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How Does Mass Transfer Affect the Effectiveness of AQ?

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## **How Does Mass Transfer Affect the Effectiveness of AQ?**

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### **Abstract**

Many researchers have performed various studies to discover the reasons for the impressive catalytic effect of anthraquinone. Discussions and experiments have been conducted on the chemistry, kinetics, and physical properties of anthraquinone (AQ). However, most of the previous research has neglected the role of mass transfer in AQ pulping. This paper describes our analysis and interpretation of published experimental data based on both chemical (kinetics) and physical (mass transfer) effects. This new analysis of the historical data has led to a proposed “AQ uptake” mechanism that incorporates the mass transfer effects. Explanations are given for previously unexplained and/or underexplained phenomena involved in the AQ mechanism. This analysis leads to an acknowledgment of physicochemical effects by which AQ is concentrated into the wood chips in the early stages of pulping. Previous work described the reason for this as the physical attraction between the AQ and the wood. However, our analysis of recent published data has shown that a more likely explanation is immobilization of AQ molecules due to reaction with lignin that causes solid AQ to precipitate out of the liquid phase and deposit on internal chip surfaces. Acknowledgment of the role of mass transfer in pulping with AQ could lead to improved pulping conditions that can take better advantage of the catalytic abilities of AQ.

## **Introduction**

Ever since anthraquinone (AQ) was first introduced to the paper industry as a pulping additive in 1977 [1], researchers have been attempting to discover the reasons behind the effectiveness of AQ in accelerating delignification and preserving yield. Studies ranging from forays into elucidating the chemical mechanism of the AQ-lignin reaction to exploration of the chemical reaction kinetics have led to the current understanding of the pulping additive. The most significant findings include: (a) that the redox cycle mechanism between AQ (insoluble anthraquinone) and AHQ (reduced, soluble forms of anthraquinone) leads to accelerated delignification and reduced carbohydrate peeling reaction [2,3,4]; (b) the effect of AQ on delignification kinetics is proportional to the square root of AQ charge on wood weight [5,6,7]; (c) AQ is effective in alkaline-to-neutral pH range, but not in the acidic pH range [8,9].

Despite these findings, some interesting and possibly important observations have never been satisfactorily explained. For example, researchers do not fully understand the reason that the delignification kinetics is proportional to the AQ charge on wood and not dependent on the AQ concentration in the liquid phase as it is normally found for other pulping chemicals such as sulfide and hydroxide. Another interesting finding, by Fleming et al. [10], is that AQ is “concentrated” into the wood chips at the early stage of bulk delignification, and this “concentrating” effect is then diminished as delignification proceeds to a higher degree. More recently, it was reported in a number of studies [11,12] that AQ is less effective in displacement batch pulping operations, such as RDH and SuperBatch™, than it is in conventional batch cooking.

To provide a more satisfactory explanation for these observations, many of these earlier studies are here reexamined to include not only the effect of redox cycle, but also the effect of AQ mass transfer processes. This involves transfer between bulk liquid phase and chips and intrachip transfer, as well as the solubility of different forms of AQ. By employing this approach, many earlier findings can be explained. More importantly, if these mechanistic interpretations can be confirmed by experimental study, they could provide guidance toward improving the efficiency of AQ in alkaline pulping.

### **Effect of AQ Dosage on Delignification Kinetics**

Many studies around the world have been conducted in the last quarter-century on the effect of AQ on delignification kinetics. It is well established that the kinetics of kraft-AQ or soda-AQ delignification [5,6,13] can be expressed as

$$-\frac{dL}{dt} = k_{AQ}^* AQ^{1/2} [OH^-]^a [HS^-]^b L^c \quad (1)$$

where  $dL/dt$  is the delignification rate,  $L$  is the lignin content in wood,  $k_{AQ}^*$  is the rate constant for the delignification reaction,  $[OH^-]$  and  $[HS^-]$  are the concentrations of hydroxide and hydrosulfide ions, **AQ is the weight percentage of AQ charge based on oven-dry wood weight**, and  $a$ ,  $b$ , and  $c$  are constants. For soda-AQ cooking, the  $[HS^-]$  term can be ignored. It is important to note that this equation holds only over the limited range of concentrations studied here.

