Chlorine Dioxide Bleaching

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ABSTRACT

The paper higlights the characteristics of chlorine dioxide, various generation processes, mechanism of chlorine dioxide bleaching, variables affecting chlorine dioxide bleaching, its impact on effluent, and materials of construction for various equipments in generation and bleaching.

INTRODUCTION

The demand for chlorine dioxide for bleaching pulp has increased rapidly during the last three decades due to its unique specificity for lignin removal with minimum damage to cellulose and hemicellulose of pulp. It has little effect on the molecular structure of cellulose as compared to hypochlorite. Commercial bleaching with chlorine dioxide was started in 1946 in Sweden and Canada. Originally it was used for making dissolving grade pulp and other speciality paper products where super brightness and higher strength of pulp is required. Earlier the use of chlorine dioxide was also restricted due to high cost of chlorine dioxide production and its explosive nature. However, with the development in technology and manufacturing process of chlorine dioxide by Rapson R_2–process and its other modifications and modified Mathieson process, chlorine dioxide bleaching has become an integral part of multistage bleaching in developed countries.

Inspite of its higher cost of Production and higher energy consumption, chlorine dioxide bleaching has been adopted universally as it offers high efficiency in comparison to other bleaching agents with minimum fibre degradation at wide range of pH, temperature and consistency. Main advantage of chlorine dioxide bleaching is high efficiency, improved higher yield, excellent physical properties, higher brightness 90° GE, high viscosity, lower copper number, decreased effluent colour, decreased toxicity and increased colour stability CEDED and CEHED are the commonly used bleaching sequences in multistage bleaching. With conventional CEHH sequence it is not possible to achieve higher brightness without fibre degradation. Almost every new pulp mill installed in advanced countries is using chlorine dioxide bleaching.

There has been also increase in the use of chlorine dioxide to treat drinking water for trihalomethane, taste and odor control; oxidation of iron and manganese and oxidant enhanced coagulation and sedimentation [1].

However, due to high initial capital, investment for installation of chlorine dioxide generation unit and its plant and machinery for chlorine dioxide bleaching as it requires special materials of construction due to its highly corrosive and explosive nature, use of chlorine dioxide in India is restricated only to Rayon grade pulp. It is not being used at present for paper grade pulp, but with increasing demand of brighter pulp with higher strength and colour stability and recent pollution abtement policy, Indian pulp mills are also adopting chlorine dioxide bleaching. Recently, M/s Hindustan Paper Corporation has adopted chlorine dioxide bleaching for its Nowgaon and Cachhar units and several other units are likely to follow suite.

In the present paper an attempt has been made to highlight the characterisitics of chlorine dioxide, its various generation processes, its mechanism of bleaching and trends of bleaching sequences, its impact on effluent and other aspects of chlorine dioxide bleaching parameters.

CHARACTERISTICS OF CHLORINE DIOXIDE

Chlorine dioxide is a yellow green gas at room temperature and has a characteristic smell, is toxic and spon-

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taneously explosive at higher concentration. It is one of the few compounds in nature that exist almost entirely as monomeric free radicals and is a member of oxochlorine family. It is an unstable compound and has an unpaired electron which makes it very reactive and toxic It can be liquified at 11°C and solidified at-59°C. Pure gaseous chlorine dioxide decomposes at 30°C at a measurable rate and explosively above 50°C. Dilution of gas with air to about 10% chlorine dioxide is a convenient means of reducing explosion.

Chlorine dioxide in water does not hydrolyse to any appreciable extent but remains in soloution as cissolved gas. Aqueous solutions are quite stable if kept cool, well sealed and protected from light. Slight acidification of chlorine dioxide solution (pH 6) enhances stability by inhibiting disproportionation.

Chlorine dioxide is used as preoxidant and primary disinfectant for treatment of trihalomethane and reacts with managanese iron, phenol and phenolic compounds, humic substances,taste and odor compounds other than phenolics, details of which has been reviewed by Aieta and Berg[1]. Chlorine dioxide in water decomposes rapidly by irradiation especially by ultraviolet light. The final products from this decomposition are chlorine and chlorate. Major Properties and characteristics of chlorine dioxide are given in Table 1 ([1,13])

HAZARDOUS NATURE OF CHLORINE DIOXIDE

Chlorine dioxide is a powerful oxidant, explodes violently on the slightest provocation as gas or liquid. Chlorine dioxide explodes (i) at high temperature, (ii) at high concentrations (iii) when sparked (iv) when easily reducible materials are present and (v) in contact with rust, scale and foreign material[7]. Explosion is initiated by contact with several mateirals like cobalt. difiuroamine, hydrogen, mercury, phosphorus, sulphur, sugar, phosphorus pentachloride, potassium hydroxide, on heating rapidly to 100°C or on sparking or by impact as solid at-100°C[8]. A guide on fire and explosion hazards for industrial uses of chlorine dioxide is available and preparative precautions have been discussed in detail[9].

Explosiveness of chlorine dioxide in the compressed or liquid state prohibits the transport and storage of pure chlorine dioxide By the use of higher reaction temperatures and higher acidity, the reaction rate can be increased to a point above which clorate can be exhausted within a few seconds. The hazards associated with higher operating temperature may be minimised by the use of cold inert gas to dilute the chlorine dioxide formed[7].

TABLE I :

PROPERTIES AND CHARACTERISTICS OF CHLORINE DIOXIDE DIOXIDE ([1-10,18,20,24])

Physical state	Gas or liquid
Colour	Greenish yellow
Odour	Pungent suffocating
Corrosivity	Highly corrosive
Taste	Bitter
Melting Point of Solid ClO_2	−59°C
Boiling point of Liquid ClO_2	9 9°C at 731 mm
Density[*]	309 g/lit at 11°C
Heat of formation H at 25°C	24.7 Kcl/mole
Free cnergy of formation at 25°C	29.5 Kcal/mole
Oxidation potential in water against normal hydrogen electrode	0.95 volt at pH 4-7
Threshold value	0.1 ppm in air, 0 3 mg/ cubic meter of air
Fire hazard	Dangerous, a powerful oxidiser
Explosive hazard	Severe
Disaster hazard	Dangerous shock will explode
Ultra violet absorption spectrum	Broad band with peak at 360 nm
Molar extinetion coefficient	1150 $(M cm)^{-1}$

Solubility of chlorine dioxide in waier (in gm/lit.)		
At 25°C Pressure mm Hg	34 5	3.01
	22.7	1.82
	13.4	1.32
	8.4	0.69
At 40°C Pressure mm Hg	56.2	2 60
	34.2	1.60
	18.9	0 83
	9.9	0.47
At 60°C Pressure mm Hg	105.9	2.65
	53.7	1.18
	25.7	0.58
	12 7	0.26

73

At a concentration of 45 ppm in air it has an irritating effect and its odor is noticeable even at 14-17, ppm. It is as hazardous as nitrogen dioxide.

