

A Comparison of Non-Integrated and Integrated Chlorine Dioxide manufacturing Systems in view of Environmental Aspects

Ma, R. Moser, C. and Shaw D.

ABSTRACT:-- The use of chlorine dioxide (ClO₂) for bleaching of chemical pulp has been on the increase worldwide as mills are shifting to higher substitution to meet the environmental regulations and/or market demand.

There are two primary Chlorine dioxide manufacturing alternatives- the non-integrated process requiring the purchase of sodium chlorate and other chemical feedstocks, and the integrated system where sodium chlorate is generated in-situ.

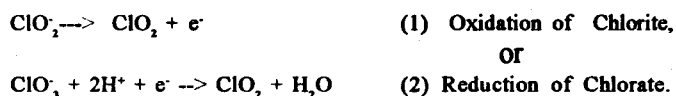
This paper compares these two alternatives, represented by the "Single Vessel" methanol based non-integrated process and the Kvaerner Chemetics Integrated Chlorine Dioxide System. A general description of both systems is provided. A summary of costs of the two processes in India is also presented.

INTRODUCTION

Since the mid 1980s, chlorine dioxide (ClO₂) has been displacing chlorine (Cl₂) as the bleaching agent of choice of chemical pulp worldwide. The key driving forces for this change are bleaching efficiency, environmental and regulatory pressures, and market demand. In 1995, over 900,000 tonnes of chlorine dioxide was used for pulp bleaching in North American mills alone.

While used in large quantities, chlorine dioxide is an unique chemical, as it is an unstable explosive gas at concentrations greater than about 10% in air. As a result, it is always generated on site and stored until use as a diluted solution.

There are only two ways of producing ClO₂ which give acceptable yield. They are:



The Chlorite route is extremely expensive and is used for laboratory and very specialized purposes. This leaves only one major route, namely the reduction of sodium chlorate (NaClO₃) in an acidic medium. All commercial chlorine dioxide processes are based on this chemistry and they differ only in the choice of acid & reducing agent, and the degree of integration.

Interestingly, only two acids have been used to date, which are sulphuric acid (H₂SO₄) and hydrochloric acid (HCl). The choice of reducing agents has also been few, limiting to chloride ion (Cl⁻), sulphur dioxide (SO₂), methanol (CH₃OH), and more recently hydrogen peroxide (H₂O₂).

**Kvaerner Chemetics Inc.,
1818 Cornwall Avenue, Van couver B.C.
Canada V6 J1C 7.**

The other distinction between the various commercial processes is the degree of integration. Non-integrated processes are those requiring the purchase of the main reacting agents, such as sodium chlorate and mineral acid. The integrated processes generate these chemicals in-situ.

Of the non-integrated systems, the standard selection in recent years has been the "Single Vessel" type sub-atmospheric methanol based process. The reactants are methanol, sulphuric acid and sodium chlorate, all of which have to be purchased, and in many cases imported over great distance, from merchant producers.

The reliance on external raw material supply is reduced with an integrated system where the main reacting agents, namely sodium chlorate, and hydrochloric acid are produced in-situ. The leading supplier of the integrated technology is Kvaerner Chemetics.

The purpose of this paper is to examine the process characteristics of the methanol based non-integrated "Single Vessel" process and the Kvaerner Chemetics Integrated Chlorine Dioxide System, and to compare the costs of two systems.

PROCESS DESCRIPTION
Sub-atmospheric, Methanol Based, "Single Vessel" Non-integrated System

A typical "Single Vessel" system is described below (Figure 1):

