Polyelectrolyte Precipitate Formation During Miscible Displacement in Porous Media

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The miscible displacement of aqueous lignin solutions (model black liquor) by water from beds formed from glass beads was studied as a function of the presence of cationic polymer in the wash water, bed structure, lignin concentration, and superficial flow rate. The displacement behaviors in homogeneous beds formed from fine beads (121 μm) were compared with results of experiments using a channel bed consisting of a bed formed from fine beads surrounding a channel of coarse beads (638 μm) running the length of the bed in the flow direction. Washing efficiencies, defined as the fraction of lignin removed when one pore volume of eluate was collected, were 84–93% for homogeneous beds washed with water compared with 31–33% for the channel bed; the range in efficiencies reflects the influence of other variables. The presence of cationic polymer in the wash water enhanced the washing efficiency by 1.7 to 2 times with a corresponding 20 to 35% decrease in the permeability of the central channel in the channel bed. The improved washing with polymer was due to selective plugging of the central channel with precipitate formed from complex formation between anionic lignin in the black liquor and the cationic polymer. Breakthrough curves obtained from 12 microconductivity probes located throughout the bed showed that mixing of lignin solution (high conductivity) with wash water (low conductivity) in the displacement front, as expressed by a mixing length, was a maximum in the coarse bead channel and was decreased when the wash water contained cationic polymer.

Introduction

Brownstock washing is an important unit operation in the production of kraft pulp. In this operation, aqueous black liquor containing spent pulping chemicals and partially decomposed lignin is separated from suspended cellulose fibers by vacuum drum washers. A fiber pad is formed on the external surface of a screen-covered washer drum and wash liquor is sprayed on top of the pad. A vacuum in the interior of the drum draws the wash liquor through the pad, displacing the black liquor from the fiber pad. The displacement washing efficiency of many commercial brownstock washers can be low. It was proposed that poor displacement washing is a reflection of nonuniform fiber pad formation which, in turn, gives premature breakthrough of wash liquor and air through the most permeable parts of the bed (Crotogino et al., 1987; Lee, 1984). Recent laboratory displacement studies support this theory (Dahllöf and Gren, 1996).

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Lee (1984) reported that displacement washing efficiency was improved by dissolving low concentrations of very high molecular weight water soluble polymers. Lee's work found little commercial application, because the polymers which gave the best washing efficiency had a high extensional viscosity which lowered the wash water flux through the pad, thus reducing production rates.

Li and Pelton (1992) proposed that displacement efficiency in brownstock washing could be improved by the addition of low molecular weight cationic polymer to the wash liquor. This proposal was based on laboratory experiments using a model packed bed of fine beads surrounding a channel of coarse beads extending the length of the bed in the direction of flow. The coarse bead channel thus represents high permeability regions in a fiber pad. The beds were initially saturated with black liquor, and displacement washing experiments were conducted with and without cationic polymer. Although the experiments were crude, it was clear that polymer

addition improved washing efficiency with no measurable change in flux. In subsequent visualization studies using a transparent flat cell, Pelton and Grosse (1994) reported that lignin and cationic polymer precipitates formed selectively in the high permeability channel. It was proposed that the precipitates lower the rate of wash liquor loss through the high permeability channel, giving better washing. Recently published results from plant trials have confirmed that it is possible to improve washing efficiency by adding cationic polymer to the displacement washing liquor (Lappan et al., 1997).

This work describes the results of more extensive displacement washing studies using the channel bed. The objective was to obtain an accurate database describing the influence of cationic polymer, bead size, lignin concentration and flow rate on the displacement washing of black liquor from channel beds. The new apparatus included 12 microconductivity probes to track the displacement front through the bed, as well as pressure and flow rate transducers. The contributions of the four variables were evaluated in a design experiment. The results from this work are compared with a semi-empirical model in a subsequent publication (De et al., 1997).

Experimental Studies

Table 1 summarizes the properties of the three model black liquor (MBL) solutions and two polymer solutions used in the displacement studies. MBL was prepared by dissolving in 0.1 N NaOH in Indulin C, which is a mixture of sodium salt of lignin (80–90%) and sodium carbonate (10–15%), was supplied by Westvaco, SC.

The polymer, Percol 1697 (Allied Colloids (Canada) Inc.), was a 40% aqueous solution of poly(diallyldimethyl ammonium chloride), which is a cationic polyelectrolyte. Polymer solutions were prepared by mixing Percol 1697 in distilled deionized water.

The density of the glass beads (Orlick Industries, Hamilton, Ont.) was approximately 2.5 g/mL. The mass average diameters for No. 3, No. 7 and No. 10 glass beads were 638 ± 7.9, 182 ± 5.6 and 121 ± 4.3 μm, respectively. The particle-size distributions of the beads are available (De, 1996).

The automated displacement washing apparatus is shown in Figure 1. Details of the fabrication of the apparatus are reported elsewhere (De, 1996). The displacement washing cell was built by modifying a 5.2-cm-ID and 30-cm-long commercial aqueous-compatible glass chromatography column, supplied by Supelco Canada Ltd. (catalog No. 5-7809). A 5.2-cm-dia. perforated stainless steel screen was placed at the bottom of the column to support the bed inside the column. The stainless steel screen (Type No. 80 P) was supplied by Paper

Table 1. Physical Properties of Various MBL and Polymer Solutions at 25°C*

Solutions	Conc. (g/L)	pH	Density (g/mL)	Viscosity (mPa·s)
MBL	25	12.35 ± 0.004	1.007 ± 0.0002	1.17 ± 0.03
MBL	13.75	12.5 ± 0.003	1.003 ± 0.0002	1.06 ± 0.006
MBL	2.5	12.56 ± 0.006	0.999 ± 0.0003	1.05 ± 0.012
Polymer	29.4	5.27 ± 0.02	0.996 ± 0.0007	3.2 ± 0.05
Polymer	14.7	5.21 ± 0.005	0.995 ± 0.006	2.24 ± 0.045

*The error limits are two standard deviations of mean values from triplicate experiments.

