Adopting The Integrated Chlorine Dioxide Process For Pulp Bleching, To Comply With CREP Regulations

Barr A., Gopalakrishnan R., Saha M.

ABSTRACT

The Charter on Corporate Responsibility for Environmental Protection (CREP) guidelines impose several new requirements on pulp and paper mills in India to adopt more environmentally friendly practices, including a reduction in AOX emissions that will require a shift away from chlorine (or hypochlorite) based pulp bleaching.

The worldwide acceptance of ECF pulp in recent years ensures that chlorine dioxide will continue to be the dominant pulp-bleaching agent for the foreseeable future.

Aker Solutions - recognizing the on-going need from the pulp and paper industry for a reliable and cost effective method to generate chlorine dioxide - offers the integrated chlorine dioxide process that produces chlorine dioxide solution at the lowest operating cost, while minimizing the dependence on outside supply, market exposure, and the need to import and store hazardous feedstocks.

This paper describes Aker Solutions' integrated chlorine dioxide process, and examines its operating costs in India, as compared to the typical methanol-based process.

INTRODUCTION

The Charter on Corporate Responsibility for Environmental Protection (CREP) regulations impose several new requirements on pulp and paper mills in India to adopt more environmentally friendly practices, including reduced AOX emission targets that will necessitate a shift away from chlorine (or hypochlorite) based pulp bleaching.

Since the 1990's, the worldwide debate over ECF vs. TCF has been settled, with ECF as the clear winner. Substitution of chlorine by chlorine dioxide, combined with other recent innovations, allows a modern ECF bleach kraft mill to produce a superior product - as characterized by high brightness & brightness stability, high cleanliness and strength - while at the same time, meet strict environmental standards.

As shown in Figure 1, ECF production has grown from less than 5% of the world bleached chemical pulp market in 1990, to about 90% in 2009, and

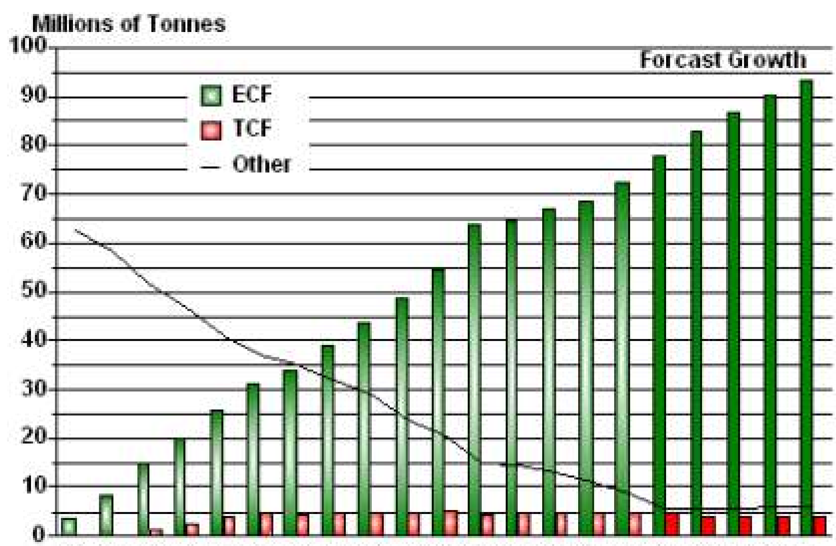

Figure 1. World Bleached Pulp production (1990-2010)* Alliance for Environmental Technology

Aker Solutions
(India and Canada)

virtually 100% of new Kraft mill capacity worldwide has adopted or is expected to adopt ECF bleaching since the publication of this data.

By contrast, TCF production has been stagnant for years and remains at 4% (and declining) of the world market. Beyond its foothold in Europe, it seems unlikely that TCF will develop into a significant process elsewhere.

The wide acceptance of ECF pulp ensures that chlorine dioxide will continue to be the dominant pulp-bleaching agent for the foreseeable future.

Essentially all industrial chlorine dioxide (ClO_2) is produced by reacting Sodium Chlorate ($NaClO_3$) with a reducing agent in acidic conditions, and there are two processes that are predominant in the pulping industry worldwide.

The integrated process produces the sodium chlorate, acid, and reducing agent 'in-situ', while the methanol process requires the purchase, transportation, storage, and handling of these feedstocks.

The integrated chlorine dioxide process offers a cost-effective alternative to the methanol-based process, and has been adopted by several world-class pulp mills - which were attracted by its low operating cost, security of supply, insulation from cyclical markets, and the convenience and safety issues of not having to transport multiple hazardous feed stocks.

This paper describes the Aker Solutions integrated chlorine dioxide process, and examines its operating costs in India, as compared to the methanol-based process.

