FIBER SURFACE STRUCTURE AND FIBER LIBERATION IN SODA-ANTHRAQUINONE KRAFT AND SODA PULPS AS DETERMINED BY CONVENTIONAL ELECTRON MICROSCOPY[1]

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ABSTRACT

Comparative studies on the surface structure of defibrated fibers and fiber liberation in nondefibrated chips from three different pulping processes, soda-anthraquinone (soda/AQ), kraft and soda pulping, were performed via conventional electron microscopy. By comparing the exposed fiber surface structure with the degree of fiber liberation, delignification processes in middle lamella regions were elucidated for these pulping systems. Soda/AQ pulping resulted in fiber liberation with less lignin removal than for either kraft or soda pulping process.

Keywords: Delignification, lignin distribution, fiber, soda/AQ, kraft, soda pulping, defibration, fiber liberation.

INTRODUCTION

The physical and chemical properties of pulps are considerably affected by residual lignin in fiber walls. Thus, knowledge of residual lignin distribution within pulps is of great importance. Both ultraviolet (UV) microscopy (Procter et al. 1967; Fergus and Goring 1969; Wood et al. 1972; Wood and Goring 1973; Kerr and Goring 1976) and the energy-dispersive X-ray analysis (EDXA) technique (Saka et al. 1978 and 1981) have been used to study the topochemistry of delignification during pulping. As a result, the topochemical patterns of delignification are well elucidated for different pulping processes.

With regard to paper production, the distribution of residual lignin on the external fiber surfaces is also important. In spite of its importance, very little work (Saka et al. 1979a) has been performed. The objectives of this study were, therefore, to characterize the fiber surface structure and the fiber liberation mechanism on fibers obtained from soda-anthraquinone (soda/AQ), kraft and soda pulping processes. The fiber surface characteristics were evaluated on fibers of varying lignin content that were mechanically defibrated after pulping. Fiber liberation studies were performed on pulped fibers not subjected to mechanical defibration. Concomitantly, the results obtained in this study were compared with those for a topochemistry study of delignification with the SEM-EDXA technique (Saka et al. 1981).

TABLE 1. *Cooking time, pulp yield, lignin content, and delignification in soda/AQ, kraft and soda pulps.*

Sample	Cooking time (min)	Pulp yield (%)	Lignin Content* (% based on wood)	Delignification (%)
Uncooked	0	100	27.6	0
Soda/AQ				
SAQ-1	25	86.5	23.9	13.4
SAQ-2	45	83.5	23.3	15.6
SAQ-3	60	78.8	23.2	15.9
SAQ-4	75	71.8	20.4	26.1
SAQ-5	100	63.7	13.8	50.0
SAQ-6	125	56.9	9.1	67.0
SAQ-7	190	48.1	4.0	85.5
Kraft				
K-1	25	86.1	24.0	13.0
K-2	50	76.5	22.6	18.1
K-3	80	66.2	17.6	36.2
K-4	95	60.7	13.8	50.0
K-5	110	55.8	9.8	64.4
K-6	130	50.2	5.4	80.4
K-7	250	44.6	2.1	92.3
Soda				
S-1	30	84.8	24.6	10.9
S-2	60	75.0	21.9	20.7
S-3	100	64.8	16.8	39.1
S-4	130	57.6	13.4	51.4
S-5	160	52.9	8.4	69.6
S-6	250	44.1	3.9	85.6

* Klason lignin plus acid-soluble lignin, based on oven-dry extracted wood.

MATERIALS AND METHODS

Pulp preparation

Guillotine-cut chips of wood (2.5 × 2.5 × 0.3 cm) were obtained from the sapwood (70th–109th annual increment) of a fresh, 109-year-old Douglas-fir (*Pseudotsuga menziesii*) log. For delignification, the following three pulping systems were utilized:

1) Soda liquor: NaOH, 25.8%.
2) Kraft liquor: effective alkali, 15.0%, sulfidity; 25.0%.
3) Soda/AQ liquor: NaOH, 23.2%; AQ, 0.1%.