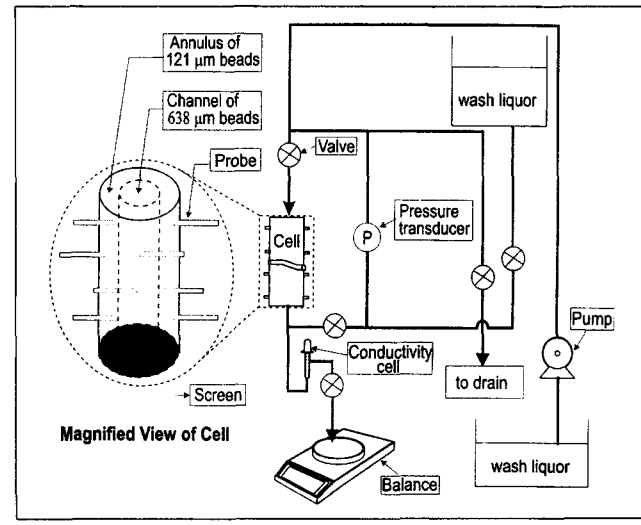

Figure 1. Displacement washing apparatus.

Research Materials, Camas, WA. The screen hole diameter was 120 μm which is a U.S. mesh equivalence of 80. The open area on the screen was 14.5%.

Conductivity measurements were used to characterize the washing. The conductivity of the MBL solutions was 14 mS/cm compared with 3.7 mS/cm for the polymer solution and 0.002 mS/cm for the water. De (1996) showed that eluate conductivities were proportional to the lignin concentration measured by UV spectroscopy. The eluate stream conductivity was measured with a flow through cell (Model CDC114, Radiometer, Copenhagen). Conductivities in the bed were measured with twelve conductivity probes based on 0.165-cm-OD syringe barrels which were fed through the holes in the wall of the column at four axial positions, that is, at 5.3, 9.4, 15.3 and 21.4 cm from the bottom screen of the column. At each of the four axial positions, one probe was placed in the annulus (0.7 cm from inner wall of column), one near the interface of fine and coarse beads (2.2 cm from inner wall of column), and the third at the center of the column (2.6 cm from inner wall of column). The location where the probes entered the column at each axial position were at 120 degree intervals. Control experiments confirmed that the probes did not have a significant effect on the flow properties of the bed (De, 1996).

Eluate conductivity values were made dimensionless using the following the relation

$$c_e = \frac{C_e - C_w}{C_{\text{mbl}} - C_w} \tag{1}$$

where C_e, C_{mbl}, and C_w were the conductivities ($\text{ohm}^{-1} \cdot \text{m}^{-1}$) of the eluate at any time t (s), initial conductivity of the MBL in the bed, and conductivity of the wash liquor, respectively. c is dimensionless conductivity. The same approach was used to convert conductivity data measured by probes in the bed to dimensionless concentrations.

Displacement washing experiments were conducted under conditions of constant flow rate. Wash liquor (water or polymer solution) was pumped through the cell with a Masterflex 7,550-60 peristaltic pump head (Cole Parmer, Chicago) fitted

with a 9-mm-OD, 7-mm-ID Tygon tubing. The eluate flow rate was computed from eluate mass/time data recorded by the Mettler PM 16 balance. The maximum Reynolds number based on particle diameter was 1.15 indicating that all the experiments in the design were conducted in the laminar flow regime (Bear, 1972).

To prepare homogeneous beds, the empty cell was partially filled with the MBL solution and glass beads (708 g) were then poured slowly into the washing cell and the cell was tapped frequently to remove air bubbles trapped inside the suspension. The glass beads were allowed to settle, and the height of the bed and final level of MBL in the column were recorded. These values were used to calculate the void volume in the bed. A second screen, identical to the bottom one, was carefully placed at the top of the bed in order to protect the bed from any disturbances. The conductivity probes were inserted into the bed through the side ports of the cell. Finally, a solid plunger with an axial channel for fluid flow was lowered and secured above the top screen.

The bed was conditioned for five minutes by pumping the MBL at a rate of 230 mL/min through the cell. At the end of conditioning, it was ensured that each probe registered the correct conductivity value of the MBL solution inside the bed and the plunger was removed. MBL was pumped from the cell until the liquid level touched the top screen. A 2-cm layer of 6-mm-dia. glass beads was formed on the screen at the top of the bed in order to distribute the wash liquor uniformly at the entrance of the bed. Wash liquor was poured slowly on the top of the bed, minimizing any mixing of MBL with wash liquor. The plunger was carefully fitted on the top of the bed, removing any voids between the plunger and 6 mm diameter glass beads.

Channel beds, consisting of a 1.7-cm-dia. central core of either coarse or medium glass beads surrounded by an annulus of fine glass beads, were prepared by the following procedure. A 1.7-cm-OD and 1.5-cm-ID glass tube was placed in the empty cell down the center axis. After partially filling the cell with the MBL solution, coarse beads (78.5 g) were slowly added inside the central glass tube and fine beads (658.5 g) to the annulus. While adding the beads, the cell was tapped frequently to drive out any air bubbles from the suspension. The glass tube was taken out of the cell vertically and very slowly to minimize any mixing of glass beads at the interface of the two kinds of beads. A procedure similar to that described for forming homogeneous beds was followed from that point onwards.