BLEACHING CHARACERISTICS OF CHLORINE DIOXIDE

Cholorine dioxide enjoys a unique position amongst the various bleaching agents as it is quite specific to lignin and does not react adversely with carbohydrates under the commonly used bleaching conditions. It is relatively cheaper per oxidising equipment and has comparable energy requirements with chlorine. It produces maximum brightness with optimum pulp quality (pulp yield, strength, cleanness), minimum colour reversion and improved effluent quality. A comparison of commonly used bleaching agents is given in Table II([10],[14]). Cost of bleaching pulp to 88-90 brightness with chlorine dioxide is actually less than the cost of bleaching to 82 brightness without chlorine dioxide[12].

TABLE II : COMPARISON OF VAKIOUS BLEACHING AGENTS [10],[12],[13],[14],[21])

Bleaching agents Mol. wt / Eq. wt.	Active chlorine per kg of oxidant, Kg	Active oxygen per kg of oxidant, Kg	Bleaching condition			Impurities			Degree of poly-meristation of cellulose
			pH	Temp.	Time/ consis-tency	Lignin and lignin compound	Hemi-cellulose	Extracti-ve colour-ing matter etc.	
1	2	3	4	5	6	7	8	9	10
Chlorine, Cl₂ 70.914/35.5	1.00	0.22	2 or lower	Am-bient Temp.	45-50 min 3-4%	Partially solubili-sed and removed	Usually little effect	Removed	Usually lttle effect under proper condition considerable degra-dation under certain condition
Caustic, NaOH 40/40	0.89	0.20	11	70°C	160 miu 10-12%	Substitu-ted and oxidised lignin com-pounds solubilised and removed	Can solu-bilise and remove to varying degree	Removed	Usually little effect
Chlorine dioxide, C10₂ 67.5/13.5	2 63	0.59	3.5-4.0	70°C	180 min 12%	Oxidised and removed	Little effect under proper condition	Removed	Relatively little effect
Calcium hypo chlorite, CaOCl₂ 127/63.5	0.52	0.12	9.5-10	35-40 °C	180 min 10-12%	Ozidised and removed	Little effect under proper con-ditions can degrade and remove	Removuud	Little effect under proper con-ditions can severely degrade under other

1	2	3	4	5	6	7	8	9	10
Hydrogen per oxide, H_2O_2 34/17	2.09	0.47	10.5	40.60 °C	1-3 hr 12-15%	Whitened not removed	Little effect under proper condition	Whitened and/or removed	Relatively little effect
Sodium hydro- sulphite. $Na_2S_2O_4$ 174/87	0.41	0.08	6.5.7.0	60-70 °C	60, min 3.5-4%	Whitened not removed	Little effect under proper condition	Removed	Relatively little effect
Oxygen, O_2 32/8	4.4	1.0	11		90-120	30–60 25-30%	Oxidised and re- moved Modifica- tion of -esidual lignin	Little effect under proper condition	Removed	Little effect under proper condition in presence of protectors, can severely degrade under other

Ultimate brightness with different bleaching agent for kraft pulp

CEH	75–80	GE	Fibre degradation more at higher
CEHH	80–85	GE	brightness in case of hypo bleaching
CED	83–85	GE	
CEDED	90	GE	
CEHDP	90	GE	

GENERATION OF CHLORINE DIOXIDE

Chlorine dioxide was first produced by Sir Humphrey Devy in 1811 by acidification of potassium chlorate with sulphuric acid and was named as euchlorine[15]. In 1843 chlorine dioxide was producd by Millon[16] by acidifying potassium chorate with hydrochloric acid, hover, it was unidentified till 1881, when Garzarolli-Thurulakh[17] identified the gas as a mixture of chlorine dioxide and chlorine.

Chlorine dioxide is prodcedcommercially by reducing sodium chlorate using sulphur dioxide, methanol, sodium chloride, all these processes is

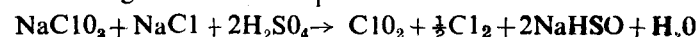$$ClO_3 + Cl + 2H^+ \rightarrow ClO_2 + \tfrac{1}{2}Cl_2 + H_2O \qquad (1)$$
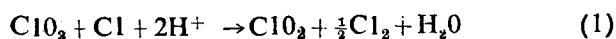
All processes except one lead to an effluent ûtilisation problem. the effluent consisting of sodium sulphate and sulphuric acid.

Sodium chlorate which is the main raw material for manufacture of chlorine dioxide is produced by electrolysis of sodium chloride which is dissolved in a weak chlorate liquor returned from chlorine dioxide plant.

$$NaCl + 3H_2O + 6 \text{ Faradays} - NaClO_3 \text{ (aq)} + 3H_2\text{(g)}$$

The reaction is very complex aud depends upon temperature, pH, electrolyte concentrations, additives, anodic and cathodic overvoltage. residence time in the electrolyser and reactor and electrolyser design[18],

RAPSON R_2 PROCESS

Rapson R_2 process (Fig, 1) ([19,20,21]) is an efficient chlorine dioxide generation process using sodium chloride, sodium chlorate and sulphuric aeid as raw materials and is characterised by quick and early start ups, shut downs, ready respose to flow changes and high yields. Salt cake and sulphuric acid are obtained as by-products. Following reaction takes place
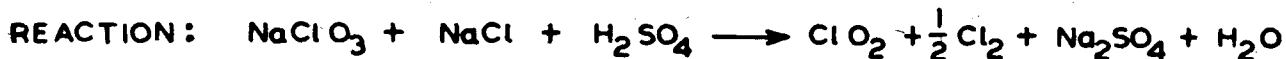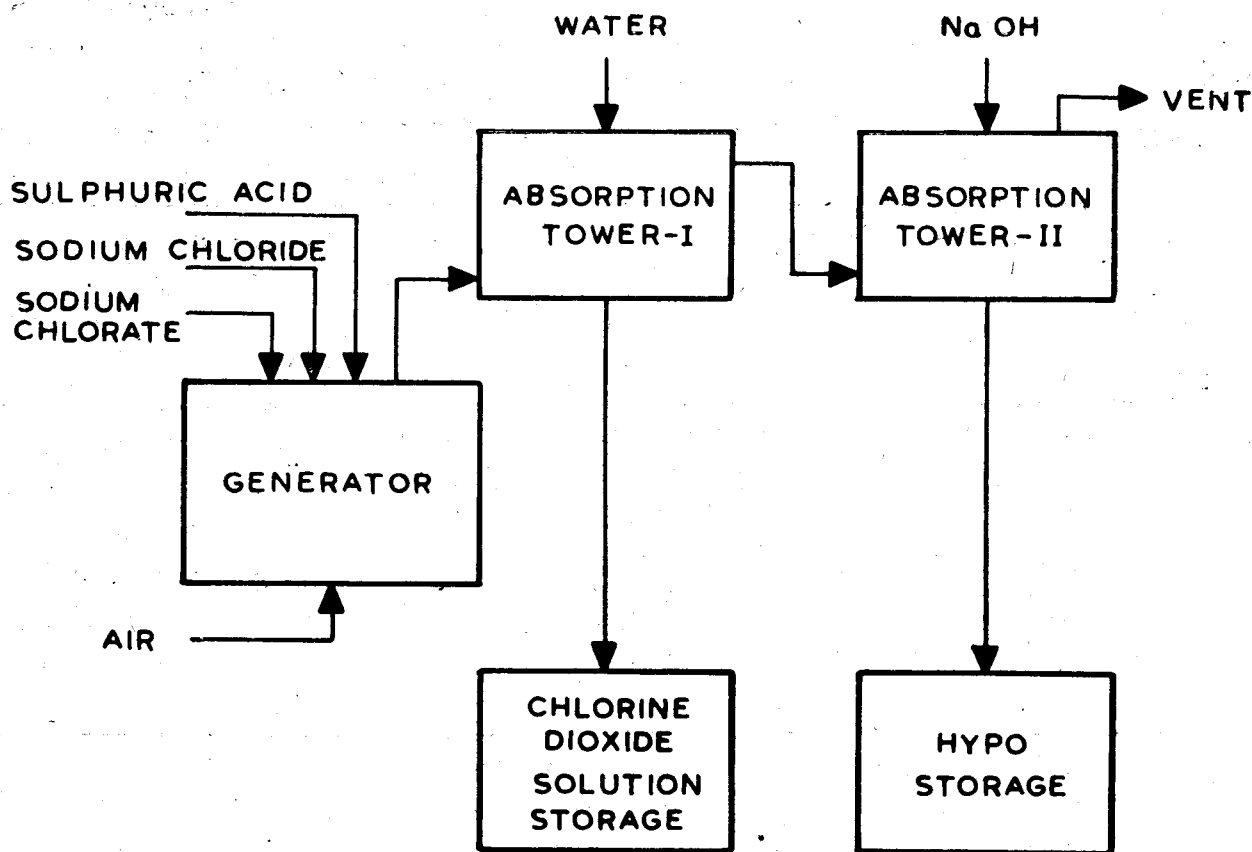
$$NaClO_3 + NaCl + 2H_2SO_4 \rightarrow ClO_2 + \tfrac{1}{2}Cl_2 + 2NaHSO + H_2O$$