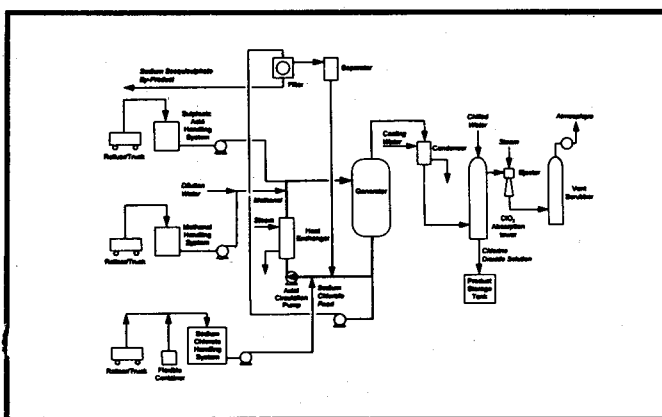
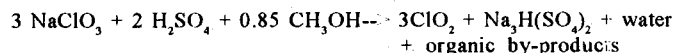


Figure 1. Methanol Based Non-Integrated ClO₂ System.

The main component of the system consists of a generator and a shell and tube heat exchanger. The overall reaction between sodium chlorate,

sulphuric acid and methanol which takes place within the generator, is as follows:



The generator typically operates at 7 to 9 Normal acidity, about 70 to 75°C and under a strong vacuum of approximately 110 to 120 mmHg absolute, induced by a large steam ejector.

The liquor within the system is circulated by an axial pump in the line between the heat exchanger and the generator. Sodium Chlorate feed solution is introduced before the pump while sulphuric acid is added at the heat exchanger outlet. Methanol can be injected into the system at either location. While not required for the reaction, this methanol feed is typically diluted with water or chlorate solution to below 20% by volume to avoid the stringent regulations governing of the use of higher strength solution due to its flammability.

Steam is supplied to the heat exchanger to evaporate the water introduced into the system from the various feed streams and from the reaction itself.

Chlorine dioxide, the majority of which is formed at the point of methanol injection, is flashed off as the liquor re-enters the generator. The evaporated water acts as the diluent to maintain the chlorine dioxide gas mixture below its explosive limit. Unreacted methanol along with methanol by-products such as formic acid leave the generator with the chlorine dioxide gas.

The gas mixture, after being cooled in a condenser, is then passed through a packed counter current flow absorption tower where chlorine dioxide is absorbed into chilled water to a typical strength of 10 g/L at the bottom of the tower. Methanol and formic acid are also absorbed into the solution which subsequently impose an additional BOD load in the bleach plant effluent.

The other by-product, sodium sesquisulphate (Na₂H(SO₄)₂) precipitates out as fine crystals in the generator and is suspended in the circulating liquor. A side stream of this slurry is pumped to a rotary drum filter when the sesquisulphate solid is removed. As the sesquisulphate contains about 18% by weight acid, care must be taken before transferring this

material to the pulp mill recovery system or to disposal. Neutralization is typically required.

The gas leaving the absorption tower, which is mostly air, goes to a final gas scrubber where low levels of chlorine dioxide and chlorine are removed before being released to atmosphere.

As a non-integrated process, the "Single Vessel" plant also requires ancillary systems for the handling and storage of the raw materials. Design and operation of these systems can be critical due to the hazardous nature of the materials involved.

For instance, handling and storage of sodium chlorate, if delivered as a solid in 1 tonne flexible containers, poses a special safety risk due to the highly reactivity nature of the chemical in the solid form and the susceptibility of the containers to contamination. Regulations governing the storage of these chlorate containers are extremely strict, but necessary in view of the recent catastrophic fires involving the same.

Methanol, being a flammable liquid, also faces many restrictions on its storage and use.

PROCESS DESCRIPTION

Kvaerner Chemetics Integrated Chlorine Dioxide System

The Kvaerner Chemetics Integrated Chlorine Dioxide System consists of plants to produce sodium chlorate and hydrochloric acid as well as the