The form of Equation (1) is an ordinary power law kinetic equation. Of particular interest is the effect of AQ dosage. It affects the rate based on the amount of charge on wood weight, instead of its concentration in the liquid phase. The effect of AQ concentration on delignification kinetics is not apparent in many published reports. It is

of importance to find out how the reaction kinetics is affected when the AQ concentration in the liquid phase is changed at a constant AQ dosage on wood. The following kinetic analysis using some published data is intended to illustrate this.

It was demonstrated that when delignification is divided into initial, bulk, and residual phases, each phase of the reaction is first-order on lignin [6,14]. However, to develop a single, overall empirical rate equation, covering at least two phases, e.g., bulk and residual, it was found that the rate is better described by the second-order kinetics [5,6,13]:

$$-\frac{dL}{dt} = k_{AQ}AQ^{1/2}L^2 \quad (2)$$

where  $k_{AQ}$  is the reaction rate constant containing the effect of hydroxide and hydrosulfide ion concentrations.

Integrating this second-order rate, Equation (2) yields:

$$\frac{1}{L} - \frac{1}{L_w} = k_{AQ}AQ^{1/2}t \quad (3)$$

where  $L_w$  is the concentration of lignin in the original wood. The concentrations of lignin in the wood and pulps can be related to the kappa numbers of the pulps with the following relationship:

$$L = \kappa \times 0.15 \times \text{yield} \quad (4)$$

for softwood, where  $\kappa$  is the kappa number of the pulp or wood. The kinetics can therefore be estimated using the kappa number in place of the lignin concentration, and Equation (3) can be rewritten as:

$$\frac{1}{\kappa_p \cdot \text{yield}} - \frac{1}{\kappa_w} = k_{AQ}^+AQ^{1/2}t \quad (5)$$

where  $\kappa_P$  and  $\kappa_W$  are the kappa numbers of the pulp and the wood, respectively, and  $k_{AQ}^+$  equals  $0.15 \cdot k_{AQ}$ . If the yield is high, Equation 5 can be estimated by Equation 6:

$$\frac{1}{\kappa_P} - \frac{1}{\kappa_W} = k_{AQ}^+ AQ^{1/2} t \quad (6)$$

It was found that Equation (6) works well for data covering bulk and residual delignification phases [13,15].

Although they were researching a different kinetic phenomenon, Abbot and Bolker [13] generated data that provide the best illustration that a change in AQ concentration in cooking liquor has no influence on its catalytic effect at constant AQ dosage on wood. Figure 1 shows the kappa number as a function of AQ charge on wood for two different liquor-to-wood ratios, 10:1 and 40:1 [13], while all other conditions, i.e.,  $[OH^-]$ ,  $[HS^-]$ , time, and temperature, were held constant.