75

WATER   Na OH

                                    → VENT

SULPHURIC ACID

SODIUM CHLORIDE

SODIUM
CHLORATE

| ABSORPTION TOWER-I | ABSORPTION TOWER-II |

GENERATOR

AIR

| CHLORINE DIOXIDE SOLUTION STORAGE | HYPO STORAGE |

REACTION : $NaClO_3 + NaCl + H_2SO_4 \longrightarrow ClO_2 + \frac{1}{2}Cl_2 + Na_2SO_4 + H_2O$

FIG·1· R_2 PROCESS

The conventional R_2 process has been modified to R_3 (Fig. 2) ([11],[13],[24],[25]), R_2H([25]), R_4 ([26],[27]), R_5 and R_6 (Fig. 3) ([28],[32]) and R_7 (Fig. 4) ([33]) processes in which chlorine dioxide is produced with reduction in either of the product chlorine saltcake and sulphuric acid in the effluent. ERCO's R_3 and other modified processes R_3H through R_7 have been discussed by Swindells et al.[95] and Fredette[33], R_7 process reduces the by product chlorine by 80-90% and reduces salt cake by 30-40%[33]. The newer processes retain the high efficiency, concentrated bleach solutions and effluent free features and utilise hydrochloric acid (alone or a mixed with sulphuric acid)and sulphur dioxide and differ only in the nature of byproducts formed.

A summary of ERCO's R_2, R_3, R_5, R_6, R_7, Mathieson and solvay processes is presented in presented in

Table III showing efficiency, raw materials requirements and by product per kg of ClO_2 produced.

MATHIESON PROCESS([10], [12], [13], [24], [34])

In this process (Fig. 5), So_2 is used as reducing agent and continuous reduction of sodium chlorate in solutions of low chlorate and high sulphuric acid concentrations takes place. Sodium chlorate, sulphuric acid, SO_2 and are added continuously in a corrosion resistance reactor, following reaction takes place

$SO_2 + Cl_2 + H_2O \rightarrow H_2SO_4 + HCL$
$2NaClO_3 + 2HCl + H_2SO_4 \rightarrow 2ClO_2 + Na_2SO_4 + Cl_2 + H_2O$
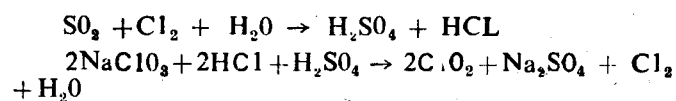
SOLVAY PROCESS([11],[21],[34],[35],[36])

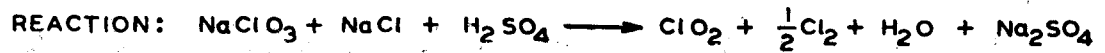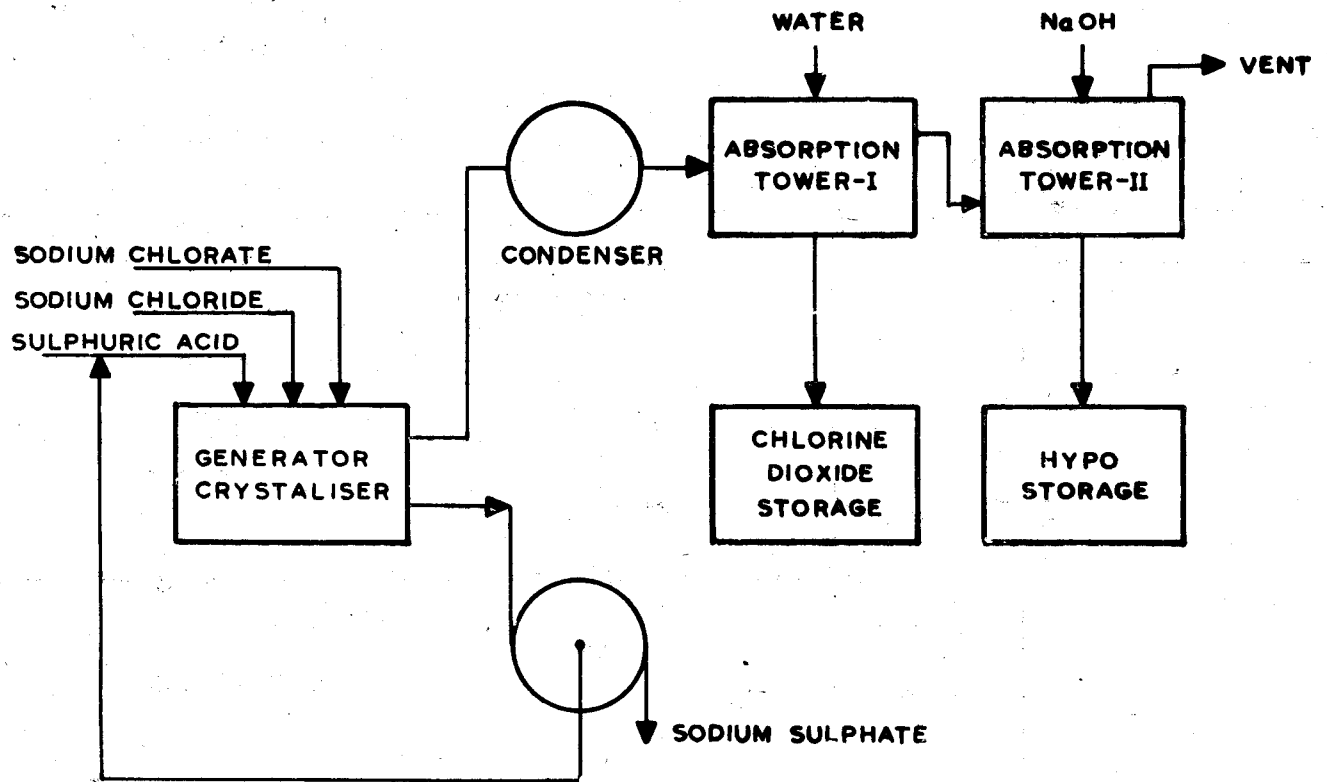In this process (Fig, 6), methanol is used to reduce sodium chlorate in pressence of sulphuric acid. Main

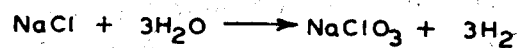REACTION: $NaClO_3 + NaCl + H_2SO_4 \longrightarrow ClO_2 + \frac{1}{2}Cl_2 + H_2O + Na_2SO_4$

FIG. 2. R-3 PROCESS.

