

Full Length Research Paper

Stabilization of manganese (Mn)-induced peroxide decomposition

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Various ways were explored to reduce Mn-induced peroxide decomposition under conditions similar to industrial bleaching of mechanical pulps. It was found that hydrogen peroxide is more stable if Mn (II) or (III) are stabilized prior to peroxide addition. Sodium silicate/magnesium sulfate solution stabilized hydrogen peroxide in the presence of both Mn(II) and Mn(III), while diethylenetriamine pentaacetic acid (DTPA) effectively stabilized alkaline peroxide in the presence of Mn(II), but not Mn(III). Magnesium hydroxide/sodium silicate solution was not effective in stabilizing both Mn (II) and (III); however, microwave assisted sodium silicate-Mn complex modification resulted in complete peroxide stabilization of both Mn (II) and (III).

Key words: Manganese, peroxide decomposition, bleaching, stabilizers, chelant.

INTRODUCTION

Hydrogen peroxide (H₂O₂) is commonly used in the bleaching of mechanical pulps. However, under bleaching conditions, H₂O₂ is very unstable especially in the presence of transition metal ions. The decomposition of H₂O₂ leads to brightness loss, low fiber strength and increased bleaching costs among others. Manganese (Mn²⁺) ion has been found to be the most potent transition metal that decompose hydrogen peroxide, (Allison, 1983). To reduce the effects of transition metal ions during bleaching, stabilizers (sodium silicate and magnesium sulfate) and chelant (diethylenetriamine pentaacetic acid) are used (Singh, 1979).

Chelating agents, such as ethylenediaminetetraacetic acid (EDTA) and diethylenetriamine pentaacetic acid (DTPA), form stable and water-soluble complexes with transition metal ions. The transition metal complexes can then be removed from the pulp in the pressing and washing stage. Stabilizing chemicals, such as magnesium sulfate and sodium silicate form complexes with Mn²⁺

or Mn³⁺ ions. It is believed that, Mn²⁺ can be incorporated into the magnesium precipitate, and hence be protected from oxidation (Lapierre, 1995).

Also, a number of patents (Jameel, 1995; Lidén, 1997) and technical papers (Leonhardt et al., 1993; Raven, 1989) have appeared, describing the utilization of zeolites-based additives in the removal of transition metal ions before the peroxide bleaching stage. Recently, it has been reported that, during peroxide bleaching, PM process results in improved ISO brightness compared to the P process (He et al., 2003). The improved ISO brightness has been attributed to better peroxide stabilization. Another study found that, DTPA can completely stabilize Mn-induced peroxide decomposition when manganese is in (II) state, but not when it is in (III) state (Ni et al., 2000). Other workers (Wekesa and Ni, 2003) have also found that, MnO₂ is less potent to decompose hydrogen peroxide compared to Mn²⁺.

Also, it has been reported that, using a combination of stabilizers and chelants leads to higher improvement in brightness as compared to when either one of them is used (Finnegan, 1998). Since paper industry is important to any economy, new innovative ways need to be developed to reduce the bleaching costs. Therefore, the objective of the study was to evaluate the order of addition of Na₂SiO₃/MgSO₄, DTPA and either Mn²⁺ or

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Abbreviations: Mn, Manganese; DTPA, diethylenetriamine pentaacetic acid; EDTA, ethylenediaminetetraacetic acid.

