

Trace Elements Measurement of Mangium Wood (*Acacia mangium*) by AAS

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Abstract

The ash and metals content of *Acacia mangium* Wild was determined following standard procedures of TAPPI T211 om-93 test method and wet ashing procedures with HNO₃ and HClO₄ solution, respectively. Measurements of trace elements were carried out by the use of atomic absorption spectrometry (AAS). Although it was fluctuating, the lowest ash content was found in a 5 years old wood and then tended to increase in older three. In the 3 and 5 years old wood, the ash content decreased from upper end to the lower end of the stems. In the 7 and 9 years old wood, the lowest ash content was in the middle part and it tends to increase to the lower end of the stem. Ash content of sapwood was higher than that of heartwood. The content of Mg decreased with increasing age of wood, and other metals tended to increase with the increase of wood age. Metallic components of acacia wood tended to accumulate more in sapwood compared to these in heartwoods. Vertically, the content of Mg and Cu decreased from upper end to lower end of the stems, and in contrary to these of other metals.

Key words: atomic absorption spectrometry, *Acacia mangium*, closed loop cycle, metallic contents, oxygen-based bleaching

Introduction

Inorganic components of wood ash consist of various metallic salts such as carbonate, silicate, oxalate, and phosphate deposited in the cell wall with the content of infrequently above 1% (Sjöstrom 1993). This author also explained that dominant trace elements in wood, successively, are Ca, K, and Mg. Furthermore, Fe and Mn can attain a concentration of 100 ppm and other metals can attain a concentration of 10 ppm. Ash content of tropical woods is commonly much higher than that of sub-tropical woods that retain an ash content of approximately 0.2-0.5% (Fengel & Wegener 1984).

Most metals are electrostatically bound in negatively charged carboxyl groups of xylan (hemicelluloses) and pectin. Its presence in wood is related to catalysis role in enzymatic biosynthesis (Sjöstrom 1993). Therefore, high concentration of metals ion are commonly found in living tissue's cells such as rays cells and resin duct parenchyma carried by negatively charged groups in resin (Sundén *et al.* 2000).

The presence of metals ion in wood has been emphasized by many pulp and paper research centers related to the development of environmentally benign technology in pulp and paper productions. The development of pulp

and paper production technology has been leading to an ultimate goal of totally effluent free (TEF) technology that compels a closed loop cycle system operation. Close loop cycle system that is aimed to reduce effluent, solid waste, and polluting emission (Ritchlin & Johnston 1999) has been incorporated in Ecocyclic Mill Research Program of Sweden, Agenda 2020 of the United State of America, TEKES of Finland, and Progressive System Closure of Canada (NCASI 2003).

TEF technology in pulp and paper mills consist of modern pulping technology, oxygen delignification, highly efficient recovery boiler, and totally chlorine free (TCF) bleaching methods (US Department of Energy 2000). It has been well understood that TEF requires the application of TCF bleaching methods. TCF methods are extremely dependent on oxygen based chemicals such as molecular oxygen, ozone, and hydrogen peroxide. However, the action of these chemicals in bleaching processes is limited by a detrimental concentration limit of transition metals ion. Hydrogen peroxide, for example, is very sensitive to decomposition by metals ion such as Mn, Fe, and Cu (Abbot & Hobbs 1998).

Process chemistry and separation process associated to the handling methods of concentrated damaging substances have been considered among the main problem in the close loop system. Trace elements substances from pulp wood, process water and chemical make up entering the system affect oxygen-based bleaching processes and possibly diminish strength properties of the resulting bleached pulp (Sundén *et al.* 2000). Furthermore, these authors have also explained that iron ions (Fe^{2+} and Fe^{3+}) in system form complexes with lignin and decrease the brightness of

pulp. Other metals ion such as Mn^{2+} and Cu^{2+} , even at a lower concentration than that of iron, was also reported decreasing pulp brightness mainly through catechol-metal complex (Yoon *et al.* 1999). Color in lignin-metal complex possibly brought about by δ - δ interaction (between δ -electron of metal ion and that of lignin) or charge transfer between metal ion and lignin or both of them (Ghosh & Ni 1998).

