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# *In Situ* Synthesis of Ferrites in Cellulosics

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Superparamagnetic cellulosic fibers were prepared by synthesizing ferrites by an *in situ* method. Five cycles of the reaction were performed on the following four substrates: sodium carboxymethylcellulose lap pulp (Na-CMC), calcium alginate fibers, continuous filament rayon tire cord, and sulfonated thermomechanical wood pulp (TMP). Vibrating sample magnetometry showed that the sulfonated TMP exhibited the highest saturation magnetization (~25 J/T/kg of sample after five cycles of reaction). TEM micrographs of sections of sulfonated TMP fibers showed that the largest concentration of ferrites (~100 Å in size) were arranged at the external fiber surfaces. The micrographs also showed ferrites of less than 20 Å in size, dispersed across the fiber cell wall. Electron diffraction indicated that the major components of the oxides were $\gamma$-$Fe_2O_3$ (needles) and $Fe_3O_4$ (disks). Room-temperature Mössbauer spectra of the sulfonated TMP, after the *in situ* reaction, indicated the presence of small superparamagnetic ferrites for the first and second cycle samples. A ferrimagnetic component was observed for the third cycle sample and predominated in the fourth and fifth cycle samples as a result of larger ferrite grains being formed both on the surface and inside the lumen of the pulp fibers.

## Introduction

Magnetically responsive cellulosic fibers allow exploration of new concepts in papermaking, information storage, security paper, and paper handling. Applications in technologies such as magnetographic printing, magnetic filters, and electromagnetic shielding could be examined. Magnetic cellulose fibers can be prepared via two routes: lumen-loading[1–4] and *in situ* synthesis.[3,5] The two approaches are complementary and lead to a range of materials which can introduce magnetic properties in applications not previously considered. Lumen-loading is a physical approach which introduces commercially prepared magnetic pigments into the lumens of softwood fibers, leading to a *ferrimagnetic* fiber. Lumen-loading was first applied as a means of introducing fillers into softwood fibers, while leaving the external surfaces free of filler. The filler is thus protected by the cell wall, preventing dislodgement during papermaking, hence the particles do not interfere with interfiber bonding and dusting problems during paper usage are greatly reduced.[1]

Magnetic cellulose fibers prepared by lumen-loading with commercial magnetic pigments were used in the conventional fashion to produce magnetic paper. Unbleached Kraft pulp, UBK, and chemithermomechanical pulp, CTMP, of the Black Spruce species have been used. The magnetic pulp is prepared by vigorous agitation in a concentrated suspension of magnetic pigment followed by a mild washing step to remove all pigment external to the lumens. Pigment which has penetrated the lumen through the pit openings is not displaced by the washing step which is under a mild agitation. Lumen-loaded fibers typically contain approximately 15% iron oxide by weight. The magnetic susceptibility of these fibers, as demonstrated by the observed hysteresis loop, was ferrimagnetic in character exactly as the pigments used. The magnetic properties of sheets prepared from the lumen-loaded pulp are comparable to those observed for the magnetic strip on subway passes and for computer floppy disks. Sheets prepared from the lumen-loaded fibers range from brownish-orange to black in color, depending on the pigment used. The color can be masked by applying a thin layer of bleached Kraft fibers as a laminate during the papermaking process.[2–4]

A more chemical approach to preparing magnetic fibers involves synthesizing ferrites within the cellulosic matrix itself.[3,5] The reaction space constraints of the substrate encourages the precipitation of particles of nanoscale dimensions which have unique magnetic and optical properties.[6] The production of small magnetic particles (<250 Å) is of interest in the area of magnetic colored toners since these ferrites have low optical density, and hence the acronym LODM for low optical density magnetics is used.[7] The superparamagnetic properties of the nanoparticles, again demonstrated by the magnetic susceptibility curve, means that while they are easily magnetized they do not retain their magnetization once the field is removed.