A miscible displacement experiment was started by pumping wash liquor into the cell at a constant flow rate, and the pressure drop across the cell was measured by the Celesco differential pressure transducer (Model DP30-0001-11) which was logged at 0.05 s intervals with the eluate and probe conductivities.

The dimensionless time, t_d, was defined as the ratio of volume of wash liquor injected into the cell up to any time t to the initial volume of MBL in the bed and is defined as

$$t_d = \frac{tQ}{\epsilon A \ell} \tag{2}$$

where Q is the volumetric flow rate (m^3/s) of the wash liquor, A is the area of bed normal to flow (m^2), ℓ is the length of the bed (m), and ϵ is the initial porosity of the bed (dimensionless).

The washing efficiency (WE) (dimensionless) of a displacement run is defined using the following relation given by Trinh et al. (1989)

$$\mathrm{WE} = \frac{\int_0^1 c_e d(t_d)}{\int_0^\infty c_e d(t_d)} \tag{3}$$

The numerator in Eq. 3 represents the amount of lignin that was removed from the bed when the volume of wash liquor injected into the washing cell was equal to one displacement volume of the bed. The denominator represents the total amount of lignin that could be removed from the bed, when washing was completed.

The permeability K_S (m^2) of a bed after complete washing was computed from Darcy's law as

$$K_S = \frac{Q\mu\ell}{A\Delta P_S} \tag{4}$$

where ΔP_S was the steady-state pressure drop (Pa) across the bed and the screens minus the corresponding pressure drops across the screens when no beads were present. μ is the viscosity of fluid (Pa·s).

Results

Figure 2 shows typical breakthrough curves for homogeneous and channel beds, with and without polymer. The homogeneous beds displayed a single breakthrough and there was little difference between washing with water or polymer solution. The channel beds displayed a double breakthrough. The first at dimensionless time (t_d) ~ 0.25 reflected displacement of model black liquor from the center channel. The second breakthrough corresponded to wash water exiting from the fine bead annulus. The presence of polymer in the wash

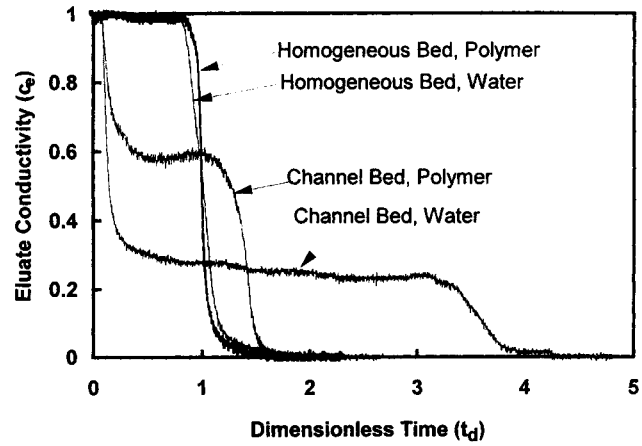

Figure 2. Breakthrough at the exit of beds for various displacement washing experiments.

Concentration of lignin in MBL was 25 g/L and flow rate was 230 mL/min.

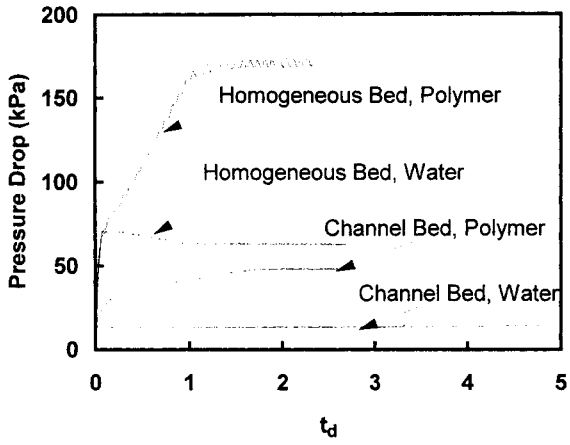

Figure 3. Pressure drop against dimensionless elution time for various displacement washing experiments.

Concentration of lignin in MBL was 25 g/L and flow rate was 230 mL/min.

water had a significant influence on the displacement behavior. With polymer in the wash water, the second breakthrough was at a t_d of ~ 1.5 compared with 3.5 without polymer. Also, the "plateau concentration" between the first and second breakthrough was much higher with polymer. A higher value for the plateau concentration corresponds to a lower dilution of MBL in the eluate with wash water from the center channel.

The washing experiments were conducted at constant flow rates, and corresponding pressure drops across the column during washing are shown in Figure 3. The initial pressure increase for all curves corresponded to the pump achieving a constant volumetric flow. The steady-state pressure drop was highest in a homogeneous bed washed with the polymer solution reflecting the low permeability of the fine bead bed and the higher viscosity of the polymer solution (see Table 1). The small amplitude pressure oscillations were caused by the pulse flow characteristics of the peristaltic pump. The shape of the pressure profiles partially reflects the fact that water was less viscous than MBL, whereas the polymer solution was more viscous than MBL (see Table 1). Thus, in the homogenous water case the pressure drops as viscous MBL is replaced by less viscous water at a constant flow rate. Also, the presence of precipitate formed with polymer contributed to the pressure drops.

The main features shown in Figure 2 have been reported before using less sophisticated measurements (Li and Pelton, 1992). The following section describes the influence of experimental variables on the displacement behavior of the channel bed based on an experimental design.

