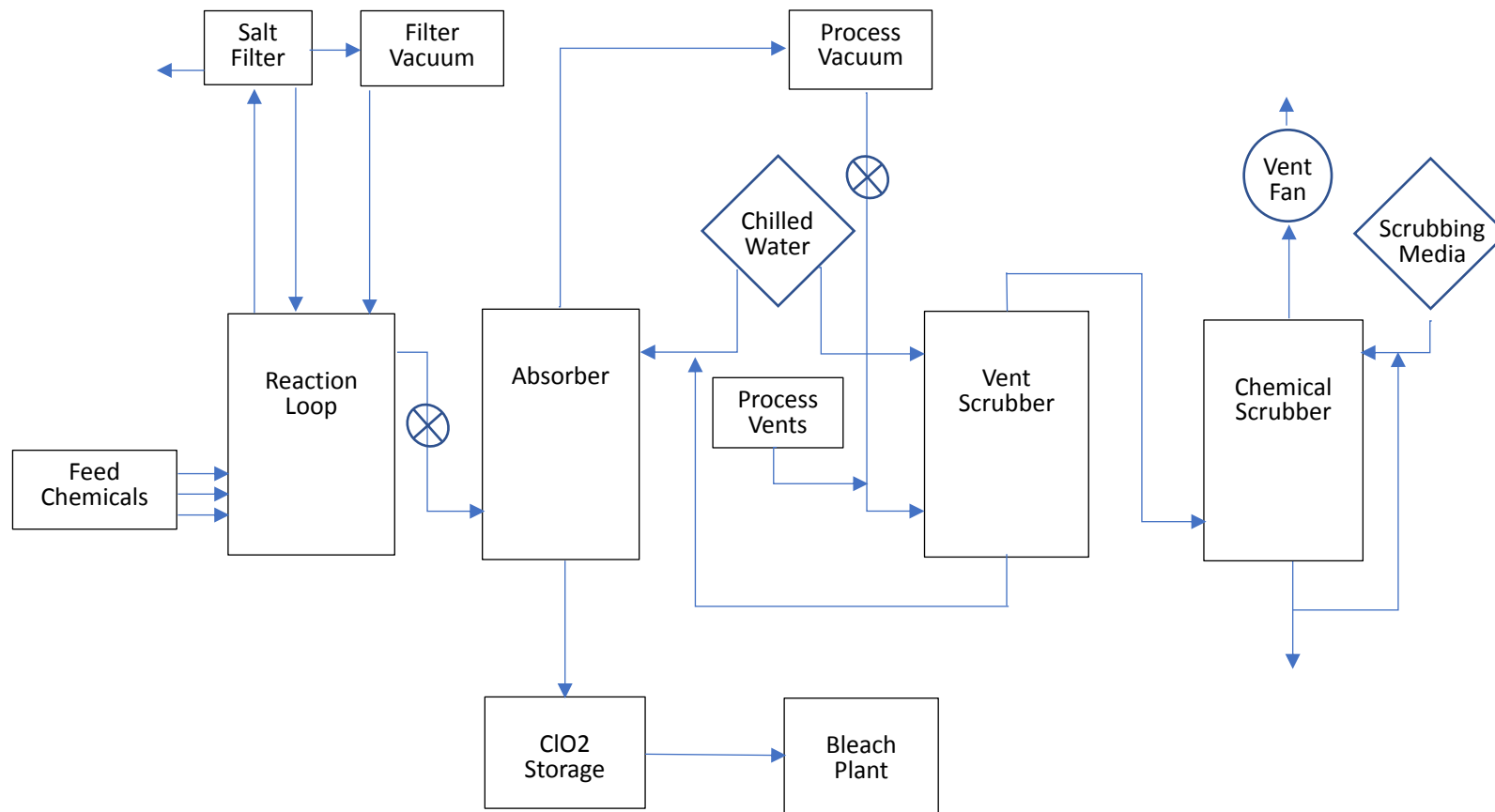**Figure 2.   Simple ClO₂ Vacuum Process Block Flow Diagram**

