

# Primer on Bleaching Recycled Fiber

*arthur.ragauskas@ipst.gatech.edu*



# *Bleaching Brightening vs. Delignification vs. Degradation*

- Brightening: Destruction/removal of chromophores  
Color/Fluorescence Dyes  
No/little yield loss
- Delignification: Removal of lignin
- Degradation: Reactions that result in yield loss

Degrading Bleaching Agents:  
Chlorine, chlorine dioxide, sodium hypochlorite,  
Oxygen and ozone  
Destroy phenols & C=C double bonds

Non-degrading Bleaching Agents:  
Hydrogen peroxide, sodium hydrosulfite, and  
Formamidine sulfinic acid (FAS), NaBH<sub>4</sub>  
Destroy carbonyl groups

# *Bleaching Abbreviations*

<b>Oxidizing Agents</b>	
C	Chlorine
H	Sodium Hypochlorite
O	Oxygen Bleaching
Z	Ozone Bleaching
P	Hydrogen Peroxide Bleaching
<b>Reducing Agents</b>	
Y	Sodium hydrosulfite (dithionite)
FAS	Formamidine sulfinic acid (thiourea dioxide)
DBI	Sodium hydrosulfite/sodium borohydride

Delignification Agents: C, H, D, O, Z

# *Reductive Bleaching*

**Brightens mechanical pulps**

**Minimal yield loss**

**Often decolorize dyes more effectively than oxidative bleaching**

**Can be combined with oxidative bleaching**

**Oxidative followed by reductive bleaching has less reversion**

# *Hydrosulfite (Dithionite) Reactions*

Principal active (reducing) species:  $S_2O_4^{2-}$  (Dithionite anion)

## **Helpful Reactions:**

Dissociation:  $S_2O_4^{2-} \leftrightarrow 2 SO_2^{\cdot -}$  (Sulfur dioxide radical ions)

Electron exchange:  $2 SO_2^{\cdot -} \rightarrow SO_2 + SO_3^{2-}$   
(Sulfur dioxide & Sulfoxylate dianion)

Bleaching:  $Pulp + Na_2S_2O_4 + H_2O \rightarrow$   
Bleached Pulp +  $2 NaHSO_3$

## **Decomposition Reactions:**

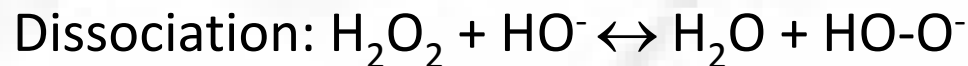
Aerobic:  $Na_2S_2O_4 + H_2O + O_2 \rightarrow NaHSO_3 + NaHSO_4$   
(Sodium bisulfite + Sodium bisulfate)

Anaerobic:  $2 Na_2S_2O_4 + H_2O \rightarrow Na_2S_2O_3 + 2 NaHSO_3$   
(Sodium thiosulfate + Sodium bisulfite)

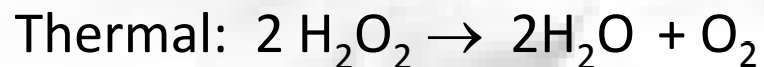
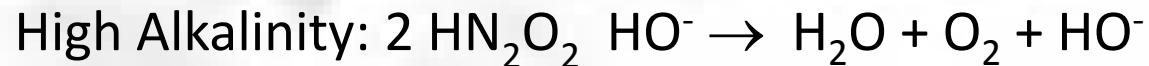
Iron-catalyzed:  $2 Fe^{3+} + S_2O_4^{2-} + H_2O \rightarrow 2 Fe^{2+} + 2 HSO_3^- + 2 H^+$   
(Bisulfite anion)

# *Hydrogen Peroxide Reactions*

## **Helpful Reactions:**



## **Decomposition Reactions:**







# Waste Paper Bleaching Conditions

Chemical	Charge/%	Csc/%	Rxn Time/h	Rxn Temp/C	pH
Cl <sub>2</sub> /NaOH	0.5 - 2.5	2-12	0.5 – 1.5	35 – 70°	9.5-11
H <sub>2</sub> O <sub>2</sub> /NaOH	1 – 3	10-30	0.5 – 4	60 -110°	9- 11
O <sub>2</sub> /NaOH	1-2	10-15	0.1 – 1	85-140°	10-11
O <sub>3</sub>	0.2-3	10-40	0.02-0.08	20-60°	2-10
Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub>	0.5-2	3-12	0.25-1.5	40-80°	5 – 8
NH <sub>2</sub> C(NH)SO <sub>2</sub> H NaOH	0.3-1	3-12	0.5-1.5	40-80°	8-11

A variety of bleaching sequences have been developed/explored  
 ZP, YP, Y(FAS), PY, (FAS)P, P(FAS), HH, CH, HC, YZP, ZPY, (FAS)ZP, PZY, PZP, PZ(FAS)  
 P<sub>HT</sub>Y , YP<sub>HT</sub>  
*- Need to be tailored for waste paper furnish*