

## RESEARCH NOTES

## Possible Mechanism for Anthraquinone Species Diffusion in Alkaline Pulping

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An analysis of the effectiveness of anthraquinone (AQ) in kraft-AQ pulping in terms of its mechanism of transport has been conducted. Our previous work showed that caustic solutions of wood lignin can decrease the membrane exclusion for anthraquinones, i.e., the presence of wood lignin enhances the ability of AQ to pass through a membrane when a reducing agent is present in the acceptor stream. This work seeks to demonstrate that a similar behavior may occur during pulping. The adsorption behavior of AQ species was analyzed, and it was shown that anthraquinone-2-sulfonic acid (AQ-S), a water soluble derivative of AQ, selectively adsorbed on wood. The adsorption of AQ dispersed in a caustic lignin solution also showed selective adsorption on wood, to an even greater extent than the AQ-S. This adsorption behavior, along with the membrane penetration behavior described in our previous work, leads to a mechanism for the transport of AQ into wood chips during kraft pulping.

## Introduction

With the presence of anthraquinone (AQ) as a chemical additive in the alkaline pulping process, the delignification rate and the preserved pulp yield can be improved. This can be mainly attributed to the redox cycle mechanism between oxidized and reduced anthraquinone, that is, AQ and anthrahydroquinone (AHQ), respectively. Through such a redox cycle, the aldehyde end groups of carbohydrates can be converted into aldonic acid groups, which stabilize the carbohydrates from further degradation.<sup>1,2</sup> At the same time, the AHQ reacts with lignin in wood chips, which accelerates the delignification. Since AQ is insoluble in caustic solutions, the effectiveness of AQ during the alkaline pulping process could be limited by many factors, mainly mass transfer. Many researchers have conducted various studies in order to discover the reason for the impressive catalytic effect of AQ not only chemically, but also physically.<sup>3–5</sup> Unfortunately, the limited information was unable to explain some interesting and important phenomena that they observed in their studies. One reason might be the lack of an adequate analytical method that can quickly and efficiently determine the AQ content in process liquors, especially in sulfide-containing pulping liquors. There are powerful methods for measuring AQ in liquors,<sup>6,7</sup> but these have not been used extensively to explain observed behavior. In our previous work,<sup>8</sup> we developed a novel method for determination of AQ species in alkaline cooking liquor. It is based on separating AQ species from cooking liquor using a Nafion membrane interface and then converting the AQ species to AHQ by reaction with dithionite in the acceptor solution. The AHQ is then detected spectroscopically at a wavelength of 505 nm.

A previous work attempted to separate AQ or AHQ from black liquor using a Nafion membrane that has a negative surface charge and a pore size below 10 nm.<sup>9</sup> It was found that AHQ is blocked by the membrane. When caustic solutions of AHQ species at moderate concentration were used as the liquor to be analyzed, the spectrum obtained on analysis of the acceptor stream (i.e., after the membrane) showed no response for the AHQs. However, further experimentation showed that at very high concentrations, measurable amounts of the AHQs were detected. In yet another previous study, we demonstrated the mechanism by which AQ can penetrate through a Nafion membrane based on many of these observations.<sup>10</sup> We showed that very high concentrations of AHQ were created at the surface of the membrane from the reaction between AQ adsorbed on the membrane surface and dithionite anions penetrating from the acceptor stream. This enabled the AHQ to partially penetrate the membrane and enter the acceptor stream, as the membrane was swamped by sodium ions from the caustic and sodium dithionite. That work also studied the effect of the addition of lignin to alkali suspensions of AQ. It was shown that the presence of dissolved lignin enhanced the membrane penetration of AQ, perhaps by acting as a dispersant. This then enabled AQ to cover more of the membrane surface area, creating more sites for reaction and membrane penetration.

In this work, we explore the behavior of AQ species in various liquors for this membrane system. This, combined with the adsorption behavior of AQ species and wood, leads to a mechanism by which AQ species diffuse into wood chips during pulping. The effectiveness of AQ on delignification with different process conditions of pine and maple pulping was also investigated.