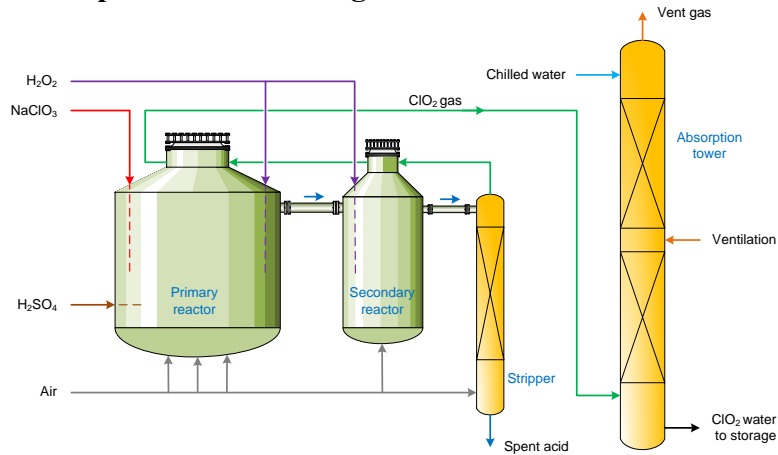## Figure 3. Typical Atmospheric Process Diagram

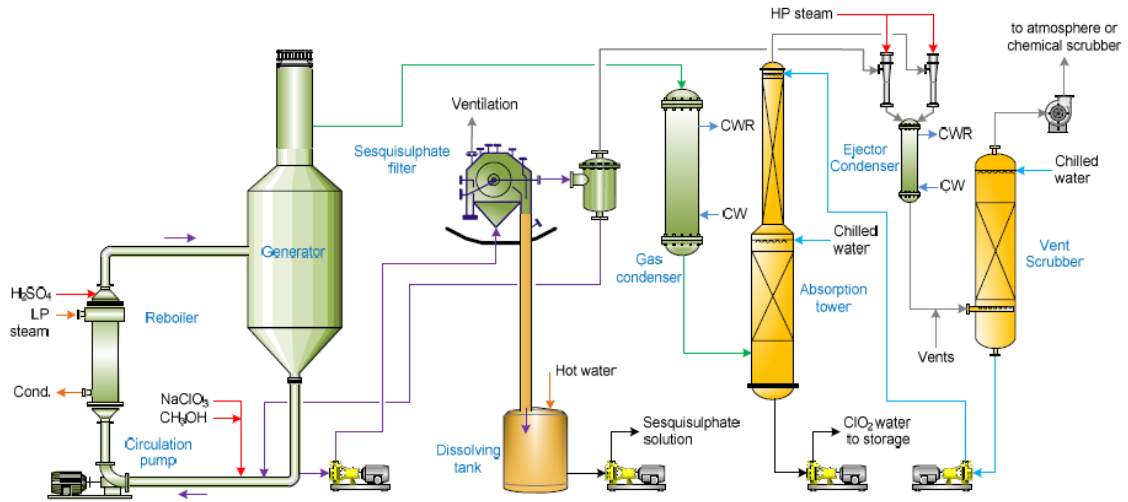
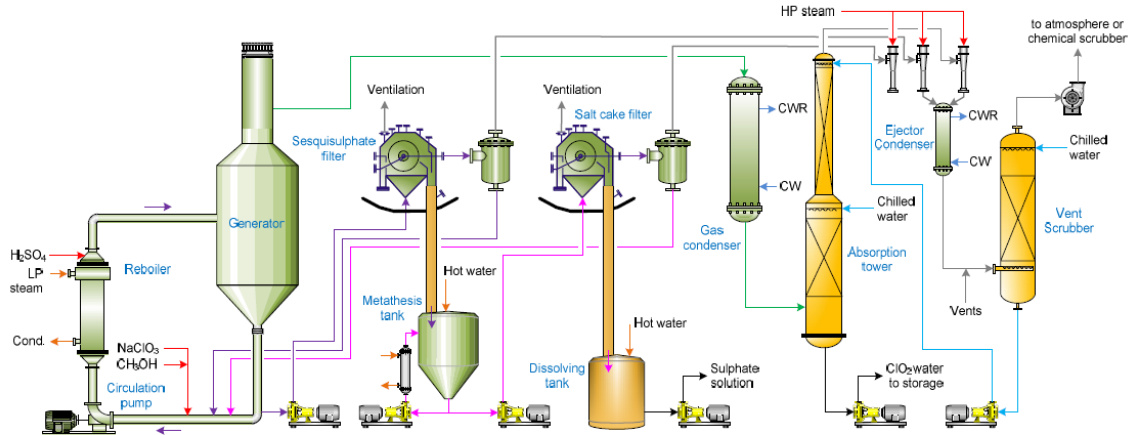## Figure 4. Typical Vacuum Process Diagram