Experimental Design

The effects of four variables on miscible displacement behavior of MBL were studied. The variables were: the concentration of lignin in the MBL; the concentration of cationic polymer in the wash liquor; the flow rate of the wash liquor; and the permeability of the center channel which was controlled by the selection of the diameters of glass beads in the center channel of the model beds. The variables were tested at two levels, given in Table 2, using a two level factorial experimental design. An experiment at the center of the levels of the variables was also performed to examine the nonlinear behavior of the response. For analysis, the values of each variable were encoded; the center value was 0 and the extremes were $+1$ and -1 (see Table 2).

Table 2. Conversion of Experimental Variables to Dimensionless Variables Linearly Transformed to be Between ± 1 for the Regressions Analysis*

Variables	Notation	High $= +1$	Central $= 0$	Low $= -1$
Conc. of Lignin (g/L)	L	25	13.75	2.5
Conc. of polymer (g/L)	P	29.4	14.7	0
Flow rate (mL/min)	F	230	130	30
Dia. of beads in channel (μm)	D	638	182	121

*For example, for a 25 g/L lignin solution, $L = 1$ whereas $L = -1$ for a 2.5 g/L lignin concentration.

Each of the 17 sets of experiments were run in triplicate to give a total of 51 runs. The design matrix and the random order in which all the runs were performed are reported in Table 3.

Washing efficiencies and permeability values were calculated from the breakthrough curves and pressure drop profiles, respectively, and are reported in Table 4. Multiple regression analysis was performed and the details are described by De (1996). Stepwise regression generated the coefficients summarized in Table 5. The definition and units of the variables are summarized in Table 2. Plots of the residuals against run numbers (not shown, De, 1996) were randomly distributed about 0, and all residuals were within three standard deviations of the regression.

The factors influencing washing efficiency are illustrated by the contour plots shown in Figure 4. Four plots show lines of constant washing efficiency plotted as functions of bead

Table 3. Design Matrix of 24 Factorial Design with an Experiment at Center and with Three Replicates of Each Experiment*

Exp. No.	Conc. of Lignin	Conc. of Polymer	Flow Rate of Wash Liquor	Bead Size in Channel	Order of Runs
1	−	−	−	−	12,3,35
2	+	−	−	−	48,20,27
3	−	+	−	−	43,2,28
4	+	+	−	−	1,4,22
5	−	−	+	−	36,31,44
6	+	−	+	−	5,34,47
7	−	+	+	−	39,14,38
8	+	+	+	−	17,33,51
9	−	−	−	+	19,13,37
10	+	−	−	+	46,23,40
11	−	+	−	+	25,15,9
12	+	+	−	+	26,49,24
13	−	−	+	+	7,45,16
14	+	−	+	+	18,10,8
15	−	+	+	+	30,41,29
16	+	+	+	+	32,11,21
17	c	c	c	c	50,42,6

*(−), (+), and (c) denote low, high, and central levels of variables.

Table 4. Responses Evaluated for the 24 Factorial Experimental Design*

Exp. No.	Response 1 (WE) Washing Efficiency	Response 2 (K_S) Permeability $\times 10^{-8}$ (cm^2) After Washing
1	0.940(12),0.917(3),0.924(35)	10.2(12),9.1(3),8.41(35)
2	0.927(48),0.917(20),0.923(27)	6.28(48),8.96(20),8.76(27)
3	0.925(43),0.945(2),0.939(28)	6.66(43),8.54(2),7.14(28)
4	0.941(1),0.930(4),0.939(22)	8.28(1),8.23(4),8.28(22)
5	0.853(36),0.860(31),0.811(44)	7.47(36),7.63(31),6.51(44)
6	0.849(5),0.850(34),0.819(47)	8.72(5),8.25(34),7.02(47)
7	0.760(39),0.810(14),0.777(38)	6.38(39),6.82(14),6.47(38)
8	0.794(17),0.786(33),0.790(51)	7.6(17),8.2(33),7.64(51)
9	0.332(19),0.334(13),0.312(37)	35.8(19),36.5(13),35.7(37)
10	0.318(46),0.31(23),0.312(40)	34.7(46),35(23),35.2(40)
11	0.541(25),0.631(15),0.565(9)	33.6(25),34.7(15),32.6(9)
12	0.642(26),0.632(49),0.637(24)	23.5(26),20.7(49),23.9(24)
13	0.336(7),0.333(45),0.318(16)	33.8(7),33.7(45),34.4(16)
14	0.31(18),0.337(10),0.312(8)	32.2(18),31.6(10),29.1(8)
15	0.528(30),0.511(41),0.514(29)	31.6(30),25.4(41),31.7(29)
16	0.574(32),0.580(11),0.574(21)	20.2(32),28.9(11),25.6(21)
17	0.873(50),0.86(42),0.84(6)	5.06(50),5.44(42),4.61(6)

*Numbers in the parentheses indicate the order in which runs were carried out.

diameter and polymer concentrations for each combination of lignin concentration and eluant flow rate. The center channel bead diameter D (dimensionless) dominated washing efficiency. When fine beads were used in the center channel ($D = -1$) giving homogeneous beds, washing efficiencies were high (> 0.8). By contrast, more permeable center channels ($D = 1$) gave low washing efficiencies. Polymer addition increased WE for constant D values > -0.5. The polymer was most effective at improving washing when the lignin concentration (dimensionless) was high ($L = 1$), and the flow rates were low ($F = -1$).