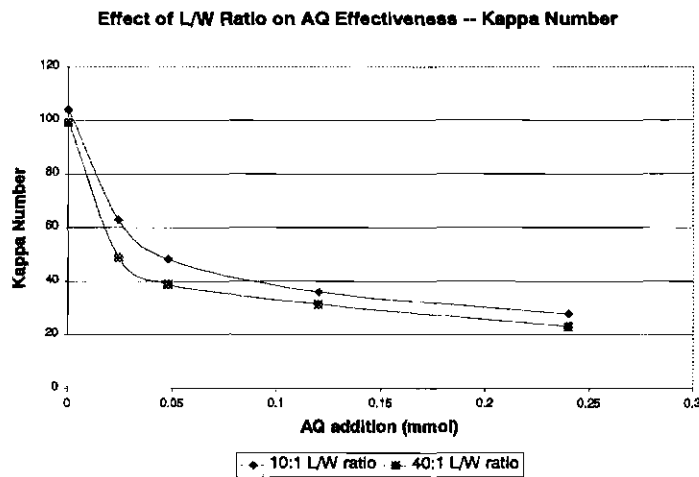
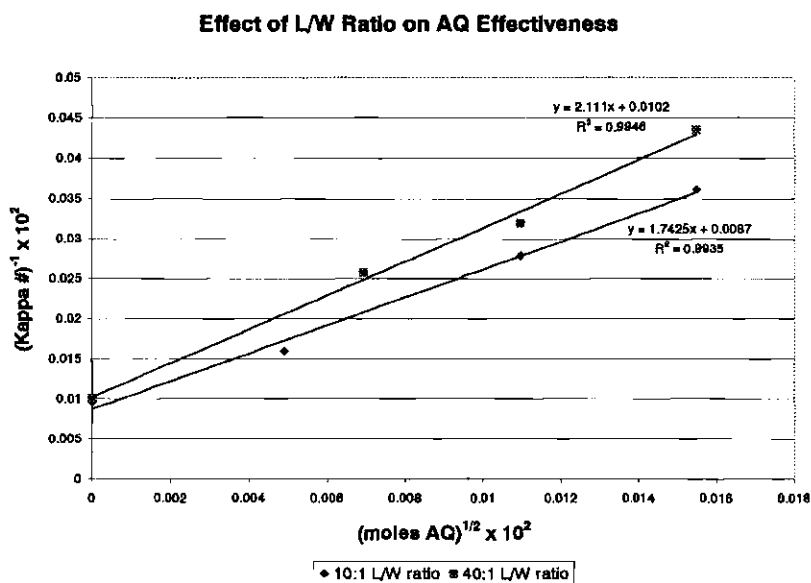


Fig. 1: Plot of kappa number versus AQ charge for different L/W ratios [13]. Notice that the higher L/W ratio has a lower kappa number for each AQ addition.

The pulps at higher liquor-to-wood ratio, i.e., 40:1, reached a slightly lower kappa number at any given AQ addition. This may be due to the greater availability of caustic in the 40:1 case. The important point to take from this plot is that the trend is the same for both cases. Removing the effect of alkali availability, the addition of AQ has the same effect on delignification, and this cannot be explained by the effect of change in the concentration of AQ in the liquid phase. Increasing the L/W ratio by a factor of 4, from 10:1 to 40:1, with the same amount of AQ dosage effectively decreases the concentration of AQ in cooking liquor to 25% of the concentration at a 10:1 liquor-to-wood ratio. If AQ were always soluble in alkaline pulping, this concentration decrease would be evident in a decrease in AQ effectiveness, i.e., a flatter trend in the graph for the higher L/W ratio. The experimental results indicated otherwise.

This phenomenon is more clearly demonstrated when the data in Figure 1 are analyzed based on Equation (6). Figure 2 shows the plot of the inverted kappa number as a function of square root of AQ charge, which yields a straight line for each liquor-to-wood ratio. The straight lines indicate that these results can be described by the kinetic Equation (6). The slopes of the lines give the rate constants,  $k_{AQ}^+$ . The rate constant for 40:1 liquor-to-wood ratio is slightly higher (not lower!) than that for 10:1 liquor-to-wood ratio. This may also be due to the greater availability of caustic in the 40:1 case. However, the similar trend between the two plots confirms that the AQ concentration based on liquid volume is irrelevant to the AQ kinetics.





**Fig. 2:** Plot of the kinetic effect of AQ addition on kappa number at different L/W ratios [13]. Pulp made using liquor with an EA of 2.0M NaOH. Note the increase in kappa reduction rate for higher L/W ratio.

### The Mechanistic Interpretation of the Kinetic Behavior

The fact that the data do not support the kinetics based on AQ concentration in liquid phase implies that another mechanism is occurring. The most likely explanation is that AQ is concentrated into the wood chips by some physicochemical effects. Therefore, the amount of AQ uptake by wood chips is a function of AQ available in the digester, and the kinetic rate of delignification is only affected by the amount of AQ available in the wood chips. This explanation fits well with the kinetics based on AQ charge on wood rather than the concentration of AQ in the liquid phase. Therefore, the question of what phenomenon causes the AQ to concentrate in the wood chips arises.