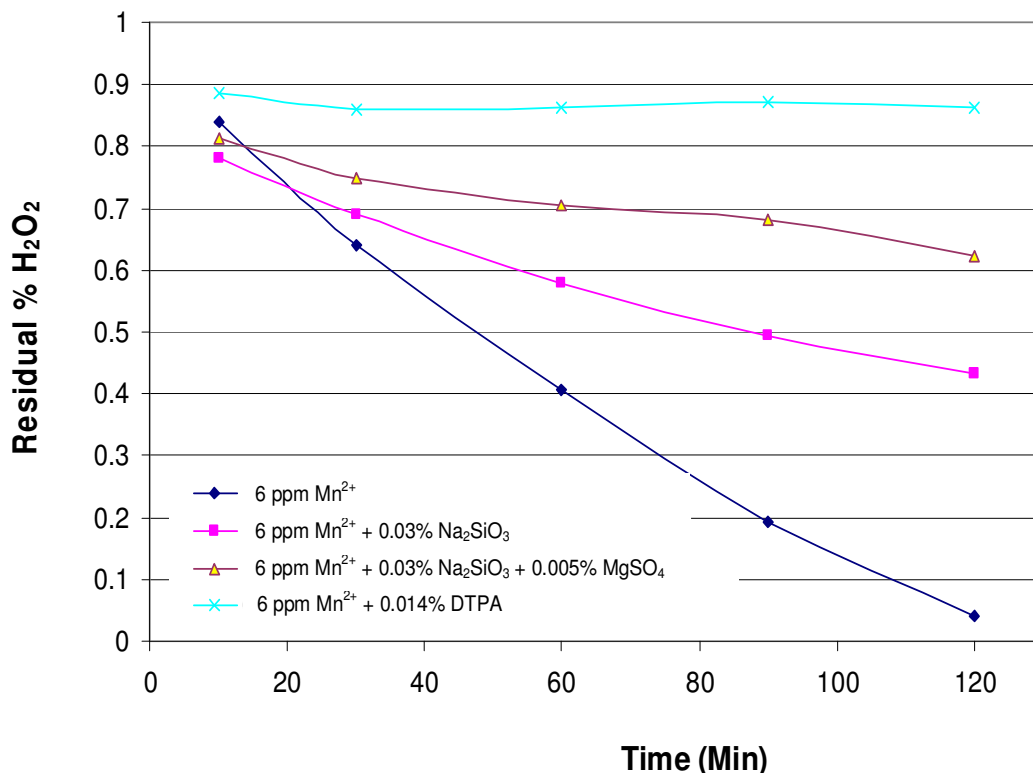


Figure 1. Stabilization of Mn-peroxide decomposition by DTPA and MgSO₄ at 25°C.

Mn³⁺, and modified Na₂SiO₃-Mn on alkaline peroxide solution.

MATERIALS AND METHODS

All the instruments used were purchased from Fisher Scientific. The pH meter was AB 15 model and the microwave was Profile model. The hotplate used was Corning PC-620D. All chemicals were analytical grade quality except when stated otherwise. Commercial sodium silicate was clear solution (SiO₂: Na₂O = 3.22), magnesium sulfate, DTPA, magnesium hydroxide, manganese sulfate, manganese (III) acetate, potassium iodide, starch, ammonium molybdate were obtained from Sigma-Aldrich,

All peroxide decomposition runs were carried out in 500 ml polyethylene beakers supported on a hotplate. The beakers were cleaned between runs using a mixture of dilute sulphuric acid and hydrogen peroxide, rinsed with water, and finally multiple washing with distilled deionized water.

Decomposition runs were carried out in hydrogen peroxide solution with initial concentration of 0.75% prepared by the addition of 5 ml of 30% hydrogen peroxide to an appropriate volume of distilled-deionized water containing the chelating agent; DTPA or stabilizing chemicals; Na₂SiO₃ and MgSO₄. The pH was finally adjusted to 10.0 with sodium hydroxide. The total volume of the solution was 200 ml. The initial amount of manganese introduced was 6 ppm in all the decomposition runs. The extent of the reaction was monitored by titrimetric determination of 5 ml sample withdrawn at 10 min interval. The samples were acidified with sulphuric acid and excess potassium iodide added with a few drops of 3% ammonium molybdate solution. The liberated iodine was titrated against standardized sodium thiosulphate solution. The order of

addition of chemicals is indicated in Figures 1 to 5.

RESULTS AND DISCUSSION

Figure 1 shows the stabilization of Mn-induced peroxide decomposition by Na₂SiO₃, MgSO₄, and DTPA. Without the addition of any stabilizers, manganese induces extensive peroxide decomposition under the typical bleaching conditions. When Na₂SiO₃ alone was added to the manganese containing system, the peroxide decomposition was decreased. However, with the addition of Na₂SiO₃ and MgSO₄, it was observed that, further additional stabilization effect was obtained. The addition of DTPA to manganese containing system completely stabilized peroxide decomposition. These results are shown in Figure 1, and they are in agreement with the results of other workers (Qiu, Z, 2000; Ni and Ohi, 2000) which can be attributed to the stabilization of Mn²⁺; hence it is not involved in Mn²⁺ ↔ Mn³⁺ redox cycle that is responsible for peroxide decomposition.