Cellulosics, such as wood pulp fibers, in water, can be viewed as swollen ionic networks which can act as ion-exchange resins.[8] The *in situ* reaction used in this study may be summarized in the form of a process cycle, as seen

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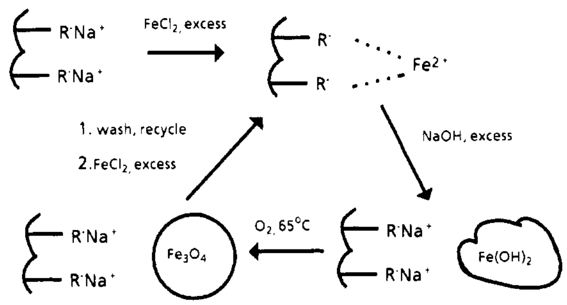
**Scheme 1**[a]



[a] R = carboxylate (–COO⁻) and sulfonate (–CSO₃⁻) acid groups.

in Scheme 1, whereby the anionic functional groups of the fibers appear to serve as catalysts for the production of ferrite. Here, careful oxidation of ferrous hydroxide, precipitated from the ferrous ion-exchanged form of a cellulosic matrix such as sodium carboxymethylcellulose, yields superparamagnetically responsive fibers containing $Fe_3O_4$ particles of approximately 100 Å in size.[5] This approach was previously referred to as "biomimetic" since the physical properties of the product mimic magnetic bacteria.[9–11] In the presence of oxygen these bacteria intracellularly biomineralize ferrites of small size (~500 Å) and high level of crystal perfection which organize, necklacelike, parallel to the rod axis. The resulting bar magnet allows the bacteria to orient in the earth's magnetic field.

## Methods

**Materials.** Sample of Na-CMC (sodium carboxymethylcellulose) was obtained from the Buckeye Cellulose Co., Inc. (Memphis, TE) in the form of a lap pulp. Wet-spun calcium alginate fibers were obtained from the Government Industrial Research Institute of Shikoku in Japan. The sulfonated TMP was made by sulfonation of Black Spruce TMP with $NaSO_3$ in a bomb at a temperature of 160 °C for 1 h. The TMP was a commercial wet pulp with a consistency of 12% (i.e., 12 g of pulp/100 g of suspension). A commercial continuous filament rayon tire cord was also used (Courtaulds Canada, Ltd.). The rayon filament was heterogeneously etherified with sodium 2-chloroethanesulfonate (CES) and 2,2-dichloroacetic acid (DCA) to produce sulfonic and carboxylic groups on the rayon, respectively.[12]

**Functional Group Quantification.** Conductometric titration was used to quantify the number of acid functional groups available for ion exchange with iron in the first step of the *in situ* synthesis.[13] The pulps, alginate fibers, and rayon filaments were acidified by washing three times in 300 mL of 0.1 M HCl solution at a low stirring rate for 30 min. Following acidification, the pulp was washed three times in deionized water to remove excess acid. The pulp was filtered and redispersed in 450 mL of 0.001 M NaCl and 5 mL of 0.1 M HCl in a 1000-mL round-bottom flask. In the case of the Na-CMC, 5 mL of 95% ethanol was added to the suspension prior to the titration in order to reduce the swelling and ease the filtration of the material.[3] The titration was performed in a sodium chloride solution for the purpose of creating a "Donnan"[14] equilibrium between the ions inside the fiber and those in the external solution. The titrations were performed according to a previously published methodology.[3]

