# Alkaline Peroxide Mechanical Pulping of Wheat Straw

## Part 2: Significance of Peroxide Stabilization to the Brightening of Wheat Straw

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## ABSTRACT

The present investigation aimed at improving the performance of wheat straw peroxide bleaching by using various chelating agents for pretreatment and during bleaching. Among the process variables in the pretreatment, the pH was the most important factor influencing the pulp brightness and peroxide consumption. While low pH pretreatment (e.g. pH 2 - 3) promoted removal of transition metals, other mechanisms may also contribute to the brightening enhancement resulting from the pretreatment. In addition, inclusion of a small amount of chelating agent in alkaline peroxide liquor further increased the bleaching efficiency of the pretreated straw. This study would provide a process that eliminates the need of adding sodium silicate and magnesium sulfate as peroxide stabilizers.

## KEYWORDS

Wheat straw (*Triticum aestivum*), mechanical pulping, bleaching, hydrogen peroxide, transition metal, chelating agent, stabilizer, sodium silicate, magnesium sulfate, brightness

## INTRODUCTION

Our earlier study has demonstrated that wheat straw fibers are difficult to bleach and at a given peroxide dosage their achievable brightness level is much lower than that of wood fibers [1]. In order to produce high brightness straw pulps using economical levels of peroxide charge, it is important to choose appropriate bleaching conditions, which should be based on the characteristics of straw fibers. Although the fundamentals of wheat straw pulping and bleaching are not well documented, it is widely recognized that wheat straw is different from wood

chemically and morphologically [2]. This paper addresses factors relating to the bleaching response and identifies conditions giving improved brightness.

Hydrogen peroxide is unstable in alkaline conditions and readily decomposes, particularly in the presence of certain transition metals [3]. This metal-catalyzed decomposition of hydrogen peroxide is generally considered undesirable in the bleaching operation, because it leads to a loss of brightening capacity. It is generally recognized that certain transition metals, particularly copper, iron and manganese, are an active catalyst of peroxide decomposition and have a detrimental impact on brightness development [3]. Therefore, removing or deactivating the transition metals is essential to minimizing the occurrence of catalytic peroxide decomposition. In practice, two approaches, commonly used together, are used to achieve this goal: pretreatment of pulp before bleaching and stabilization of bleach liquor. Chelation is an effective way to complex and wash out metals from pulp using chelating agents such as DTPA and EDTA [4]. Alternatively, acid wash (pH 1.5 – 3.0) has been reported to be equally effective in removing transition metals [5]. The second approach to minimizing catalytic peroxide decomposition is bleach liquor stabilization. Sodium silicate and magnesium salts have proven stabilizing effects and have widespread industrial application [6, 7]. In addition, chelating agents such as DTPA and DTPMPA are also used as organic stabilizers for bleach liquor stabilization [4, 8].

It has previously been demonstrated that pre-washing wheat straw with hot water (70$^{o}$C) significantly improves the performance of subsequent alkaline peroxide impregnation [1]. This pretreatment not only improves the accessibility to the chemicals due to wheat straw softening, but also causes the dissolution of lignin, hemicelluloses, extractives, and inorganics to varying extent. It is reasonable to anticipate that incorporation of chelating agents into the above-mentioned pretreatment would more effectively remove transition metals thereby enhancing the peroxide bleaching.

## MATERIALS AND METHOD

Wheat straw collected at the University of Alberta farm was cut by a hammermill into a length of about 20 mm and screened to remove fines. All chemicals are commercial products and were employed as received. The chelating agents used in pretreatment or impregnation are as follows.

- DTPMPA: Diethylenetriaminepentamethylene phosphonic acid
- DTPA: Diethylenetriaminepentaacetic acid
- H EDTA: N-(2-hydroxyethyl)ethylenediaminetriacetic acid
- NA: Nitrilotriacetic acid
- STPP: Sodium tripolyphosphate

Each trial used approximately 10 g (o.d.) of wheat straw. Both pretreatment and chemical impregnation were conducted in polyethylene bags. Pretreatment was performed with a water-to-straw ratio of 25:1 (ml/g) by varying other parameters. The treated straw was washed to neutral pH.