The liquor : wood ratio used was 4:1 in all cases. Prior to pulping, 100 grams (oven-dry weight) of fresh chips were soaked in cooking liquors for 16–20 h in order to allow the pulping liquor to penetrate the chips. Several cooks were made for each pulping process, and the extent of the lignin removal and pulp yield was controlled by varying cooking times (Table 1). Time to the pulping temperature of 170 C was 95 min for all cooks. After pulping, the chips were washed to remove residual alkali. Samples from each cook were used to determine pulping yield, Klason lignin content, and acid-soluble lignin (Table 1).
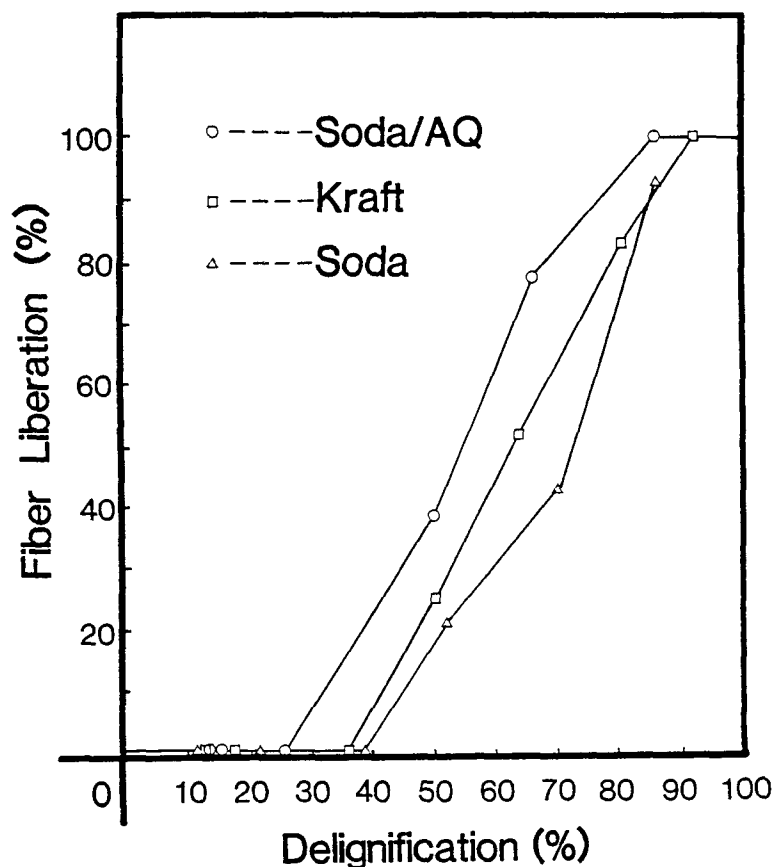
FIG. 1.   Relationship between fiber liberation and degree of delignification for three different pulping systems.

Electron microscopy

Electron microscopy observations of nonbrominated defibrated fiber[3] surfaces and cross sections of brominated nondefibrated fibers were made for each stage of delignification.

For detailed characterization of exposed fiber surfaces, direct carbon replicas (Côté et al. 1964) of handsheets formed from defibrated pulps were evaluated.

Nonbrominated fibers, which were not defibrated, and brominated fibers were embedded in epoxy resin (Luft 1961). Ultrathin sections were subsequently cut with a diamond knife mounted on a Porter Blum MT-2 ultramicrotome. Prior to examination with an electron microscope, the sections were shadowed with platinum. Nonbrominated fibers were used for studying fiber liberation and the brominated fibers for observing cell corner lignin.

Both ultrathin sections and replicas were examined with a Siemens Elmiskop 1A transmission electron microscope at an accelerating voltage of 80 kV.

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[3] In the following discussion, the term "fiber" refers to the longitudinal tracheid which constitutes 90 to 95% of the cells found in softwoods.
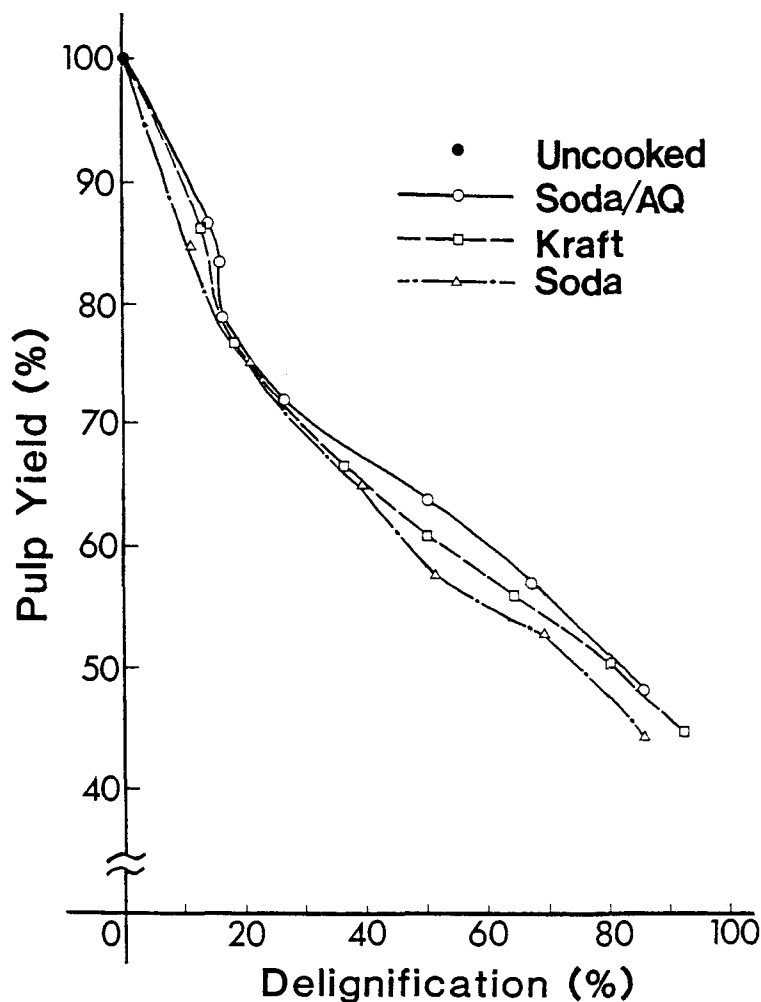
FIG. 2. Relationship between pulp yield and degree of delignification for three different pulping systems.