REACTION : $NaClO_3 + 2HCl \longrightarrow ClO_2 + \frac{1}{2}Cl_2 + H_2O + NaCl$

$\frac{1}{2}Cl_2 + \frac{1}{2}Cl_2 \text{ (PURCHASE) } + H_2 \longrightarrow 2HCl$

$NaCl + 3H_2O \longrightarrow NaClO_3 + 3H_2$

FIG.3. R_6 PROCESS

REACTIONS:

$$NaClO_3 + HCl + \frac{1}{2}H_2SO_4 \longrightarrow ClO_2 + \frac{1}{2}Cl_2 + \frac{1}{2}Na_2SO_4$$

$$\frac{1}{2}Cl_2 + \frac{1}{2}SO_2 + H_2O \longrightarrow \frac{1}{2}H_2SO_4 + HCl$$

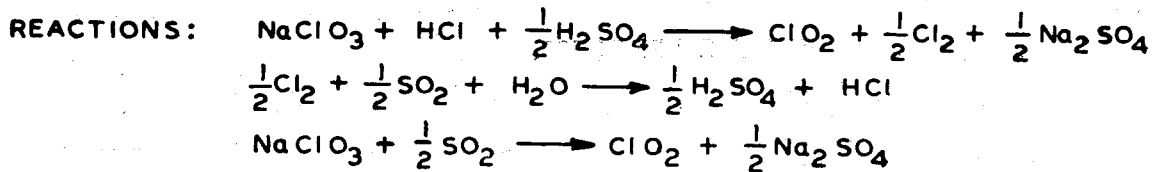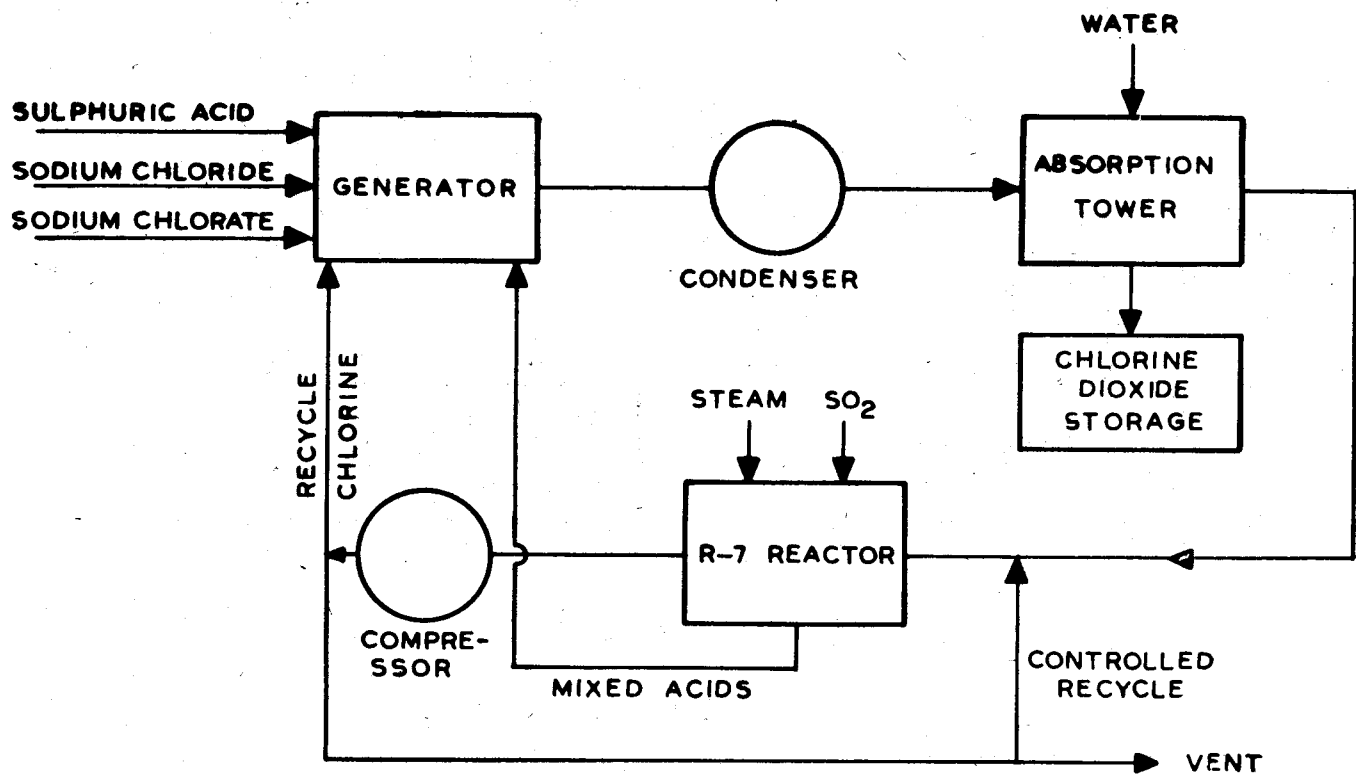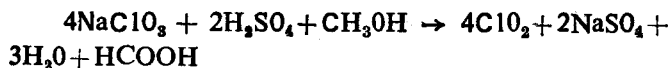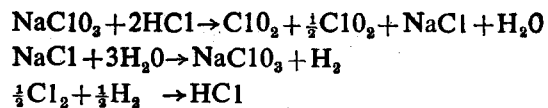$$NaClO_3 + \frac{1}{2}SO_2 \longrightarrow ClO_2 + \frac{1}{2}Na_2SO_4$$
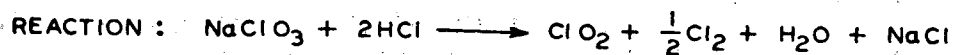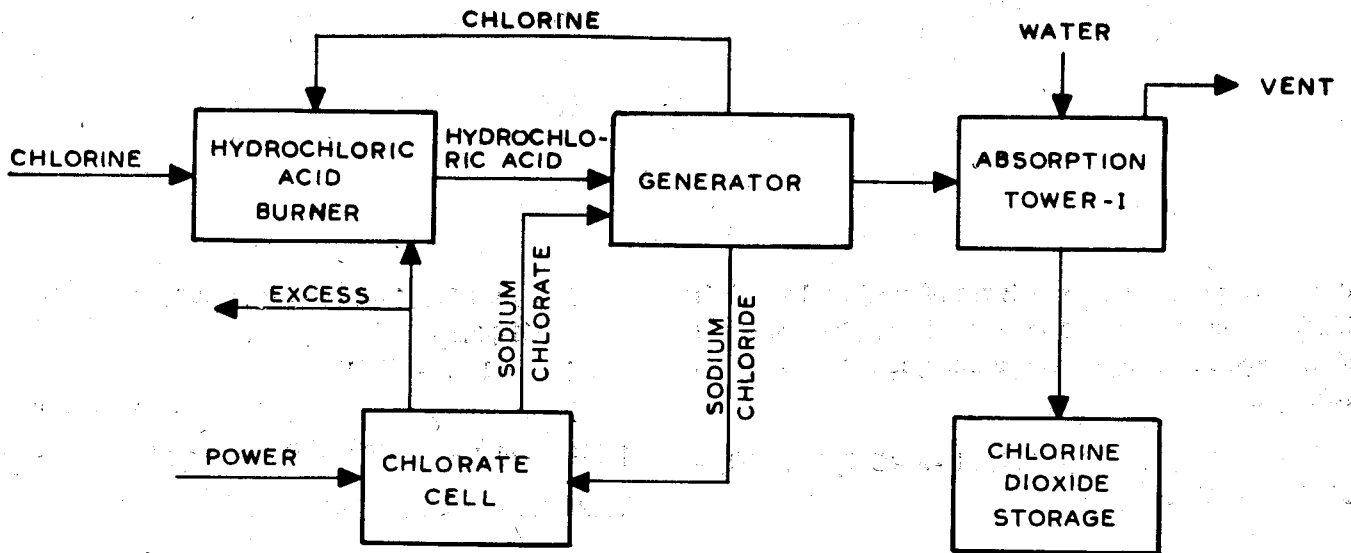
FIG. 4. R-7 PROCESS