Bed permeability values were calculated from pressure drop/flow rate data at the end of the washing experiments. Figure 5 shows K_s contours as functions of the concentrations of polymer and lignin. As expected, the dominant parameter was the diameter of the center channel beads. Large beads $D = 1$ gave permeability values of 2.5×10^{-11} to 3.5×10^{-11} m^2, whereas the fine bead center channels values were a factor of three less. Furthermore, conditions corresponding to polymer/lignin precipitate formation (that is, going from lower left to upper right on the $D = 1$ curves) gave the lowest

Table 5. Multiple Regression Relating Washing Efficiency and Bed Permeability to L, D, P and F

Terms in WE Reg. Eq.	Coeff. for WE	Terms in K_S Reg. Eq.	Coeff. for K_S
Constant	0.857667	Constant	1.042
D	−0.211104	D	0.2604
P*D	0.069146	D^2	1.074
P	0.058563	P	0.2604
L^2	−0.19685	P*D	0.2604
F	−0.036396	L*D	0.2604
F*D	0.022271	L	0.2604
P*F	−0.016479	L*P*D	0.2604
L*P	0.009563	F	0.2604
L*P*D	0.007729	L*P*F*D	0.2604
L	0.005979		

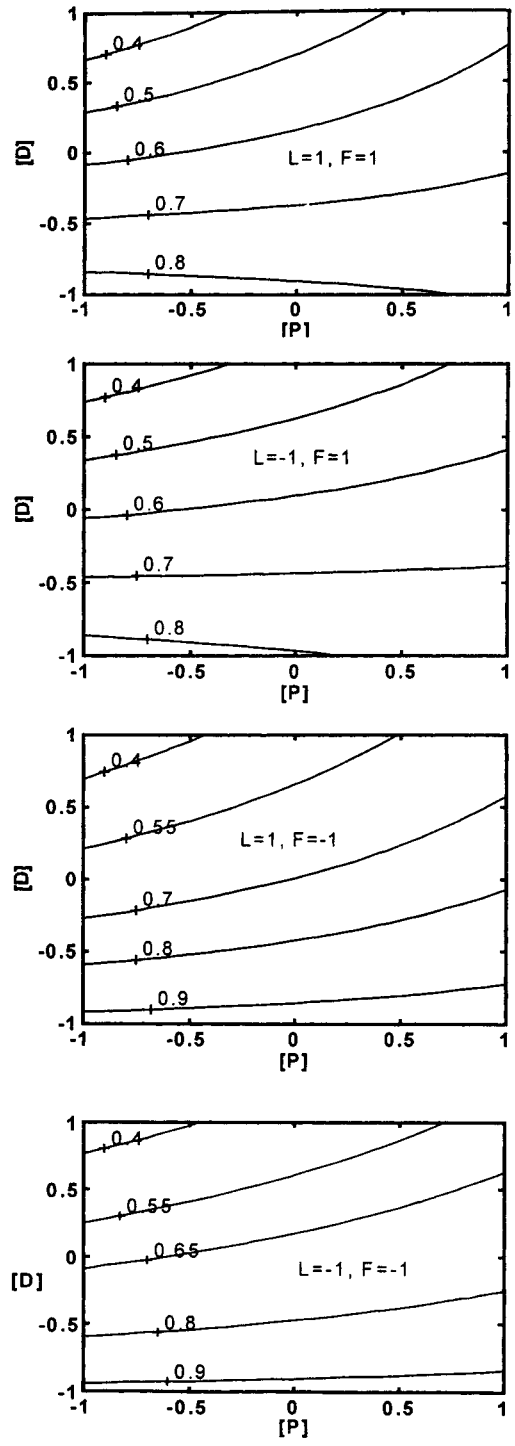

Figure 4. Constant washing efficiency as functions of bead diameter and polymer concentrations for different combinations of lignin concentrations and eluate flow rate.

permeability. By contrast, the permeabilities in the homogeneous beds ($D = -1$) were rather insensitive to polymer and lignin concentrations.

The channel beds showed ~30% decrease in permeability when the concentrations of lignin and polymer were high. In previous work with a thin, flat, transparent cell, precipitates

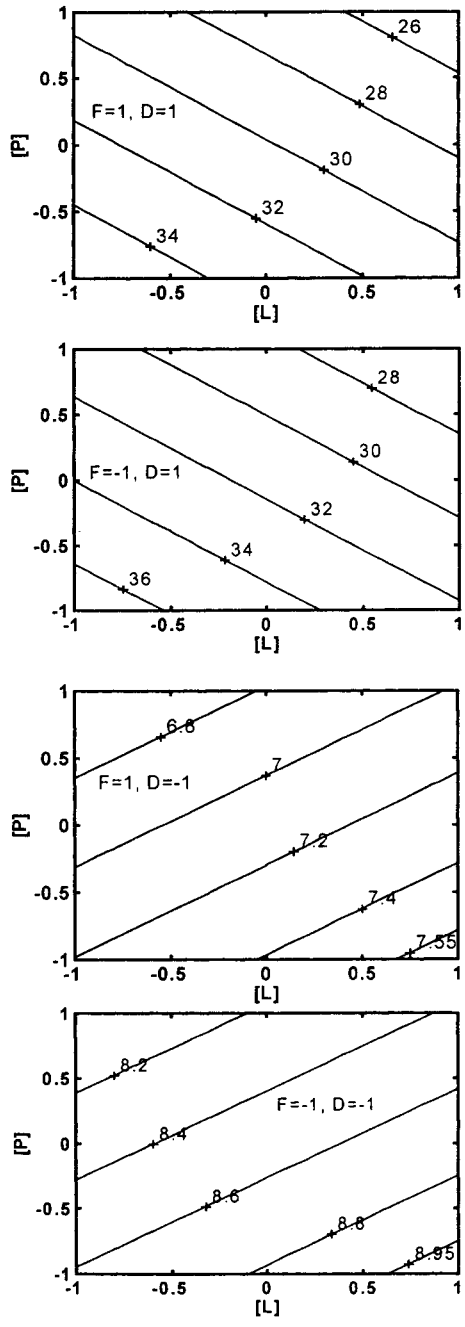

Figure 5. Constant bed permeability as functions of polymer concentration and lignin content calculated from the regression equation (Table 6).