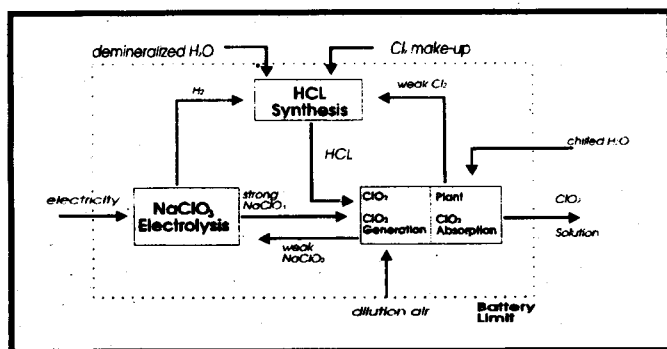
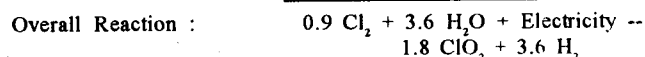
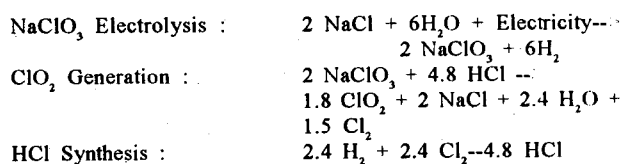


Figure 2. Kvaerner Chemetics Integrated Chlorine Dioxide System

final product, chlorine dioxide. A simplified inter-connection of the three main plants is shown in Figure 2.

The overall chemistry of the system can be summarized in the following equations:



As shown by the above overall reaction equation, the only raw materials required to produce chlorine dioxide are chlorine, water and electricity. Sodium chlorate, sodium chloride and hydrochloric acid are generated and consumed internally.

A description of each of the three plants is provided below:

Chlorine Dioxide Plant

The chlorine dioxide generator is a horizontal titanium vessel divided into a number of compartments (Figure 3). Sodium chlorate solution from the electrolysis plant and hydrochloric acid from the HCl synthesis unit are fed into the first compartment. Chlorine dioxide and chlorine are formed as the solution flows by displacement from compartment to compartment. Air is added to strip out the product gases and to maintain the chlorine dioxide gas concentration at a safe level. Liquor temperature is raised by internal steam heaters to maintain reactivity as the reactant concentration is reduced. Spent liquor from the last generator compartment overflows to the weak chlorate evaporator where excess water is removed before the solution is recycled back to the sodium chlorate plant.

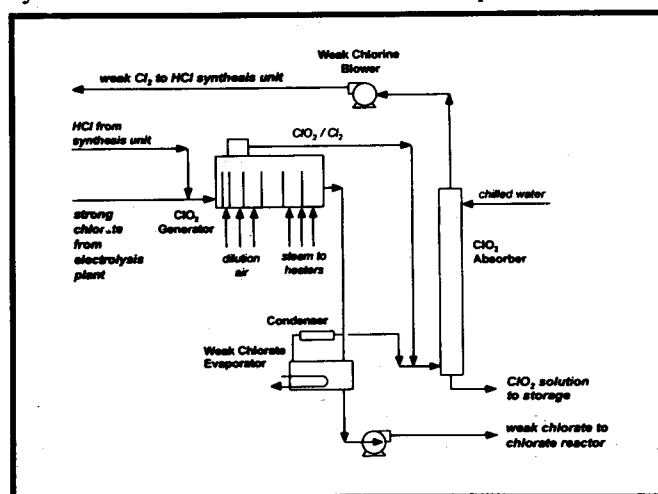


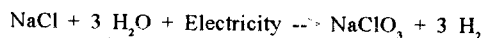
Figure 3. Chlorine Dioxide Plant

Chlorine dioxide and chlorine gases stripped out of the solution by the dilution air are collected along the top portion of the generator and are sent to the counterflow "Linder" tray absorption tower. Almost all of the chlorine dioxide and some chlorine are absorbed into the chilled water to produce a solution containing about 10 g/L ClO₂ and 1.8 g/L of Cl₂ at the bottom of the tower. Further processing is necessary to produce a chlorine free product solution if needed.

The non-absorbed chlorine gas, along with air, leaves the top of the tower and is transferred to the hydrochloric acid plant for regeneration into acid. A stand-by chlorine gas scrubbing system (not shown) is provided for the start-up and shutdown of the integrated system.