Figure 5. Typical Vacuum Process with Secondary Washing Diagram

Management of Highly Hazardous Chemicals

Based on TLV's[11] the two bleach plant chemicals designated under PSM[6] as "Highly Hazardous" are methanol (extremely flammable, potentially explosive, toxic) and chlorine dioxide gas (toxic, potentially explosive). However, given the scale of operations, all chemicals and intermediates applied in a pulp mill and ClO_2 process are potentially hazardous to health and safety, including H_2O, depending on state, temperature and/ or pressure. [6, 13]

Health, safety and environmental considerations, including regulatory compliance, are cornerstones of industry and organizational sustainability. ClO_2 is designated as a highly hazardous chemical under PSM[6] because it is stored in high concentrations and volumes. [6] ClO_2 has the potential to spontaneously decompose should gas concentrations reach approximately 10% by volume. Therefore, great attention is lent to designing continuous negative pressure vent sweeps across storages, which pull fugitive ClO_2 gas off the tanks and into the Vent Scrubber. Furthermore, all ClO_2 storage tanks are required to have appropriate positive pressure relief vents in the event of sweep air failure. Design of such storage relief venting was historically based on a peak pressure of 6 psig at approximately 10% ClO_2 gas by volume with a relief area/volume ratio of 0.02. [8] However, more recent models for relief lid sizing have been developed based on vented deflagrations. [24] Experimental results have indicated that the lower concentration limit for the explosive decomposition of chlorine dioxide gas is 9.5% ($[ClO_2]/[air]$), whereas there is no corresponding upper concentration limit. [7, 8, 24, 63]

Site specific PSM[6] programs must incorporate the following fourteen elements:
1. Employee Participation
2. Process Safety Information
3. Process Hazard Analysis
4. Operating Procedures and Protocols
5. Operator Training
6. Contractor Training
7. Pre-Startup Safety Review
8. Mechanical Integrity Program
9. Hot Work Permits
10. Management of Change (MOC[8])
11. Incident "Root Cause" Investigations
12. Emergency Planning and Response
13. Compliance Audits
14. Protection of Process Trade Secrets

Given the potential for catastrophic release of ClO_2 gas in the unlikely event of storage tank failure there may be further PSM[6] requirements based on population densities surrounding the mill site. Examples include RMP[9] and coordination with local first responder organizations and site ERT[21].[63] In addition to explosion potential ClO_2 gas is also toxic to the human respiratory system. Either acute exposure to elevated levels or extended chronic exposure to low levels can result in mild to extreme mucosal irritation and ultimately cause chemical pneumonia. Therefore, extreme caution and appropriate PPE[26] are advised when entering any PSM[6] designated or process area that may have ClO_2 gas present.

Emergency Response Planning Guidelines (ERPG) published by the American Industrial Hygiene Association provides the basis for established human exposure limits to ClO_2 gas. The ERPG findings for chlorine dioxide are based on collective acute and subacute lethality data in animals. NIOSH[18] REL-STEL[15] (Recommended Exposure Limits - Short Term Exposure Limit) (NIOSH[18] 1997) is defined analogous to the ACGIH[19] TLV[11]-TWA[17]. and IDLH[16]. The NIOSH[18]/ OSHA[4] "Standard Completions Program" only defines exposures for respirator selection representing a maximum concentration from which, one could escape exposure without experiencing any escape-impairing or irreversible health effects. [6, 9, 28, 29, 63]

Established Human ClO_2 Gas Exposure Limits
NIOSH[18] IDLH[16] 5 ppm - exposure
NIOSH[18] STEL[15] 0.3 ppm - 15 minutes, 3 times per 8-hr day, with 20-minute minimum interval between exposures
OSHA[4] PEL-TWA[17] 0.1 ppm - 8 hr. exposure

Further safety precautions routinely include installation of gas detection monitors on each level of the ClO_2 plant, and at strategic locations in the process storage areas and throughout the bleach plant. Depending on site specific safety protocols these monitors are usually set to alarm audibly at either 0.1 or 0.3 ppm ClO_2. Some mill sites also require use of personal gas monitors.