Transition metals ion detrimental to oxygen based bleaching chemicals can be removed by complexing agents such as EDTA and DTPA. However, EDTA and DTPA are less environmentally benign due to its low degradability and nitrogen content (Prasakis *et al.* 1996). More environmentally friendly complexing agents for transition metals are available and have been tested, but the complexing ability of the chemicals has not been able to succeed those of the EDTA and DTPA (Granhölm *et al.* 2009).

In Indonesia, fast growing acacia (*Acacia mangium*) is a preferred pulp wood. Acacia is a tropical species of wood that has been only well known for its fast growing nature and acceptable content of chemical components for pulp and paper raw materials. Its trace elements information important for the close loop system of pulp production has been very limited. It has been mentioned that tropical woods retain higher ash content compared to those of sub-tropical woods (Fengel & Wegener 1984). Therefore, as for other tropical woods, this can be a significant drawback for acacia as well when pulp mill applies close loop cycle system.

Ash content is commonly a measure of inorganic (metals) content of wood. Considering that tropical woods seem to

be more problematic for a close loop system compared to sub-tropical woods, comprehensive information about the types, content and distribution of metal in tropical wood is paramount. The present works was aimed to determine the types, content and distribution of metal ion in acacia wood (*A. mangium*) by the use of Atomic Absorption Spectrometry (AAS) method.

Materials and Methods

In the present works, *A. mangium* of 3, 5, 7 and 9 years old were obtained from industrial plantation of Perum Perhutani at Bogor District-Indonesia. The wood stems were divided into three divisions, i.e. lower end, middle part, and upper end, each with the length of 25 cm. Heartwood was separated from sapwood, chipped and air dried. Demineralized water was used to clean air dried chips, and these chips were then oven dried at 60 °C to air dried moisture content. The chips were milled and sieved to obtained wood meal of 40–60 mesh size. Ash content measurement of the samples was based on standard methods of TAPPI T211 om-93 (TAPPI 1993).

Wet ashing procedure with HNO₃ and HClO₄ (reagent grade) was involved in sample preparation. In this procedure, 0.50 g of wood meal were dissolved over night with 5 ml HNO₃ and 0.5 ml HClO₄ in a digesting tube. The solution was then heated in a digestion block at 100 °C for an hour, and then the temperature was increased to 150 °C until no yellowish vapor was visible. The heating temperature was further increased to 200 °C until white vapor was visible and approximately 0.5 ml of the extract left. Digestion block was then removed and allowed to gradually cold. The extract was diluted with dionized water to 50 ml and homogenized.

The content of Ca, Mg and Na was measured by the use of Perkin Elmer Atomic Absorption Spectrometry (AAS). Extract and its standard (1 ml each) were pipetted into different reaction tube and each was added with 9 ml 0.25% La solution. The solutions were then homogenized in a tube shaker. Ca and Mg were measured at 422.7 and 285.2 nm, respectively, and Na was measured with flame photometer at 200 nm.

Fe, Al, Mn and Cu were directly measured from the extract by the use of Hitachi Atomic Absorption Spectrometry with their respective standard. Al was measured with N₂O-acetylene flame and the rests (Fe, Mn and cu) were with air-acetylene flame. Fe, Al, Mn and Cu were measured at 248.3, 309.3, 279.6, and 324.8 nm, respectively. Two measurements (duplo) were carried out for every sample, and the content was calculated with the following equation:

$$\text{Ca, Mg, Na (\%)} = p \times 0.1 \times fp \times fk$$

$$\text{Fe, Al, Mn, Cu (ppm)} = p \times 100 \times fk$$

where:

p = Ppm standard curve that is sample content from the relationship between content of standards and AAS reading corrected to the blank

100 = Conversion factor (to %)

fp = Dilution factor

fk = Moisture content correction factor = 100/(100-%MC).

Results and Discussion

Ash content

In the longitudinal division of the stem (Figure 1), two distribution trends of the ash content of acacia were distinguished. In the 3 and 5 years old wood, the ash content decreased from upper end to the

lower end of the stems. The 7 and 9 years old wood have a similar ash distribution pattern, i.e. the lowest ash content were in the middle part and it tends to increase to the lower end of the stem.