BACKGROUND

The typical methanol-based chlorine dioxide process reacts sodium chlorate, methanol and sulphuric acid to produce chlorine dioxide and by-products formic acid (3HCOOH) and sodium sesquisulphate ($4Na_3H(SO_4)_2$), according to the overall reaction below:

$$12NaClO_3 + 3CH_3OH + 8H_2SO_4 \quad 12ClO_2 + 3HCOOH + 9H_2O + 4Na_3H(SO_4)_2$$

This reaction requires the transportation and storage of the three feedstocks at site. Since very little sodium chlorate is currently produced in India, the methanol process would require the import of this feedstock from foreign suppliers.

Figure 2 illustrates the methanol process.

The **integrated chlorine dioxide process** produces the sodium chlorate, acid, and reducing agent feedstocks in-situ, and produces chlorine dioxide according to the overall reaction:

$$Cl_2 + Electricity + Water \quad ClO_2$$

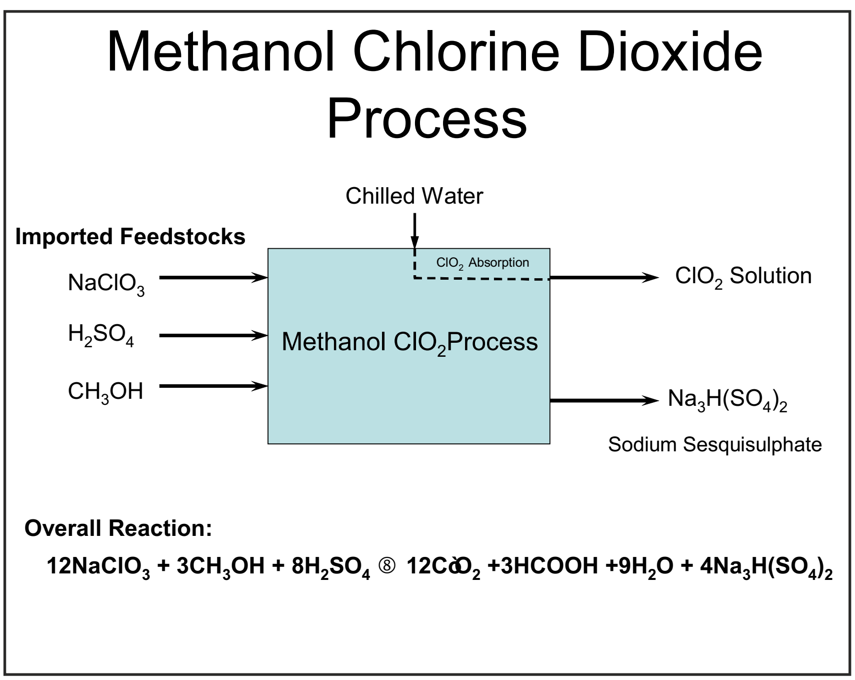

Figure 2. Methanol-Based Chlorine Dioxide Process

The main feedstock, chlorine, is readily available in India, and can be sourced from local suppliers or produced (from common salt) by a chloralkali plant at the mill site.

For most mills that are using chlorine for pulp bleaching now, the infrastructure and current sourcing agreements for chlorine exist already. However, if the supply of chlorine is an issue, it is also possible to feed the integrated process with clean hydrochloric acid.

Aker Solutions Integrated Chlorine Dioxide Process Overview

An overview of the Aker Solutions Integrated Chlorine Dioxide System is shown in Figure 3 which consists of three plant areas to produce the two intermediate products; sodium chlorate (NaClO3), hydrochloric acid (HCl), and the final product, chlorine dioxide (ClO_2).