disadvantage of this process is use of methanol which is likely to stimulate explosive conditions, the reaction is slower and needs higher temperature, following reaction takes place

$$4NaClO_3 + 2H_2SO_4 + CH_3OH \rightarrow 4ClO_2 + 2NaSO_4 + 3H_2O + HCOOH$$

DAY KASTING PROCESS([10], [21], [37], [38])

In this process (Fig. 7) reduction of of sodium chlorate takes place in psesence of hydrochloric acid. The spent liquor containing NaCl is recycled for chlorate electrolysis. Following reaction takes place

$$NaClO_3 + 2HCl \rightarrow ClO_2 + \tfrac{1}{2}ClO_2 + NaCl + H_2O$$
$$NaCl + 3H_2O \rightarrow NaClO_3 + H_2$$
$$\tfrac{1}{2}Cl_2 + \tfrac{1}{2}H_2 \rightarrow HCl$$

Investment in this process is high as chlorine dioxide preparation is combined with chlorate production.

PERSON PROCESS([34], [39])

In this process chromic sulphate which is formed by reaction of chromic acid with SO_2 is used to reduce sodium chlorate. Following reaction takes place
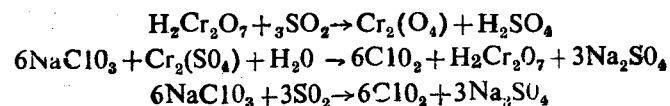
$$H_2Cr_2O_7 + 3SO_2 \rightarrow Cr_2(O_4) + H_2SO_4$$
$$6NaClO_3 + Cr_2(SO_4) + H_2O \rightarrow 6ClO_2 + H_2Cr_2O_7 + 3Na_2SO_4$$
$$6NaClO_3 + 3SO_2 \rightarrow 6ClO_2 + 3Na_2SO_4$$

TABLE III :   RAW MATERIAL REQUIREMENT AND BY PRODUCT OF YARIOUS CHLORINE DIOXIDE GENERATION PROCESSES ([13],[53],[15],[25])

Process	Raw material kg per kg of chlorine dioxide						by products kg per kg of chlorine dioxide				Na_2SO_4 kg per ton of pulp		Efficiency
	$NaClO_2$	NaCl	A_2SO_4	SO_2	CH_3OH	HCL	Na_2SO_4	NaCl	H_2SO_4	Ol	2.75@	4.0%	
1	2	3	4	5	6	7	1	9	10	11	12	13	14
R_2	1.66	0.98	4.85	—	—	—	2.30	—	3.2	0.58	87.0	92.0	95
R_3	1.66	0.95	1.70	—	—	—	2 3	—	—	0.6	63.0	92.0	97
R_5	1.73	—	—	—	—	1.40	—	1.1	—	0.7	—	—	95
R_6	1.74	—	—	—	—	1.42	—	—	—	—	—	—	91
R_7	1.63	0.45	0.68	0.30	—	—	1.60	—	—	—	44.0	64 0	97
Mathieson process	1.80	—	1.55	0.65	—	—	1.30	—	1.70	—	36,0	52.0	84
Solvay process	1.81	—	2.90	—	0.21	—	1.30	—	1.70	—	36 0	52.0	—

REACTION $SO_2 + Cl_2 + H_2O \longrightarrow H_2SO_4 + HCl$

$2NaClO_3 + 2HCl + H_2SO_4 \longrightarrow 2ClO_2 + Na_2SO_4 + Cl_2 + H_2O$

FIG. 5.   MATHIESON PROCESS.

WATER

VENT

ABSORPTION
TOWER

SODIUM CHLORATE

METHANOL

SULPHURIC ACID

GENERATOR
NO·1

GENERATOR
NO·2

CHLORINE
DIOXIDE
STORAGE

AIR

REACTION: $4NaClO_3 + 2H_2SO_4 + CH_3OH \longrightarrow 4ClO_2 + 2Na_2SO_4 + 3H_2O + HCOOH$

FIG·6· SOLVAY PROCESS

ABSORP-
TION
TOWER

WATER

ELECTRO
LYSIS
CELL

AIR

I

II

III

IV

V

VI

STEAM

STEAM

SODIUM CHLORATE

HYDROCHLORIC ACID

CHLORINE
DIOXIDE
STORAGE

GENERATORS

STORAGE TANKS

REACTIONS :