Sodium Chlorate Electrolysis Plant

The spent liquor from the chlorine dioxide generator, now rich in sodium chloride, is fed to the chlorate reactor to be converted electrochemically back into sodium chlorate. The overall reaction as stated previously is as follows:



The key component of the sodium chlorate plant is the electrolyzer, which is interconnected with the reactor via the cooler (Figure 4). The electrolyzer is essentially a series of electrochemical cells with internal anodes and cathodes. Each cell is separated from its neighbouring cells by a heavy composite metal current carrier plate. The carrier plate consists of a titanium plate explosion

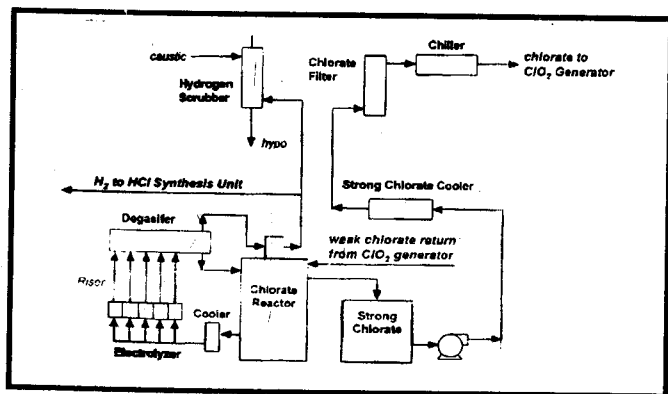


Figure 4. Sodium Chlorate Plant

bonded to a special steel plate. The anodes are welded into milled slots on the titanium side, and the

cathodes are similarly attached to the steel side of the carrier plate. The anodes are made of flat titanium sheets coated with a mixed metal oxide coating. The cathodes are constructed of a special steel which is extremely resistant to hydrogen blistering. The electrodes (anodes and cathodes) are intermeshed with each other with a small gap in between for liquor flow. There is no membrane to separate the anode and cathode compartments as in a chloralkali cell. The cells in the electrolyzer are arranged in parallel for liquor flow and in series for current flow.

When direct current is applied to the cell, hydrogen gas is produced at the cathode surface causing the resulting mixture within the cell to rise. This "hydrogen lift" phenomena creates a high rate of circulation from the bottom of the reactor, through the cooler, into the bottom of each cell in the electrolyzer and finally into vertical piping (riser) at the top discharge of the cell. A high circulation rate is desirable in order to minimize power consumption.

Meanwhile, at the anode surface, chlorine is formed which immediately reacts with the hydroxide ions in the solution to form hypochlorite ions and hypochlorous acid, which in turn, react to produce sodium chlorate. These latter reactions are slower and the time necessary to achieve the desired conversion is provided by the reactor volume.

The two phase mixture leaving the cells is discharged into a degasifier where the H₂ gas is separated. The liquor is returned to the reactor whereas the hydrogen gas is sent to the HCl plant. A stand-by hydrogen gas scrubber is provided in the event that the acid plant is not available.

The rate of sodium chlorate production in an electrolyzer is directly proportional to the DC current applied. Depending on design, operating current can range from 20 kA to about 100 kA. The incoming weak chlorate liquor from the chlorine dioxide plant contains about 330 g/L NaClO₃ and 150 g/L NaCl. About 30% of this sodium chloride is electrochemically converted to sodium chlorate giving an outlet concentration from the chlorate reactor of approximately 450 g/L NaClO₃ and 110 g/L NaCl. This strong chlorate liquor is cooled, filtered, and chilled before returning to the chlorine dioxide generator.