Further studies on the effect of the order of addition of DTPA, Mn²⁺, and Na₂SiO₃/ MgSO₄ on alkaline peroxide solution were carried out and the results are presented in Figure 2. In Run 1, DTPA was added to alkaline peroxide followed by Mn²⁺ and in Run 2, Mn²⁺ was mixed in a separate container before being added to alkaline peroxide. It is clear that, the peroxide decomposition in

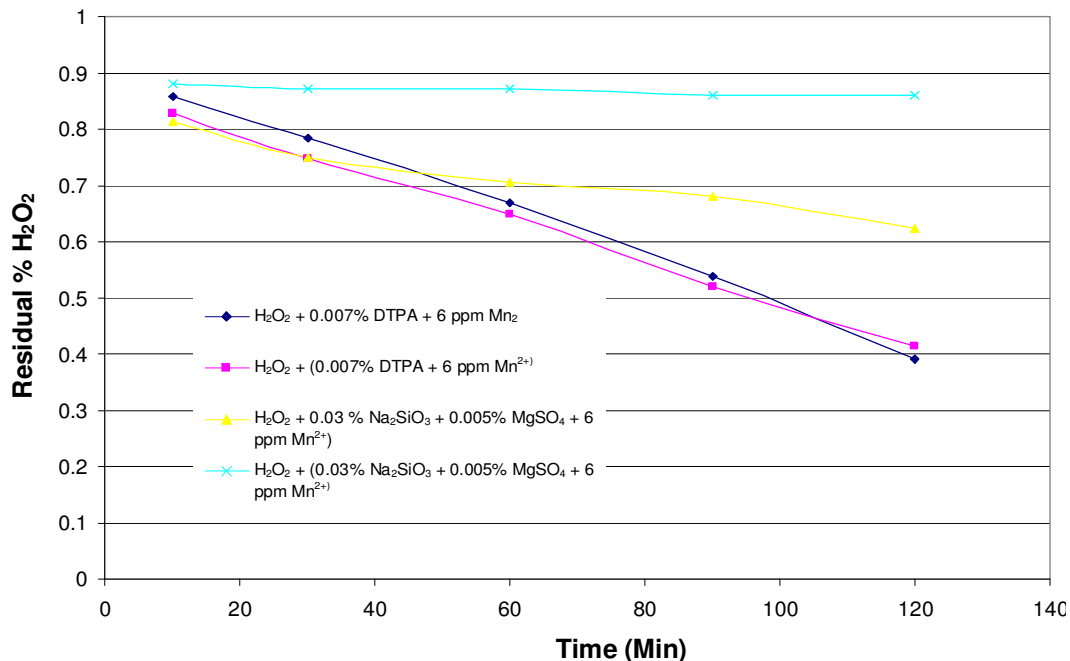


Figure 2. The effect order of mixing chemicals on peroxide decomposition.

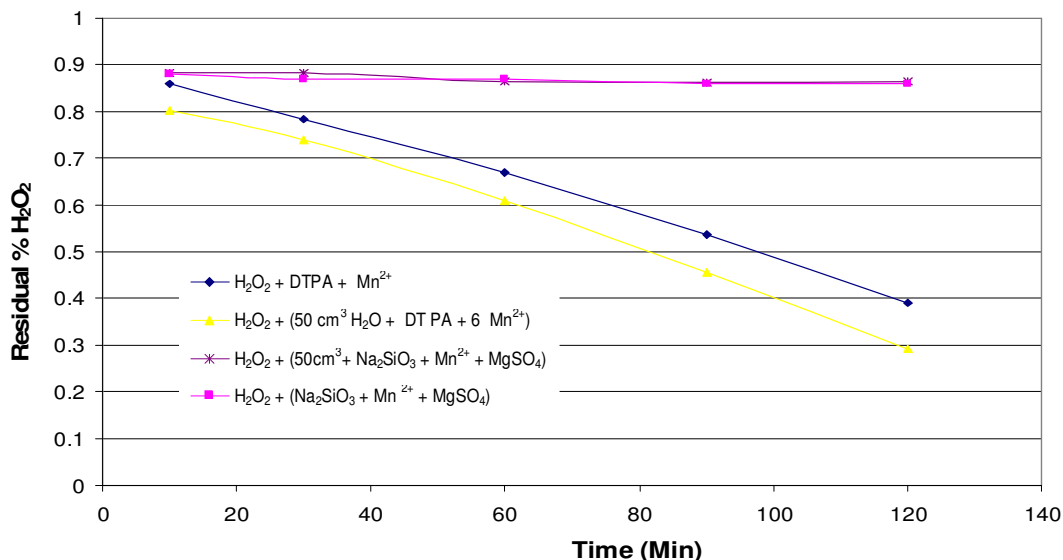


Figure 3. The effect of adding the chelant or stabilization agents as dilute or concentrated.

these two runs is the same. The same runs with Na₂SiO₃/MgSO₄ as the stabilizing agent was tried instead of DTPA. It was found that Run 3, where Na₂SiO₃, MgSO₄ and Mn²⁺ were mixed together before addition to alkaline peroxide solution had effective peroxide stabilization compared to Run 4 where Na₂SiO₃, MgSO₄ and Mn²⁺ were added to alkaline peroxide solution in the order. These results were expected because in Run 3,

Mn²⁺ was effectively trapped. However, in Run 4, some of the Mn²⁺ that was not trapped was involved in the catalytic Mn²⁺ ↔ Mn³⁺ cycle.