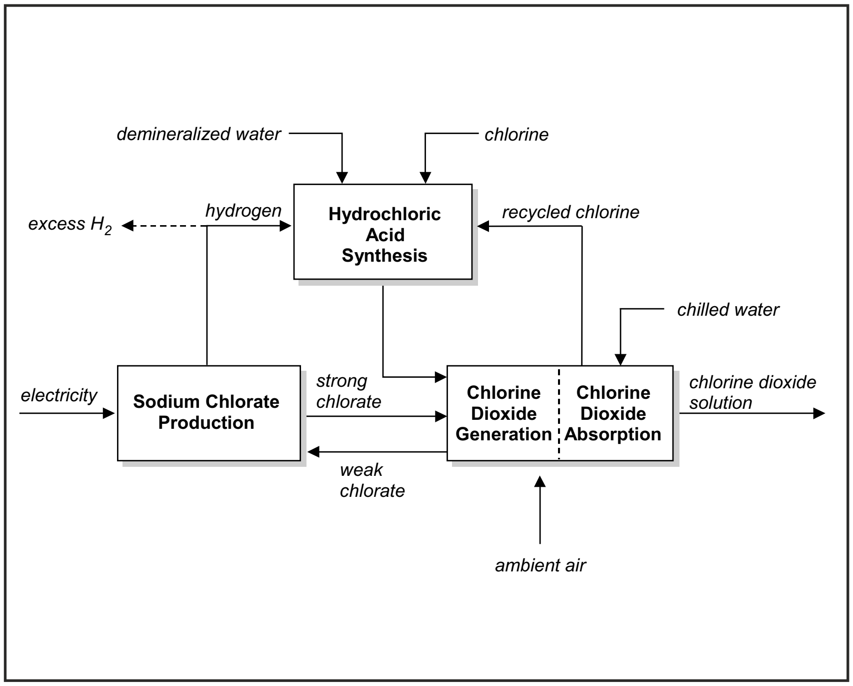

Figure 3. Block Diagram of Aker Solutions Integrated Chlorine Dioxide System

The $NaClO_3$ is produced on-site as a solution and the required HCl is produced through the combustion of hydrogen (H_2) and chlorine. Overall, the process consumes power and chlorine to produce chlorine dioxide. No sodium chlorate crystal, sulphuric acid, and methanol feed stocks are necessary and the process has no acidic effluent or by-product saltcake as produced by the methanol processes.

As some pulp mills also have on-site chloralkali plants, the Aker Solutions Integrated Chlorine Dioxide system is a chlorine consumer, and thereby allows mills to enjoy an improved balance in sodium hydroxide (NaOH) to chlorine

Integrated Chlorine Dioxide System Chemistry

$NaClO_3$ Electrolysis:	$2NaCl + 6H_2O + \text{Electricity} \rightarrow 2NaClO_3 + 6H_2$
ClO_2 Generation:	$2NaClO_3 + 4.8HCl \rightarrow 1.8ClO_2 + 2NaCl + 2.4H_2O + 1.5Cl_2$
HCl Synthesis:	$2.4H_2 + 2.4Cl_2 \rightarrow 4.8\ HCl$
Overall Reaction:	$0.9Cl_2 + 3.6H_2O + \text{Electricity} \rightarrow 3.6H_2 + 1.8ClO_2$

OR: $$\mathbf{Cl_2 + 4H_2O + Electricity \rightarrow 2ClO_2 + 4H_2}$$

The key inputs required to produce chlorine dioxide by the integrated system are chlorine, water and electric power.

Figure 4. Chemetics Integrated Chlorine Dioxide System Chemistry

consumption that would not be possible with other chlorine dioxide processes.

During sodium chlorate electrolysis, sodium chloride, water, and electricity are combined to form sodium chlorate and hydrogen gas. Chlorine dioxide generation occurs when the sodium chlorate is reacted with hydrochloric acid. The reaction products are chlorine dioxide, chlorine gas, salt, and water. Hydrochloric acid synthesis involves the combustion of hydrogen gas with chlorine gas to produce hydrogen chloride.

The simplified chemistry of the three steps is shown in Figure 4.

All the by-products produced in the Chlorine Dioxide Generator are recycled; chlorine gas is returned to Hydrochloric Acid Synthesis, and the salt produced during chlorine dioxide generation is returned to Sodium Chlorate Electrolysis. Of note is that all hydrochloric acid added to the integrated system is consumed in the process. In contrast, the sulphuric acid used in the methanol-based process is purged from the system as by-product sodium sesquisulphate or sodium sulphate (saltcake).

Hydrochloric acid reduction of sodium chlorate to produce chlorine dioxide is not a new process. It is an established process dating back to the 1950's and is known as the Kesting or Day Process.

Considerable research and development efforts by Aker Solutions have advanced this technology to result in a proven, reliable, and efficient system that Aker Solutions has supplied to over 25 installations worldwide (including India), ranging in production capacity from 4 tonnes/day to 70 tonnes ClO_2/day.

Aker Solutions delivers integrated chlorine dioxide plants in India via a collaborative effort involving the supply of technology, proprietary equipment, and specialized site services by the Aker Solutions office in Vancouver, and the supply of engineering, materials/equipment, and project management services by the Aker Solutions office in Mumbai.

Chlorine Dioxide Generation Area

Hydrochloric acid is added to sodium chlorate in the Chlorine Dioxide Generator where they react together according to the simple reaction shown on the second line in Fig. 4. This is actually a simplified expression for the two competing reactions shown in Fig. 5.

The reaction efficiency (90 % was used in the example) is defined as the percent of the sodium chlorate which reacts according to reaction number 1. The undesirable reaction number 2 involves the conversion of sodium chlorate to chlorine gas.

The following illustration (Fig. 6) shows a typical chlorine dioxide generation area. The chlorine dioxide plant includes the Generator, Evaporator, Condenser, Absorber, and Weak Chlorine Blower.

