Alkaline Peroxide Bleaching of Chemical Pulps And Metal Management Concepts

Raghuveer S.

ABSTRACT: The growing global environmental and market pressures for Elemental Chlorine free pulp and Total Chlorine free chemical pulps have resulted in an accelerated the use of oxygen based oxidising chemicals, including O_2, O_3, H_2O_2, peroxy acids in chemical pulp bleaching. Among these, hydrogen peroxide has established a key role in pulp bleaching strategies and sequences because of its ability, when necessary, to deliver low investment, cost effective bleaching performance, environmental benefits and fiber properties advantages. Therefore, in order to get an optimum performance from H_2O_2 stages, it is essential that the metal ion impurities, both the detrimental transition metal ions (mainly Fe, Mn and Cu) and the bothersome "hardness" ions (Ca, Mg and Al) are controlled in bleaching operations. To control these the metal management concepts are to be understood and adopted.

INTRODUCTION

The idea of using oxygen and related compounds such as hydrogen peroxide and ozone dates back to the early decades of this century. Hydrogen peroxide was the first among these which was applied commercially, namely in the bleaching of cotton fibers, and some what later in bleaching of mechanical and other high yield pulps (CTMP). In India more recently, it has been used in the bleaching of chemical pulps in the final stages to improve not only brightness, but also brightness stability. Lately, hydrogen peroxide has found increasing use of reinforcing oxygen delignification or alkali extraction, alone or in combination with oxygen.

Oxygen and Peroxide bleaching commercially implemented purely for environmental reasons, and has since then emerged as the most prominent alternative to chlorination. This has resulted in significant environmental benefits, such as substantial reduction in colour, BOD and formation of chloro-organics. The use of oxygen, alone or in combination with oxygen operoxide in reinforcing alkali extraction, results not only in enhanced lignin retained in the fibers towards subsequent treatment with chlorine dioxide. Consequently, less chlorine dioxide in the following stages, respectively, less chlorine in the preceding stage, is required to achieve the desired level delignification and brightness. Thus, substantial reduction in the generation of chloro-organics. Due to the presence of various heavy metals in the raw materials, process water, bamboo and wood pulps, the transition metal ions such as Mn, Fe and Cu are strong hydrogen peroxide decomposition catalysts, and cause wasteful decomposition to oxygen gas while at the same time generating the highly oxidising free radicals such as OH that can degrade cellulose and cause darkening reactions. Hence, there need to be metal management while doing oxygen and peroxide bleachings.

ITC-Bhadrachalam Paperboards LTD.
SARAPAKA - 507 128,
Distt. Khammam (A.P.)

UNDERSTANDING THE OXYGEN BLEACHING MECHANISM AND EFFECT OF METAL IONS

Reaction mechanism involving oxygen and lignin is not yet fully established, extensive research has been carried out to understand the basic chemistry of oxygen delignification and comprehensive summaries can be found in the literature (1-3). The reaction of oxygen with lignin is as follows. Two unpaired electrons are present in an oxygen molecule. So, it can react easily but selectively with organic molecules. In these reactions, oxygen itself is reduced to water (HOH) or alcohol (ROH). Ionised phenolate or enolated species in the lignin can be initially attacked by oxygen. Various intermediates such as, peroxides, peroxy, hydroxy and organic radicals are formed by radical chain reactions. Hydrogen Peroxide is formed as a by-product. High molecular weight lignin is oxidised to low molecular weight acid (i.e. degradation of lignin occurs) which dissolve in alkaline medium. The relations of oxygen with lignin include inhibition of a phenolic hydroxyl group in the lignin to form a phenoate ion. This ion reacts with oxygen to form a reactive intermediate called a phenoxy radical. This intermediate then undergoes fragmentation whereby the polymer structure of lignin breaks up into fragments which are fairly soluble. Also hydrogen peroxide can further react with both the lignin and the carbohydrate portion of the pulp (4).

The intermediate radicals formed are non-selective oxidising agents. Hence, they can attack carbohydrates as well as lignin. Carbohydrate reactions occur mainly by the cleavage of chain like cellulose molecules. This cleavage of cellulose chain is belived to start with the formation of Carbonyl groups in the chain thereby decreasing the chain length. Consequently, this results in lowering the pulp strength which is characterised by decrease in viscosity of the pulp. Such cellulose degradation in the major factor that limits the extent of delignification than can be achieved in the oxygen stage.