The effect of adding DTPA and Na₂SiO₃/MgSO₄ systems as dilute or concentrate to an alkaline peroxide solution was investigated and the results are presented in Figure 3. In Run 1, DTPA was added to 50 cm³ of H₂O to which Mn²⁺ was added. This was compared with Run 2 in

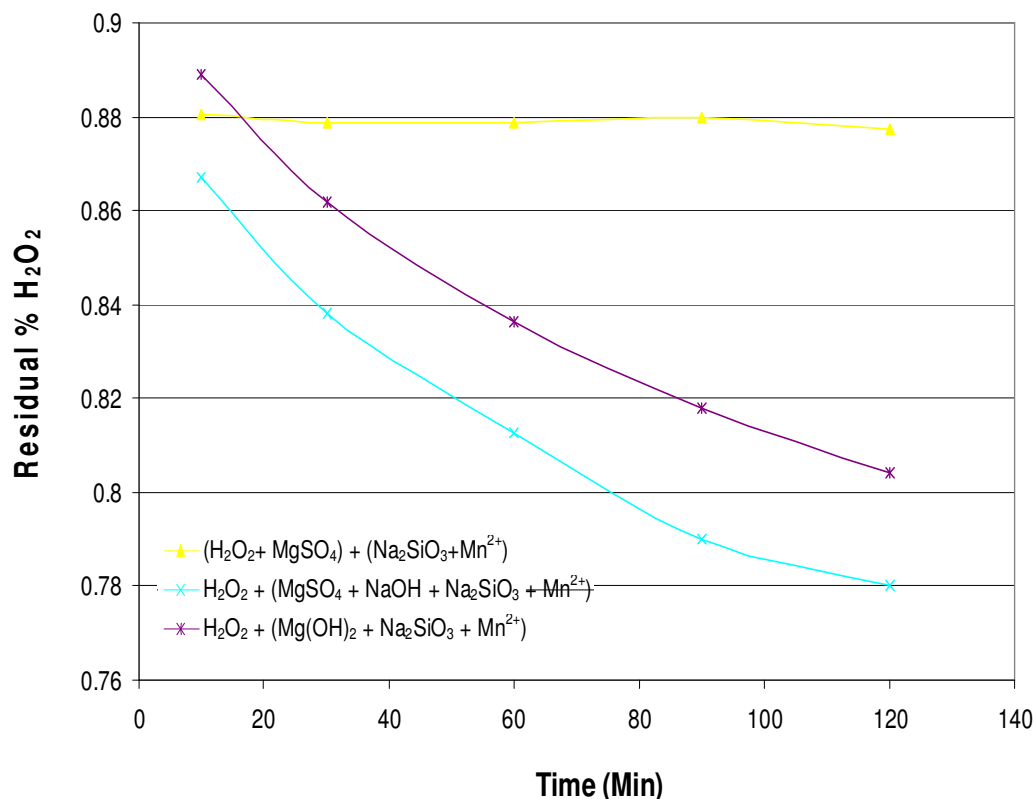


Figure 4. The effect of Mg (OH)₂ on peroxide stabilization by Na₂SiO₃/MgSO₄ system (0.015% Na₂SiO₃, 0.005% MgSO₄, 6 ppm Mn²⁺, 0.01% Mg(OH)₂).

which DTPA was added to alkaline peroxide solution followed by Mn²⁺. We found that in Run 2, there was better peroxide stabilization compared to Run 1. This was expected because, the addition of DTPA as dilute, limited the potential of Run 2 to trap Mn²⁺ which was involved in Mn²⁺ ↔ Mn³⁺ redox cycle. This process was repeated for Na₂SiO₃/MgSO₄ system, whereas in Run 3, Na₂SiO₃ mixed with Mn²⁺ followed by MgSO₄ and in Run 4, 50 cm³ H₂O was added to Na₂SiO₃, followed by Mn²⁺ and then MgSO₄. The solution was then added to alkaline peroxide solution. The results from the two runs were the same.

The reduction of Mn-induced peroxide decomposition using Na₂SiO₃/MgSO₄ system by looking at the order of mixing chemicals prior to peroxide addition was focused on. In Run 1, Mg(OH)₂ was mixed with Na₂SiO₃ and then Mn²⁺. The resulting solution was then added to alkaline peroxide solution. In Run 2, NaOH was added to MgSO₄ to form Mg(OH)₂ to which Na₂SiO₃ was then added followed by Mn²⁺. The resulting solution was then added to alkaline peroxide solution. Peroxide decomposition was observed in these two runs. In Run 3, MgSO₄ was added to alkaline peroxide solution and separately Na₂SiO₃ was mixed with Mn²⁺ and then added to the first solution. In Run 3, there was no peroxide decomposition. This implied that, the mixing of Na₂SiO₃/MgSO₄ system resulted in the formation of Mg(OH)₂, which is not

effective in stabilizing Mn-induced peroxide decomposition.