$NaClO_3 + 2HCl \longrightarrow ClO_2 + \frac{1}{2}Cl_2 + NaCl + H_2O$

$NaCl + 3H_2O \longrightarrow NaClO_3 + H_2$

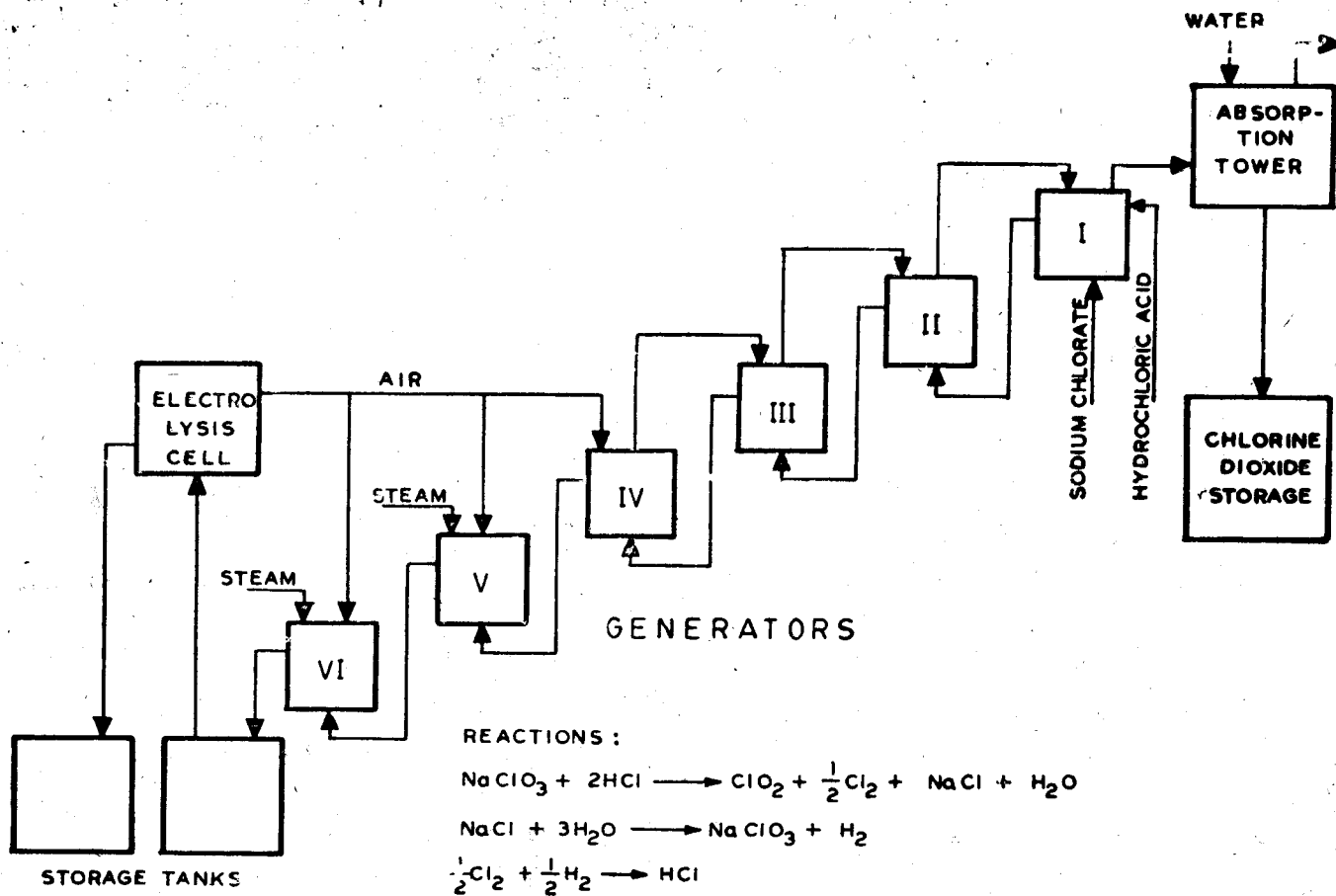$\frac{1}{2}Cl_2 + \frac{1}{2}H_2 \longrightarrow HCl$
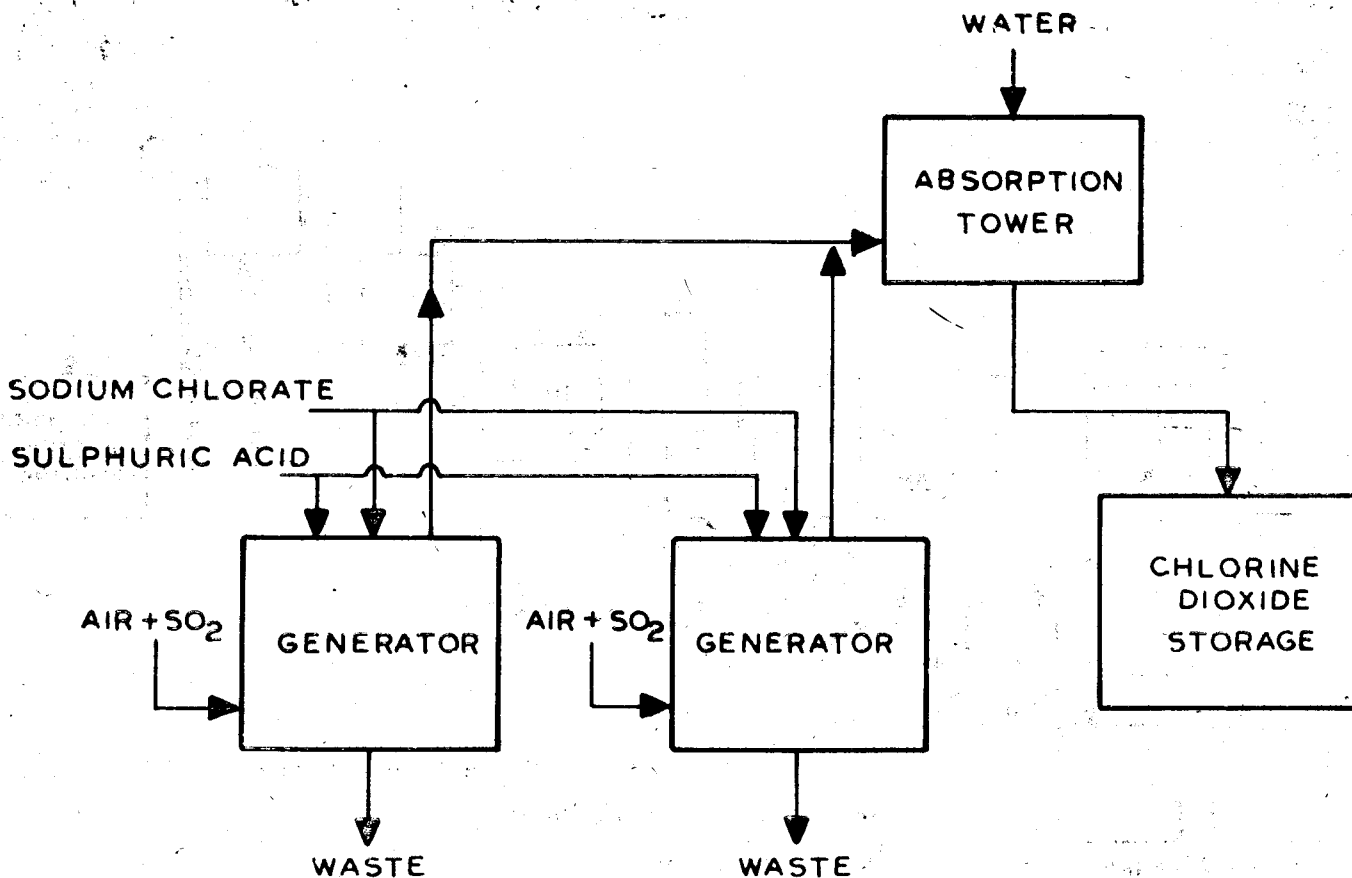
FIG. 7. DAY-KESTING PROCESS

FIG 8. HOLST PROCESS

HOLST PROCESS[40]

In this process (Fig. 8) sulphur dioxide, sodium chlorate and sulphuric acid are reacted batchwise to produce chlorine dioxide. Capital investment and maintenance cost is low.