Different combinations of flow rate and center channel bead diameter are shown in the four plots.

were observed to form in the center channel (Pelton and Grosse, 1994). The results in Table 5 confirm that the precipitates influence the permeability properties of the beds.

Characterizing the Displacement Front

Twelve microconductivity probes were placed in the bed to monitor the passage of the displacement front. Three probes were placed at each of four axial (horizontal) planes. At each

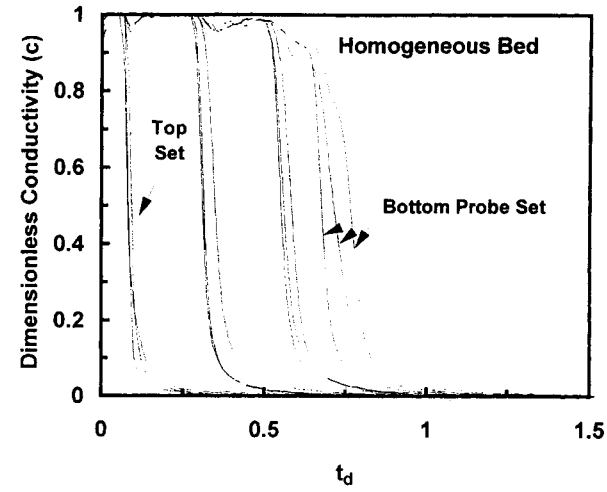

Figure 6. Breakthrough collected by groups of three probes located at four axial positions in a homogeneous bed of fine beads.

See Figure 2 for details of probe positions.

axial position, one probe was near the wall, one probe was in the center, and the third probe was near the interface between the two types of beads. Each probe generated a breakthrough curve and examples of results from a homogeneous bed of fine beads are shown in Figure 6. The displacement front passed by the first set of three probes simultaneously. By contrast, the front passed the three probes in the last layer at different times. The reasons for the initial fluctuations in the microprobe conductivity results are not known.

Probe data were used to measure the rate at which the displacement front moved in the annulus and the center of the channel bed. Figure 7 shows the dimensionless breakthrough times as a function of probe distance from the top of the bed for runs with and without polymer. The plotted points

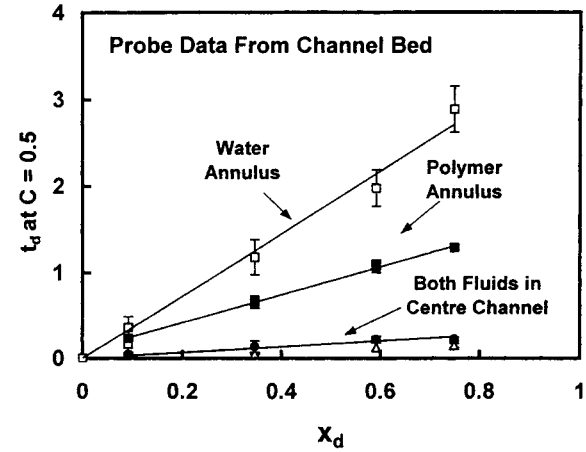

Figure 7. Breakthrough times (t_d at $c = 0.5$) vs. dimensionless distance of the probes from the top of the channel bed.

Data points are average of three experiments and the error bars correspond to 2 standard deviations of the mean. The wash liquor flow rate was 230 mL/min and the lignin concentration was 25 g/L.

are the average of three experiments, and in all cases the results were linear. The displacement front traveled quickly through the center channel and the polymer had no significant effect. Previous flow visualization work with a flat cell geometry showed that precipitates formed slowly in the center channel mainly after breakthrough had occurred (Pelton and Grosse, 1994). By contrast, the times for the displacement front to pass the annulus probes were about twice as long with water displacement than with polymer displacement. Furthermore, the polymer/annulus data, although linear, did extrapolate to the origin (y intercept was at $t_d = 0.1$). Initially, the polymer front should move at approximately the same rate as the water case. However, as precipitate forms, the permeability of the center channel decreases giving a lower slope. The results in Figure 7 indicate that the center channel permeability is reduced before the front reaches the first probe ($t_d < 0.25$), which is long before precipitates were observed to form in flat cell experiments (Pelton and Grosse, 1994).

The entire set of probe data for the coarse bead channel bed are summarized in Table 6, which gives the slopes of the lines fitted to the breakthrough time vs. position data. The slopes are the inverse of the dimensionless flow front velocities. In the last section it was shown that the washing efficiency in channel beds with polymer was better when the lignin concentration was high. The results in Table 6 confirm that the displacement front moved more quickly (lower slope) when the lignin concentration was high.

In general, the slopes from the interfacial probes were close to the annulus values. The transition zone between the coarse and fine beads could be as thin as 2 coarse bead diameters so it was unlikely that probes could be located accurately within the transition zone. Video microscopy was used to observe directly the transition zone during a displacement washing experiment. For this work, it was necessary to use a flat cell in which the coarse bead channel spanned the cell width rendering the mixing zone visible through the transparent cell wall. Initially, some fine beads, next to the coarse ones, were observed to move in flow and lodge in the spaces around the large beads which would tend to lower permeability. Polymer/lignin precipitated complex particles were observed to

Table 6. Slopes and Correlation Coefficients (R2) of Lines Regressed through Breakthrough Times as a Function of x_d for Conductivity Probes in the Bed*

Type of Bed and Wash Liquor	Location of Probe	Concentration (25 g/L) (slope)$^{-1}$	Concentration (25 g/L) R^2	Concentration (2.5 g/L) (slope)$^{-1}$	Concentration (2.5 g/L) R^2
Homogeneous Bed					
Water	Annulus	0.98	0.997	0.96	0.997
Water	Interface	1.06	0.999	1.01	0.999
Water	Center	1.15	0.998	1.05	0.998
Polymer	Annulus	0.96	0.999	0.99	0.998
Polymer	Interface	0.98	0.998	1.00	0.999
Polymer	Center	1.00	0.998	1.00	0.999
Channel Bed					
Water	Annulus	0.27	0.982	0.25	0.998
Water	Interface	0.28	0.990	0.27	0.989
Water	Center	4.96	0.913	4.91	0.903
Polymer	Annulus	0.56	0.985	0.44	0.995
Polymer	Interface	0.78	0.934	0.63	0.931
Polymer	Center	2.96	0.706	3.43	0.877

*The flow rate was 230 mL/min.