As the present investigation focused on the impact of pretreatment, we used an identical impregnation condition: liquor-to-straw ratio 6:1 (ml/g), 4% $H_2O_2$, 4% NaOH, 0.1% DTPMPA, 70$^o$C, 2 h. The charges of all chemicals were based on the o.d. straw weight before the pretreatment. In this study, we only measured ISO brightness and residual peroxide. Pulp yield would be around 85%, as observed by our earlier study [1]. Upon completion of impregnation, the straw was defibrated in a Waring blender. The resulting pulp was acidified to pH 5 and washed with distilled water.

The concentration of hydrogen peroxide was determined iodometrically. Handsheets were prepared following the TAPPI standard method T-218. Lignin, ash and extractives were also analyzed according to the TAPPI standard methods. Brightness values were recorded in a Technibrite Micro TB-1C instrument. For determination of metal content, the wheat straw samples were dissolved with a mixture of $HNO_3$ and $HClO_4$ in a microwave digester and the solutions were measured by ICP. Detection limit was 0.1 – 0.01 ppm depending on the metal species.

## RESULTS AND DISCUSSION

### Metal Content of Wheat Straw

Metals are initially present in plants and are commonly measured as the ash content. Despite a low percentage of the plant fiber weight, the metals from plant fibrous materials, together with those introduced from the bleaching chemicals, process water and equipment, can have a significant effect on bleaching, and their levels are an important factor in choosing bleaching conditions. In hydrogen peroxide bleaching, transition metals, particularly iron, copper and manganese, are considered as catalysts of peroxide decomposition, and, in contrast, alkali-earth metals like magnesium and calcium as well as silica are considered as peroxide stabilizers. Therefore, it is of great interest to find out the content of metals in wheat straw. As shown in **Table I**, in comparison to several typical pulping wood species in the literature [9], wheat straw has a considerably different metal profile: a lower content of manganese and a higher content of iron, magnesium, calcium and silica. Especially interesting is that manganese, known as the most active catalyst of peroxide decomposition [3], is remarkably low in wheat straw. The question arising here is how such a unique metal profile influences the performance of alkaline peroxide bleaching.

| Sample | Al | Ca | Cu | Fe | Mg | Mn | Si |
|---|---|---|---|---|---|---|---|
| | | | ppm | | | | |
| Whole straw | 6.9 | 1915.4 | 1.9 | 42.8 | 474.6 | 11.2 | 2275.3 |
| Internodes | 0.7 | 1102.9 | 1.5 | 15.5 | 213.9 | 5.9 | 1952.7 |
| Cut/screened | 1.1 | 1896.4 | 1.5 | 31.7 | 410.5 | 5.9 | 2251.9 |
| Chelated * | 2.9 | 1176.8 | 1.5 | 17.7 | 159.0 | 0.7 | 1929.7 |

* Treatment conditions: cut/screened straw, 0.5% HEDTA, pH 3, 60$^{o}$C and 1 hour

**Table I. Metal Content of Different Wheat Straw Preparations**

It is reported that there is heterogeneity of chemical composition within a wheat straw [10]. The internodal material contains more cellulose and less ash and silica than other parts such as the nodes and leaves. Table I indicates that there also is a heterogeneous distribution of metals in wheat straw. Overall, the internodal fraction has a lower metal content, especially two key transition metal ions, manganese and iron. It is evident that the internodes are an ideal fibrous material for pulping because of higher cellulose content and lower transition metal content. Indeed, our earlier result has demonstrated that using solely internodes for the APMP leads to higher pulp brightness and lower peroxide consumption [1]. It is interesting to notice that comminuting/screening can selectively eliminate straw fractions rich in these two metal ions, most likely nodes and leaves. This process can be considered as the first step to remove the transition metals from the wheat straw thus enhancing bleaching efficiency in the APMP process.

Influences of Pretreatment Parameters

In order to find out how the pretreatment pH influences the bleaching efficiency, wheat straw samples pretreated with various chelating agents and at varying pH levels were bleached with alkaline peroxide. The bleaching results are shown in **Figures 1 and 2**. As the pH decreased, the brightness increased and the peroxide consumption decreased. Furthermore, both the enhancement in brightness response and the reduction in peroxide consumption are more significant at a pH of below 5. It is interesting to note that a simple acid wash (pH 2 - 3) was far more effective than chelations, typically performed at a pH of about 5, in enhancing the bleaching efficiency.