Measurements of fiber liberation

Examination of pulp that has not been mechanically defibrated reveals the amount of fiber separation due entirely to the cooking action of the pulping liquor. Generally 60 to 80 double cell walls in several ultrathin sections were observed for separation of each pulp. Isolated single fibers were obviously regarded as separated. In addition, fibers that showed complete separation along the double cell walls but that were still connected in the cell corner region, were also regarded as fully separated fibers. For fibers partially separated along the double cell wall, the percentage of separation was obtained from the ratio of the separated double cell-wall length to the whole length from one cell corner to the other. The relationship established between fiber liberation and delignification is shown in Fig. 1.

FIG. 3a–3c. Replicas of (3a) kraft (delignification = D:13%), (3b) soda/AQ (D:13%) and (3c) soda (D:11%) pulp fibers. Note that the cell-wall layers, S_1 and S_2, are exposed. Arrows indicate the direction of the fiber axis.

RESULTS AND DISCUSSION

A relationship between pulping yield and delignification

The relationship between the pulping yield and delignification is graphically illustrated in Fig. 2 for each pulping system. Note the obvious yield differences between soda/AQ, kraft and soda at various stages of delignification. Above 25% delignification, pulping yield was found to be highest for soda/AQ pulping, followed by kraft, and finally by soda pulping process. However, above 75% delignification, the yield difference between soda/AQ and kraft pulping was not significant.

Fiber liberation

Although acid pulping treatments do not cause fiber liberation with the removal of middle lamella lignin (Kibblewhite 1973), fiber liberation of alkaline pulped wood is very dependent on the amount of residual lignin in the middle lamella region (Kibblewhite and Harwood 1973). Therefore, during alkaline pulping, the more delignified the middle lamella regions, the more double cell walls are separated. Thus a direct measurement of fiber separation in nondefibrated pulps provides an indication of delignification in middle lamella regions.

Although fiber liberation increases as delignification proceeds, little separation occurred below the 30% delignification level (Fig. 1). The amount of lignin present in the middle lamella region is only 15% of the total lignin in springwood Douglas-fir tracheids (Saka 1980). Therefore, this observation suggests that delignification proceeds predominantly in the cell wall in the early stages of pulping as observed in delignification studies on kraft (Procter et al. 1967; Fergus and Goring 1969; Saka et al. 1981), soda/AQ and soda pulps (Saka et al. 1981).

As is obvious in Fig. 1, fiber liberation initiates and terminates at a lower degree of delignification with soda/AQ than with either the kraft or soda process. This finding confirms the result obtained by the SEM-EDXA technique, which revealed that soda/AQ pulping removes middle lamella lignin more extensively than either kraft or soda (Saka et al. 1981).

Characterization of fiber surface structure

Mechanical agitation, or defibration, after cooking insures complete separation of the individual fibers. The place of separation, i.e., middle lamella, primary wall, S_1 or S_2, may vary depending upon the degree of delignification and the pulping process used. Examination of separated fiber surfaces at different delignification levels should reveal the effect of pulping processes on the place of fiber separation. Since 90 to 95% of Douglas-fir wood consists of longitudinal tracheids, characterization of fiber surface structure was performed on tracheid cells. In order to eliminate the variation due to the cell-wall direction, only springwood radial walls that were identified by presence of bordered pits were studied.

Figures 3 through 8 show representative examples of exposed fiber surfaces in different pulps. Abbreviations K, SAQ, and S used in the figures indicate kraft, soda/AQ, and soda pulp fibers, respectively. The numbers associated with these abbreviations indicate the percent delignification. The line on all micrographs represents 0.5 μm.