## Experimental Details

**Chemicals and Sample Preparations.** All chemicals, including the lignin (Aldrich) used in making lignin-enriched liquors,

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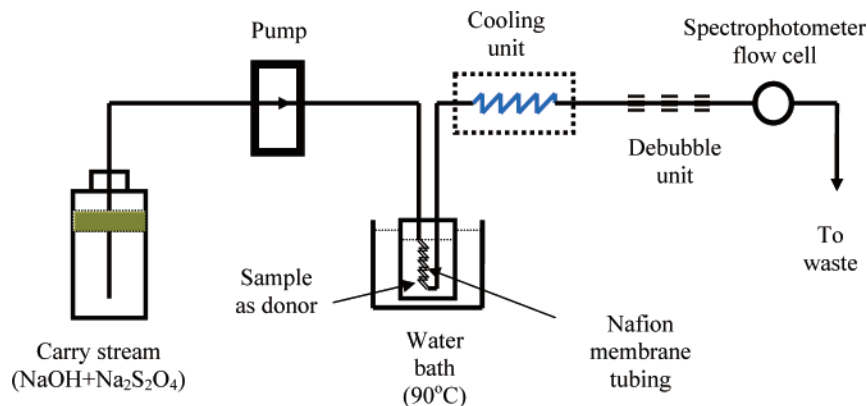


Figure 1. Flow diagram for membrane system.

used in the experiment were from commercial sources. Distilled water was used in the preparation of all solutions.

Sample liquors were withdrawn at different times from several alkaline pulping processes with various sulfidity (10, 20, and 30%  $\text{Na}_2\text{S}$ , Fisher) and AQ charges (0.025, 0.05, and 0.10% on wood) at different ending times (H-factor). All other factors were held constant so that analysis could be made based on only the above changes in conditions. The active alkaline was 18 and 16% for pine and maple cooks, respectively. Soda cooking liquor was obtained from a pine wood pulping terminated at an H-factor of 1000, in which the initial alkali charge is 18%. The liquor to wood ratio used in the pulping experiments was 4:1. In the AQ and AQ-S adsorption studies, the liquor to wood ratio was 5:1.

**Apparatus and Procedures.** The determination of AQ (Acros) and anthraquinone-sulfonate salt (AQ-S, Aldrich) is conducted by a flow analysis method based on a membrane separation and spectroscopic measurement.<sup>8</sup> All conditions (flow rate, dithionite and caustic concentrations, etc.) are the same as in ref 8. A flow diagram of the system is shown in Figure 1.

A coiled length of tubing made from a Nafion polymer through which flows an aqueous acceptor stream is placed into a sealed vial containing the liquor sample to be analyzed. The acceptor stream is then fed through a spectrophotometer flow cell, and changes in the spectrum are measured over time. The acceptor stream consists of at least sodium hydroxide (NaOH, J.T. Baker) and in some instances sodium hydrosulfite ( $\text{Na}_2\text{S}_2\text{O}_4$ , Aldrich). When  $\text{Na}_2\text{S}_2\text{O}_4$  is not present in the acceptor stream initially, it is added shortly before the spectrophotometer (Agilent 8453) to reduce any AQ that passes the membrane to AHQ for spectrophotometric analysis.

Adsorption studies of AQ and AQ-S in soda and kraft liquors were carried out in a beaker placed in the water-bath. Pulping was conducted using a bomb digester. Cooks utilized a 90-min rise to temperature time.

## Results and Discussions

**Behavior of AQ in Alkaline Pulping Process Liquors.** As shown in Figure 2, the presence of lignin greatly increases the ability of AQ species to penetrate the membrane. The liquor containing pure alkaline lignin (70 g/L lignin in 1.5 M NaOH) had an order of magnitude greater response than the pure sodium hydroxide solution (1.5 M). We have previously reported that this may be due to the decrease in the particle size of AQ in the presence of lignin.<sup>10</sup>

Figure 2 also shows that the response of AQ in a soda black liquor ( $H = 1000$ ) is lower than that in the alkaline lignin solution when adding the same amount of AQ solids. This is

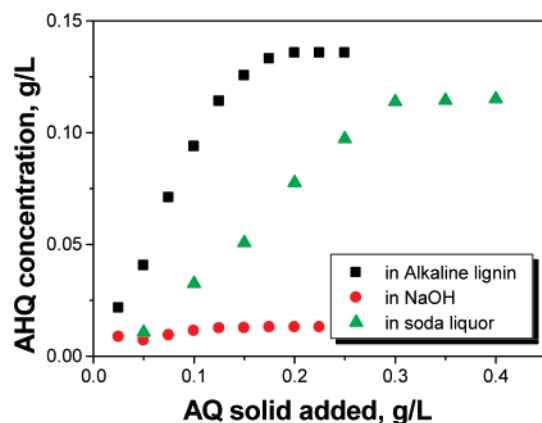


Figure 2. AHQ concentration detected in the acceptor stream for various liquor compositions at 90 °C.