Hydrochloric Acid Plant

Hydrochloric acid is produced by the combustion of hydrogen and chlorine gases to form hydrogen chloride gas which is absorbed in water to form a 32% by weight solution (Figure 5). The hydrogen gas is supplied from the sodium chlorate plant as mentioned above. The chlorine gas is a mixture of by product chlorine and air from the chlorine dioxide plant and pure chlorine from an external supply. This external supply of chlorine is required to

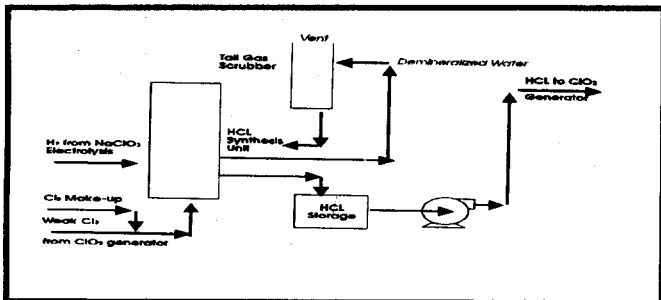


Figure 5. Hydrochloric Acid Plant

balance the chlorine atoms leaving the integrated system as chlorine dioxide in the product solution.

The HCl synthesis unit burns the hydrogen and chlorine gases and absorbs most of the resulting hydrogen chloride gas in demineralized water. Demineralized water is used to minimize impurities from entering the integrated plant circuit.

The tail gas scrubber removes the residual acid vapour before the non-condensable gas, nitrogen and hydrogen, is vented to atmosphere.

Comparison of the Chemical and Process Differences of the Two Systems

The major chemical and process differences of the non-integrated and integrated systems involve process inputs, by-product production, residual chlorine in ClO_2 solution and mill chemical balance.

- The integrated system uses electric power and chlorine to produce chlorine dioxide while the non-integrated system has to purchase, transport and handle sodium chlorate and other feed materials. This places a significant cost burden on the non-integrated process, especially in regions where raw material price is high and/or supply is unreliable. Also, the most common operational problem faced by the non-integrated system is feed stock contamination. By design,

this type of problem is eliminated for the integrated system.

- The non-integrated system produces a sizable quantity of by-product sodium sesquisulphate which may exceed the amount required for mill chemical make-up. Direct discharge of excessive sodium sesquisulphate to mill effluent, which had been practiced in the past, may now not be possible given the increasingly stringent effluent regulations. The integrated process produces no solid or effluent by-product.
- The methanol based non-integrated process generates organic compounds which pass through the bleaching plant and increase the BOD load to the mill's effluent treatment system. It has been estimated that a BOD burden of about 80 kg is imposed for each tonne of chlorine dioxide generated by the "Single Vessel" process. No organic compounds are used in the integrated system; therefore, no BOD burden is generated.
- The non-integrated process produces a chlorine dioxide solution containing about 0.2 g/L of chlorine, whereas the chlorine content is higher at about 1.8 g/L for the integrated system. This chlorine content meets all bleaching requirements; however, if a mill required a lower concentration of chlorine, additional processing is needed and available for the integrated process.
- The integrated system is a consumer of chlorine; therefore, it reduces or eliminates the imbalance between caustic and chlorine requirements experienced by most mills. The non integrated process is a consumer of caustic, thereby worsening the imbalance.
- Both systems typically offer good on-time availability. However, for the non-integrated process, a periodic boilout of the chlorine dioxide generator is required to remove deposit on the heat exchanger surface. Improper boilout, or lack of, has been known to cause corrosion of the titanium heat exchanger tubes. Boilout is not required as no solids are involved in the integrated process.

Table 1

Chlorine Dioxide Systems Cost Comparison

Basis of Comparison: India Cost

Plant Capacity	(MT of ClO ₂ /Day)	MT/Day	5
Kvaerner Chemetics	Total Equipment Cost	Million Rs	198
Kvaerner Chemetics	Total Installed Cost	Million Rs.	356
Methanol Non-integrated	Total Equipment Cost	Million Rs.	79
Methanol Non-integrated	Total Installed Cost	Million Rs.	244
Operator Hourly Cost		Rs/HR	200