In the initial delignification stages, the defibration of pulps caused separation predominantly within the cell wall for all three different pulps (Figs. 3a, 3b, and
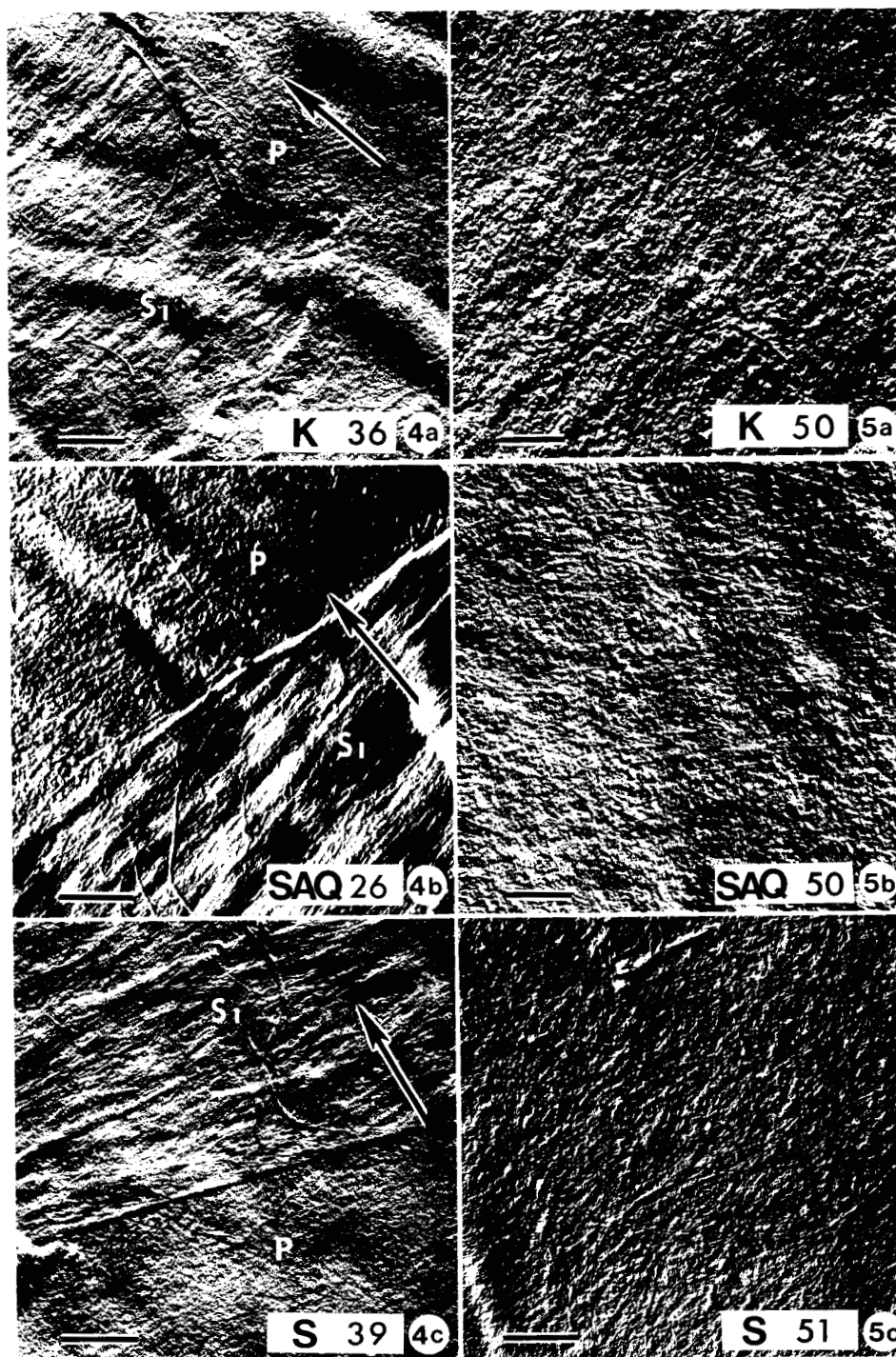
FIG. 4a–4c. Replicas of (4a) kraft (D:36%), (4b) soda/AQ (D:26%) and (4c) soda (D:39%) pulp fibers. Outer cell-wall portions consisting of S_1 and P wall layers are exposed. Arrows indicate the direction of the fiber axis.

3c). In most instances, both the S_1 and S_2 layers of the secondary wall were visible on the fiber surfaces.

At a higher stage of delignification (15 to 40%), although the S_2 layer was detected on some fibers, the exposed surfaces were mainly the outer cell-wall portions consisting of the S_1 layer or the S_1 and primary (P) wall layer. Note the encrusting amorphous material partly obscuring the P wall microfibrils (Figs. 4a, 4b, and 4c).

As calculated from Table 1 and Fig. 2, all three pulping processes up to 40% delignification showed a maximum 33–35% yield loss that consisted of 11% lignin and 22–24% carbohydrates, based on the original wood substances. The SEM-EDXA technique revealed that lignin removal during the early stages of delignification takes place primarily in the cell wall (Saka et al. 1981). Furthermore, most of the carbohydrate loss in early delignification stages is in the form of hemicelluloses, and hemicellulose dissolution takes place mainly in the S_1 and neighboring layers, P and S_2 (Polcin et al. 1967). Therefore, mechanical defibration caused fiber liberation within the cell-wall regions weakened by lignin and carbohydrate removal.