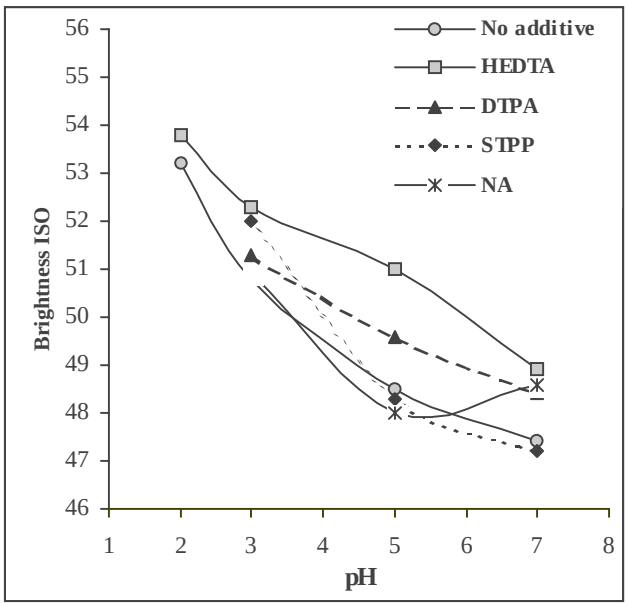


**Figure 1. Effect of Pretreatment pH on Brightness in Impregnation (pretreatment: 0.5% chelating agent, 60°C and 1 hour)**

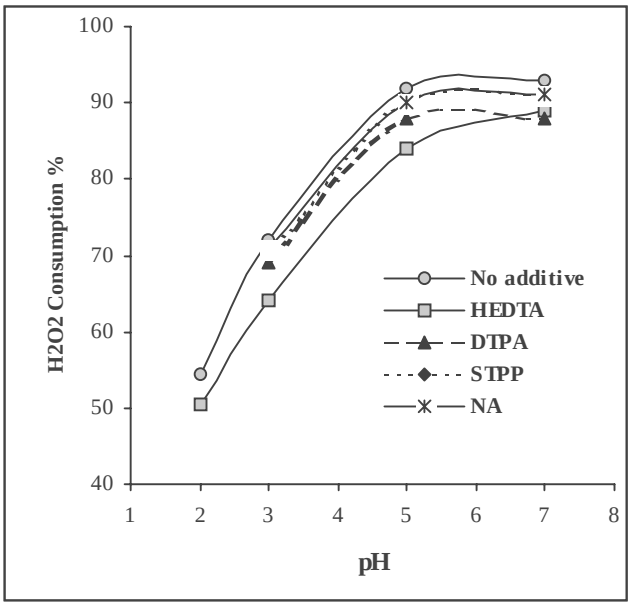


**Figure 2. Effect of Pretreatment pH on Peroxide Consumption in Impregnation (pretreatment: 0.5% chelating agent, 60°C and 1 hour)**

**Figure 3** illustrates the variations of the content of manganese and iron in the wheat straw samples used in the above bleaching trials. Since copper is very low in the original wheat straw, the variation of the copper content is only marginal and not included here. As shown in Figure 3, the manganese and iron contents decreased with lowering the pH. Moreover, the addition of chelating agents helps further remove the transition metals no matter what pH level is used. Nevertheless, the magnitude of the variation of the two transition metals within the range between pH 7 and pH 3 appears to be steady and unable to explain the much sharper change of both the brightness and peroxide consumption from pH 5 to pH 3. Hence, it is hard to correlate the change in the transition metal profile due to the pretreatment and the performance of peroxide bleaching in terms of pulp brightness and peroxide consumption.