### *Xylophilicity and Hydrophilicity*

Werthemann gives one possible explanation [16]. He discussed the unique kinetics of AQ charge on wood in 1981. His paper stated that AQ concentrated into wood chips due to the phenomenon that he dubbed the xylophilicity of AQ. This is a measure of the additive's affinity toward wood versus water in a pulping system. This is in contrast to the principle of hydrophilicity, which is a measure of the additive's affinity to water; i.e., an additive with higher hydrophilicity tends to remain mostly in the liquid phase. AQ has a low hydrophilicity, but not so low as to make it unable to move into the liquid phase. In comparison, anthraquinone-2-sulfonate (AQ-S) (a highly soluble derivative of AQ) has a very high hydrophilicity because of its high solubility [16]. While in the liquid phase, AQ-S can diffuse out of the chip as easily as it can diffuse into the chip. This is used to explain the fact that AQ-S has much lower effectiveness than AQ does since AQ-S cannot selectively concentrate in the chips where it can be effective.

Although the concept of xylophilicity and hydrophilicity works well to explain the kinetic behavior of AQ and AQ-S, the experimentally measured AQ distribution in wood chips and bulk cooking liquor during a cook did not confirm it [10]. Actually, the fact that a large amount of AQ is released into bulk cooking liquor during the bulk delignification represents convincing evidence that xylophilicity is not the phenomenon responsible for the apparent behavior of AQ.

### *The Proposed "AQ Uptake" Mechanism*

After analyzing many published reports on AQ kinetics, the catalytic mechanism on delignification, and the fade of AQ during alkaline pulping, we attribute the "AQ

uptake” phenomenon to the “soluble and insoluble” cycle resulting from the redox reaction cycle.

Initially, the insoluble AQ particles are suspended in the cooking liquor. Some of the AQ could also be sitting on the surface of the chips. The AQ cannot enter the chips because the suspended particles are not dissolved and are unable to diffuse through the fiber wall. As the temperature rises, the AQ begins to be reduced to soluble AHQ by carbohydrates dissolving out into the liquor. The mobile AHQ molecules can then diffuse into the chip. Once inside the chip, the AHQ can react with lignin, becoming AQ again. **Because AQ is insoluble, it becomes immobile, thus staying in the wood chips until it is reduced by carbohydrate reducing end groups. As more AHQ diffuses into the chips, more AQ is formed, and thus trapped in the chips. At this stage, the insoluble AQ is only reproduced from AHQ in the chips because most reactive lignin only resides in the chips. On a macro scale, it appears as though AQ is adsorbed or deposited into the wood chips, or one could even say that AQ is adsorbed by the lignin in wood.**

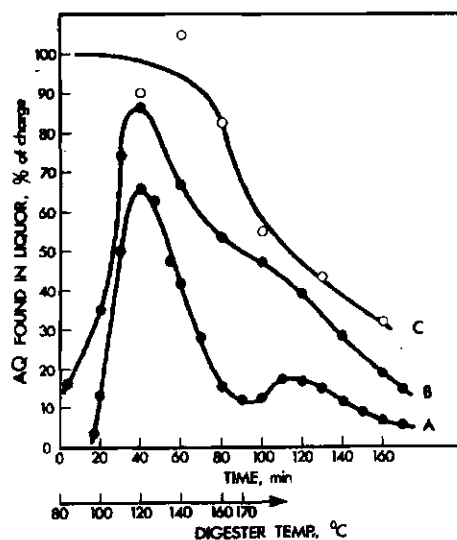
The amount of AQ uptake by the wood chips is only a function of the amount of AQ available in the system, not its concentration. The amount of lignin depolymerization induced by AHQ depends on the amount that is taken up into the chip. Thus, the AQ effectiveness becomes proportional to its dosage on wood weight.