At about the 50% delignification stage, separation within the middle lamella occurred for fibers pulped with either kraft or soda/AQ process (Figs. 5a and 5b). Note that middle lamella amorphous substances obscure most of the randomly oriented microfibrils of the P wall. Although structural differences in the exposed fiber surfaces were not observed between the two, the degree of fiber liberation at this stage of delignification was significantly higher in soda/AQ pulps than in kraft (Fig. 1). For soda pulps, however, so-called "fibrillation" (Koran 1970) was observed on the exposed surfaces (Fig. 5c). The separation, therefore, presumably occurred at the interface between the P wall and middle lamella region, producing "fibrillation" from the P wall microfibrils. Although delignification study with SEM-EDXA (Saka et al. 1981) revealed that delignification patterns in the middle lamella regions were essentially the same for kraft and soda pulping, some structural differences existed between the two (compare Figs. 5a and 5c). This may be explained by the fact that fiber separation due to defibration action is the result of carbohydrate degradation as well as delignification. For example, the yield is lower in soda than in kraft pulps at 50% delignification (Fig. 2). This yield difference is due to the removal of carbohydrates, particularly hemicelluloses.
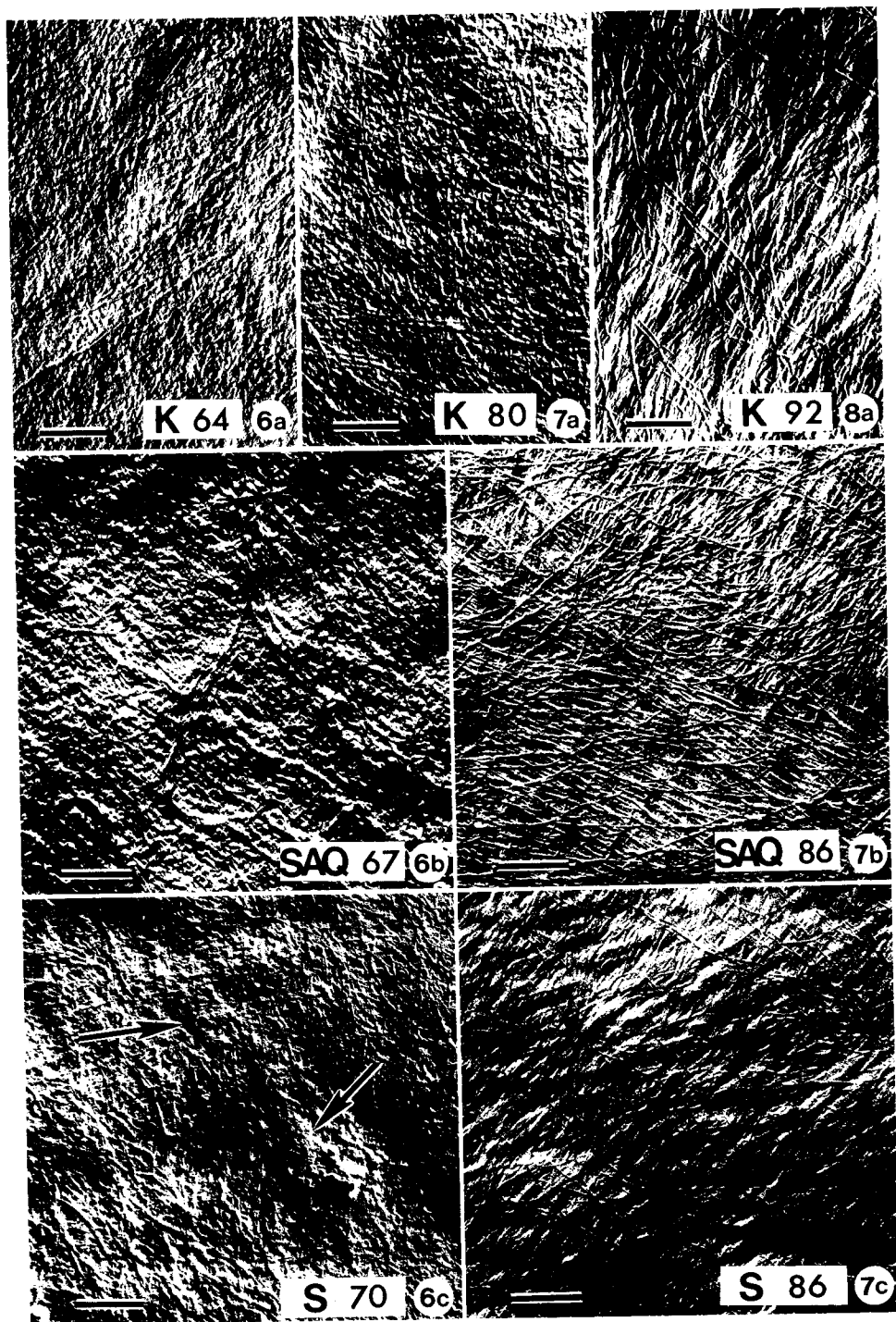
As delignification proceeds further, microfibrils that have been embedded in matrix substances become more visible (Figs. 5 through 8). Comparative studies using potassium permanganate ($KMnO_4$) stained sections and replicas indicated that matrix substances observed in replicas corresponded to the $KMnO_4$ stained materials seen in sections (Saka et al. 1979a). Therefore, the matrix substances

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Fig. 5a. Replica of middle lamella in a kraft pulp fiber (D:50%). Residual middle lamella lignin completely covers P wall microfibrils.

Fig. 5b. Replica of middle lamella in a soda/AQ pulp fiber (D:50%). Residual middle lamella lignin completely covers P wall microfibril.

Fig. 5c. Replica of the interface between P wall and middle lamella regions in a soda pulp fiber (D:51%). Note the "fibrilation" from the P wall microfibrils.

detected in replicas are regarded as residual lignin. The clarity with which microfibrils can be seen thus provides a qualitative measure of lignin removal such that Figs. 5 through 8 illustrate the sequence of lignin removal from external fiber surfaces.

Although Figs. 5a, 5b, and 5c illustrate slight differences in lignin removal among these three pulping processes, the next higher delignification stage (Figs. 6a, 6b, and 6c) more clearly reveals differences. Note that for soda/AQ pulps, the microfibrils appear to be less encrusted with lignin at the 67% delignification stage than those in the 64% delignified kraft pulps (compare Figs. 6a and 6b). Soda pulps at 70% delignification level (Fig. 6c) revealed a rather irregular lignin removal from the external fiber surfaces, often showing large, isolated clumps of residual lignin (see arrows). Although not as common, these clumps were also observed in kraft pulps (Saka et al. 1979a).