Fortunately, ClO_2 gas is self-alerting presenting a faint odor of bleach or chlorine at 0.1 ppm levels or less, thus necessitating area evacuation or use of respiratory protection. Based on ERPG data, such low-level exposure to ClO_2 gas is not life-threatening. In fact, more recent studies indicate that ClO_2 gas at low levels, well below the TWA[17] of 0.1 ppm, could be useful as an antimicrobial in the presence of humans to mitigate and/ or prevent viral infection and possibly other related respiratory tract infections. The *Journal of General Virology* reported that continuous exposure to 0.03 ppm ClO_2 gas inactivated highly pathogenic aerosol H1N1 virus in experiments using mice. Specifically, ClO_2 gas could be used in places such as hospitals, clinics, offices, hotels, schools and airport buildings without interrupting normal activities. [25]

Control and Safety Interlocks

Distributive control systems (DCS) provide the interface between real-time process data and remote operational process control. In ClO_2 vacuum process areas a typical DCS incorporates over 100 control loops. Each loop may include local and/ or remote indication and remote operator manipulation of flow valves, motors and switches. In total the DCS usually facilitates remote operational control of 15 to 20 motor starters and 25 to 30 flow valves. [20]

Safety interlock functions programmed into the DCS functional loops initiate automated emergency shutdown of the ClO_2 vacuum process. Typically, more than 20 interlock functions are programed into the DCS logic for purposes of protecting personnel, equipment and the environment from release of and exposure to hazardous process chemicals.

Process safety does not rely solely on DCS interlocks to protect personnel, equipment and the environment. Ultimately, system safety rests with the process operators while interlock emphasis is focused on preventing serious and costly incidents from occurring. Vacuum processes additionally incorporate dozens of safety features ranging from in-line check valves, back-flow preventors and pressure relief devices to automated block flow valves. Within the US routine PHA[7] review and functional testing of safety systems and DCS interlocks is required under PSM[6] regulation and are highly recommended activities for all operating ClO_2 processes.

To further enhance efficient, reliable and safe production of ClO_2 many plants have added advanced process control (APC) systems to interface with their DCS. APC software is configured to monitor manipulated process variables and issue feedback control variable set-points to the DCS. APC systems focus on four key control variables: $NaClO_3$, CH_3OH and H_2SO_4 chemical feed flow rates and steam flow to the Reboiler. Optional control variables may include acid dilution water flow rate, saltcake filter motor VSD[20] and/ or saltcake filter feed pump VSD[20]. APC systems do not interfere with DCS interlocks or safety systems and APC systems do not replace operators or the need to conduct routine generator liquor analysis. However, they significantly improve the simulation of a steady state "Batch Reaction" thus optimizing overall chemical conversion efficiencies and process reliability. [20]

Maintenance

Predictable availability of ClO_2 is critical to the production of bleached pulp. Consequently, reliability centered maintenance programs, safety protocols, appropriate specifications, technology enhancements, and ready access to spare process components are keys to reliable ClO_2 production.

The materials used in the vacuum process are intentionally robust and specific for the intended purpose providing extremely long service expectations. However, these facts do not preclude the need for routine maintenance and internal inspection of plant and equipment. With proper care titanium equipment can last a lifetime. However, loss of containment of either sesquisulphate

and/or generator liquor presents a significant risk of corrosion and service life reduction. External surfaces of titanium equipment do not have passivating sodium chlorate present, therefore acidic chemicals will attack the alloy from the outside. Steel components such as heat exchanger shells and structural beams are vulnerable to acid attack as well as ClO_2 corrosion, which can result from insufficient process ventilation. Implementation of a "zero leak policy" within the entire process area is highly recommended to ensure maximum service life and ultimately reduce costly plant and equipment maintenance, repairs and/or replacements. FRP equipment is durable but does not have an indefinite service life like titanium. Absorbers and scrubbers typically last 15-20 years before needing replacement or major repair. Ceramic packed beds may need replacement every 5-10 years depending on quality of ceramic, chilled water quality, and operations. Motor-driven equipment requires appropriate routine maintenance per OEM[22] specification. PTFE[24] gasket material should be replaced with every flange break or every 8 to 10 years without flange break.

Well-planned preventative and reactive maintenance programs in coordination with routine and periodic process inspection schedules are imperatives for sustaining reliable ClO_2 production. [15]

Troubleshooting

Given the instability of ClO_2 gas, process upsets occasionally occur and typically result in decompositions within the reaction loop. It is possible, yet quite rare, for decompositions to occur in other areas of the process. The reaction loop is designed to contain and mitigate the impact of decompositions. ClO_2 decompositions are instantaneous, taking place in fractions of a second to produce oxygen, chlorine and heat, resulting in the significant rise of generator gas pressures and temperatures proportional to the reaction magnitude. In general, the root cause of decompositions can be traced to mechanical, chemical or operational origins per the following examples.