The Chlorine Dioxide Generator is a horizontal titanium vessel designed with a number of internal compartments of varying size to

Chlorine Dioxide Generator Chemistry

Reaction 1	$.9NaClO_3 + 1.8HCl \rightarrow .9ClO_2 + .45Cl_2 + .9NaCl + .9H_2O$
Reaction 2	$.1NaClO_3 + 0.6HCl \rightarrow .3Cl_2 + .1NaCl + .3H_2O$
Overall Reaction:	$NaClO_3 + 2.4HCl \rightarrow .9ClO_2 + .75Cl_2 + NaCl + 1.2H_2O$

Figure 5. Chorine Dioxide Generator Chemistry

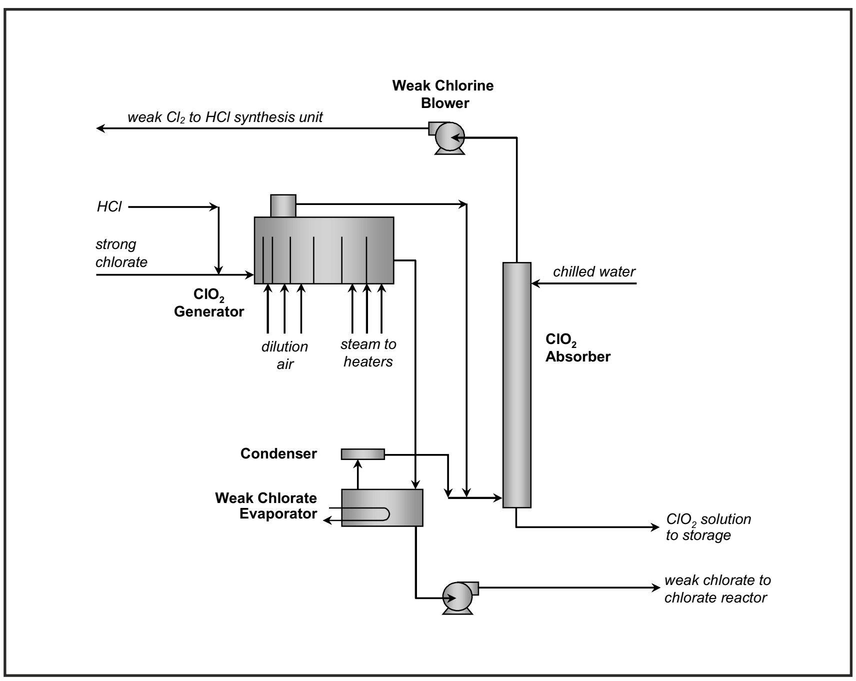

Figure 6. Chorine Dioxide Generator Area Block Diagram

promote the optimum reaction efficiency. The Generator is, in effect, a series of reactors. Internal steam heaters progressively increase the temperature along the Generator to compensate for a decrease in reaction rate due to decreasing reactant concentrations. Temperatures are adjusted to maximize the reaction efficiency and to provide a stable chlorine dioxide gas mixture.

Spent liquor from the final generation compartment overflows to the Weak Chlorate Evaporator where excess water is removed prior to the return of the weak chlorate liquor to the Sodium Chlorate Plant. This stream is the salt recycle, as discussed above. It is necessary to evaporate water to maintain the water balance in the integrated system. Water is added to the process in the hydrochloric acid plant and is produced by the reactions in the Generator. Water is consumed during electrolysis in the sodium chlorate plant and some leaves the process with the chlorine dioxide gas stream. The net effect would be an increase in the amount of water in the process if it were not removed by evaporation.

Chlorine dioxide gas is unstable at high concentrations. For this reason, dilution air supplied from the Generator Dilution Air Compressor is added to each generator compartment to keep the chlorine dioxide concentration low enough to avoid decomposition.

Chlorine gas is produced simultaneously with the chlorine dioxide gas. These gases, along with water vapour and dilution air, are drawn through the chlorine dioxide absorption system by the weak chlorine blower. The system is run under a slight vacuum for safety; and any leaks in the system will result in air ingress and further dilution as opposed to chlorine dioxide venting to atmosphere.

In the Chlorine Dioxide Absorber, chlorine dioxide and a small amount of chlorine is absorbed in chilled water to produce a chlorine dioxide solution. Chilled water at approximately 7C is added to the top of the absorber and the solution product flows by gravity to a pump tank. A typical product specification is 8 g/L chlorine dioxide. The absorber is an FRP tower with beds of high efficiency packing.

By-product chlorine gas, the majority of which is not absorbed with the chlorine dioxide, leaves the top of the absorption tower and is normally transferred by the Weak Chlorine Blower to the hydrochloric acid plant. A portion of this gas is also recycled to the Generator to minimize the dilution air requirement.

Sodium Chlorate Electrolytic Area

Sodium chlorate is produced by the electrolysis of sodium chloride (NaCl) solution in the electrolyzers. Each electrolyzer consists of a number of cells. The number of electrolyzers and cells in the overall integrated plant are customer specific and is dependent on such factors as power cost and chlorine dioxide production requirement.