As delignification proceeds further, microfibrils on fiber surfaces from all three pulping processes were more clearly delineated. Furthermore, clumps of residual lignin were less frequently observed on both soda and kraft pulp fibers. However, by comparing Fig. 7b with 7a, 8a and 7c, the greater clarity with which the P wall microfibrils are exposed in soda/AQ pulps than in either kraft or particularly soda pulps can be seen. This is a further indication of the higher lignin removal from the middle lamella region by soda/AQ pulping process.

The observed differences in external fiber surface structures throughout delignification supports the obtained relationship between fiber liberation and degree of delignification. Soda/AQ pulps at 50% delignification level revealed approximately the same fiber liberation as soda pulps at 70% delignification, despite the fact that the P wall microfibrils are slightly more delineated in 70% delignified soda pulps (Fig. 6c) than in 50% delignified soda/AQ pulp (Fig. 5b). The lower fiber liberation of soda pulps is probably due to an irregular removal of lignin from the middle lamella regions which tends to prevent complete cell wall separation.

Cell corner region

Representative transmission electron micrographs of ultrathin cross-sections of cell corner areas are shown in Figs. 9 through 13. After pulping, the nondefi-

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Fig. 6a. Replica of the P wall in a kraft pulp fiber (D:64%). The middle lamella residual lignin obscures the P wall microfibrils.

Fig. 6b. Replica of the P wall in a soda/AQ pulp fiber (D:67%). Although the residual lignin is still visible, the microfibrils are more delineated than those in Fig. 6a.

Fig. 6c. Replica of the P wall in a soda pulp fiber (D:70%). Note large and isolated clumps of residual lignin (arrows).

Fig. 7a. Replica of the P wall in a kraft pulp fiber (D:80%). The microfibrils are well delineated because of middle lamella lignin removal.

Fig. 7b. Replica of the P wall in a soda/AQ pulp fiber (D:86%). Note that the residual lignin is completely removed, resulting in complete exposure of the P wall microfibrils. The greater clarity with which microfibrils can be seen compared to Figs. 7a, 7c and 8a provides an indication of more extensive removal of lignin from both middle lamella and P wall layers.

Fig. 7c. Replica of the P wall in a soda pulp fiber (D:86%). The residual lignin is completely removed, but the microfibrils are less delineated than those in Fig. 7b.

Fig. 8a. Replica of the P wall in a kraft pulp fiber (D:92%). Note that the residual lignin is completely removed.

0.5μm

K 36 9a

K 50 10a

SAQ 26 9b

SAQ 50 10b

S 39 9c

S 51 10c
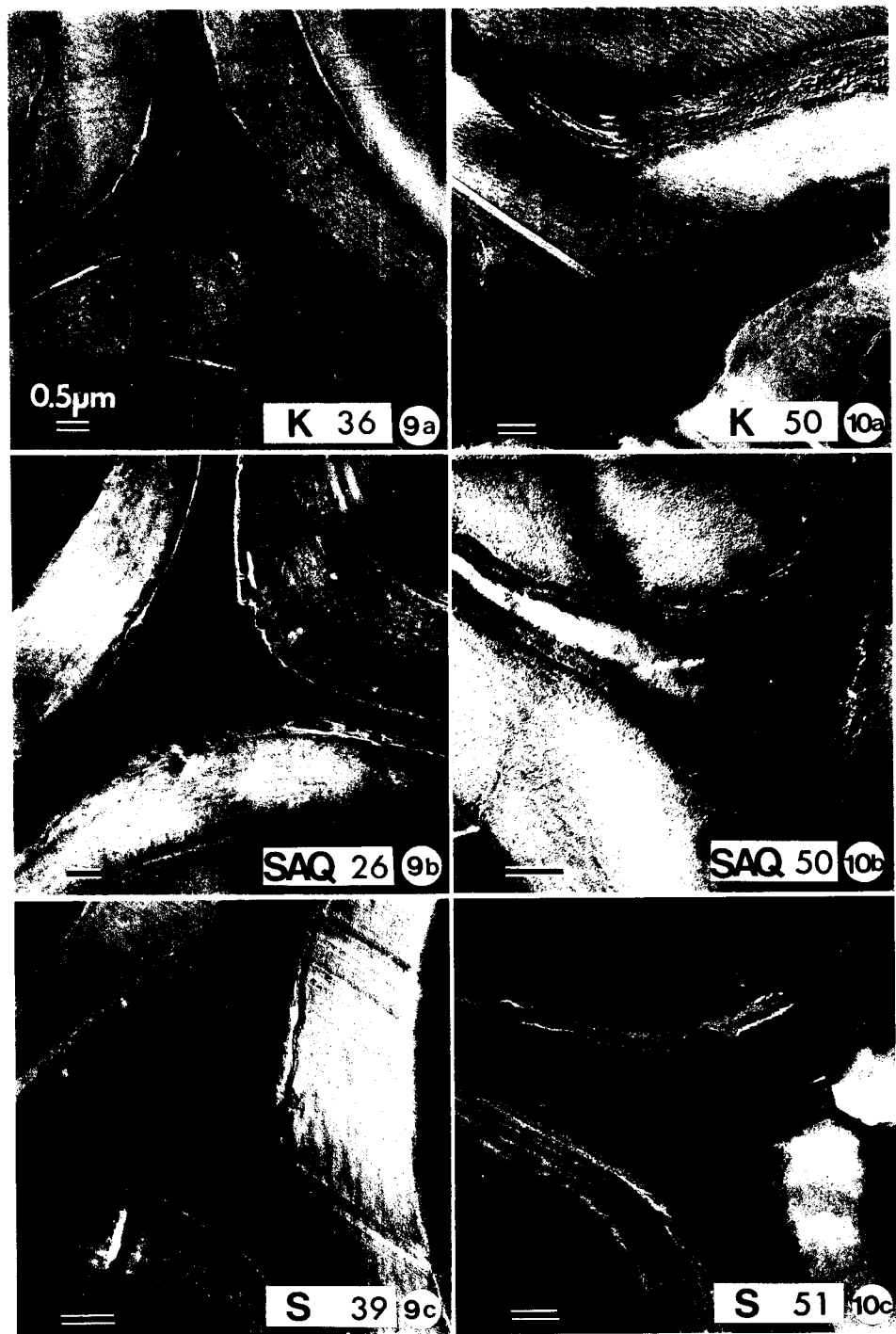
brated pulp samples were carefully handled to avoid any physical separation of the fibers. Thus the structural changes observed at different stages of delignification are due only to the individual pulping process.