Various metal ions are almost always present in bamboo and wood pulps, beleaching chemicals and other raw materials and process waters used in pulp mills. Among these, the ubiquitous transition metal ions such as Mn, Fe and Cu are strong H_2O_2 decomposition catalysts, and cause the formation highly energetic and non-selective free radical intermediates such as OH, OOH that degrade cellulose. Cations such as Mg, Ca, Al, while being generally innocuous in alkaline peroxide oxidation, can seriously deplete valueable chelating agents or silicates used to control transition metal ions, In an extreme situation, these cations can form insoluble resinates or salts of organic acids (e.g. oxalates), carbonates or silicates during bleaching and cause particulate contamination in the paper, deposits on the equipment, wires and discharge pipes and scales in heat exchangers and boilers.

METAL MANAGEMENT

The development of chlorine free bleaching employing oxygen, hydrogen peroxides (Peroxy compounds in general) and Ozone constitute milestones in bleaching technology. Planned or desired conversions to Elemental chlorine free and particularly Total Chlorine Free bleaching also means that the higher acidic stages such as C, C/D will be replaced by lower acidity-higher pH - sequences (e.g. high to 100% D) or alkaline Oxygen or Peroxide stages. This will result in less efficient purging of detrimental metal ions from the system and unless optimally managed will result loss of efficiencies in the oxygen and hydrogen peroxide reinforced extractions and H_2O_2 stages (5).

The detrimental effect of transition metal ions is not limited to H_2O_2, and other oxygen based bleaching agents are similarly susceptible to decomposition or damaging activation. Thus it has been shown that in oxygen bleaching of pulps, peroxide radical intermediates and transition metal ions are involved in carbohydrate degradation and magnesium ions effectively deactivate the metal ions, and thereby stabilise peroxide intermediates and hinder carbohydrate degradation and magnesium ion effectively deactivate the metal ions, and thereby stabilize peroxide intermediates and hinder carbohydrate degradation.

The "Metal Management" concepts and strategies discussed in this paper are aimed at promoting a systematic, logical, non-empirical and broad approach to the sources, control, elimination and/ or deactivation of metal ions to make alkaline peroxide bleaching, and more broadly oxygen based bleaching, more efficient, selective and cost effective.

METAL MANAGEMENT STRATEGIES-1

* Analyse for metals in:

-- Bamboo and wood chips

-- Bleaching chemicals

-- Brown stock,

-- Fresh and recycle water

-- Recycle chemicals E.G. Sodium Sulphate and Caustic

-- Fiber before and after each stage

-- Pressates, Recycle streams

-- Downstream additives that may be present in recycle water.

-- Finished Fiber

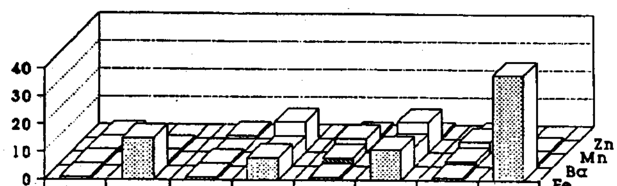
* Develop metal material balance around the system

* Improve raw material quality if necessary, possible or economical.

Tabl-1 shows typical metals profile in hard wood kraft mill and Table-2 shows another typical metal profile in pulp and paper mill. Table-3 shows Fe and Mn distribution in pulp and water.

TABLE NO. 1

METALS PROFILE
HW KRAFT MILL



	C-PULP	Pm-STK	SCREENING		Bs-WAT	Bs-BLP	Bs-WAT	NaOH
Zn	1	u	1	0	1	1	1	0
Mn	1	1	0	11	5	11	4	1
Ca	1	105	185	470	245	540	225	2
Na	620	275	46	200	255	125	145	571000
Mg	1	270	1	.60	42	205	34	1
Ba	1	1	1	6	3	7	2	1
Fe	1	15	1	8	1	11	1	38
Si	1	355	4	49	9	130	7	66

Zn, Cu, Ni, ALL (1

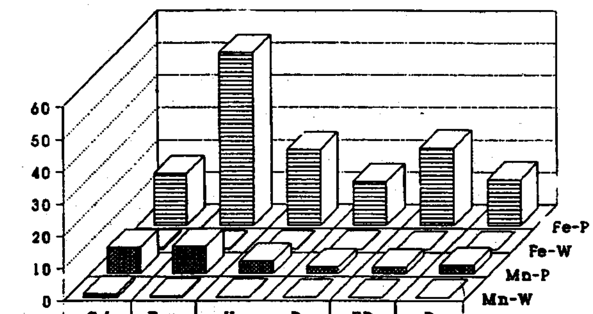
Table-2

Metal Content in pulp bleaching, lime and water

	PPM				
	Fe	Mn	Ni	CO	Cu
UNBLEACHED PULP	48	7	1	Nil	5
ALKALI EXTRACTED PULP	93	4	1	Nil	1
HYPO STAGE PULP	90	3	Nil	Nil	3
ClO_2 PULP	93	3	1	Nil	3
QUICK LIME					
PARTY NO.					
1.	2320	Nil	Nil	Nil	280
2.	3740	320	60	Nil	260
3.	4060	1200	40	Nil	260
4.	5740	40	--	Nil	300
WATER	Nil	Nil	Nil	Nil	Nil