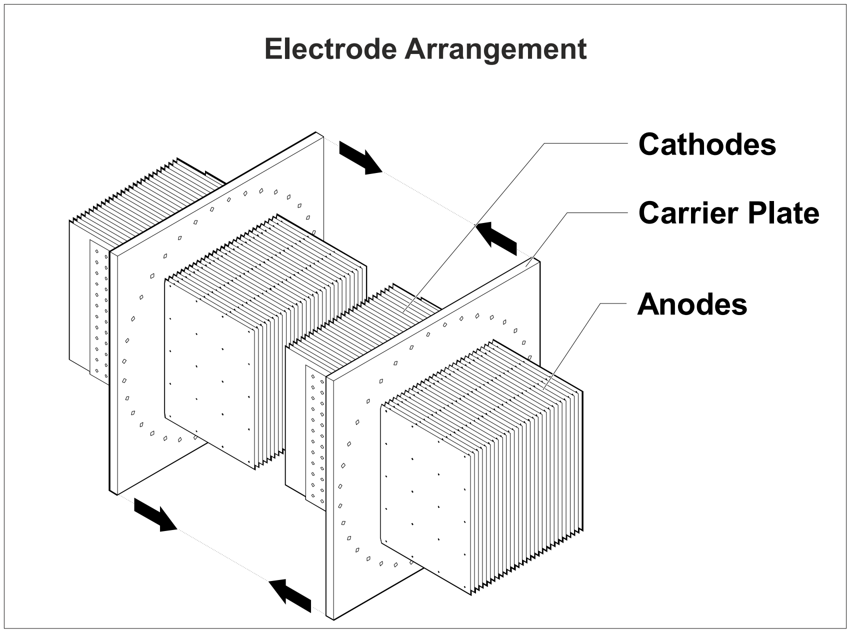

Figure 7. Sodium Chlorate Electrolyzer Schematic

Each cell consists of a set of anodes, a set of cathodes, a cell cover, and two gaskets. Cells are separated from each other by a heavy composite metal current carrier plate. The titanium anodes are welded into milled slots on the titanium side of the carrier plate and the steel cathodes are similarly attached to the steel side. Thus, a carrier plate with its attached set of anodes and cathodes form a compact electrode assembly. In each cell, the anodes of one electrode assembly inter-meshes with the cathodes of the adjacent electrode assembly (Fig. 7). The inter-meshed anodes and cathodes are enclosed by a titanium cell cover that is bolted to the adjacent carrier plates.

When direct current is applied to the cells, chlorine is produced at the anodes and hydrogen gas and hydroxide ions are produced at the cathodes. Heat is also produced. The hydroxide ions react with the chlorine to form hypochlorite ions and hypochlorous acid which, in turn, react to produce sodium chlorate. The principal overall reaction (previously shown on the first line of Fig. 3) is as follows:

$$2NaCl + 6H_2 0 + \text{Electricity} \rightarrow 2NaClO_3 + 6H_2$$

The sodium chlorate production rate is controlled by varying the direct current to the electrolyzers. The efficiency of chlorate production is dependent upon temperature, pH, composition and concentration of the electrolyte, anode and cathode potentials and over-voltages, and the design of the electrolyzers and the electrolytic system. The following illustration (Fig. 8) shows a typical sodium chlorate plant.

The Chlorate Reactor provides the retention time and reaction conditions for the effective conversion of sodium hypochlorite and hypochlorous acid to sodium chlorate. Weak chlorate liquor returning from the chlorine dioxide generator is added to the Chlorate Reactor. This volumetric addition displaces a strong chlorate solution which overflows into the Strong Chlorate Feed Tank. The feed tank provides a buffer between the sodium

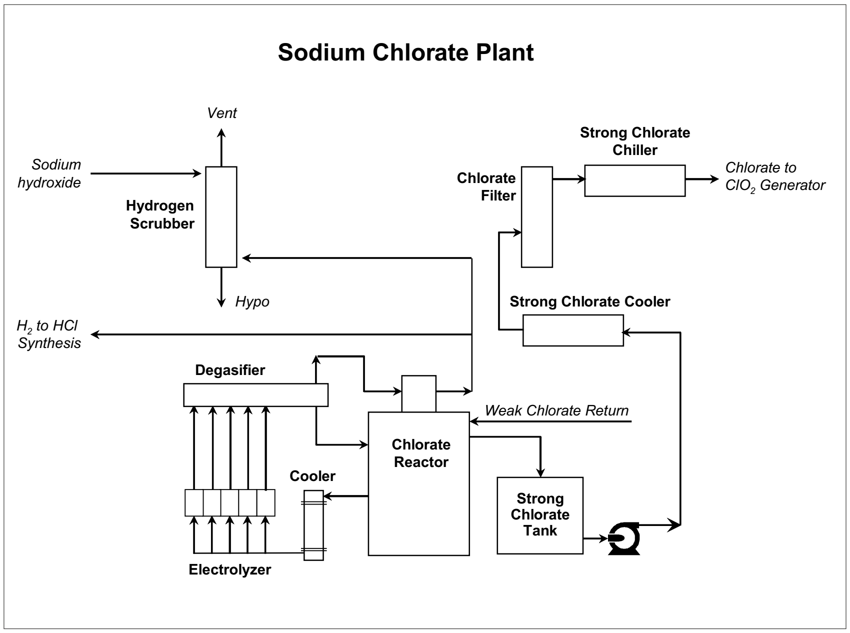

Figure 8. Sodium Chlorate Area Block Diagram

chlorate plant and the chlorine dioxide plant.