Since it was demonstrated that bromine reacts specifically with lignin and that the amount of bromine incorporated is proportional to the lignin content (Saka et al. 1978 and 1981), the samples were carefully brominated prior to electron microscopic observations. In the examination of ultrathin sections, lignin-rich areas are revealed as dark zones because bromine is an electron-dense element specific for lignin. Thus, the darkening provides a qualitative measure of lignin (Saka et al. 1979b). However, as delignification proceeds, less bromine is incorporated into the pulps. As a result, a low contrast image of delignified pulps was obtained. In order to overcome this difficulty and improve image contrast, ultrathin sections were shadowed with platinum after bromination.

Up to about 40% delignification structural changes were not observed (Figs. 9a, 9b, and 9c), and uniform darkening in the cell corner area was apparent for all three pulping processes. But, at approximately 50% delignification stage, cell corner lignin in soda/AQ pulps has been partly removed (Fig. 10b) whereas neither soda nor kraft pulps revealed visible structural modification in the cell corner area (Figs. 10a and 10c).

As delignification proceeded, soda/AQ pulps at 67% delignification level revealed further removal of lignin from the center of the cell corner (Fig. 11b), whereas kraft pulps (65% delignification) revealed no obvious qualitative changes (Fig. 11a). For 70% delignified soda pulps, a partial removal was observed in the cell corner area (Fig. 11c). Observed difference between kraft and soda pulps would be due to further delignification in soda pulps, compared to kraft pulps. The SEM-EDXA technique (Saka et al. 1981) revealed that above 50% delignification, cell corner lignin is extensively removed. Thus, a 6% (70–64%) difference in delignification between soda and kraft pulps caused the observed difference.

Surprisingly, in the next stage of delignification (Figs. 12a and 12c), both kraft and soda pulping processes have removed lignin completely from the center of the cell corner. However, residual lignin is still present adjacent to the P wall (arrows). Even at a higher delignification level (92%), as reported previously (Saka et al. 1979a), residual lignin showed resistance to removal (arrow, Fig. 13a). On the other hand, soda/AQ pulps generally did not retain residual lignin in the cell corner (Fig. 12b).


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FIG. 9a–9c.   Ultrathin cross sections of brominated (9a) kraft (D:36%), (9b) soda/AQ (D:26%) and (9c) soda (D:39%) pulp fibers. Structural changes were not noted and uniform darkening in the cell corner area is due to bromine incorporated into lignin.

FIG. 10a.   Ultrathin cross section of brominated kraft pulp fibers (D:50%).

FIG. 10b.   Ultrathin cross section of brominated soda/AQ pulp fibers (D:50%). Cell corner lignin is partly removed.

FIG. 10c.   Ultrathin cross section of brominated soda pulp fibers (D:51%). Structural changes are not apparent.