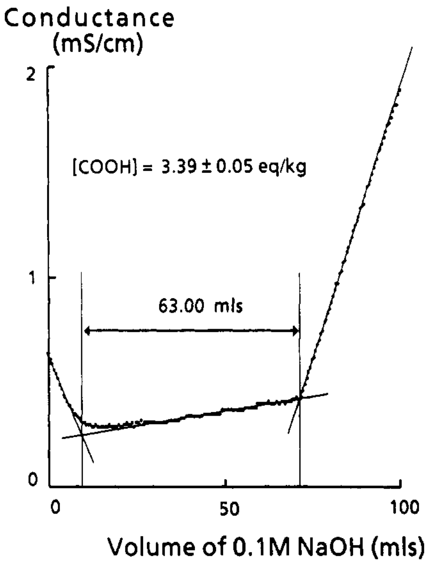


**Figure 1.** Conductometric titration curve of sodium carboxymethylcellulose.

***In Situ* Synthesis.** Ferrites were synthesized in the materials according to Scheme 1. Approximately 1 g of material was stirred gently in 100 mL of excess $FeCl_2{\cdot}4H_2O$ solution (0.01 g/mL) to form a yellowish-brown suspension. Ferrous hydroxide was precipitated by addition of an excess (50 mL) of 0.1 M NaOH. The greenish-black suspension was heated to 65 ± 5 °C and maintained at this temperature for 2 h while bubbling $O_2$ through the solution at a rate of 6 mL/min. The reaction mixture was stirred gently and turned a muddy-rust color with time. Five cycles of the *in situ* reaction were performed on each of the materials and a sample was collected after each cycle. The samples were washed several times by stirring in deionized water followed by filtering on a medium porosity glass fritted filter in order to remove any physisorbed ferrites prior to analyses.

**Vibrating Sample Magnetometry.** The magnetic properties of the materials were studied using a vibrating sample magnetometer (Physics Department of McGill University). Approximately 15 mg of sample was inserted into a sample holder and was vibrated within a magnetic field of up to 1.5 T. A plot of the response of the material as a function of applied magnetic field was plotted on line in the form of a magnetic hysteresis loop.[15]

**Transmission Electron Microscopy.** Transmission electron microscopy was performed on sections of samples of sulfonated TMP after each of the five cycles of the *in situ* reaction. For sectioning, the pulps were swollen in water and successively solvent exchanged with ethanol and propylene oxide and embedded in a Spurr resin which was cured at 70 °C overnight. Ultrathin sectioning of the resulting blocks was performed with a Reichert ultracut E microtome equipped with a diamond knife. The TEM instrument was a Philips EM 400 operated at 120 kV for imaging by diffraction contrast in the bright-field mode and for selected-area (SA) electron diffraction.

**Energy-Dispersive X-ray Spectrometry.** The samples were supplied as ultramicrotome sections mounted on Cu grids. Detailed TEM observations combined with EDS (energy-dispersive X-ray spectrometry) microanalysis were performed to facilitate the determination of iron distribution across the sulfonated TMP wood fibers after one and five cycles, as well as the sulfur distribution across these sulfonated fibers. The ultramicrotome sections were examined using an analytical electron microscope (Philips CM30) at an accelerating voltage of 100 kV with an X-ray energy dispersive spectrometer (Link AN10/85S system) equipped with an ultrathin window allowing the analysis of light elements down to boron. Measurements

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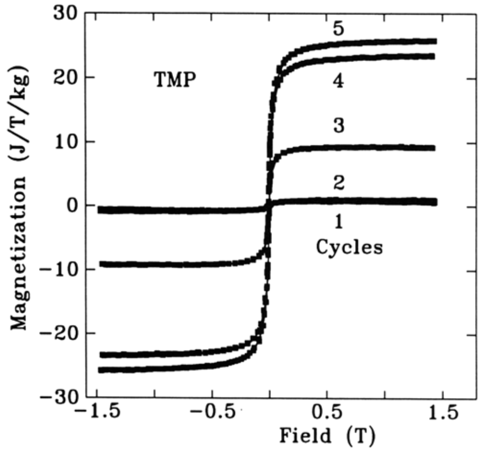