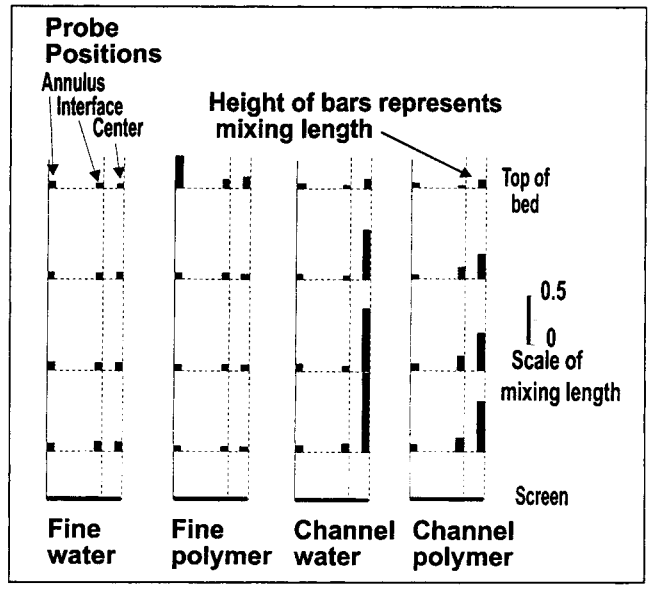

Figure 8. Mixing lengths of fronts in model beds during displacement washing experiments.

"Fine" refers to homogenous beds of fine beads. The wash liquor flow rate was 230 mL/min, and the concentration of lignin was 2.5 g/L.

deposit onto the large beads, and to be filtered in pore throats in the transition zone and in the coarse bead channel. There was no evidence of complex being retained in the fine beads.

The probe data also gave information about the extent of mixing in the displacement front at the 12 locations in the bed. Following the approach of Blackwell (1962), a mixing length was calculated from the probe breakthrough curves by the following relationship

$$\frac{t_d(c=0.1) - t_d(c=0.5)}{t_d(c=0.5)} x_d \tag{5}$$

where x_d is the distance of the probe from the top of the bed divided by total bed length (dimensionless).

The dimensionless mixing lengths are shown in Figure 8 for the two types of beds with and without polymer. For the homogeneous beds, the mixing lengths at the fronts in the three radial positions were similar except for the three probes near the entrance. Thus, the near ideal behavior of the homogeneous beds obtained from the analysis of the eluate breakthrough curves is confirmed by the probe data. The mixing lengths from the final set of probes in the homogeneous beds were shorter with polymer than without indicating that the polymer solution had a stabilizing influence on the displacement boundary.

The mixing lengths in the coarse bead center channels were much longer than in the fine beads. As with the homogeneous beds, the presence of polymer in the displacing fluid shortened the center channel mixing length while increasing the mixing length in the interface region.

Discussion

Previous studies with similar channel beds showed that: (1) cationic polymer in the wash water improved MBL displace-

ment washing (Li and Pelton, 1992); (2) precipitates selectively formed in the center channel when washing with polymer (Pelton and Grosse, 1994). The proposed explanation of these results was that the precipitate in the center channel lowered the center channel permeability which in turn caused a larger fraction of the total flow to be directed through the fine beads giving improved washing. The current results support this explanation. Comparison of channel bed breakthrough curves with and without polymer (Figure 2) shows that the conductivity values of the plateau part of the curves, between center channel and annulus breakthrough, were higher in the presence of polymer. Higher conductivity reflects a lower fraction of wash liquor in the eluate steam.

Further support for the concept that precipitate formation in the center channel improves washing efficiency comes from plotting bed permeability at the end of the experiments (that is, after precipitate formation) as a function of the corresponding washing efficiency. The results, shown in Figure 9, confirm that good washing corresponded to lower permeabilities in most cases. The washing efficiencies fell into three groups. The group around WE = 0.325 corresponds to the channel bed experiments with no polymer, giving high permeabilities and poor washing. The washing efficiencies between 0.5 and 0.6 corresponded to polymer with high flow rates or low lignin concentrations. The very best washing (WE > 0.6) corresponded to high concentrations of polymer and lignin in conjunction with a low flow rate. The points marked with squares in Figure 9 correspond to the three runs of experiment number 11 ($L = -1$, $P = 1$, $f = -1$, $D = 1$), which is the channel bed with high polymer, low lignin, and low flow rate. P is the transformed cationic polymer concentration for regression (dimensionless). This experiment gave good washing with minimal impact on permeability, which is ideal for a washing application.