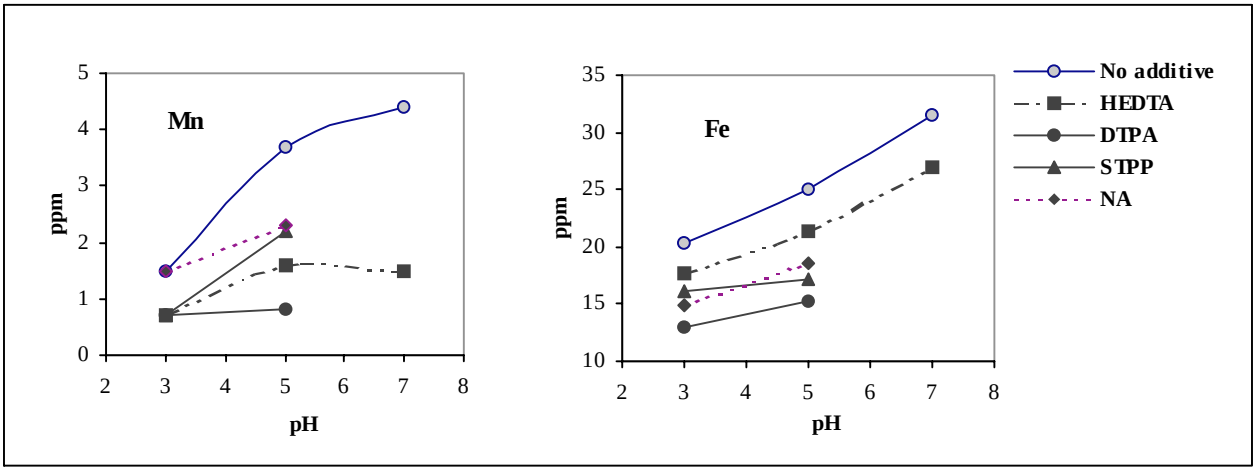


**Figure 3. Effect of Pretreatment pH on Metal Removal (pretreatment: 0.5% chelant, 60°C and 1 hour)**

To find out the impact of the pretreatment on the chemical composition of wheat straw, we examined the dissolution of wheat straw components during the pretreatment. As shown by **Table II**, low pH wash resulted in higher yield of material recovery. In other words, the water-solubility of wheat straw components was reduced when the pH was lowered. In comparison to the neutral wash (pH 7), the acid wash (pH 3) resulted in higher ash and extractives contents, but a similar lignin content. So far, we are not able to fully explain the high dependence of the bleaching efficiency on the pretreatment pH. Presumably, there could be other factors influencing the alkaline peroxide bleaching.

| Sample | Original | pH 7 | pH 5 | pH 3 |
|---|---|---|---|---|
| Straw Recovery Yield,% | 100 | 93.0 | 94.0 | 94.7 |
| Klason Lignin,% | 17.4 | 17.6 | | 17.3 |
| Acid Soluble Lignin,% | 1.9 | 1.6 | | 1.7 |
| Ash,% | 6.5 | 4.5 | | 4.9 |
| Toluene-Ethanol Extractives,% | 3.4 | 1.6 | | 2.1 |

**Table II. Effect of pH on Recovery Yield and Chemical Composition of Hot Water Washed Wheat Straw at 60°C for 1 hour**

**Figure 4** illustrates the effect of chelant dosage on the removal of manganese and iron and the performance of alkaline peroxide bleaching. Here, HEDTA is taken as an example. It should be noted that in this experiment no acid was added for pH adjustment. It is not surprising that as the HEDTA charge was increased, both the manganese and iron contents decreased, the pulp brightness increased, and the peroxide consumption dropped. Nevertheless, the efficiency increment considerably slowed down when the HEDTA dosage was increased from 0.5% to 1.5%. Similar observations were made with the other chelating agents. This result suggests that a chelant dosage exceeding 0.5% is not necessary.

