Mechanism of Transition Metal Catalyzed Decomposition of Hydrogen Peroxide in Pulp Bleaching

Alkaline peroxide as a delignifying agent

- Used mainly in lignin retaining bleaching
  - bleaching of mechanical pulps
- Also in chlorine-free bleaching (TCF bleaching sequences)

Alkaline peroxide

- H_2O_2 is a nucleophilic bleaching agent (HOO^--anion)
- Reacts with chromophoric compounds
  - ***carbonyl or conjugated carbonyl structures***
- Hydroxyl radicals may also be formed (*see oxygen delignification)*
  - ***reactions with double bonds of lignin (radical reaction)***
- The formed structures have lower light absorption coefficient than the original structure

Metal catalyzed decomposition of hydrogen peroxide

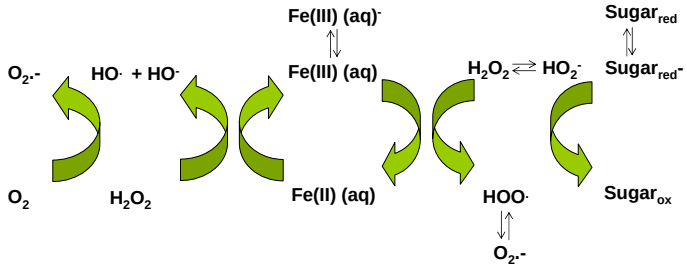
- Alkaline peroxide is decomposed during bleaching
  - Increased consumption of chemicals
  - Decreased selectivity
    - Formation of non-selective free radicals (O_2.- and HO·)
    - Depolymerization of carbohydrates
- *In addition to transition metal ions oxygen and reducing sugars are likely to participate the catalytic cycle of decomposition*

Removal of transition metals

- Harmful transition metals (Mn, Cu, Fe) are often removed before the alkaline peroxide bleaching:
  - Chelation step before the bleaching and
  - Addition of chelants and magnesium in the bleaching stage

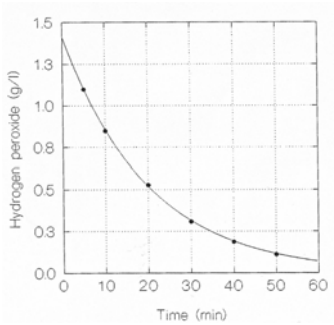
    Formation of inactive metal complexes

Mechanism of metal ion catalyzed decomposition of H_2O

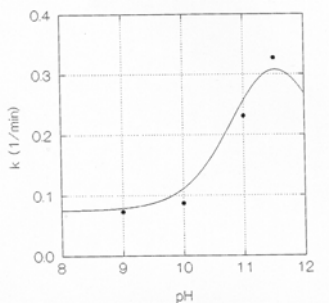


Decomposition of hydrogen peroxide

Decomposition of peroxide by ferrous/ferric ions at pH 10 at 80 ºC.



Reducing sugars

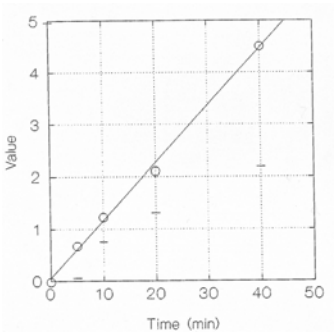


Effect of pH on the rate of decomposition of H_2O_2 by manganese ion in the presence of a reducing sugar (arabinose 2 g/l)

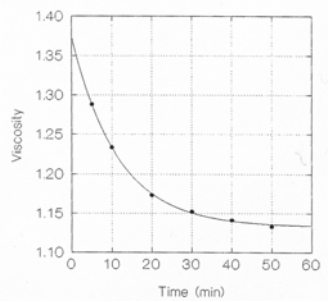
Presence of Oxygen

Kinetic expression for the cuprous / cupric ion catalyzed decomposition of H_2O_2 at pH 10 under oxygen pressure of 5.5 bar

Value = $\ln([H_2O_2]_0 / [H_2O_2]) + k_5[O_2](1/[H_2O_2]_0 - 1/[H_2O_2])/k_1$



Depolymerization of polysaccharides



Development of the viscosity of a dextran solution during ferrous / ferric ion catalyzed decomposition of H_2O_2 at pH 10 at 80 ºC

$\eta = \eta_0 - \Delta\eta_\infty(1-e^{-kt})$

Depolymerization of polysaccharides

Correlation between the decrease in viscosity of dextran and decomposition of H_2O_2 by ferrous / ferric ion at pH 10 at 80 ºC