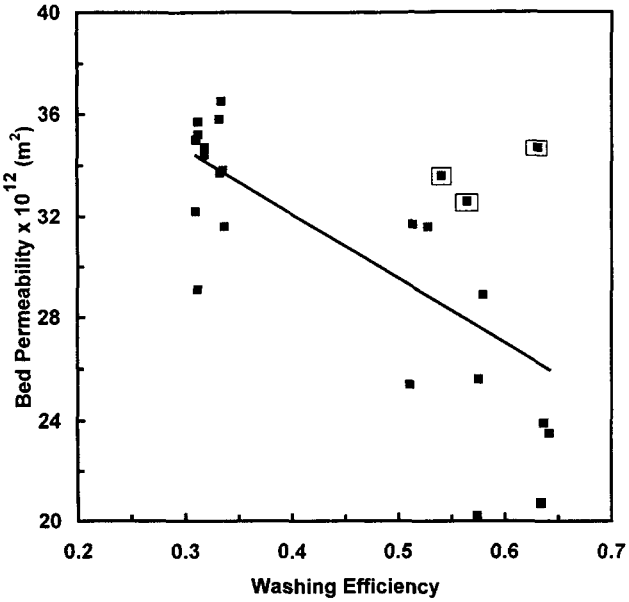

Figure 9. Washing efficiencies from the channel bed (coarse beads) experiments as a function of the measured overall permeability values of the beds at the end of the washing experiments.

The data points marked with squares correspond to experiment 11 (see Table 4).

The permeability change in the center channel due to precipitate formation was estimated by assuming: (1) the channel bed could be treated as a coarse bead column in parallel with a fine bead column with the same cross-sectional area as the corresponding zones in the channel bed; (2) precipitation only occurred in the coarse bead column. The second assumption is reasonable based on the observed location of precipitates in other work (Gross and Pelton) and the fact that the homogeneous fine bead beds showed little variation in permeability values (see Table 4, experiments 1 through 8). Based on this analysis, the highest decrease in overall permeability corresponded to a 35% decrease in the permeability of the center channel (De, 1996).

The factors influencing precipitate formation (Lappan et al., 1997) and the reason for selective precipitate formation in the center channel (Lappan et al., 1996b) have been addressed elsewhere. In this work, computational fluid mechanics calculations were used to support the hypothesis that radial pressure differences cause some MBL to flow laterally from the fine beads into the center channel causing lignin to mix with cationic polymer solution to form precipitate. Furthermore, it was proposed that the radial pressure drop arose because the resistance to flow in the zone where the fine beads met the bottom screen was much higher than the corresponding coarse bead/screen interface.

An unexpected finding in this work was that the mixing lengths for the homogeneous fine bead beds were lower and washing efficiencies were increased when the wash water contained cationic polymer (see Figure 8) with no evidence of precipitate formation. We propose that soluble lignin/cationic polymer complex formed in the mixing zone giving perhaps a local increase in viscosity which in turn could inhibit dispersion of the displacement front.

Conclusions

The presence of a cationic polymer in the wash liquor increased the washing efficiency in a channel bed by 1.7 to 2 times compared with a channel bed that was washed with water. The improved washing was a result of lignin/cationic polymer precipitate formation in the high permeability center channel, which lowered the loss of wash liquor. Cationic polymer also slightly improved the washing efficiency of homogenous fine bead beads by inhibiting dispersion in the displacement front. Micro-conductivity probes confirmed the absence of anomalous flow behavior in the channel bed.

Acknowledgments

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Literature Cited

Bear, J., *Dynamics of Fluids in Porous Media*, Elsevier, New York (1972).

Blackwell, R. J., "Laboratory Studies of Microscopic Dispersion Phenomena," *Soc. Petrol. Eng. J.*, **2**, 1 (1962).

Crotogino, R. H., N. A. Poirier, and D. T. Trinh, "The Principles of Pulp Washing," *Tappi*, **70**, 95 (1987).

De, D., "Reactive Polymer Enhanced Miscible Displacement in Porous Media," PhD Thesis, McMaster Univ., Hamilton, Ontario, Canada (1996).
De, D., A. N. Hrymak, and R. Pelton, "A Network of Zones Model for Polymer Precipitate Formation in Channel Beds," *Chem. Eng. Sci.*, in press (1977).
Dahllöf, H., and U. Gren, "Displacement Washing of Pulp Fibre Beds—Comments on the Role of Permeability," Preprints CPPA/TAPPI Meeting, Vancouver, 9 (Oct. 7–10, 1996).
Lappan, R. E., R. Pelton, I. McLennan, J. Patry, and A. N. Hrymak, "Kraft Lignin-PolyDADMAC Precipitate Formation," *Ind. & Eng. Chem. Res.*, **36**(4), 1171 (1997).
Lappan, R. E., A. N. Hrymak, and R. Pelton, "Polymer Enhanced Brown Stock Washing," *Tappi J.*, **79**(11), 170 (1996a).
Lappan, R., A. H. Hrymak, and R. H. Pelton, "Dependence of *in situ* Precipitate Deposition on Flow Characteristics in Multi-Permeablity Porous Media," *Chem. Eng. Sci.*, in press (1996b).
Lee, P. F., "Channeling and Displacement Washing of Wood Pulp Fiber Pads," *Tappi J.*, **67**(11), 100 (1984).
Li, P., and R. H. Pelton, "Wood Pulp Washing: 2. Displacement Washing of Aqueous Lignin from Model Beds with Cationic Polymer Solutions," *Colloids and Surfaces*, **64**, 223 (1992).
Pelton, R., and B. Grosse, "Polymer Enhanced Displacement of Lignin Solution from Model Packed Beds," *J. Pulp Paper Sci.*, **20**(3), 91 (1994).
Trinh, D. T., N. A. Poirier, R. H. Crotogino, and W. J. M. Douglas, "Displacement Washing of Wood Pulp—An Experimental Study," *J. of Pulp and Paper Sci.*, **15**(1), J28 (Jan., 1989).

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