K 64 11a

K 80 12a

K 92 13a

SAQ 67 11b

SAQ 86 12b

S 70 11c

S 86 12c
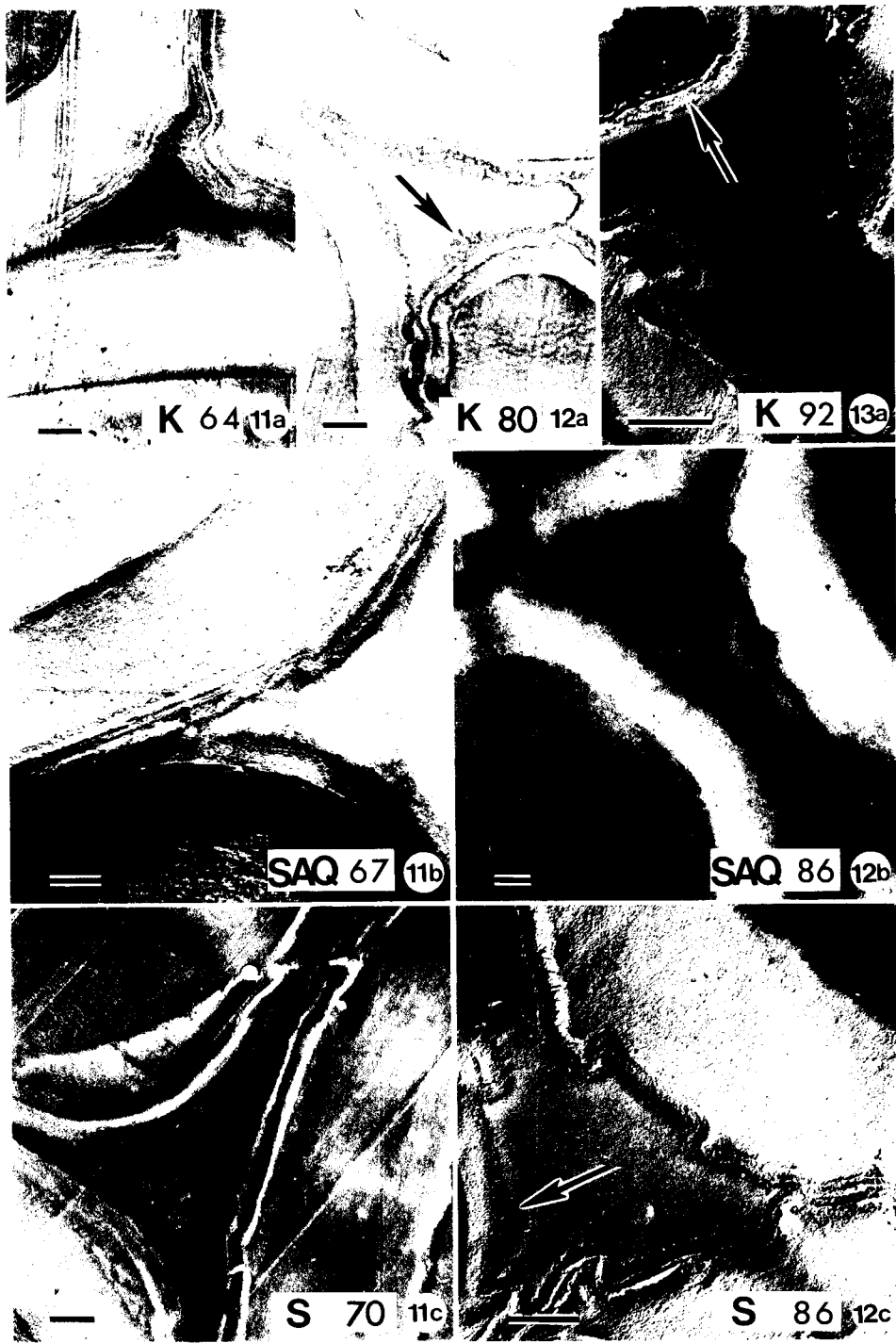
As a result, the overall trend of delignification indicated that soda/AQ pulping removes lignin more extensively in the cell corner regions than either soda or kraft pulping. These observations are in good agreement with the results obtained from the SEM-EDXA study (Saka et al. 1981).

SUMMARY AND CONCLUSIONS

1) Up to 30% delignification, no fiber liberation occurred regardless of the pulping processes. Above 30% delignification, fiber liberation initiates and terminates at a lower delignification level with soda/AQ pulps than with either kraft or soda pulps.

2) Characterization of defibrated fiber surface structures indicated that in an early stage of delignification (up to 15%), defibration of pulps caused separation predominantly within the cell wall, exposing S_1 and S_2 layers. Between 15 and 40% delignification, the outer cell-wall portions such as S_1 and P wall layers were exposed. After 50% delignification, separation occurred only in the middle lamella region. At higher delignification levels, the matrix substances, mainly lignin, in the middle lamella region were removed, exposing randomly oriented P wall microfibrils.

3) Above 50% delignification, soda/AQ pulping more extensively removed middle lamella lignin than either kraft or, in particular, soda pulping.

4) Studies of cell corner regions showed the soda/AQ to be more effective than kraft or soda pulping in removing cell corner lignin.

5) Soda/AQ pulping results in fiber liberation with less lignin removal, compared to kraft or soda pulping process.

6) These observations confirmed the results obtained for a topochemistry study of delignification with the SEM-EDXA technique.

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Fig. 11a. Ultrathin cross section of brominated kraft pulp fibers (D:64%). As yet, structural changes have not been observed.

Fig. 11b. Ultrathin cross section of brominated soda/AQ pulp fibers (D:67%). Note the extensive removal of lignin from the center of the cell corner.

Fig. 11c. Ultrathin cross section of brominated soda pulp fibers (D:70%). A partial removal of lignin at the cell corner area can be seen.

Fig. 12a. Ultrathin cross section of brominated kraft pulp fibers (D:80%). In contrast to Fig. 11a, lignin has been completely removed from the center of the cell corner. However, note residual lignin is still present adjacent to the P wall (arrow).

Fig. 12b. Ultrathin cross section of brominated soda/AQ pulp fibers (D:86%). Lignin has been completely removed from the cell corner region and residual lignin is not observed.

Fig. 12c. Ultrathin cross section of brominated soda pulp fibers (D:86%). Although lignin has been completely removed from the center of the cell corner, residual lignin is still present adjacent to the P wall (arrow).

Fig. 13a. Ultrathin cross section of brominated kraft pulp fibers (D:92%). Residual lignin is still present adjacent to the P wall (arrow).

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