**Figure 2.** Magnetic hysteresis loops for sulfonated TMP after one to five cycles of the *in situ* reaction.

**Table 1. Functional Group Quantification of Starting Materials**

| substrate | [COOH] (equiv/kg) | [$SO_3H$] (equiv/kg) |
|---|---|---|
| Na-CMC lap pulp | 3.5 ± 0.1 | |
| Ca-alginate fibers | 0.929 ● 0.018 | |
| sulfonated TMP | 0.169 ● 0.008 | 0.518 ± 0.003 |
| rayon (sulfonated) | | 0.197 ± 0.010 |
| rayon (carboxy) | 0.254 ± 0.010 | |

were made in the TEM imaging mode with a focused 80-nm diameter electron probe. Spectra were acquired in about 300 s.

**Mössbauer Spectroscopy.** The Mössbauer spectra were obtained at room temperature with a conventional constant-acceleration spectrometer in transmission geometry using a 1 Gbq $^{57}$Co$\underline{\text{Rh}}$ source. Spectra of the standards, $\gamma$-$Fe_2O_3$ (Pfizer Pigments Inc., MO-2228, lot no. 179020) and $Fe_3O_4$ (Pfizer Pigments Inc., MO-4232, lot no. 129015), were obtained by using approximately 50 mg of the magnetic pigment mixed uniformly with BN. The spectra were fitted using a standard Mössbauer computer fitting program. Spectra for each of the *in situ* cycles were obtained for the sulfonated TMP samples. The samples were prepared by drying the pulp in a Teflon cuvette into a uniform square of paper which was subsequently folded once to increase absorption.

## Results and Discussion

**Conductometric Titration.** As previously noted, conductometric titration was used as a method for functional group quantification. Figure 1 is a typical titration curve for a weak acid, in this case sodium carboxymethylcellulose, which contains carboxylic acid groups. The first branch of the curve corresponds to the neutralization of the $H^+$ ions from the 5 mL of 0.1 M HCl added prior to the titration. The "plateau" region is a result of the weak carboxylic acid groups dissociating and being neutralized, and hence little contribution to the total conductance of the solution occurs here. The third upward branch is due to an excess of base being added to the suspension.[13] The equivalence points may then be determined by the intersection of the three branches, and the number of equivalents of acid group may be calculated. For materials such as the sulfonated TMP sample which contains both carboxylic and sulfonic acid functional groups, the first equivalence point for the neutralization of the strong acid sulfonic groups is the point at which the plateau region begins, taking into account the volume of titrant required to neutralize the HCl added initially. The carboxylic acid group content is calculated as described above. The advantage of conductometric titration over other methods for functional group quantification, such as potentiometric determinations, is its ability to produce two distinct endpoints for strong and weak acids, which are present in the sulfonated TMP sample.[13]

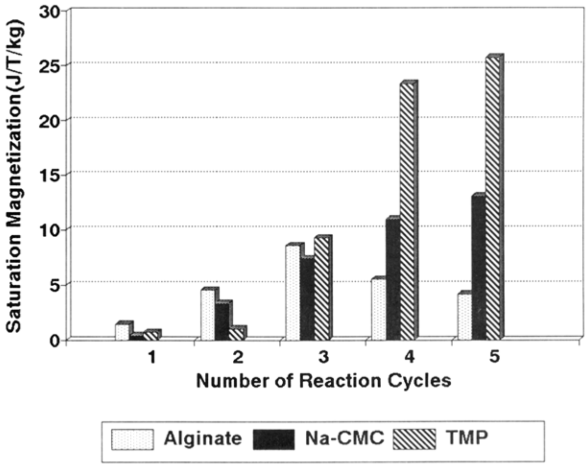

**Figure 3.** Saturation magnetization as a function of the number of cycles of the *in situ* reaction.

Table 1 shows the results obtained for the number of acid groups for each of the materials.