Ash content distribution toward horizontal division of wood stem is shown also in Figure 1. Due to the amount of heartwood in the 3 years old wood was negligible, horizontal division was not possible. Therefore, horizontal divisions were carried out only to wood of 5, 7, and 9 years old. It can be seen from Figure 1 that except for the 5 years old wood, ash content of sapwood was higher than that of heartwood. It seemed that the age of wood and longitudinal and horizontal stem divisions of wood influenced the ash content. Sapwood consists of living cells where water transportation within a tree takes place. Large content differences of ash forming

element in different plant tissues were found in four Scandinavian wood species possibly due to the differences of natural processes involving mineral uptake and element transport in the tree (Werkelin *et al.* 2005).

Metal in wood

Ca, Mg, and Na usually present in wood in a higher amount (>100 ppm) compared to other metals content, and considered as macro element. On the other hand, the content of Fe, Al, Mn and Cu in plant is lower than 100 ppm and thus considered as micro elements. Distribution of Ca, Mg, and Na in sapwood and heartwood is shown in Figure 2. It can be seen (Figure 2) that the content of Mg in sapwood tends to decrease with increasing age of wood and reaching a minimum at 7 years old wood, and tends to increase afterward.

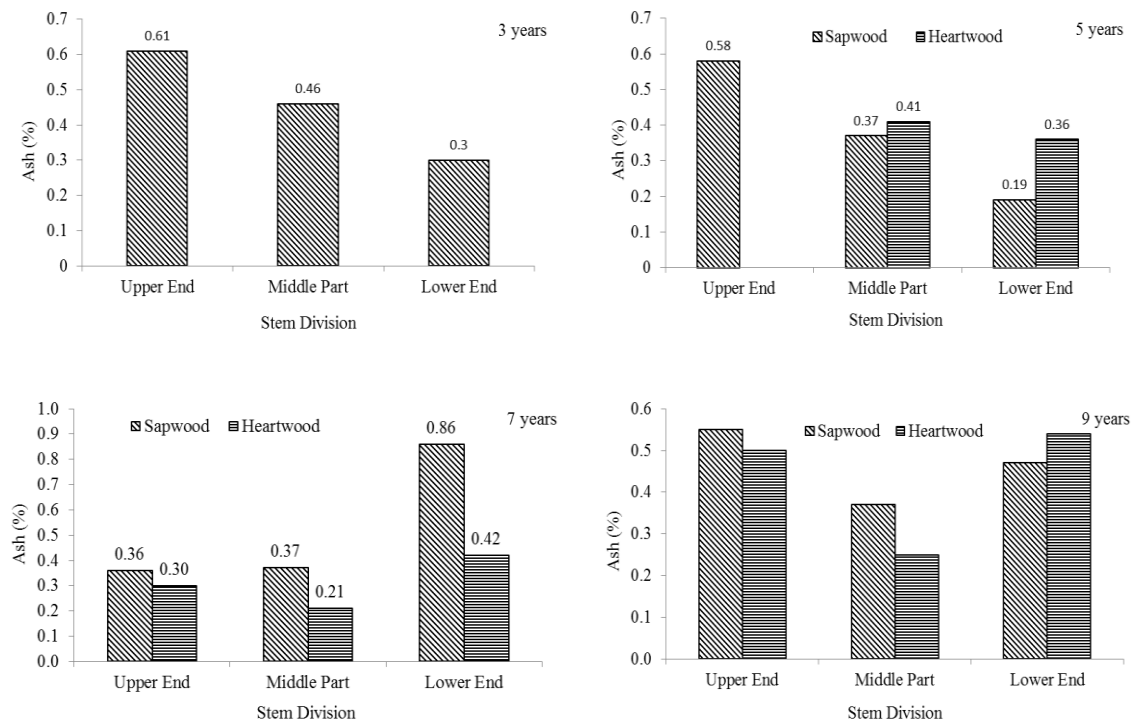


Figure 1 Ash content of the 3-9 years old mangium wood.