Before the strong liquor is fed to the Chlorine Dioxide Generator, it is cooled and filtered. Cooling is required to ensure stable and efficient operation in the Generator and filtration removes any suspended solids.

Hydrogen gas produced in each cell displaces liquor and reduces the specific gravity of the cell and outlet piping contents. The resultant specific gravity difference between the liquor in the cells and that in the Chlorate Reactor creates a high liquor circulation rate from the bottom of the Chlorate Reactor, through the Electrolyte Cooler into the bottom of the cells, up the riser pipes to the Degasifier, and back to the top of the Chlorate Reactor. In the Degasifier, the hydrogen, containing small amounts of oxygen and chlorine, separates from the bulk liquor and is directed to the hydrochloric acid area.

To deliver the hydrogen to the HCl Synthesis Unit, and to eliminate any potential for air ingress, the sodium chlorate plant is operated under pressure (typically 20 kPa(g) minimum is required.

When the HCI Synthesis Unit is shutdown, the gas is vented to atmosphere via a packed tower scrubber which removes any chlorine present in the gas mixture with a dilute sodium hydroxide solution, where the chlorine is converted to sodium hypochlorite and sodium chloride. This (bleach) solution can be used for general cleaning and disinfection at the mill.

Hydrochloric Acid Area

Hydrochloric acid is produced by the combustion of hydrogen and chlorine gases, according to the reaction shown on the third line of Fig. 2, to form hydrogen chloride gas. This gas is subsequently absorbed in demineralized water to form a 32% (w/w) solution. Demineralized water is used to prevent detrimental impurities from entering the integrated process.

As shown in Figure 9, the major components in the hydrochloric acid plant are the HCI Synthesis Unit and the Tail Gas Scrubber.

The HCl Synthesis Unit has the dual purpose of burning the hydrogen and chlorine gases and absorbing most of the resulting hydrogen chloride gas in demineralized water. To ensure safe operation of the HCl Synthesis Unit, the gas mixture consists of excess hydrogen, to fully burn the chlorine.

Residual hydrogen chloride gas is absorbed in the Tail Gas Scrubber. The vent gas from this scrubber consists of the excess hydrogen gas as well as inerts such as nitrogen which are in the feed chlorine gas.

The only chemicals supplied to the HCl Synthesis Unit are hydrogen and chlorine. Hydrogen is supplied from the sodium chlorate plant. Chlorine is partially supplied from the chlorine dioxide plant and the balance is imported to the process from an on-site chloralkali plant, or from a local merchant chloralkali plant.

Operation of the Aker Solutions Integrated Chlorine Dioxide System

As shown in Figure 3, the Integrated Chlorine Dioxide System utilizes three steps to convert chlorine to chlorine dioxide. Figure 10 shows the three blocks in more detail to illustrate the interaction of the various parts of the integrated plant.