This AQ deposition process continues until the temperature reaches a point at which the delignification reaction rate is very high. As delignification continues, large numbers of lignin fragments diffuse out of the chip into the liquor. These fragments are not completely depolymerized. Therefore, the AHQ in the chips can diffuse back out of

the chips to react with the lignin in the liquor. At this stage, the apparent AQ accumulation in wood chips stops. The AQ concentration in wood starts to decrease.

#### *Experimental Confirmation from AQ Concentration Variation during Pulping*

The AQ uptake mechanism proposed above is well supported by the study reported by Fleming et al. [10]. Polarographic analysis conducted by Fleming et al. shows that the concentration of AQ in the chips and liquor varies with time during the cook [10]. The data, obtained in soda-AQ cooking of black spruce chips, are presented in Figures 3 and 4. These plots display a very interesting picture of the location and oxidation state of AQ during the course of a cook.



**Fig. 3:** Distribution of AQ in pulping liquor as a function of time and temperature [10].

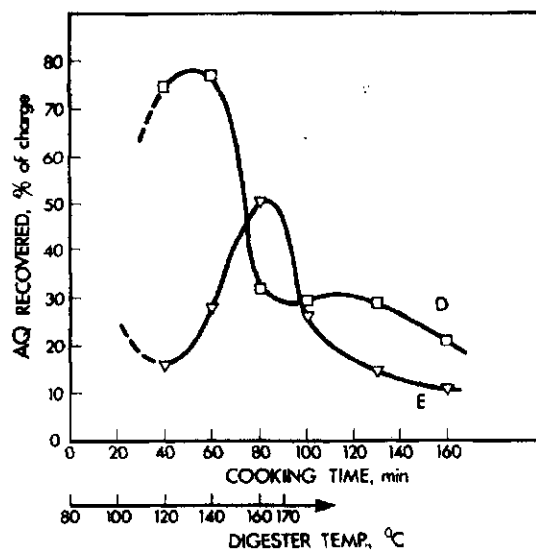


Fig. 4: Distribution of AQ between free liquor (D) and wood chips (E) [10].

Curve A in Figure 3 represents the change in the concentration of reduced AQ forms ( $AHQ^{\ominus}$  and  $AHQ^{\ominus 2}$ ) during the cook. Curve B represents the total AQ in the pulping liquor. Curve C represents the total AQ in both the liquor and the chips. Curve D in Figure 4 is the amount of AQ in free or bulk cooking liquor, while Curve E is the amount of AQ in wood chips [10].

Initially, there is very little AQ in any reduced form (AHQ) present in the system. As carbohydrates begin to dissolve into the liquor, these begin to reduce the AQ and render it soluble, accounting for the rise in Curves A and B. As the temperature rises, the rate of AQ-lignin reaction increases, causing the concentration of AHQ in the bulk liquor to decrease as AHQ diffuses into and is retained in the chips. This accounts for the drop in Curves A and B at above 120°C. Once cooking temperature is reached, Curve A, i.e., AHQ in bulk cooking liquor, increases somewhat, possibly because the AHQ diffuses out of the chips to react with the large amount of dissolved lignin. The widening gap

between Curves B and C in Figure 3 shows that AQ was depositing on the chip surface [10]. This is supported by the curves in Figure 4. At the approximate cooking temperature, total AQ (AQ and AHQ) reaches a maximum in the chips as shown in Curve E. At the same time, Curve D displays a minimum. The total liquor-to-wood ratio used in this study was 5:1 L/kg, and the liquor residing in wood chips when temperature reached 170°C is about 1.5-2 L/kg wood; thus, bulk cooking liquor should be about 3-3.5 L/kg wood. Using these liquor distribution figures and the AQ distribution at 90 minutes in Figure 4, one can calculate that the AQ concentration in the liquor within the wood chips is 2.5-4 times higher than that in the bulk liquor. The only way for this to happen is that a large portion of the AQ within the chips is not in soluble form.