Finally, we investigated the effect of microwave-assisted chemically modified Na₂SiO₃-Mn complex on alkaline peroxide solution and the results are presented in Figure 5. In Run 1, Mn³⁺ was added to Na₂SiO₃ and then put in a microwave for 2 min prior to the addition of alkaline peroxide solution. No peroxide decomposition occurred. In Run 2, Mn³⁺ was added to alkaline peroxide solution without any stabilizer, extensive peroxide decomposition occurred. In Run 3, Mn²⁺ was used instead of Mn³⁺, as indicated in Run 1, again no peroxide decomposition occurred.

Conclusion

The order of addition of Na₂SiO₃, MgSO₄ and Mn²⁺ was very important in reducing the peroxide decomposition. However, when DTPA was used as the chelant, there was no difference in the stabilization; whether DTPA and Mn²⁺ were mixed together prior to the peroxide addition or DTPA was added to peroxide followed by Mn²⁺. The stabilization effect of Na₂SiO₃/MgSO₄ system was independent whether it was added as diluted or as concentrated; however, DTPA was a better chelant when

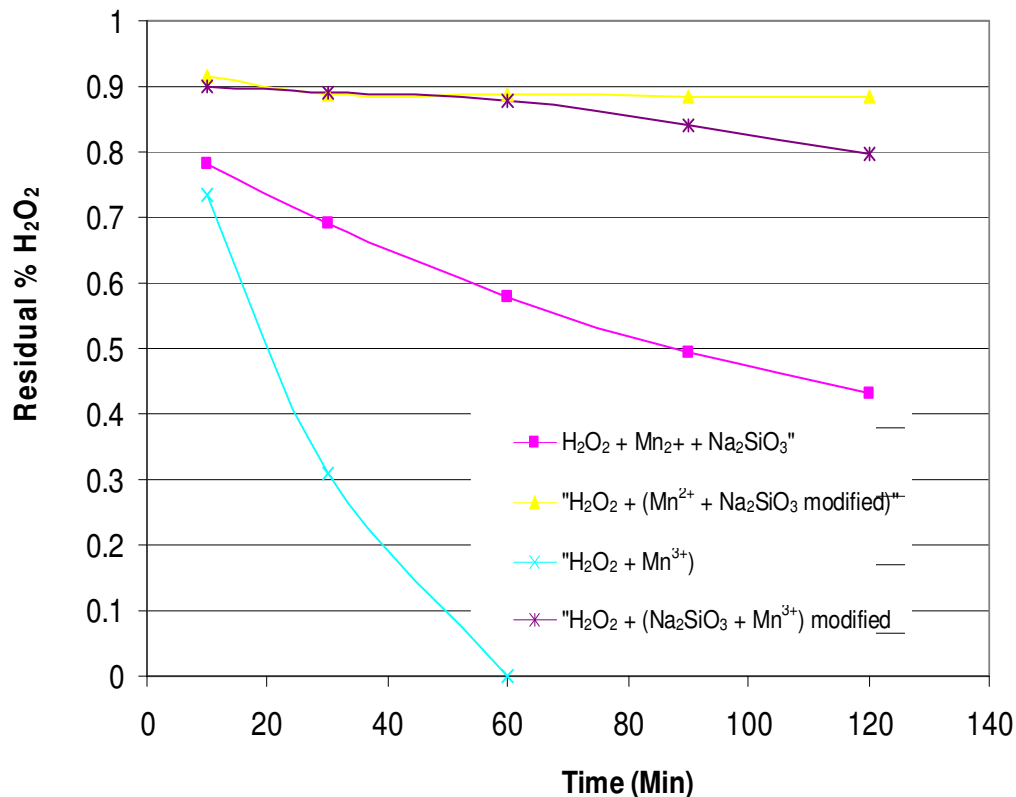


Figure 5. Reducing peroxide decomposition by modified Na₂SiO₄ (6 ppm Mn²⁺ and Mn³⁺, 0.03% Na₂SiO₃, 25°C, pH 10.0).

it was added as concentrated. Microwave-assisted modification of SiO₃-Mn complex had no effect of alkaline peroxide solution for Mn²⁺ or Mn³⁺ species.

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