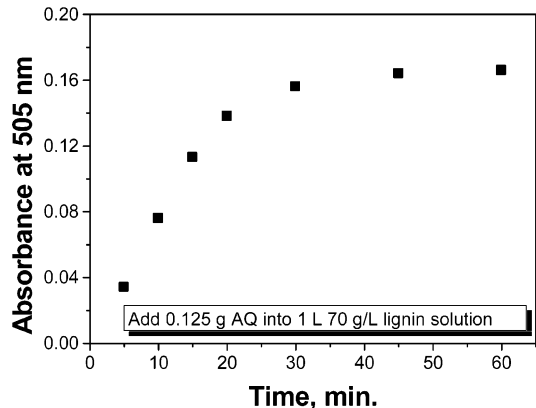


Figure 3. Time dependent profile for AHQ in acceptor stream.

due to the significant amount of carbohydrates that soda liquor contains, which can convert a part of the AQ into AHQ in the bulk solution, rather than at the membrane surface. Again, AHQ cannot pass through the polymer membrane at the low concentrations present in the bulk solution. The response of AQ is also limited by the concentration of the dissolved lignin in the soda liquor.

As shown in Figure 3, it takes about 30–60 min to reach a steady rate of diffusion for 0.14 g AQ powder in 1 L of lignin-enriched alkaline solution at a temperature of 90 °C. It is unknown if the rate of AQ diffusion is affected by higher temperatures during the pulping process.

**Possible Mechanism for AQ Diffusion.** Originally, we attempted to explain the observed behavior through analysis of the chemistry of AQ in pulping. It was thought that since AQ is insoluble, it cannot pass through the membrane directly.

Therefore, a “protected AHQ” model was suggested, based on previous work.<sup>11,12</sup> This theory was based on the reduction of AQ to AHQ either by carbohydrates or the lignin present in the analyzed liquors. The AHQ formed could then form complexes with quinone methides (QMs). It has been shown previously that this can occur at low temperatures (<100 °C).<sup>11</sup> Thus, the AHQ, which cannot normally pass through the membrane, is protected and can pass through the membrane. Then, these adducts can be broken down to release AQ,<sup>12</sup> which subsequently can react with Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> on the other side of the membrane. However, further investigation has shown this mechanism to be incorrect.

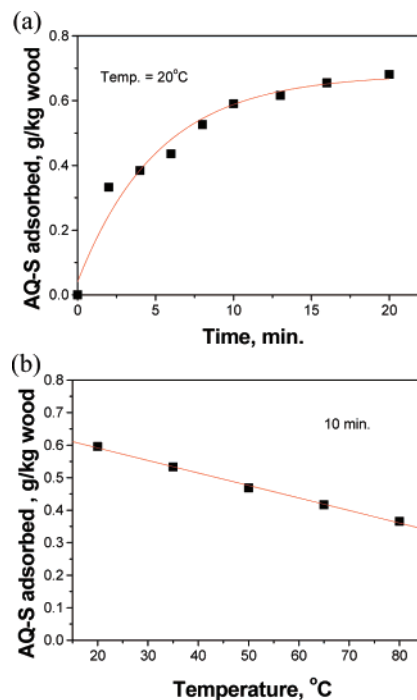
When the experiments that resulted in Figure 1 were repeated without the presence of Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> in the accepts stream, but instead added after the stream exited the analyte vial, no AHQ spectrum was seen, even over long periods of time. This shows that AQ is not in fact being dissolved in the liquor due to lignin matrix effects. The answer to this riddle may lie not in the chemistry of AQ, but instead in the physical properties of both the AQ and the solution.

It has been shown previously that lignin, especially high molecular weight lignin, can act as a surfactant when in solution with alkali.<sup>13</sup> Therefore, it is proposed that the lignin in the enriched liquors is behaving as a dispersant for the AQ, thus breaking up the AQ particles. This could be due to (1) a redox reaction cycle with the lignin (or lignin-carbohydrate complexes (LCCs) or carbohydrates if they are present), (2) the surface activity of the dissolved lignin, or (3) a combination of these. This allows the AQ to cover more of the surface of the membrane tubing. Then, since Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> can freely move out from the inside, AQ is reduced right at the outer surface of the membrane, and the resulting AHQ can move into the membrane, thus bypassing the hindrances it experiences when it is formed in the bulk solution.