The reaction between AHQ and lignin has been shown to be a single electron transfer (SET) reaction [17]. This report stated that the redox cycle was most likely between  $\text{AHQ}^\cdot$  (radical anion) and  $\text{AHQ}^{2-}$  (dianion). In contrast, the data presented here suggest that the AHQ in the chips is oxidized all the way to the immobile AQ. Therefore, the data suggest that the redox cycle during alkaline cooking is more likely between AQ and  $\text{AHQ}^\cdot$ , rather than  $\text{AHQ}^\cdot$  and  $\text{AHQ}^{2-}$ .

Figure 4 shows that in the later part of the cook, where a large amount of dissolved lignin has diffused into bulk liquor, the AQ distribution becomes similar to the liquor distribution inside and outside of the wood chips. This is because the redox cycle can take place also in bulk liquor; i.e., AHQ can react with the dissolved lignin in bulk liquor. The AQ distribution in this part of the cook also suggests that the concept of xylophilicity cannot be true since AQ is no longer “concentrated” inside the wood chips when the bulk liquor has a high enough concentration of dissolved lignin.

## **The Effect of AQ Mass Transfer Mechanism on Its Efficacy in Pulping and Industrial Implications**

Similar to other heterogeneous chemical reactions, the AQ mass transfer mechanism can have a significant impact on its catalytic effectiveness. Depending on how the pulping conditions are designed, the rate of AQ penetration, the AQ concentration in wood chips, and the reaction rate with lignin can be varied greatly. The following are attempts to analyze how AQ mass transfer can affect the delignification rate and how its efficacy can be improved.

### *Soluble vs. Insoluble*

Since AQ must be reduced to AHQ before it can diffuse into wood chips, and because it is in insoluble form after AHQ reacts with lignin in wood, the mass transfer of AQ to the center of wood chips is lower than completely soluble AQ derivatives, such as AQ-sulfonate (AQ-S). However, the slow mass transfer due to the insoluble AQ phase is a two-edged sword. Although it decreases the mass transfer rate of AQ, it can be beneficial in alkaline-AQ pulping. The insolubility of AQ causes AQ to be retained on the sites in the chip where it can be effective. If AQ remains soluble (i.e., in the forms of  $AHQ^-$  and  $AHQ^{\cdot-}$ ) at all times in the cooking cycle, it would be able to diffuse out of the chip as readily as it can diffuse into the chip. This will make for speedier diffusion, and thus more homogeneous pulp, but the decreased concentration inside the chip where AQ is effective can be detrimental to its overall effectiveness. **This analysis suggests that it**

**may not provide any economical paybacks to develop or use completely soluble AQ derivatives.**

### *Initial Soluble Form*

Although the completely soluble AQ derivatives may not provide an advantage over regular AQ, if AQ is initially in a soluble form, such as prereduced to AHQ, or SAQ, but can still undergo the soluble-insoluble redox cycle, it can be more effective in short heating-time cooks. This is because it eliminates the time required for the initial solubilization.

An article by Dutta and Biermann supports this effect [18]. These researchers discuss the differences between 1,4-dihydro-9,10-dihydroxyanthracene (DDA, also known as soluble AQ or SAQ) and AQ. Their data show that DDA is a more effective additive than AQ. DDA is soluble in aqueous solution. Its solution can be easily dispersed into the white liquor. Dutta and Biermann used an “instantaneous” or very short heating time to the final cooking temperature by preheating the hot oil bath to the cooking temperature before the bomb digesters were placed into the bath [18]. The short rise to cooking temperature does not allow AQ to be reduced by dissolved carbohydrates in the liquor before the alkali in the digester reacts with the wood components. Since it cannot be reduced until later in the cook, by the time AQ has diffused into the chips it would be too late to provide the catalytic benefits. However, Dutta and Biermann’s results would be applicable to digesters with very short heating time, e.g., vapor phase cooking using direct steaming.