TABLE NO. 3

Fe, Mn DISTRIBUTION IN PULP AND WATER



	Cd	Eop	H	D	EP	P
Fe-P	16.1	53.5	23.4	13.5	24	14.2
Fe-W	0.65	0.38	0.28	0.24	0.08	0.08
Mn-P	8.1	8.5	3.8	2.2	2.1	2.7
Mn-W	1.14	0.49	0.26	0.24	0.08	0.08

WATER(W): PULP(P): METALS STAY ON PULP

METAL MANAGEMENT STRATEGIES-2:

* Pretreat before bleaching

-- Mineral acid, pH 2-4 for high iron

-- Mineral acid + chelant, pH 2-4 for high iron

-- Chelant, pH 4-6, for Mn, Cu, Ca, Mg etc.

* Device ways to purge chelated or acid soluble metal ions from the system.

-- Better washing, Dewatering

-- Purging front and concentrated metal streams.

* Stabilise during bleaching:

-- Chelants, Silicate, Mg^{++}

-- Amounts of chelants, silicates would be sufficient for all Bi and Tri valent metal ions.

Table - 4 Shows the metal removal by acid chelation.

Table-4

Metals removal by acid chelation

METAL (PPM)	KRAFT BROWN STOCK	pH_2 (H_2SO_4)+0.5% DTPA 65 C, 30 MIN., 10% CONS.
Mn	29	1
Fe	10	2
Cu	2	<1
Ni	<1	<1
Cr	<1	<1
Si	250	20
Na	5200	49
Mg	590	17
Ca	1900	52
Al	24	3

METAL MANAGEMENT STRATEGIES-3:

* Optimise bleaching chemistry
  - Time, temp., pH, consistency
  - Peroxide reuse or recycle
  - Reduce temp. or pH if Iron removal is difficult.
  - Improved flexibility and benefit with good metal management.
* Identify sources of corrosion in the bleaching loop.

MATERIAL OF CONSTRUCTION FOR ALKALINE PEROXIDE BLEACHING

The corrosion problem in pulp and paper industry is very serious and various forms of corrosion in some or other way are experienced in almost all sections. The bleaching equipments are also exposed to variety of corrosive chemicals at each stage exposed to variety of corrosive chemicals at each stage and paper material of construction to combat corrosion is very important. The recommended material of construction especially at alkaline peroxide stage is as follows (6);

	Equipment and Accessories	Material
1.	Chemical Mixer	SS 316
2.	Towershell/lining	Mildsteel/ Tile
3.	Nozzles	SS 316
4.	Washer vat	SS 304, concrete Tile lined.
5.	Drum	SS 304 L
6.	Piping	SS 304 L
7.	Heater Mixer	SS 304
8.	Pumps	SS316

CONCLUSION

Since there is a need for pulp and paper industry to adopt clean technology, there is going to be increased utilisation of oxygen and peroxide in pulp bleaching, it is important to know its optional utilisation and prevention from transition metal decomposition.

Considerable knowledge exists in the literature on the nature and the negative influence of transition metal ions in peroxide bleaching. The use of acids, silicates, chelating agents and Mg ions to control Fe, Mn and Cu has been well investigated. In its push towards elemental chlorine free and totally chlorine free bleaching technologies, the pulp and paper industry is recycling more and more on peroxide and oxygen chemicals for pulp bleaching. Significant improvement in H_2O_2 efficiency may be achieved by a sound metal management that includes pinpointing the source of metals, defining the metals material balance in bleach sequences and applying the most cost effective chemistry or engineering to control, eliminate or deactive the undesirable ions.

REFERENCES

1. R.P. Singh, The Bleaching of Pulp, Tappi Press 3rd Ed. (1979)
2. K. Gratzl, J. Gratzl and P. Claus, Adv. Chem. Ser. 59 157 (1966)
3. O. Samuelson and L. Stolpe, Tappi 52 1709 (1969)
4. J.S. Gratzl, Chemistry of non-chlorine bleaching oxygen and Peroxides 1993. Workshop proceeding at NCSU, USA
5. Madhu D. Jayawant, Edward I. De Graw, Dupond Presentation at NCSU, USA 1993.
6. Kenneth W. Britt, Hand Book of Pulp and Paper Technology, 1984 Ed. 303.