An Experimental and Modeling Study on Carbonate Formation in the Effluent of Oxygen Delignification of a SW Kraft Pulp and Its Applications

Dongcheng Zhang and Arthur J. Ragauskas, Institute of Paper Science and Technology, Georgia Institute of Technology, Atlanta, GA 30332-0620.

ABSTRACT

A quantitative model of carbonate formation in the effluent of one-stage oxygen delignification for a softwood (SW) kraft pulp was developed and tested in terms of the experimental results. This model quantitatively described carbonate formation in the effluent of oxygen delignified SW kraft pulps and its kinetic characteristics, which could be used as an approach to predict pulp kappa number in the solid phase (fiber) from carbonate content in the liquid phase (filtrate). From the kinetic behavior of carbonate formation and its relationship with pulp kappa number, a control strategy was suggested and constant kappa number curves used for parameter selection were developed to achieve target pulp kappa number with retained pulp viscosity and total fiber charge property.

INTRODUCTION

Oxygen delignification

- An dominant bleaching technology for both ECF and TCF operations.
- The chemicals applied and materials removed from the pulp are compatible with the kraft chemical recovery system.
  - ➢ enables the recycling of oxygen-stage effluent to the recovery furnace by way of the brown stock washing, decreasing the potential environmental impact of the bleach plant.
  - ➢ reduce the levels of chlorinated organic by-products in subsequent chlorine dioxide bleaching, and other environmental parameters associated with bleach plant effluents, such as BOD, COD, and color.
- Acidic groups and other oxidative structures are formed in residual lignin and pulp carbohydrate, which further leads to the formation of carbonate in alkali aqueous solution when exposure to heat and alkaline environments.
- The carbonate formed will contribute to the carbonate content in black liquor when the filtrate used for brown stock washing.

Carbonate in black liquor

- Typically in a range of 1.6-1.8 g/L for production of a bleachable-grade kraft pulp, corresponding to ~18% of the total carbonate in black liquor.
- The major species responsible for fouling and scaling in kraft mill evaporators during chemical recovery and the solubility of carbonate is strongly dependent on the total solids content in the black liquor.
  - ➢two types of carbonate precipitates are formed during black liquor evaporation. Burkeite, a double salt ($2Na_2SO_4•Na_2CO_3$), is precipitated first, and then burkeite plus sodium carbonate is precipitated
- To date, no detailed work has been reported to quantify carbonate formation and its kinetic behavior during oxygen delignification.

OBJECTIVES

- Examines the dynamic formation of carbonate in the effluent of a series of one-stage oxygen delignification of a SW kraft pulp
- Develop an empirical dynamic model to predict the amount of carbonate in the effluent and its application for pulp kappa number prediction.
- Suggest a control strategy based on the carbonate formation characteristics to achieve a pulp kappa number with desirable pulp viscosity and total fiber charge.

EXPERIMENTAL

- All one–stage oxygen delignification were conducted in a 1.00 liter inclined rotary stirred Parr reactor using a commercial southern pine kraft pulp with a kappa number (KN) of 32.5. Experimental conditions are summarized in Table 1.
- Sodium carbonate content in filtrate was measured using Head Space Gas Chromatography (HSGC) with a standard deviation less than 2.0%.

Table 1. oxygen delignification conditions

Parameter	Symbol	Conditions
NaOH (%)	N	1.5, 2.5, 3.5
Temperature (°C)	T	85, 100, 115
Oxygen (MPa)	P	0.64, 0.80, 0.96
Time (min)	t	0, 10, 20, 30, 45, 60, 80

Note: 10% pulp CSC and the molar ratio of Mg:Mn = (31-33):1

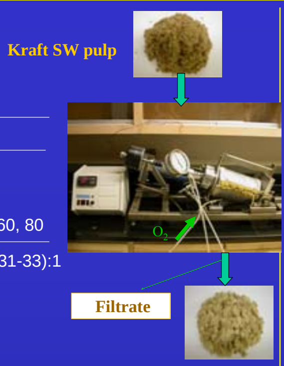

Fig. 1. An inclined rotary Parr reactor for oxygen delignification

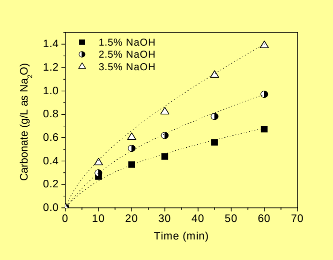

Fig. 2. Dynamic change of carbonate content in the effluent of one-stage oxygen delignification of a SW kraft pulp

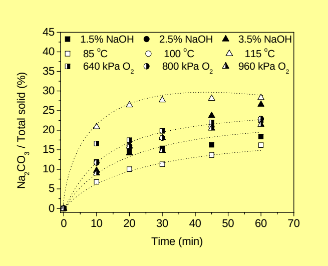

Fig. 3. Percentage of carbonate to total solid in the effluent of oxygen delignified SW kraft pulps

RESULTS

- The carbonate formation rises rapidly in the first 10 minutes reaction and then increases steadily with further oxygen delignification (Fig.2)
- As sodium hydroxide increases from 1.5% to 3.5%, the carbonate content in the filtrate increases over 100%, suggesting that the process parameters such as caustic charge have a significant impact on the carbonate formation.
- At the end of oxygen delignification reactions, the carbonate concentration typically ranged from 0.60-1.40 g/L in the effluent, corresponding to 16 - 28% of total solid in the effluent (Fig.3).