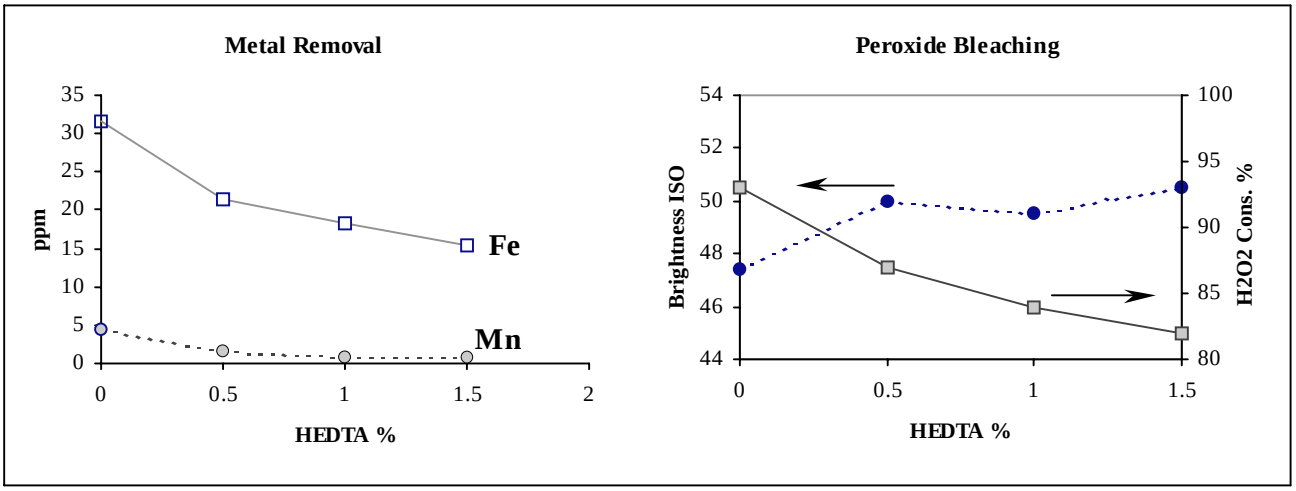


**Figure 4. Effect of HEDTA Dosage on Metal Removal and Peroxide Bleaching (pretreatment: 60°C and 1 hour)**

In contrast to the above parameters, the influence of temperature and time is relatively small. Varying the pretreatment temperatures from 50°C to 70°C resulted in a little change in the chelation efficiency and the pulp brightness. It appeared that a pretreatment for 1 hour was optimal.

Role of Chelating Agents or Stabilizers in Alkaline Peroxide Impregnation

In this section, our research was focused on the role of chelating agents or stabilizers in the alkaline peroxide impregnation of pretreated wheat straw. Our preliminary study has shown the necessity of adding a chelating agent in the impregnation in order to maximize the brightness response. As demonstrated in the preceding section, the pretreatment of wheat straw with particular conditions is effective in removing the transition metals and enhancing the peroxide bleaching. However, the presence of metal impurities in the bleaching chemicals and process water justifies the use of a small amount of chelating agent, preferably DTPMPA to further stabilize peroxide.

The wheat straw used here was pretreated under the following condition: 0.5% HEDTA, pH 3, 60°C and 1 hour. Overall, as shown in Table I, the chelation decreased the content of all the metals to varying degree. Among the transition metals, the manganese content was reduced to a very low level. On the other hand, iron seemed to be difficult to remove by chelation and only less than half the iron was removed. This phenomenon has been reported previously [11].

To evaluate the role of chelating agent, the pretreated wheat straw was impregnated under the standard bleaching conditions using varying amounts of DTPMPA. As can be seen from **Figure 5**, adding certain amounts of DTPMPA increased the brightness by a few ISO points. 0.1% to 0.2% may be a reasonable range of DTPMPA dosage.