This mechanism can be used to explain the results in Figure 2. In pure NaOH, there is no dispersant present, and therefore, the small response seen is to be expected. The AQ is probably in large particles which do not allow for a good covering of the polymer membrane. With only a fraction of the total surface area covered, much of the Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> that exits the membrane will react with AQ in the bulk rather than at the surface, leading to a very low response.

The spent soda cooking liquor contains much lignin, thus it is able to disperse the AQ more widely across the surface of the membrane, resulting in a higher response. However, the liquor also contains many dissolved carbohydrates which can reduce the AQ in the bulk solution rather than at the membrane surface, thus limiting the amount of AHQ that can pass through the membrane. Remember, AHQ formed in the bulk phase cannot pass through the membrane because of the low concentration. Much of the carbohydrates in the spent liquor will have undergone the stopping reaction and, therefore, be unable to reduce the AQ. However, there will still be some carbohydrates existing as either single sugars or as polymers which have not undergone the stopping reaction, and there will still be some contribution from the lignin/LCCs.

The lignin-enriched soda solution provides a nearly ideal environment for promoting the transfer of AQ through the membrane. The solution contains much lignin for the dispersing of the AQ particles, and it lacks carbohydrates which can reduce the available AQ. Some of the AQ can be reduced by the lignin itself, but this is a slow process and may have only a small effect. Thus, the model predicts that this solution will have the



**Figure 4.** (a) Kinetic adsorption of AQ-S on wood chips. (b) Temperature effect on AQ-S adsorption.

greatest response. This is the behavior seen for the lignin-enriched solution in Figure 2.

This has direct implications for pulping and may explain the reasons for the improvement seen in AQ pulping when a surfactant is added.<sup>14,15</sup> In pulping, the polymer membrane is replaced by the chip surface, and the Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> is replaced by carbohydrates that are leached out of the chip by alkali. A surfactant can disperse the AQ into smaller particles, which then adsorb onto more of the chip surface than without surfactant. Carbohydrates leached from inside the chip then react with the AQ coating, forming a high concentration of AHQ directly at the surface. The concentration here would be much higher than the concentration if all of the AQ were reduced in the bulk liquor. This high concentration enables rapid diffusion through the chip and, thus, improved delignification and yield enhancement.

**Study of AQ Adsorption Behavior on Wood Chips.** It is difficult to study the adsorption behavior of AQ on wood chips due to a solubility limitation of AQ in the solution. Instead, we use anthraquinone-2-sulfonic acid (AQ-S), a water-soluble derivative of AQ, to observe its adsorption behavior on the wood chips. This can then be used as an estimation of the behavior of AQ in pulping. The study shows that the dissolved AQ-S can adsorb onto the wood chips, and the amount of AQ-S adsorbed on the chips is a function of the time and temperature as shown in Figure 4a and b. The equilibration of adsorption can be achieved within 20 min. The amount of AQ-S adsorbed is inversely proportional to the temperature of the system. Therefore, this adsorption should be regarded as a physical adsorption.

The study also showed that the adsorption of AQ-S on wood chips is selective, because its reduced form, anthrahydroquinone-2-sulfonic acid (AHQ-S), does not significantly adsorb on the wood chips under the same conditions. We also conducted a single AQ adsorption test by impregnating wood chips in a suspension of AQ in a caustic lignin solution (0.03% AQ in a 40 g/L alkaline lignin solution) at a temperature of 80 °C. The

results showed that the equilibrium amount of AQ adsorbed was higher than that for AQ-S under the same experimental conditions.

**Mass Transfer of AQ in Wood.** It is very important in the pulping process for the acting agent to be able to diffuse into the wood chips. The penetration behavior of AHQ in wood chips could be similar to that demonstrated with the Nafion membrane. AHQ formed in the bulk phase may have a lesser ability to diffuse into the chip due to reasons stated above. If this is the case, we can easily explain why the soluble AHQ does not provide an advantage over regular AQ in the pulping process.<sup>16</sup> Falk et al. showed that using AHQ as a starting material improved results over AQ only when the chips were impregnated with AHQ prior to cooking, thereby bypassing the diffusion limitations of AHQ.<sup>17</sup>