Mechanical:

➢ Vacuum leaks: intrusion of ambient air into the process between the reaction loop and vacuum source.
➢ Power failure: complete loss of process vacuum, resulting in an intense decomposition
➢ Instrumentation or transmitter failure: control valve sticking or broken stem, inaccurate data transmitted to the DCS

Chemical:

➢ Organic or alloy (primarily iron) contamination of feed chemicals and/ or process waters entering the reaction loop
➢ Excessive foam formation on the surface of the liquor in the generator, typically caused by impurities in the chemical feeds and/ or waters entering the process

Operational:

➢ Low generator level resulting in circulation pump cavitation
➢ Exposure of the generator gas space to local UV[25] light or heat sources
➢ Improper position of manual process valves
➢ Poor control of target chemical concentrations in the reaction loop

Successful troubleshooting and elimination of such process disruptions requires comprehensive process understanding and knowledge of site-specific operations. Strict application of the KT[23] system for solving such process upsets usually produces favorable results in the shortest time possible. KT[23] involves the identification and prioritization of causational changes in normal process functions and then strict adherence to implementing one corrective action at a time. [16] In this sense KT[23] methodology is like classic "factorial experimental design" involving multivariable processes where; one and only one variable is manipulated while holding all other variables constant. Analysis of subsequent data may then lead to conclusions regarding single variable manipulation impact on the entire process. Review of DCS data historians, such as PI or Parkview, can often significantly aid in the identification of causational process changes. The

ClO2 vacuum process is a dynamic multivariable process, therefore identification and elimination of problems require a patient, knowledgeable, systematic and disciplined approach.

Experienced and knowledgeable operations and maintenance personnel are critical assets to successful ClO2 production. Over the past three decades pulp mill labor forces have aged along with plant and equipment. As these experienced operators retire local knowledge and experience is lost. Less experienced operators replacing this generation would benefit from routine process, technology and safety education and training specific to ClO2 production.

Conclusions

For decades ClO2 vacuum processes have proven safe, reliable and predictable for pulp bleaching applications. Thus, remaining the "best available global technique" for ClO2 production based on rather simple reaction chemistry, the molecule's physical properties, and a robust multi-variable process designed to control fundamental parameters of physics; pressure, temperature, volume, concentration and fluid flow. [14-22, 30-46]

Commitment to "Reliability-centered Maintenance" including timely and appropriate investment in plant and equipment in combination with the implementation of sound operational and chemical safety; education, training and procedural protocols are the keys to sustainable ClO2 production and ultimately competitive advantage in bleached pulp market sectors. [15, 16]

Through evergreen license agreements NA industry retains access to ClO2 OEM[22] process and support services for design, engineering, operation, troubleshooting, regulatory compliance, education, training, plant maintenance and spare parts.

Acknowledgements

Definition of Terms:

1. CSTR (Continuous Stirred-Tank Reactor)
2. PFR (Plug Flow Reactor)
3. STP (Standard Temperature and Pressure)
4. OSHA (US Occupational Safety and Health Administration)
5. EPA (US Environmental Protection Agency)
6. PSM (Process Safety Management)
7. PHA (Process Hazard Analysis)
8. MOC (Management of Change)
9. RMP (Risk Management Plan)
10. SDS (Safety Data Sheet)
11. TLV (Threshold Limit Value)
12. ELG (Effluent Limitations Guidelines)
13. R (Rapson)
14. SVP (Single Vessel Process)
15. STEL (Short Term Exposure Limit)
16. IDLH (Immediately Dangerous to Life and Health)
17. TWA (Time Weighted Average)
18. NIOSH (US National Institute for Occupational Safety and Health)
19. ACGIH (American Conference of Governmental Industrial Hygienists)
20. VSD (Variable Speed Drive)
21. ERT (Emergency Response Team)
22. OEM (Original Equipment Manufacturer)
23. KT (Kepner Tregoe)
24. PTFE (polytetrafluoroethylene, trade name Teflon)
25. UV (Ultraviolet)
26. PPE (Personal Protective Equipment)

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