# THE HIDDEN COST OF CHLORINE DIOXIDE

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**SUMMARY**

The pulp industry is being driven by the markets to become more sustainable and to further reduce adverse impact to the environment in its mill emissions. Reducing, or eliminating, the use of chlorine dioxide will reduce the formation of AOX (adsorbable organic halides) which helps the industry achieve these goals. There are new technologies, such as bleaching enzymes, which could help with this goal; however, the perception is that they are marginally more expensive than using chlorine dioxide to bleach pulp. Most mills underestimate the true cost of chlorine dioxide by as much as 30% and do not consider many intangible costs. Properly considering these factors allows new technologies to become not only competitive, but in some cases, less expensive than the status quo.

**Keywords: Bleaching, Chlorine Dioxide, Cost, ECF, Enzymes, Sustainability, TCF**

**INTRODUCTION**

The use of elemental chlorine in the bleaching of pulp was basically abandoned in the 1990s due to concerns with the formation of dioxins in the resulting effluent. Chlorine was primarily replaced with chlorine dioxide ($ClO_2$) as it proved to produce much less AOX in the effluents than chlorine. The Elemental Chlorine Free (ECF) process quickly became the predominant method for bleaching, as Total Chlorine Free (TCF) bleaching at the time proved too expensive and produced a pulp of inferior quality. Today, emerging technologies which include the use of enzymes, are providing the opportunity to revisit the potential to increase TCF production as fibre quality is beginning to approach that of ECF processed pulps. One of the primary barriers is that these new technologies are proving to be marginally more expensive when compared to current ECF methods. This may or may not be the actual case when the true cost of $ClO_2$ is considered. This paper will explore the true cost of $ClO_2$, so that realistic comparisons can be made when a mill considers technologies which will allow them to move to either TCF bleaching, or at least reduce their $ClO_2$ footprint via the use of bleaching enzymes.

**DISCUSSION**

The production of $ClO_2$ in most mills is done through the use of sodium chlorate, sulfuric acid and methanol. There are multiple processes used in the manufacture of chlorine dioxide. For this review we will focus on the R-8 and SVP-Lite processes. The chemicals are metered into a reactor in the proper sequence and proportions, the ClO2 gas generated is drawn off and absorbed in chilled water for storage, and the resultant acidic sulfate salts are purged. The basic (unbalanced) reaction is as follows:

$$NaClO_3 + CH_3OH + H_2SO_4 \rightarrow ClO_2 + Na_3H(SO_4)_2$$

(Sodium Chlorate) (Methanol) (Sulfuric Acid) (Chlorine Dioxide) (Sodium Sesquisulfate)

Through stoichiometry, the theoretical amounts of sodium chlorate, sulfuric acid and methanol are determined. A mill then has to simply multiply each component by its associated cost, and a cost of $ClO_2$ can be determined. This cost is reduced by credits taken when the spent acid/neutral saltcake is introduced as a source of sodium and sulphur make up to the Kraft system. In some mills, these inputs and credits are calculated by multiplying the theoretical chemical inputs by their cost providing a cost per unit for $ClO_2$ produced. This financial calculation can be done as little as once every several years or can be done in a continuous real time method through the mill's Distributive Control System (DCS).

Typically, input costs are updated either monthly or quarterly.

This method is crude and grossly underestimates the true cost of what it takes to produce a kilogram of $ClO_2$. In reviewing the chemical portion of the equation, several factors need to be considered, including

1) Chlorate conversion efficiency- By far, the price of sodium chlorate is the major contributor to the cost of $ClO_2$. If conversion of the chlorate to $ClO_2$ is complete, it takes about 1.58 kg of sodium chlorate to produce 1 kg of $ClO_2$. Typical generator systems operate in the 90 to 95% conversion efficiency range with some mills as low as 80%. This efficiency loss needs to be considered.

2) Chemical recovery credits - The by-product spent acid/neutral saltcake is rich in sodium and sulphur, and many mills take advantage of this by introducing them into the Kraft liquor cycle. As mill systems become more efficient, they require less of these materials to be used to maintain the mill's soda/sulphur balance, and they are not totally used. This should be considered into the cost calculations.

3) Handling losses – While usually minimal, leaks in lines and storage vessels can be common, and bulk unloading procedures can leave product in the transports, not into the process.

Many mills address these factors by taking physical inventory of the bulk chemicals used. This is typically done on a monthly basis. Monthly inventory is done primarily for cost accounting purposes, but it can give insight into actual plant efficiencies by providing overall usage data. It is surprising that this data is not always shared between the mill's accounting and production/technical departments. This practice is useful for monitoring plant efficiencies over time; however, it only measures the chemical costs associated with producing $ClO_2$. It does not consider other important measurable inputs, such as energy, fixed costs, $ClO_2$ process losses and potential production issues. It also does not consider other intangible costs; such as system safety, environmental impact and plant lifecycle.