Unit	Unit Cost Rs/MT	Kvaerner Chemetics Integrated		Methanol Based Non-Integrated		
		Unit/T	Cost Rs/MT	Unit/T	Cost Rs/MT	
Purchased Feedstocks						
Chlorine	MT	3,200	0.75	2,400	0	0
Sodium Chlorate	MT	37,000	0	0	1.65	61,050
Sulphuric Acid	MT	2,000	0	0	1.01	2,020
Methanol	MT	17,000	0	0	0.16	2,720
Caustic Soda	MT	21,000	0	0	0.2	4,200
DC Power	kWh	3.3	8,600	28,380	0	0
Utilities						
Sub Power	kWh	3	350	1,050	400	1,200
Steam	MT	600	6.7	4,020	7.5	4,500
Cooling Water	m ³	2	1,020	2,040	195	390
Chilled Water	m ³	4	120	480	95	380
Demineralized Water	m ³	3	3.4	10.2	0	0
Nitrogen Purge Gas	m ³	8	0.1	0.8	0	0
Royalty			No Royalty	0		1,346.4
By-Products (Credits)/Costs						
Cl ₂ in ClO ₂ Solution	MT	-3,200	0.18	-576	0.02	-64
Saltcake	MT	-9,700	0	0	1.45	-14,065
BOD	MT	18,000	0	0	0.08	1,440
Other Operating Costs						
Maintenance (5% yr. of Equipment Cost)		5%		5,647		2,261
Operators		# Opt'r/Shift	1.5	1,440	1.0	960
Total Manufacturing Cost	Rs/MT			<u>44,892</u>		<u>68,339</u>
Total Saving Per Tonne	Rs/MT			23,447		
Total Annual Savings	Million Rs/Yr			41		
Total Capital Cost Difference	Million Rs			112		
Simple Payback	Yr			2.7		

Cost Comparison

The different chemical and process requirements of the two systems give rise to very different capital and operating costs. In simple terms, the integrated process has a higher capital requirement due to the additional equipment involved, but gives a much lower operating cost. Conversely, the opposite is true for the non-integrated process.

To illustrate these differences, a comparison of capital and operating costs for a green field 5 tonne per day chlorine dioxide plant in India is provided in Table 1, based on the following assumptions:

- Raw material consumptions are those published by the suppliers, on a 100% basis.
- The installed cost for a generic "Single Vessel" plant is 244 million Rupees.

- The installed cost for the Kvaerner Chemetics Integrated Chlorine Dioxide Plant is 356 million Rupees.
- Power is available at approximately 3.0 Rs/kWhAC.
- All by-products from either system are considered usable and are fully credited.
- A royalty fee of 1350Rs/tonne is applied to the non-integrated process as it is industry standard.
- Annual maintenance cost is fixed at 5% of the total equipment cost.
- On-line time for both plants is approximately 350 days per year.

Based on the above, the total manufacturing costs per tonne of chlorine dioxide, which include maintenance and labour, are estimated to be about 44900 Rs for the Kvaerner Chemetics integrated system approximately 68300 Rs for the non-integrated system. This represents a cost savings of some 23400 Rs per tonne of chlorine dioxide produced by the Kvaerner Chemetics integrated sys-

tem over the non-integrated process. this huge difference in costs is largely due to the high cost of chemical feedstocks in India, in particular, sodium chlorate at 37000 Rs/tonne or higher.

The resulting savings for a 5 tonne per day ClO₂ plant, assuming a 95% load factor, is calculated to be in excess of 41 million Rs. per year for the integrated system over the non-integrated process. This level of savings clearly justifies the higher capital cost of the integrated system. The simple payback for the additional capital required is calculated to be 2.7 years.

Conclusion

The non-integrated and integrated chlorine dioxide manufacturing processes differ in many aspects. The integrated process offers a number of process advantages, such as no effluent and better chemical balance. It has a higher capital requirement which is well justified given its significantly lower manufacturing cost, as compared to that of the non-integrated process. Given the current cost of raw materials, and challenges associated with the importation and transportation of sodium chlorate in India, the Kvaerner Chemetics Integrated Chlorine Dioxide System is clearly the preferred alternative.