For many years Solvay, Mathieson R_2 and other processes were the main source for chlorine dioxide generation, however, R_3 and other modified ERCO processes have replaced these older technologies. A major incentive for change has been due to marked reduction in the amount of by product saltcake, elimination of an acidic effluent and ability to increase chlorine dioxide solution strength while maintaining the efficiencies of process. A comparison of various chlorine dioxide manufacturing process is given in Table III([12],[13],[25])

MECHANISM OF CHLORINE DIOXIDE BLEACHING

The reation involved in chlorine dioxide bleaching is of complex nature. Chlorine dioxide reacts with water leading to a group of reaction products. The

relative amounts of the products and the speed of their formation depend largely on temperature and pH[21],

Chlorine dioxide reacts with water forming chlorate and chlorite ions

$$2ClO_2 + H_2O \rightarrow HClO_3 + HClO_2 \qquad (i)$$
$$6ClO_2 + 3H_2O \rightarrow 5HClO_3 + HCl \qquad (ii)$$
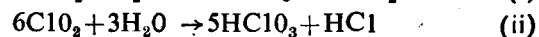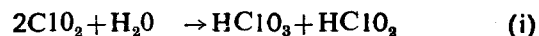
According to Virkola[11] reaction (i) and (ii) are catalysed by chlorine and further that chlorine catalyess decomposition of chlorine dioxide in solution according to followiog reaction

$$2ClO_2 \rightarrow Cl_2 + 2O_2 \qquad (iii)$$

Chlorine dioxide reacts readily with unsaturated compounds that have no carboxyl groups and with phenols and most of the ethers. Lignin is oxidiscd by chlorine dioxide and made water soluble, chlorous acid hypochlorous acid are formed[41].
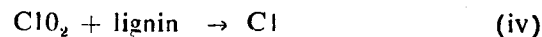
$$ClO_2 + lignin \rightarrow Cl \qquad (iv)$$
$$ClO_2 + lignin \rightarrow HClO_2 \qquad (v)$$
$$HClO_2 + lignin \rightarrow HOCl \qquad (vi)$$
$$HOCl + lignin \rightarrow Cl \qquad (vii)$$

82

TABLE IV : BLEACHING CONDITION IN CHLORINE DIOXIDE BLEACHING

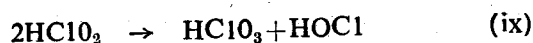| Parameters	C	E	D	E	D	H+
Chemicals%	5—7	3—4	0.6—1.0++	0.5	0.3—0.5	1.0
Consistency%	3.5	10—12	11—12	11—12	11—12	11—12
Temperature, °C	20—30	65—70	70	65—70	70	30 40
Time in min	30—40	120	180	120	180	180
pH	2—3	11	3.5—4.0	11	5.6	9.5—10

+   when used after first caustic extraction stage.

++   amount of ClO_2 varies depending on bleaching sequence.

Chlorine dioxide does not react at significant rates with saturated aliphatic groups such as alcohols, amines, croboxylic acid, nitrites, amides, etc. Following reaction was reported by Paulson[43].

$$5ClO_2 + lignin \rightarrow 2ClO_3 + 3Cl \qquad (viii)$$
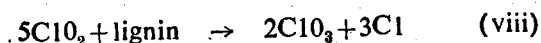
Chlorous acid, $HClO_2$ reacts with itself or at higher pH with chlorite ion

$$2HClO_2 \rightarrow HClO_3 + HOCl \qquad (ix)$$

Strumila and Rapson[44] have shown that most important role of hypochlorous acid is regeneration of chlorine dioxide from chlorous acid during the reaction of chlorine dioxide with acetovanillone

$$2HClO_2 + HOCl \rightarrow 2ClO_2 + H_2O + HCl \quad (x)$$

The rate of chlorine dioxide bleaching increases with increasing pH but consumption of chlorine dioxide by pulp to achieve a constant bleaching result is independent of the reaction pH[45].

The carbohydrates in rhe pulp are not attacked by chlorine dioxide to any noticeable degree under the normal bleaching conditions. The optimum pH for chlorine dioxide bleaching is 4.5-6.0. Adjustment of pH controls the side reactions in bleaching which can be foliowed by the formation of chlorite and chlorate.

Phenolic substances react rapidly with chlorine dioxide, but the reaction between non phenolic compounds and chlorine dioxide is comparatively slow. Chlorine dioxide attacks phenolic groups in the lignin during first part of bleaching[33].

Wartiovaara[46] in his recent work proposed a new type of reaction mechanism on the basis of bleaehing experiments, reaction kinetics and information in the literature. He showed that effective bleaching depends chiefly on the conditions immediately after mixing of chlorine dioxide. At this point the optimum amount of chlorine dioxide is decomposed by alkali to chlorite and peroxochlorous acid. The chlorite anion is then regenerated to chlorine dioxide by the monochlormonoxide produced by the bleaching reactions.

The rate of reaction in chlorine dioxide bleaching increases significantly in the presence of of ultraviolet light, however, the pulp brightness at a given consumption of chlorine dioxide is reduced[47].

Chlorine dioxide from all the generating processes contains some amount of elemental chlorine amount of which depends upon generator efficiency, operating pressure and conditions in absorption tower, however, no adverse affect of moderate amount of chlorine in chlorine dioxide on bleaching efficiency throughout a wide range of pulp quality, pH and ratio of applied chlorine removide to pulp has been observed[42].

CHLORINE DIOXIDE SUBSTITUTION IN CHLORINATION STAGE

Substitution of chlorine dioxide in chlorination stage to rmprove bleaching efficiency in respect of pulp quality and effluen load, has received much attention in the recent years and extensive work has been carried out by various workers and a review of available literature as chlorine dioxide substitution in the chlorination stage has been presented by kutney et at.[48]. Optimum pulp quality, lower consumption of oxidising chemicals and sodium hydroxide is obtained with low chlorine dioxide substitution. High chlorine dioxide substitution has no advantage over low chlorine dioxide substitution so far pulp yield, shive and dirt removal, physical strength, total organic content and chlorinated phenolics content is concerned, however, high substitution has marginal advantage in pulp delignification, chemical consumption, COD and toxicity[48]. The available literature confirm that use of 10% chlorine

dioxide substitution produces similar pulp quality to 50% or substitution. High substitution does not reduce BOD and toxicity, however, colour decreases[49]. Reeve and Rapson[42] lfound than chlorine dioxide solution containing 7.5% chlorine as well as 100% chlorine diox de behave similarly in bleaching efficieney and preserving viscosity throughout a wide range of pulp quality, pH and chemical does. Histed[50] observed that by addition of HCl and ClO_2 (0 2% on pulp) during chlorination stage viscosity loss at high chlorination levels and temperatures can be minimised. Formation of organically bound chlorine (TOCl) low molecular chlorinated substances (OCl-ether) decreases linearly with increasing chlorine dioxide substitution from 10% to 90%([51-53]). In full-scale mill trial, Peter Axegard([54,55]) showed that formation of organically bound chlorine, low molecular chlorinated substances and chlorinated acttic acids, chlorinated phenolic compounds decreased linearly with decreased chlorine consumption. No significant effect on pulp quality, LOD, COD and colour was observed.