$ClO_2$ is a toxic substance and exists as a gas at standard conditions. At atmospheric conditions the partial pressure of $ClO_2$ gas exceeds 40 kPa at 49°C and will cause the material to spontaneously decompose (auto detonate).[1] To facilitate storage and transport, the gas is absorbed into chilled water as it is drawn off the generator and sent to storage which is kept under a slight vacuum. Gases are swept off the storage tanks and either sent back to the absorption tower as a recycle stream or to a destructive scrubber. The $ClO_2$ concentration is typically kept at about 10 g/l or 1%. This means that for every kilogram of $ClO_2$ produced and used, 99 kilograms of water is associated with it, and this water must be chilled and then reheated when used in the bleaching process. Storage temperatures of the solution vary, but 4-8°C are common. In most systems, this requires the use of mechanically chilled water to accommodate storage. The amount of energy required to achieve this cooling varies widely depending upon geographical location and water source. As an example, a mill in a northern climate that has access to consistent groundwater may require little to no chilling, whereas a mill using surface water in warmer climates may need significant chilling capacity, as the inlet water can be greater than 30°C.

The $ClO_2$, along with the associated water used in the bleaching process, must be heated from this storage temperature to that of the process. This can be anywhere from 43°C to 88°C depending upon the mill's bleaching procedures. Many mills utilize waste heat from the process to preheat the $ClO_2$ solution, so the cost for heating is reduced, but not eliminated. It should be noted that some mills have discontinued use of $ClO_2$ preheaters due to handling and safety exposure concerns. Actual energy cost associated with the use of $ClO_2$ vary widely depending upon mill configuration and location. It should be noted that the cost of chilling water is typically much higher than the cost of heating the solution for the process.

Because $ClO_2$ requires cold temperatures to remain in solution, some of it is lost in the bleaching process. This is evidenced by the fact that most bleach plants have destructive gas scrubbers which collect the fugitive $ClO_2$ from the towers and washers and remove them before the fumes are discharged to the atmosphere. This is done by means of neutralizing them via a caustic/sulphur scrubbing medium. The amount of $ClO_2$ lost to the scrubbers varies widely based on the type of equipment and bleaching control.

Fixed costs are rarely considered in the manufacture of $ClO_2$. These costs are usually incorporated into the overall mill operational fixed costs as it is difficult to segregate the money spent specifically on a $ClO_2$ plant. This is understandable; however, there are significant costs associated with operation and maintenance of a $ClO_2$ plant. Electrical costs to operate the rotating equipment and to light the building are very small, but they are not zero. What is more substantial are the costs associated with maintaining the plant. Due to its nature, specialized and expensive materials such as titanium, fiberglass and other Fibre Reinforced Plastics (FRP) are commonly used. These materials are not only expensive to purchase, they require maintenance resources with specialized skills to install and maintain.

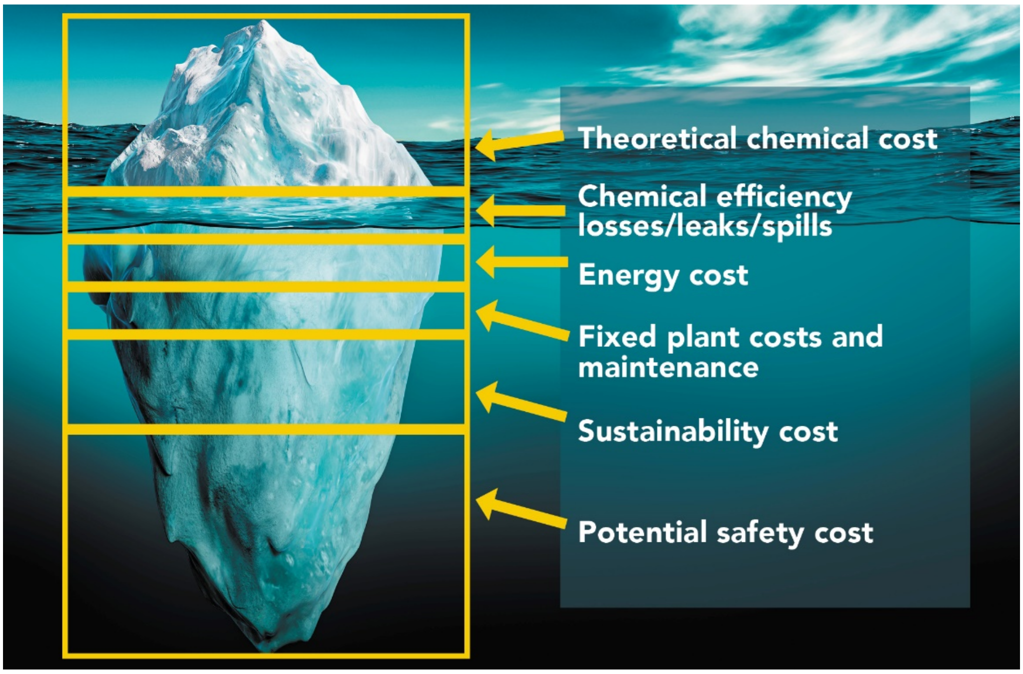
In addition to skilled maintenance resources, skilled operational resources are also required. The Original Equipment Manufacturers (OEM) of $ClO_2$ plants have done an excellent job in the design of these plants and the DCS controls that make the plants highly efficient. Despite this, these plants still require skilled operational resources not only to operate the plants, but to unload the bulk chemicals required to run the plant. In addition to the operators, all aspects of the plant, from scheduling chemical deliveries and logistics, to operator training and certification, to scheduling maintenance and handing $ClO_2$ inventories must be managed. This takes time away from the basic operations of pulping, washing and bleaching.