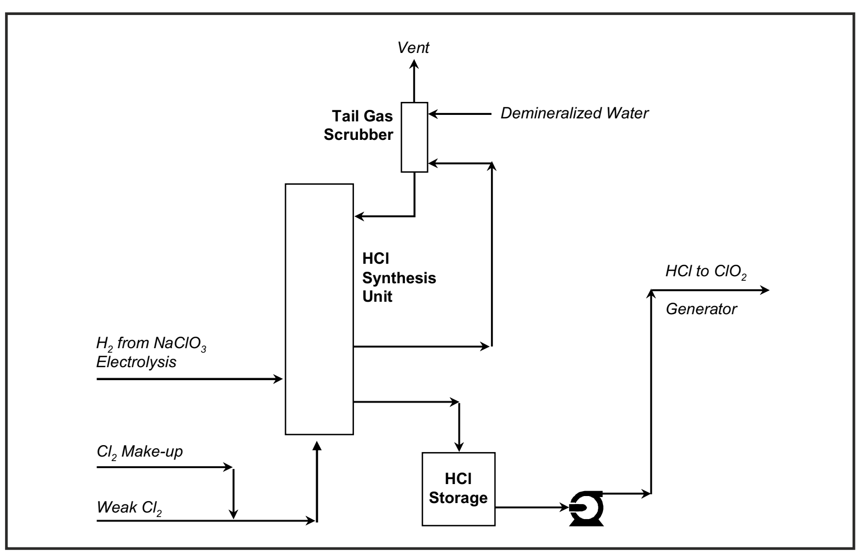

Figure 9. Hydrochloric Acid Area Block Diagram

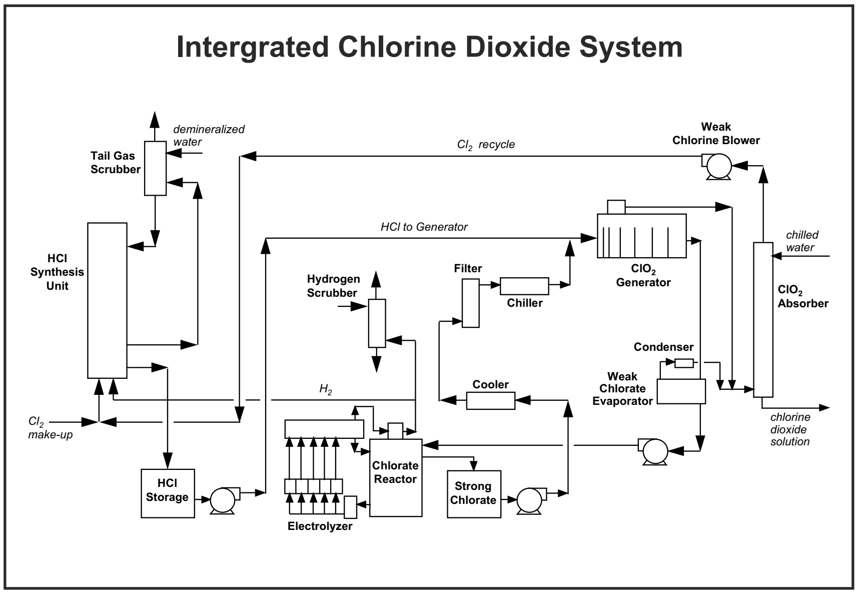

Figure 10. Overall Integrated Chlorine Dioxide Process Schematic

The system is designed to operate on a continuous basis at its maximum production level. System start-up and shutdown is straight forward. Operator attention involves routine process monitoring and simple analytical tests.

The normal start-up of the sodium chlorate plant, from a standby condition, involves purging the hydrogen system with nitrogen and subsequent application of direct current power to the electrolyzers. The desired strong liquor concentration is obtained by regulation of current to the electrolyzers, and steam flow to the Weak Chlorate Evaporator.

The normal start-up of the chlorine dioxide plant from a standby condition involves setting the dilution air flows to the Generator, checking the temperature profile of the Generator, and setting the flow of steam to the heaters in the Generator. Production is initiated by the addition of hydrochloric acid and strong chlorate to the Generator and chilled water to the Chlorine Dioxide Absorber. The flows of hydrochloric acid and strong chlorate are regulated to obtain the desired chlorine dioxide production rate. The chilled water flow is regulated to obtain the desired chlorine dioxide concentration.

The hydrochloric acid plant is started after the chlorine dioxide plant has reached a stable production level. The normal start-up of the acid plant involves the ignition of hydrogen in air. Chlorine gas is substituted for air once a flame has been established. The absorption water flow is adjusted to obtain the desired acid strength.

The integrated system can be turned down to rates as low as 40% of design while maintaining efficient and stable operation.

No special normal procedures are required to maintain the integrated system in operation. Fouling of heat exchangers is not normally expected and since no by-products such as sodium sulphate are produced. No boil outs are required in the Generator and Evaporator. All process streams are in solution form thereby avoiding the difficulties associated with handling solids and slurries.

ECONOMIC COMPARISON BETWEEN INTEGRATED AND METHANOL PROCESSES

The integrated system has very different capital and operating costs when compared to the methanol process. In simple terms, the integrated process has a higher capital requirement due to the additional equipment involved, but has a much lower operating cost. Conversely, the opposite is true for the methanol processes.

Capital cost quotations can be prepared for specific mill requirements upon request.

To illustrate the operating cost differences, a side-by-side comparison of the typical operating costs for chlorine dioxide plant in India is provided in Table 1, based on the following assumptions:

Raw material consumptions are representative estimates of prevailing market prices, on a 100% basis, delivered to the mill site, and including any applicable customs duties.

Power is available from internal mill generation system or from the local grid at the prevailing price of 3.5 Rp/kWh.

A royalty fee of 1850 Rp/tonne of chlorine dioxide produced is applied to the methanol process, whereas no royalty is charged for the integrated process.

Annual maintenance cost is roughly estimated as 1% of the total investment cost.

On-line production for both plants is assumed to be 350 days per year.

Rough estimates of unit costs for utilities such as steam, water.

'MT' = metric tonnes.

Based on the above, the total operating costs per tonne of chlorine dioxide, which include maintenance and labour, are estimated to be about 45,000 RP/tonne ClO_2 for the Aker Solutions integrated system and approximately 90,000 Rp/tonne ClO_2 for the methanol-based system. This represents a cost savings of some 45,000 Rp per tonne of chlorine dioxide produced by the Aker Solutions integrated system over the methanol process. This difference in operating costs is largely due to the high cost of chemical feedstocks in India, particularly the sodium chlorate at a delivered, duty-included cost of approximately 45,000 Rp/tonne.