VARIABLES IN CHLORINE DIOXIDE BLEACHING

The variables which play important role in chlorine dioxide bleaching are ƒH temperatuıe, consistency and time.

Hydrogen Ion Concentration :

The pH has been found to be an important variable affecting the effectiveness of both prebleaching and final bleaching with chlorine dioxide([58-62]). Chlorine dioxide has been found effective in the range of 2 to 7. As pH increases the reaction of chlorine dioxide with water is faster and pH above 7 the cellulose is attacked resulting in lower viscosity The attack on cellulose is negligible at lower PH however, below pH 3 viscosity is lowered due to hydrolosis of carbohydrate. Optimumı pH for effective cnlorine dioxide bleaching is 4. 5-6. Control of pH in the first stage is more important than in second stage of bleaching.

Temperature

The optimum temperature for chlorine dioxide bleaching is 70°C. Reaction is faster at lower temperature in the beginning of reaction when lignin content is high, but reaction is slow at latter stage when lignin content is low and higher temperature is needed to achieve maximum brightness. At temperature above 70°C, the reaction is accelerated quickly and causes brightness loss and fibre weakening.

Consistency :

There is insignificant effect of consistency on the efficiency of chlorine dioxide bleaching. However, medium consistency is maintained as higher heating cost will be there in case of low consistency and too high consistency will lead to mechanical problem in pumping high eonsistency pulp. The optimum consistency being maintained is 11-12%.

Time :

The consumption of chlorine dioxide by pulp on time basis follows the asymptotic curve being very fast initially and become slower and slower as the driving forces diminish[18], optimum time is 3 hrs. Higher retention time causes colour reversion.

COMMON BLEACHING SEQUENCES USED IN CHLORINE DIOXIDE BLEAHING

To obtain high degree of pulp brightness with minimum fibre degradation and colour stablity commonly used bleaching sequences are CEDED, CEHDED and CEHD, however, CEDED sequence is most widely used in advanced countries([12,14,21]). The most common four stage sequence is CEHD. About two thirds of the Canadian kraft mills are almost evenly split between the two bleaching sequences-CEDED and CEHDED[63]. Consumption of chlorine dioxide in CEDED, CEHDED and CEHD are about 16.78 Kg, 6.80 Kg. and 6 80 Kg/ton of pulp[63]. Amount of ClO_2 being used in 1st chlorine dioxide stage, is about 82-85% in CEDED and 77% in CEHDED. The optimum condition for chlorine dioxide multistage bleaching in CEDED sequence is given in Table IV. For a 100 TPD pulp mill chlorine dioxide required will be about 0.7.16 tons/day depending upon the sequence and Kappa No. of pulp.

EQUIPMENT AND MATERIAL OF CONSTRUCTION CHLORINE DIOIDE GENRATION AND BLEACHING

As chiorine dioxlde is highly corrosive and explosive in certain conditions, choice of proper materlal of construction for various equipment used in chlorine dioxide generation and bleaching is very imporjant. Chlorine dioxide is even corrosive to SS 304 and SS 316. Majority of the bleaching equipment and components including those used in chlorine dioxide generation require special material of construction and as higher capital investment is involved, utilixation of chlorine dioxide is restricted and majority of papcr mills in India are not having chlorinc dioxide bleaching.

84

Titanium is very resistant to chlorine dioxide and use of this metal has increased considerably. Other materials suitable for chlorine are SS 317L and Hastelloy C. Rubber is unsuitable for chlorine dioxide service as it is highly explosive in contact of rubber and even gaskets and other accessories made of rubber cannot be used. Teflon impregnated asbestos has been found satisfactory. FRP using Hetron 197 resin, steel shells lined with PVC, acid proof brick tiles or lead and titanium are the materials used for chlorine dioxide generators[63][64]. Unplasticised PVC[40] has also been found satisfactory for chlorine dioxide generator. For piping FRP, titanium, saran lined or glass lined steel has been found satisfactory. Absorption towers are made of PVC, stoneware, pordelain or steel that is lined with glass or brick and same type of materials used for storage of chlorine dioxide solutions.

In case of heater mixer for heating pulp prior to bleaching SS 304 is a satisfactory material. In chemical mixer titanium or titanium lined shell and Hastelloy crotors are being used. Plumb bob distribution, tower circulators and dilution nozzles are of Hastelloy C or SS 317 L. For bleach plant washer and conveyor repupler SS 317 has been commonly used[12-14].

Although vast majority of chlorine dioxide washers have been made of 317 SS, but in close bleach plant system haviug more and more recycle water system, 317 SS is no longer adequate for long term service[66] and many mills are using higher alloy stainless steels, nickel based alloys and titanium for better corrosion resistance[67]. 6% Mo stainless Avesta 2545 Mo, Ni-based Hastelloy G and C-276 and titanium are best suited in high y corrosive washer environments[64]. Anodic protection technique has been found successful in increasing the resistance to corrosion[55]. The washer life can be greatly extended if the washer is cathodically polarised from the oxidising potentials imposed by residual oxiant to a more negative passive potential by use of rectifier and a platinised anode mounted in the washer vat[66] FRP has been successfully used for pipe line, washer sprays, washerhood. ducts and fans lining. Synthetic wire mesh also being used for washers.

The washers and auxiliary equipment can be protected from corrosion by adding SO_2 or NaOH after chlorine dioxide bleaching as 25 ppm ClO_2 has been identified as the level above which corrosion reactions are driven by residual oxidants. Following reactions takes place

$$2ClO_2 + 5SO_2 + 6H_2O \rightarrow 2HCl + 5H_2SO_4$$
$$2ClO_2 + 2NaOH \rightarrow NaClO_3 + NaClO_2 + H_2O$$
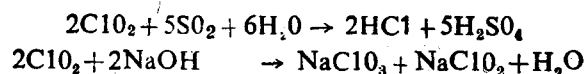
The amount of acid formed by reaction of SO_2 has a negligible effect on washer corrosion and sufficient SO_2 should be added to maintain a trace of residual SO_2 at all times, however, higher SO_2 percentage may also cause corrosion. Normally, the pH is raised to 5 or 6 by addition of NaOH to the pulp leaving tower to keeping residual ClO_2 below 25 ppm.

CONCLUSION

Although the initial investment in multistage bleaching using chlorine dioxide is high in comparison to conventional CEH or CEHH system commonly used by majority of pulp mills in india as major equipment and auxiliaries usd are made of special material 317 SS, titanium, hastelloy C and other higher alloy stainless steel, still use of chlorine dioxide bleaching could be a profitable proposition as it will result in improved pulp quality with higher brightness and colour stability, better yield due to less degradation and improved effluentnt quality. The improved quality of pulp with higher strength will also facilitate, the utilisation of more short fibre pulp and waste paper. With recent advancement and improvement in the chlorine dioxide generation technology and manufacturing facilities available in india use of chlorine dioxide is going to be very popular.

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