Human error is always possible in any system, and failure of any of the maintenance, operational or management components can result in significant downtime of the $ClO_2$ plant. This also includes the auxiliary equipment required for plant operations, such as water chillers and solution storage tanks. There are times when this downtime can become significant enough to result in a loss of production either through not being able to maintain budgeted production rates or through a full shutdown of the plant operations caused by $ClO_2$ generator issues. These costs are rarely if ever considered in calculating $ClO_2$ costs. The ability to reduce the amount of $ClO_2$ required can mitigate these types of errors by providing a larger buffer in existing storage capacity. In addition to potential loss of production due to human error, some mills are faced with the simple fact that the $ClO_2$ plant is under-designed for the mill's production. This is typically caused by incremental improvements made in other parts of the process which eventually cause a "bottleneck" at the $ClO_2$ generator plant.

In addition to the tangible costs of $ClO_2$, there are three primary intangible costs to be considered. They are equipment lifecycle management, sustainability and safety.

Fugitive $ClO_2$ gas will form hypochlorous acid when contacted by water vapour. This acid is highly corrosive to most materials including lower grade stainless steels, aluminium, and even concrete. To address this, most mills have infrastructure preservation programs which include painting, protective coatings and routine replacement procedures. Mills that use FRP type materials to transport $ClO_2$ solution around the mill have to maintain costly piping integrity programs as the FRP materials deteriorate over time. A few mills have discontinued the use of FRP materials in favour of expensive titanium as replacement piping. In addition to issues brought about by fugitive $ClO_2$ gas emissions, the waste liquor discharged by the generator can contain a large amount of sulfuric acid, which is very corrosive, or it can contain a neutral saltcake containing sulphur salts which can be erosive. The type of by-product discharge is dependent upon the type of $ClO_2$ generator process used.

As our world becomes more aware of the environmental impact industries have upon the planet, the expectation is that all industries work toward further reducing adverse environmental effects from their manufacturing facilities. While the pulp and paper industry has made great strides in sustainable forestry practices, carbon neutrality, fibre recycling and a reduction in overall emissions, the subject of reducing chlorinated organic compounds is resurfacing, despite studies showing relatively no difference in toxicity of ECF and TCF effluents [2,3]. When the elimination of elemental chlorine happened in the 1990s, the AOX discharges of most mills were greatly reduced. Today, most mills can comfortably comply with AOX discharge permits set forth by their governments; however, public pressure is building once again and many governments, primarily in the European Union, are examining reducing AOX discharge permits to the point where many mills would not be able to comply given their current configurations. In a recent study done by the EU's Joint Resource Centre of Science for Policy, if AOX discharge limits were reduced from 0.17 kg/ton to 0.10 kg/ton as has been proposed, only 38% of European mills would be capable of compliance today.[4]




Chlorine dioxide is by nature a hazardous material and there are multiple regulations concerning its manufacture and use. In the United States, manufacture and use of the quantities of $ClO_2$ typically found in a bleached pulp mill fall under strict Federal Process Safety Management regulations. These laws heavily regulate all facets on the manufacture and use of $ClO_2$. The industry has done an excellent job of designing, maintaining and managing these systems. While infrequent, exposures to $ClO_2$ still occur, and they often result in medical attention being required for workers exposed to the material. While the economic cost of these exposures is tangible, the human cost in suffering injuries related to $ClO_2$ exposure is not. In addition to the manufacture and use of $ClO_2$, there are additional safety exposures related to the unloading and handling of the bulk chemicals used in the process. Sodium chlorate, sulfuric acid and methanol are all hazardous materials, and every bulk transport that is unloaded provides an opportunity for a significant exposure. If a mill is able to reduce its $ClO_2$ consumption by 20% through the use of bleaching enzymes, it also reduces its exposure to hazards associated with unloading of these chemicals by 20%. This simple fact is rarely considered when evaluating the use of bleaching enzymes.

**CONCLUSIONS**

When mill managers are weighing their options for choosing the best path forward in balancing costs versus environmental impact, they often grossly underestimate the cost of using chlorine dioxide in their process. This precludes proper economic assessment of new technologies, such as bleaching enzymes, or of considering capital projects, as in the case of TCF pulp. The costs of using chlorine dioxide are significantly more than the price of the chemicals used in producing it, perhaps by as much as 30%. In addition to the tangible costs, such as energy, water, maintenance and operations, there are intangible costs such as plant lifecycle, environmental perception and safety that need to be considered.

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