The resulting operating cost savings for an integrated chlorine dioxide plant are significant and, offer a return on investment for its additional capital cost.

SELECTION OF A CHLORINE DIOXIDE PROCESS

Generally, capital cost, raw material & power costs, chemical balance and operational reliability are the deciding factors when selecting a suitable chlorine dioxide process several mills worldwide have selected the integrated process, based on the following:

Process Inputs and Operating Costs	Cost of Inputs (Est.)		Inputs - Integrated		Inputs - Methanol	
	Unit	Unit Cost Rp/unit	Unit/T ClO_2	Cost Rp/MT	Unit/T ClO_2	Cost Rp/MT
Feedstocks						
Chlorine, delivered.	MT	7500	0.73	5475	0	0
Caustic Soda, delivered.	MT	17500	0.015	263	0.02	350
Sodium Chlorate (delivered incl. freight and duty)	MT	45000	0	0	1.64	73800
Sulphuric Acid, delivered	MT	7500	0	0	1.01	7575
Methanol, delivered.	MT	17500	0	0	0.15	2625
Technology Royalty (/tonne of ClO_2)	MT	1850	0	0	1	1850
Utilities						
Electrolytic Power, as AC feed.	KWh	3.75	9000	33750	0	0
Motor Power	KWh	3.75	250	938	150	563
Steam	MT	50	7	350	6	300
Cooling Water	m^3	0.5	1200	600	400	200
Chilled Water	m^3	5	140	700	125	625
Demineralized Water	m^3	5	5	25	0	0
Nitrogen Purge Gas	Nm^3	300	0.46	137	0	0
Instrument Air						
Total Variable Costs				**42237**		**87888**
Other Operating Costs						
General Maintenance (% of est. inst. plant cost)	1%			1429		714
Labour (number of plant operators/shift)	'All-In' Rate =	250	1.5	1114	1	743
Total Production Cost (/tonne chemical)	Rp/MT			**44780**		**89345**

TABLE 1: Typical *Operating Cost Comparison for Chlorine Dioxide Processes - Integrated vs. Methanol*

The significant operational cost savings of the integrated process more than adequately justifies the higher capital requirement. Dependent on local mill conditions, operating cost for an integrated chlorine dioxide system are about 50% lower than that of the non-integrated process.

Security of chlorine dioxide supply to the bleach plant is improved, since the reliance on the foreign-supplied sodium chlorate is eliminated.

The overall reaction of the integrated process is: $Cl_2 + 4\ H_2O + \text{Electricity}\ \ 2\ ClO_2 + 4\ H_2$. Therefore, as a large consumer of chlorine, the integrated system reduces the "out of balance" caustic requirements. Mills that have moved away from chlorine bleaching can continue to enjoy the benefit of purchasing more balanced units of caustic and chlorine from local suppliers (i.e. lower price), or in consuming these from an on-site chloralkali plant.

Unlike the methanol process, there is little opportunity for feed stock contamination in the integrated process. Raw material contamination is known to be the most common operational problem faced by methanol-based systems, which typically results in product decompositions and plant downtime.

The integrated process main feeds are power and chlorine, while the methanol-based plants process must purchase, transport and handle sodium chlorate, sulphuric acid, and methanol. This places a significant cost & operational burden on the non-integrated processes, especially in regions where raw materials price is high and/or supply is unreliable.

The non-integrated systems produce a sizeable quantity of by-product sodium sesquisulphate or sodium sulphate, which may exceed the amount required by the mill chemical make-up. Direct discharge of excessive sodium saltcake to mill effluent, which had been practised in the past, may no longer be possible given the increasingly stringent environmental regulations. The integrated system produces no solid or effluent by-product.

The integrated system is an all-liquid process. In contrast, methanol process involves a solid handling systems, and its generator and heat exchangers must be periodically cleaned to remove deposits. Improper cleaning, or lack of, has been known to cause corrosion to critical titanium equipment.

CONCLUSION

Pulp mills in India now face pressure to phase out elemental chlorine (or hypochlorite based) bleaching, to adopt a more environmentally friendly process.

After much debate in the 1990's, the 'ECF' process has been accepted as the preferred bleaching sequence for Kraft pulping, and this has established chlorine dioxide as the predominant pulp bleaching agent worldwide.

The Aker Solutions Integrated Chlorine Dioxide System offers technical, economic and environmental benefits as opposed to the methanol-based processes notably an attractive return on capital investment, and no reliance on foreign supplied feedstocks.

After over 25 years of serving the chlorine dioxide industry, Aker Solutions is the world leader in supplying proven integrated chlorine dioxide technology, equipment and plants, and is well-positioned to serve to the Indian market via our office in Mumbai.