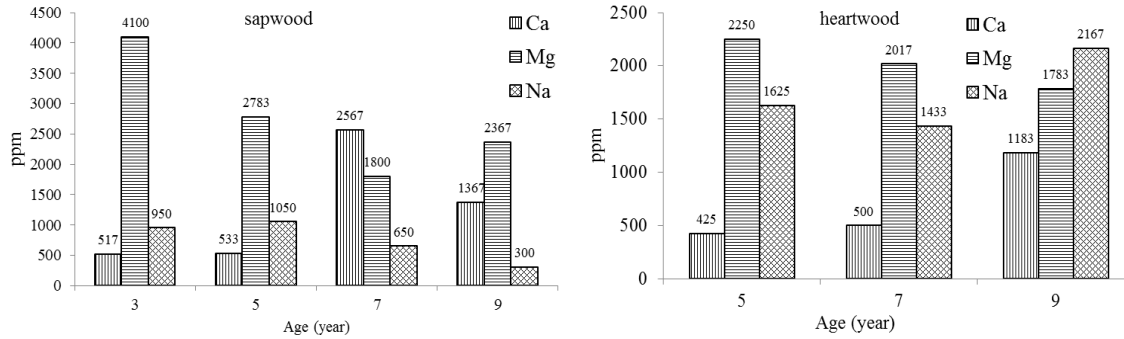


Figure 2 Distribution of macro elements in sapwood and heartwood of the mangium wood of 3, 5, 7 and 9 years old.

In contrary to the content of Mg, the Ca content of wood tends to increase with increasing age of wood, and reaching a maximum at 7 years old wood. Figure 2 also indicates that in heartwood, Mg content decreases with increasing wood age and the content of Ca increased with increasing wood age. Older tissue has been concluded to contain higher concentration of Ca than younger tissues (Rothpfeffer & Karlton 2007). The content of Na in 7 years old wood was found lower than these of 5 and 9 years old wood. Mg and Ca concentration of sapwood were higher than these of heartwood. However, the concentration of Na in sapwood was lower than that in heartwood. Literatures review carried out by Meerts (2002) cited in Rothpfeffer and Karlton (2007) concluded that Mg in sapwood is higher than that in heartwood, and was thought due to the differences of cation exchange capacity between wood with different level of cell ageing.

In a living plant tissue (in sapwood), certain metal is needed for the growth of tree (Fengel & Wegener 1984) and has important function as catalyst in enzymatic biosynthesis of plant (Sjöstrom 1993). Mg ion is an activator of several enzymes (Okada *et al.* 1990) and may involve in the cell division of

primary meristematic tissue in the apical growing point. Cell division in this point brings about longitudinal growth of the stem (Pandit & Ramdan 2002). Plant tissue obtains Mg ion from fertilizer given at the beginning of plant growth. Fertilizer might be the origin of the high content of several metals in young tree (initial growth). Metal electrostatically bound at carboxyl component of hemicelluloses (xylan). High content of xylan in young tree (Fengel & Wegener 1984) was thought to contribute to its high metal content.

Current experiments indicated that the Fe content in sapwood increased with increasing of wood age. It can be seen from Figure 3 as well that 5 years old wood contained the highest Al and both Mn and Cu seemed to be almost the same in all age of wood. In heartwood, Fe, Mn and Cu tended to increase with the increasing age of wood. The stem diameters of the present experiments were increasing with the increasing age of wood. Therefore, the present finding on the Fe, Mn, and Cu content was different to that found by Rothpfeffer and Karlton (2007) in which they reported that the content of Mn in *Picea abies* was positively correlated to the wood diameter, but negatively correlated with diameter for Fe and Cu.

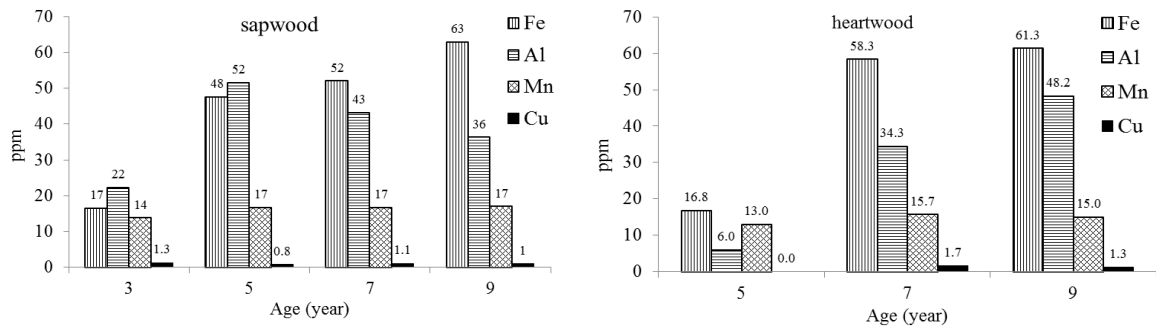


Figure 3 Distribution of micro elements in sapwood and heartwood of the mangium wood of 3, 5, 7 and 9 years old.