Thus, the following is proposed for the mass transfer of AQ during the alkaline pulping process. AQ particles adsorb onto wood chips where these react with carbohydrates leaching out from the wood to form AHQ. The addition of surfactant will improve the spreading of AQ particles across more surface area of the chip. The newly formed AHQ can immediately diffuse into the chip and react with wood lignin on-site. The redox cycle takes place on the wood phase. The effectiveness of AQ to such a redox cycle will decrease when the formed AHQ exits the chip into the bulk solution. AQ will lose its functionality in later stages of the pulping process since a large amount of dissolved lignin and carbohydrates pass into the process liquor, thus allowing the redox cycle to take place in the liquor phase rather than in the wood phase. The efficacy of AQ pulping is diminished by side reactions that consume AQ.<sup>7,18,19</sup> However, the effectiveness of the remaining, unreacted, AQ is also reduced due to the liquor phase redox cycle.

**Effectiveness of AQ in Kraft Pulping Processes. 1. Sulfide Effect.** It has been reported that the effectiveness of AQ decreases as the sulfidity of white liquor increases.<sup>20–22</sup> It is well-known that sulfide is a reduction agent and could react with AQ, an oxidant. Previous work has shown that sulfide can readily reduce AQ at high temperatures.<sup>22,23</sup> However, experiments showed that the reaction between solid AQ and sulfide in white liquor is insignificant even if the temperature is at close to the boiling point. The same experiment was conducted using AQ-S, a soluble species, to react with sulfide in the white liquor. It was found that a complete conversion of AQ-S to AHQ-S occurred within a short time at a temperature above 50 °C. Therefore, the extent of dispersion of AQ solids in the above experiment limits the reaction between AQ and sulfide. However, it can be expected that a much faster reaction between AQ and sulfide will take place during the pulping process where the surface area of the AQ is greatly increased due to the presence of the dissolved lignin in the cooking liquor. A higher sulfidity in cooking liquor can convert more AQ into the AHQ form, which can reduce the transport of AQ species into the wood chip.

**2. Process Time Effect during a Conventional Pulping.** It was found that AQ is most effective during the early stages of pulping. This was actually revealed by the work conducted by Sezgi et al., which tells the difference in kappa number for the pulp samples from kraft and AQ-kraft pulping processes at different H-factors as shown in Fig 10 of that paper.<sup>24</sup> The figure clearly indicates that the effect of AQ on delignification at an H-factor below 2000 is very significant. Cooks utilizing AQ displayed a reduction of six kappa number units over the process without AQ. However, the benefit gained by the addition of AQ disappears when the H-factor reaches 2500. Here, cooks

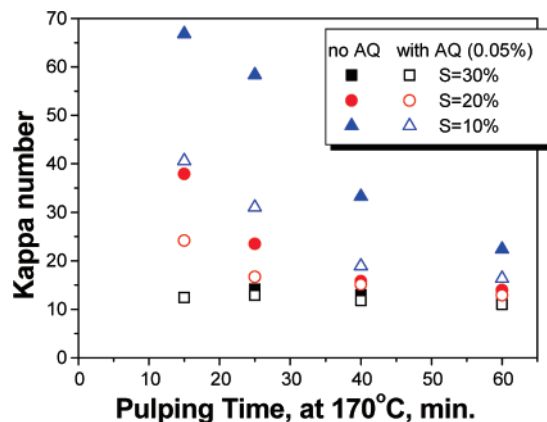


Figure 5. AQ and sulfide effect on delignification during pine kraft pulping processes.

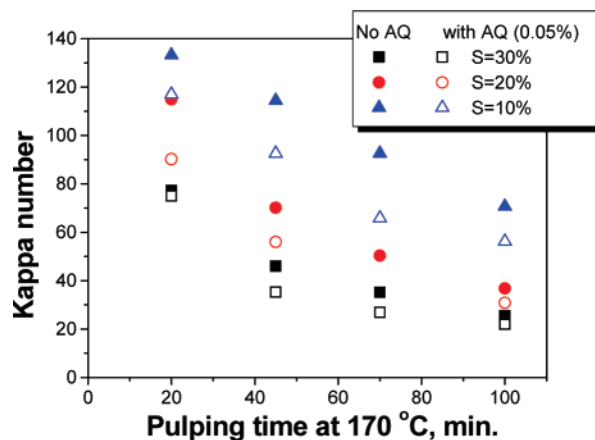


Figure 6. AQ and sulfide effect on delignification during maple kraft pulping processes.

containing AQ produce pulps with the same kappa number as that of pulps without AQ.