KINETIC MODEL DEVELOPMENT

Proposed kinetic mechanism for CO_2 and carbonate formations from an intermediate:

From lignin: $L + O_2 \xrightarrow{k_i} \sum_i L_i$ $\quad L_i + O_2 \xrightarrow{k'_i} L_i* + CO_2$

From carbohydrate: $C + O_2 \xrightarrow{k_j} \sum_j C_j$ $\quad C_j + O_2 \xrightarrow{k'_j} C_j* + CO_2$

$$CO_2 + NaOH \xrightarrow{k_3} Na_2CO_3 + H_2O$$

The kinetic carbonate formation:

$$\frac{d[CO_3^{2-}]}{dt} = \sum_i k'_i [L_i] P^{n_i} + \sum_j k'_j [C_j] P^{n_j}$$

The initial conditions:

$t = 0$, $[CO_3^{2-}] = 0$, $[L]_0 \cong 0.13*(KN)$

$[C]_0 = 100 - [L]_0$

Integrating and applying initial conditions, an equation for carbonation formation as a function of reaction parameters were obtained as follow.

$$[CO_3^{2}] = K_2'\left(\frac{K_4 L_0}{\alpha^2}(\exp(-\alpha K_3 t) - \exp(-K_2' t)) + \frac{(100 - L_0) K_6}{\beta^2}(\exp(-\beta K_5 t) - \exp(-K_2' t))\right) + \left(\frac{L_0 K_4}{\alpha} + \frac{(100 - L_0) K_6}{\beta}\right)(1 - \exp(-K_2' t))$$

Where

$$K_3 = A \cdot N^a \cdot p_{O_2}^b \cdot \exp\left(-\frac{E_L}{RT}\right) \qquad K_5 = C \cdot N^e \cdot p_{O_2}^f \cdot \exp\left(-\frac{E_C}{RT}\right)$$

$$K_4 = B \cdot N^c \cdot p_{O_2}^d \exp\left(-\frac{E_{L,0}}{RT}\right) \qquad K_6 = D \cdot N^g \cdot p_{O_2}^h \exp\left(-\frac{E_{C,0}}{RT}\right)$$

$$K_2' = E \cdot K_4 + F \cdot K_6$$

Using the experimental data and $L_0 = 32.5*0.13$, the constants and parameters were computed by least-square estimation as shown in Table 2. The experimental and predicted data are shown in Fig.4

Table 2. The estimated coefficients and constants

Coefficient constant	Estimate	± Error
E_L/R	0	-
E_C/R	0	-
$E_{L,0}/R$	1904	4
$E_{C,0}/R$	680	5
A	150	20
B	0.331	0.001
C	1	0.5
D	-0.002	0.0002
E	19.45	0.15
F	38.42	0.50
α	0.018	0.001
β	1.0	0.50
a, c, e, and g	0, 0.882, 0, and 1.384	-
b, d, f, and h	0, 0.822, 0, and -1.5	-

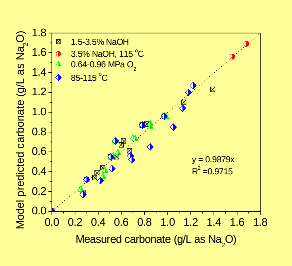

Fig.4. Actual and model predicted carbonate content in the effluent of one-stage oxygen delignified SW kraft pulps

MODEL APPLICATION-pulp kappa number prediction

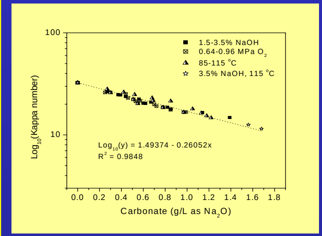

Fig.5. A relationship between pulp kappa number and filtrate carbonate content (Experimental data)

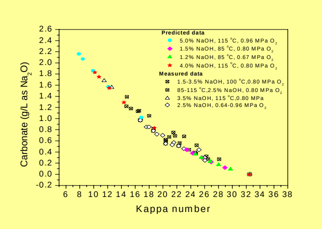

Fig.6. A relationship between filtrate carbonate content and pulp kappa number (exp. And predicted data)

MODEL APPLICATION-Process control strategy

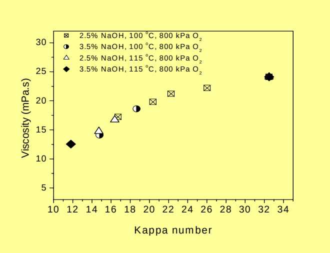

Fig.7. The relationship between pulp viscosity and pulp kappa number

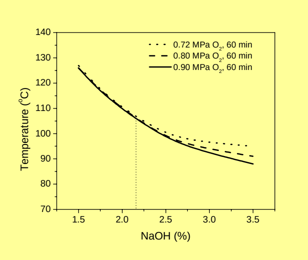

Fig.8. Constant kappa number (18.0) curves

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Georgia Tech Institute of Paper Science and Technology

CONTACT: Art.ragauskas@ipst.gatech.edu and Dongcheng.zhang@ipst.gatech.edu