Figure 2 and 3 indicate that the content of both macro and micro metals of sapwood tend to be higher than these in heartwood. Wood tissue in sapwood consists of physiologically active living cell, and these in heartwood consist of dead cell inactive in physiological processes (Pandit & Ramdan 2002). Living cells require metals ion to promote its metabolic processes (Sundén *et al.* 2000). This possibly brought about metal content found in sapwood were

higher than those in heartwood. However, in several samples, metals content were fluctuating.

In the longitudinal direction, Figure 4 indicates that the content of Ca and Na increased with the increasing age of wood. Except for the 7 years old wood, the content of Mg followed the pattern of these of Ca and Na. The middle part of the 7 years old wood contains the highest amount of Mg.

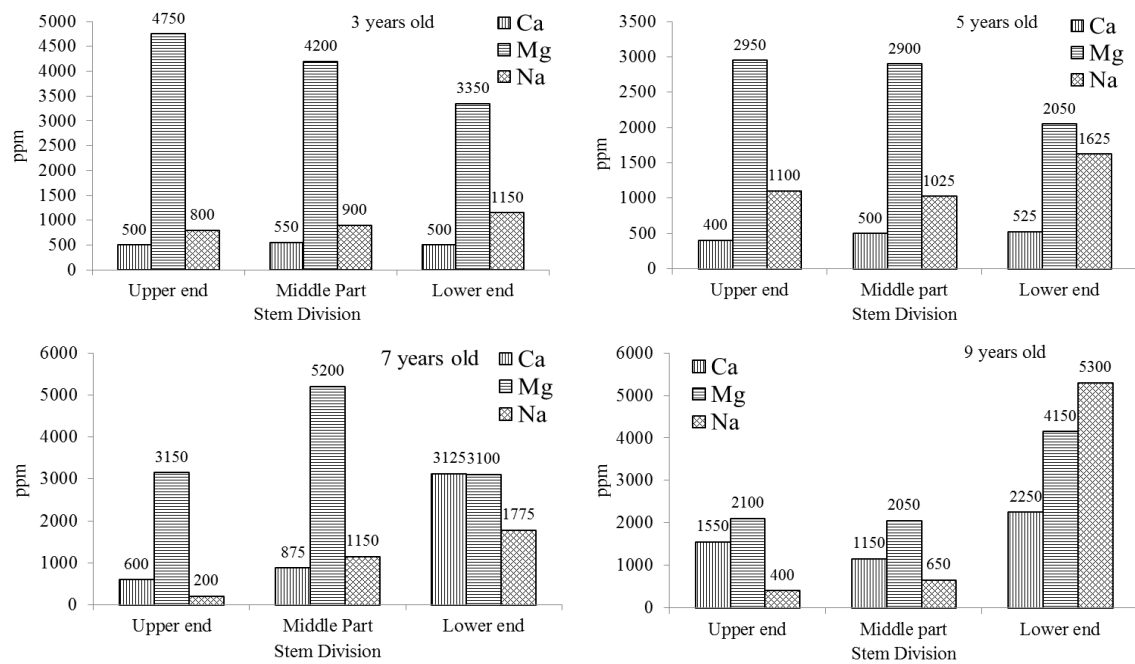


Figure 4 The content of macro elements content of 3-9 years old mangium wood.

Figure 4 indicates that for the 3 and 5 years old wood, the Ca and Mg content of wood was higher at the younger tissues (increasing from the lower end to the upper end of the stem). These finding was in accordance to these of Werkelin *et al.* (2005). However, the Ca and Mg content of the present works were found higher in the lower end of the stems.