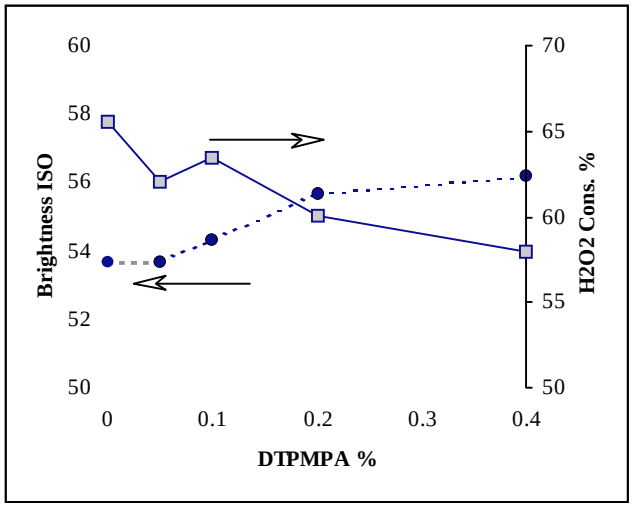


**Figure 5. Effect of DTPMPA Dosage on the Alkaline Peroxide Impregnation of HEDTA-Pretreated Wheat Straw**

In addition, alternative additives were assessed as stabilizers for alkaline peroxide bleaching. **Table III** shows that the addition of 3% $Na_2SiO_3$ offered an additional brightness gain of about 1 ISO point, but resulted in an increase in peroxide consumption. This brightness increase could be due to the higher alkalinity of the bleach liquor since the commercial sodium silicate contains 11.5% NaOH. As our previous study revealed [1], both the pulp brightness and peroxide consumption increased with increasing the alkali charge. Therefore, the silicate used here functions more likely as an additional alkali source and is superfluous. On the other hand, the magnitude of brightness increment by 3% $Na_2SiO_3$ can be achieved using 0.2% of DTPA or 0.2% DTPMPA (Figure 5).

| | **Brightness ISO** | **$H_2O_2$ Consumption%** |
|---|---|---|
| No additive | 53.7 | 65.6 |
| $Na_2SiO_3$ (3%) | 55.0 | 70.5 |
| DTPA (0.2%) | 55.0 | 64.2 |
| $MgSO_4$ (0.2%) | 52.7 | 64.5 |

**Table III. Effect of Various Additives on the Alkaline Peroxide Impregnation of HEDTA-Pretreated Wheat Straw**

As can be seen in Table III, the addition of 0.2% $MgSO_4$ had an adverse effect on the brightness development during the alkaline peroxide impregnation. We have repeatedly observed the negative impact of $MgSO_4$ at addition levels varying from 0.05% to 0.2% in our wheat straw APMP study [1]. There are many reports in the literature on the magnesium stabilization effect in hydrogen peroxide bleaching [5, 12]. Especially in the case of acid treatment which removes magnesium as effectively as the transition metals from a pulp, it is necessary to add back certain amounts of $MgSO_4$ to replace the "native" magnesium to minimize the peroxide decomposition. In our work, as shown in Table I, the wheat straw has a fairly low content of transition metals and, in contrast, a very high content of alkali-earth metals (Ca, Mg) and silicon. After the pretreatment, the transition metal content of wheat straw was reduced to very low level. Although the pretreatment also significantly decreased the content of Mg, Ca and Si, the remainder of these elements would be sufficient to serve as peroxide stabilizers. Consequently, the added $MgSO_4$ is superfluous.

As for the negative effect of $MgSO_4$ observed here, we have not established satisfactory explanations. In fact, the role of the added $MgSO_4$ is not well documented and many results are contradictory. It has been reported that adding $MgSO_4$, as well as calcium, to the peroxide bleaching liquor is beneficial, but excessive dosage is detrimental [12, 13]. Basta and co-workers observed the brightness decrease by the added $MgSO_4$ in the peroxide bleaching of both softwood and hardwood chemical pulps [14]. They assumed, but did not experimentally prove, that "native" magnesium or calcium is more efficient than its externally added counterpart.

## CONCLUSIONS

Wheat straw has a low content of transition metals (Mn and Fe) and a high content of alkali-earth metals (Mg and Ca) and silica. This characteristic allows a relatively "easy" metal management as compared with that used for wood. Pretreatment, like chelation or acid wash, is effective in reducing the amount of the transition metals thereby significantly enhancing the brightness development and reducing the peroxide consumption.

Among the pretreatment parameters investigated, pH played the most important role in the performance of subsequent alkaline peroxide bleaching. Our result suggests that pretreatment, acid wash alone or associated with chelation, is preferably carried out at a pH of 2 to 3. Such a pretreatment resulted in significant improvement of the bleaching efficiency while attaining a higher recovery yield of wheat straw upon pretreatment. In addition to transition metal removal, other mechanisms may be involved which positively affect the peroxide bleaching.

Besides, beneficial effect on the brightness development was observed by using a small amount of chelating agent, e.g. 0.1 – 0.2% DTPMPA, in the impregnation to further stabilize alkaline peroxide bleach liquor. In contrast, the addition of sodium silicate or magnesium sulfate would not be suggested as a peroxide stabilizer in the wheat straw APMP process. Significantly, eliminating the need of adding the silicate would facilitate the recycle of spent bleach liquor.

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