**Vibrating Sample Magnetometry.** After synthesis of the ferrites, the magnetic properties of the materials were studied via vibrating sample magnetometry. The materials all demonstrated superparamagnetic behavior, i.e., the magnetization curves showed no hysteresis, coercivity, or remanence, while exhibiting substantial saturation values. The curves obtained for the sulfonated TMP samples after each of the five cycles of reaction are shown in Figure 2. Fits to the magnetization curves of the loaded sulfonated TMP samples showed their magnetic response to be dominated by signals from magnetite particles of approximately 100 Å across. However, even after five cycles there was a substantial contribution from much smaller (~10 Å) particles. These two components may be attributed to grains seen by TEM on the exterior of the fiber and within the cell wall, respectively. The saturation magnetizations were recorded for each of the substrates as a function of the number of cycles of reaction. As can be seen in Figure 3, the sulfonated TMP sample shows the highest saturation magnetization (~25 J/T/kg of sample). The CMC material does not maintain its properties after one cycle of reaction: The sample dries into a brittle film following the reaction. The calcium alginate fibers show an increase in saturation magnetization up to the third cycle then a progressive decrease. The alginate fibers demonstrate behavior similar to the CMC material where the sample decomposes under the harsh reaction conditions. This phenomenon is probably a result of the "peeling" reaction which is observed in basic conditions for polysaccharides.[16] Milder reaction conditions (i.e., lower temperature, shorter reaction time, lower concentration of base, etc.) may reduce the probability of peeling of the cellulosic substrate from occurring, though reducing the effectiveness of the reaction. The rayon filaments lack the ionic group content for sufficient loading in one cycle. After one cycle of loading, the magnetic rayon filaments show a magnetic saturation of 2 J/T/kg. Higher ferrite loadings may be expected for multiple cycles.

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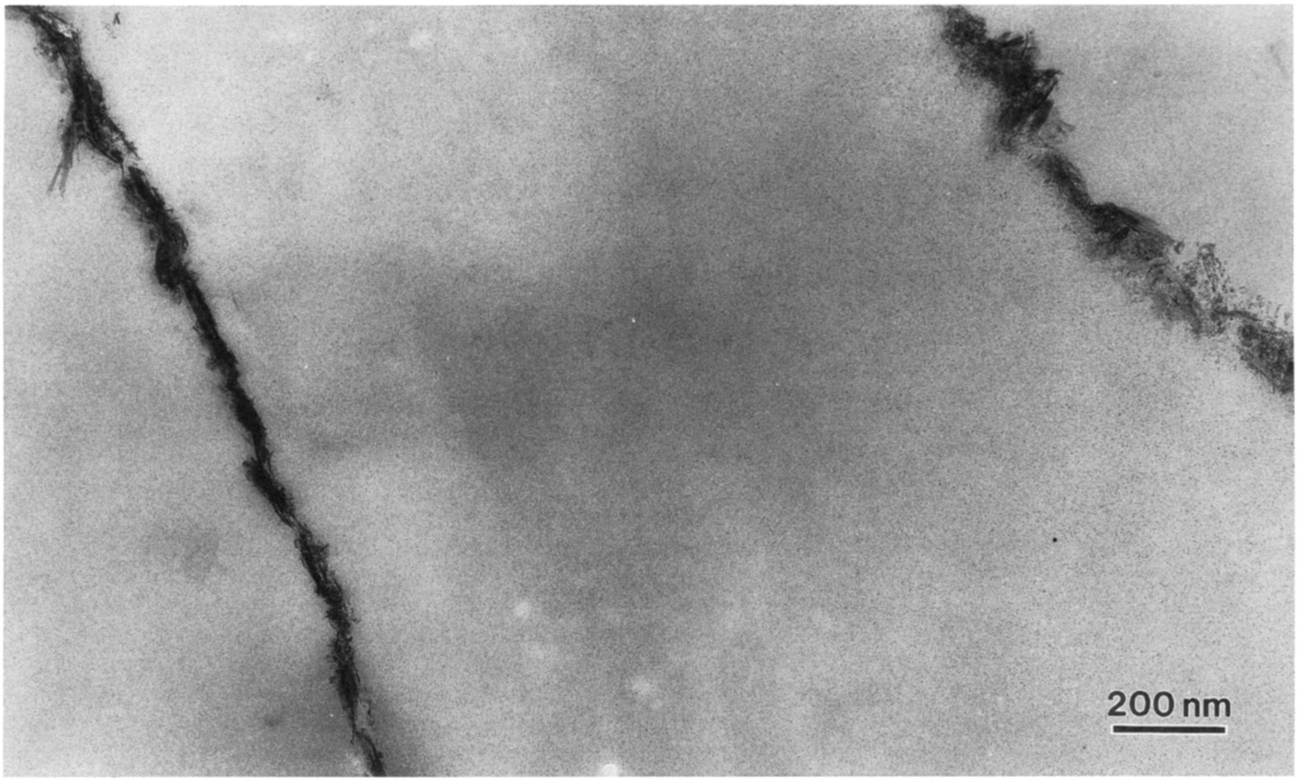