Vertical distribution of the content of micro elements of investigated acacia is shown in Figure 5. Except for the 3 years old wood, the content of Fe, Al, and Mn tended to increase from the upper end to the lower end of the stems in almost all of wood ages. It seemed that the Fe, Al, and Mn content tended to increase with the increasing wood age, as well. In the contrary to the distribution trend of Fe, Al, and Mn contents, the content of Cu tended to decrease from the upper end to the lower end of stems and with the

increasing age of woods. Rothpfeffer and Karlton (2007) again indicated that branches contained higher amount of Fe, Mn, Cu, and Al than these of wood (stem). Therefore, it seemed that the present results were not in accord with their finding.

Possible influence of trace elements on oxygen based bleaching

Accumulation of metallic ion in a closed loop cycle system will mainly affect oxygen-based bleaching processes. Oxygen-based bleaching involves treatments with hydrogen peroxide (P), oxygen (O), and ozone (Z). In an alkaline media, hydrogen peroxide is decomposed by the presence of metallic ion (Ni *et al.* 2000). It will bring about the increase of hydrogen peroxide requirement, and thus increasing production cost of pulp making.

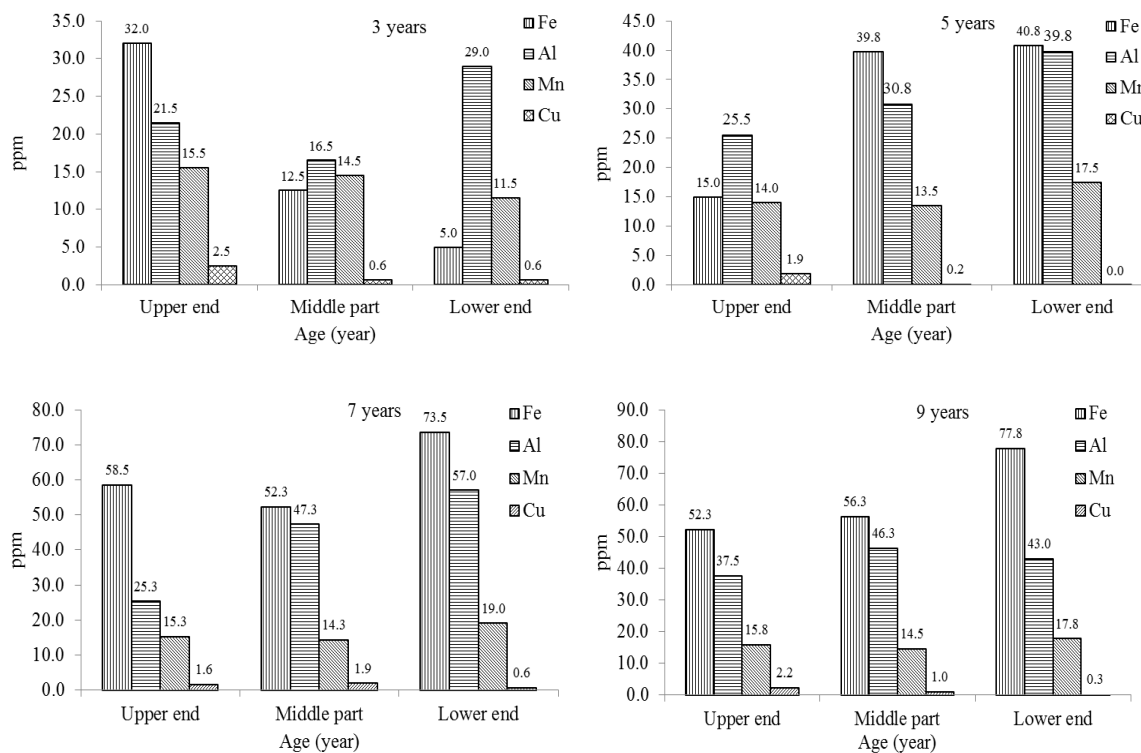


Figure 5 The content of micro elements of 3-9 years old mangium wood.

It has been realized that hydrogen peroxide decomposition created the formation of new chromophoric compound (Yang 1998 in Ni *et al.* 2000) that reduced pulp brightness.