In the present study, we conducted a set of AQ-containing (0.05%) kraft pulping experiments at varying sulfidities and H-factors using both southern pine and maple wood to compare AQ efficiency in delignification. As shown in Figures 5 and 6, the efficiency of AQ is higher at lower H-factors (shorter cooking time) and lower sulfidities. This is demonstrated by the greater change in kappa number between the AQ-containing and AQ-free cooks at these conditions.

This demonstrates that sulfidity plays a more important role on the delignification at the level of 0.05% AQ charge. Meanwhile, we found that even for the process with higher sulfidity charge (30%), the effect of AQ addition on the delignification is still significant at a lower H-factor (410) if a sufficient amount of AQ is introduced, as shown in Figure 7. However, the benefit of AQ addition will be lost gradually as the cook continues. Therefore, we can conclude that the effectiveness of AQ is limited mainly to the initial stage during the conventional kraft pulping process.

**3. Effect of Pulping Mode.** It has been reported that AQ is less effective in the displacement batch pulping operations, such as rapid displacement heating (RDH) and SuperBatch, than it is in conventional batch cooking.<sup>24,25</sup> It can be easily explained by the phenomenon we discussed above. First, the AQ adsorption on wood chips plays an important role to the delignification and a lower temperature is ideal to such an adsorption. Second, a significant amount of dissolved lignin and carbohydrates in the cooking liquor can limit the AQ to AHQ redox cycle to

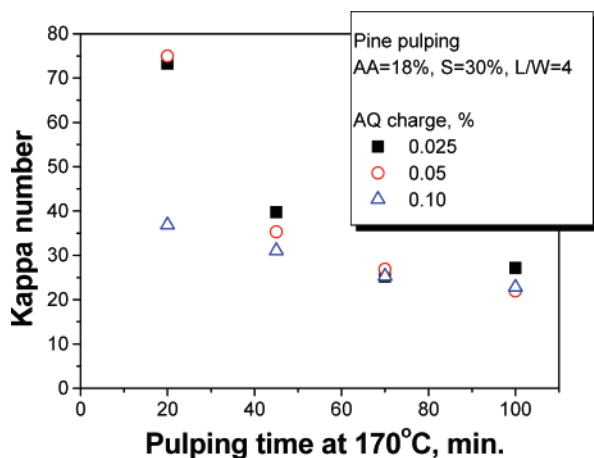


Figure 7. AQ charge effect on delignification during kraft pulping processes.

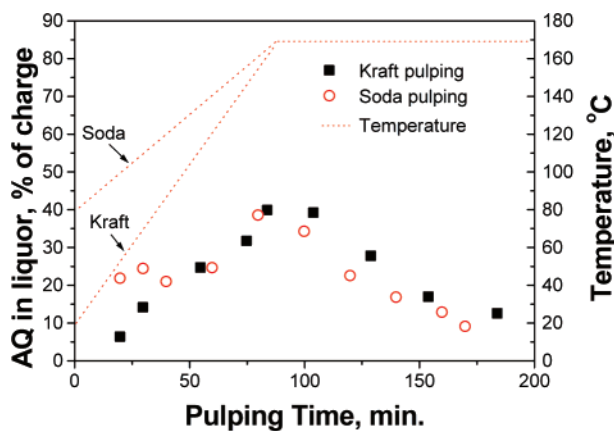


Figure 8. Suspended AQ profile during a conventional kraft pulping process; soda pulping results from subtraction of data points in Figure 5 of the work by Fleming et al.<sup>7</sup>

within the cooking liquor and affect the adsorption of AQ on the wood chips.

Also, it was found that AQ or AHQ is consumed during the late stage of the cook as shown in Figure 8. Therefore, only the process conditions at the early stage of a conventional batch process is ideal to meet the requirements. Thus, we suggest that the AQ-containing pulping research should be focused on the early stage of conventional pulping processes.

## Conclusions

This study showed that AQ dispersion can be enhanced by dissolved lignin in alkaline solution. This dispersion of AQ in lignin-enriched solution is a relatively slow process, which takes about 30–60 min to achieve a maximum. Enhancing the dispersion leads to increased adsorption on the chips. This then creates a more favorable environment for AQ species to diffuse into the chips. Studies also show that the effect of AQ on delignification is very significant during the early stage of the pulping process.

## Acknowledgment

The State of Georgia (Grant No. PP02-MP-03) is greatly acknowledged for providing the financial aid to make this work possible.

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Received for review December 7, 2006  
Revised manuscript received March 8, 2007  
Accepted May 16, 2007