Other researchers, however, found conflicting results: that AQ was at least as effective as DDA. Pekkala compared tetrahydroanthraquinone (THAQ, the oxidized form of DDA) to AQ and found it to be only 95% as effective as AQ [19]. In his experimental design, Pekkala allowed for a rise-to-temperature time of 105 minutes. This gave enough time for the AQ to be reduced to the soluble state by the carbohydrates. Under these circumstances, the initial mass transfer limitation of AQ is reduced. Pekkala's and Dutta and Biermann's results confirm that mass transfer could play an important role in making AQ more effective. **If AQ is supplied in a soluble form, it can be more effective in the pulping processes with short heating time.**

#### *Initial Presence of Dissolved Lignin in Cooking Liquor*

One important phenomenon proposed in the present report is that the "AQ uptake" by the wood chips results from the "reoxidation" of AHQ to insoluble AQ by lignin in wood. However, if there is a large amount of dissolved lignin in the bulk cooking liquor, the redox cycle can take place in the bulk liquor as well. The "AQ uptake" by wood chips would not happen to a large extent, and thus the AQ concentration in wood chips would be about the same as in bulk liquor. Therefore, the overall AQ effectiveness would be lower than that when dissolved lignin is not present in the initial cooking liquor.

Some studies performed on AQ effectiveness in RDH cooking provide the supporting evidence for the above suggestion [11,12]. It was found that when AQ was added with warm black liquor and hot white liquor, it provided little catalytic effect on delignification. When AQ was added with hot black liquor, delignification was

accelerated. The overall effect, however, was less than that seen in conventional kraft cooking. The large amount of dissolved lignin in the hot black liquor will probably react with some of the AQ.

It was observed in some mill trials that when AQ was added with the black liquor rather than white liquor in conventional batch cooking, its effectiveness was lower. The original thinking of adding AQ with black liquor was that the dissolved sugar molecules in black liquor would reduce AQ to AHQ quicker so that AQ would be able to penetrate wood chips faster. There is no evidence that such thinking is wrong. The likely explanation is that the dissolved lignin has “short-cut” the redox cycle in bulk liquor rather than in wood chips.

**The above discussion suggests that AQ’s effectiveness will be impaired when it is added to a cooking environment containing a large amount of dissolved lignin, such as all phases in RDH-type cooking and in the middle of continuous cooking.**

#### *Other Unanswered Questions*

The mass transfer mechanism for AQ proposed in this report has properly explained some phenomena related to AQ kinetics and industrial application. There are other unanswered questions in “AQ science and technology” that could be related to mass transfer. One example would be the well-known sulfidity effect: the effectiveness of AQ decreases as sulfidity of white liquor increases [20,21,22]. Could this be related to the mass transfer rate of hydrosulfide and AQ? One explanation could be that parallel reactions, one involving  $\text{HS}^-$  and another involving AQ, might be occurring, thereby

decreasing the chemical effectiveness of AQ. However, the much higher diffusion rate of HS<sup>-</sup> ions might preclude the AQ from “concentrating” in the chips by degrading the lignin before AQ has a chance to react with it. Correct answers to this question, and possibly others, could lead to modifications of the cooking process to enhance the effectiveness of AQ in pulping.

### **Concluding Statements**

The “AQ uptake” mechanism proposed here explains the catalytic effect of AQ in terms of the kinetics, chemistry, and physical properties of AQ and wood. The proposed mechanism bridges the gaps between prior conclusions that previously could not be explained. This mechanism is based on prior work, and new work is currently underway to more fully understand the implications of mass transfer in AQ pulping.

Exploring and understanding this mechanism could lead to a fundamental shift in the way that AQ is utilized in pulping operations. Improved understanding of the role of mass transfer could lead to methods to improve the use of AQ to increase its effectiveness. This could, in turn, lead to improved product quality and savings in terms of fiber use. For some mills, the fiber savings alone could total millions of dollars.

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