Ions of Fe, Cu and Mn have been found to decompose hydrogen peroxide (Dahl 1999). Among these three metals, in alkaline media, Mn brings about the most detrimental effect in hydrogen peroxide bleaching (Ni *et al.* 2000). Decomposition of hydrogen peroxide by ion of Mn^{2+} started to occur at a very low concentration of about 1 ppm (Dahl 1999). Mn^{2+} oxidized to form Mn^{3+} that actively decomposes hydrogen peroxide. Although some of the metal may dissolved during pulping process, in a closed loop cycle system, precaution should be given when pulping acacia wood. At three years old, it contains 11.5 ppm of Mn. It dramatically increased into more than 20 ppm when the wood reaching the age of 7 and 9 years (as shown by Table 1). Ni *et al.* (1996) reported that Mn did not merely decompose hydrogen peroxide, but it also decomposed ozone. Ozone decomposition reduced its reaction selectivity to lignin. Hydroxyl radicals from the decomposition of hydrogen peroxide and ozone by metallic ion can attack cellulose (Gierer 1997 in Sundén *et al.* 2000), and consequently reduced strength properties of pulp (Sundén *et al.* 2000).

At as low as 2 ppm, iron's ion (Fe^{2+} and Fe^{3+}) start to decompose hydrogen peroxide. At 3 years old, acacia wood contained 5 ppm of Fe, and the content was found as high as 80 ppm at 7 and 9 years old (Figure 5). Fe's ion has been reported to have the highest capacity to decompose hydrogen peroxide (Dahl 1999) via Fenton reaction (Acero *et al.* 2001).

The content of Cu^{2+} in acacia wood was found as high as 1.9 ppm at 5 years old wood, and reached more than 3 ppm at 9 years old. Detrimental concentration limit of Cu on hydrogen peroxide was reported only as low as 0.5 ppm (Dahl 1999). Current research indicates that the content of Fe, Mn and Cu of acacia wood were higher than the limit of suggested detrimental concentration.

Ions of magnesium (Mg^{2+}) and sodium (Na^+) can prevent hydrogen peroxide decomposition through the formation of magnesium sulfate and sodium silicate, respectively. Both of these compounds inhibit the oxidation process of Mn^{2+} into Mn^{3+} , thus the decomposition of hydrogen peroxide by Mn can be hindered.

The formation of chromophoric lignin-metal complex by the presence of metallic ions has been reported to reduce pulp brightness (Sundén *et al.* 2000). Brightness reduction mainly brought about by ions of Fe and Cu, and to a lower extent by Mn and Al (Ghosh & Ni 1998). The minimum amount of metallic ions enable the formation of lignin-metal complex and brightness reduction has not been established yet.

Chelating agents such as EDTA (*ethylenediaminetetraacetic acid*) and DTPA (*diethylenetriaminepentaacetic acid*) are commonly used to remove metal from the system (Li *et al.* 2000). However, in a closed loop cycle system, continuous accumulation of metallic ions will increase the required dose of chelating agents. Acidic washing has been used to remove certain metal, as well. It can be carried out in the pH of 1.5-3.0 with H_2SO_4 . Although, this method has been reported to remove Mg that is beneficial to stabilize hydrogen peroxide in stage P bleaching, it was

considered a better way of removing metallic ions due to the waste was recyclable and reusable (Bouchard *et al.* 1995). The use of chelating agents and acid washing has not been successful to remove all metallic ions from the system. Fe's ion was found the most difficult to be removed, due to its strong attachment to the fibers (Li *et al.* 2000).

Conclusion

Ash content, indicative to inorganic component of acacia wood tended to reduce from upper end to lower end of the stems. The content of Mg decreased with increasing age of wood, and other metals tended to increase with the increase of wood age. Trace elements of acacia wood tended to accumulate more in sapwood compared to these in heartwoods. Vertically, the content of Mg and Cu decreased from upper end to lower end of the stems, and in contrary to these of other metals. The content of metals examined in the present research was found higher than the minimum limit of detrimental concentration allowed in oxygen-based bleaching. Taking into consideration of metals content, 5 years old acacia wood is the most suitable for raw material of pulp making when totally effluent free technology is applied.

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