**Figure 4.** TEM micrograph of a section of sulfonated TMP fiber after one cycle of the *in situ* reaction. Needlelike crystals at the exterior wall surface (left side) and at the lumen surface (right side) are visible.

The sulfonated TMP showed the highest saturation magnetization ever obtained for both the lumen-loading and the *in situ* method of inducing magnetic susceptibility in cellulosic fibers (cf. Figure 3).[2–5] The fibrous properties of the material were retained, i.e., the pulp fibers dried down into a paperlike film, showing high potential for conversion of *in situ* magnetic fibers to paper.

**Transmission Electron Microscopy.** TEM microscopy was used to study the chemical and physical properties of the ferrites throughout sections of the TMP fibers. Figure 4 is a section of the TMP fiber after one cycle of the *in situ* reaction. The ferrites are distributed primarily on the exterior of the fiber as well as in the lumen. Only a small amount seems to be present in the cell wall. Ferrites in the form of needles are the largest fraction, whereas the remaining number is found to be in the form of disks. The needles, identified as $\gamma$-$Fe_2O_3$ by electron diffraction (see next section), range from approximately 30 to 50 Å in width and 500 to 1000 Å in length and are distributed along the exterior fiber surfaces. The ferrites within the cell wall are approximately 10 Å in size and dispersed across the cell wall: no crystallinity could be detected by electron diffraction, probably due to their very small size. The disks found on the exterior of the fiber are of the order of 50 Å in size and were identified as $Fe_3O_4$.

Figure 5 shows the TEM micrographs of sections of TMP fibers after five cycles of reaction. Here, the largest fraction of ferrites is found in the form of disks with a smaller portion of needles. The needles, found along the exterior of the fiber and in the lumen, range from approximately 25 to 130 Å in width and 650 to 1300 Å in length. The disks also appear larger after five cycles of reaction ranging from 65 to 260 Å on the exterior fiber surfaces and 15 to 30 Å in the cell wall where still no crystallinity can be detected. The disks were identified as $Fe_3O_4$ by electron diffraction on those on edge. Aggregation is not apparent in the cell wall due to reaction space constraints causing a stabilizing effect.[18–20] The increase in size and concentration of the ferrites is a result of an increase in iron content from the first to the fifth cycle. The material was found to contain 15% iron after one cycle and 34% iron after five cycles, as determined by ashing.[21]

TEM shows that the heterogeneous chemical and physical properties of the sulfonated TMP influence the ferrite distribution. As shown in Figures 4 and 5, the ferrites are primarily distributed along the fiber surfaces. Sulfonation of TMP pulp probably occurs at the benzylic position in units having free phenolic groups in the lignin structure. For high yield pulps, such as sulfonated TMP, the middle lamella, primary wall, outer secondary wall (S1) and the internal lumen surfaces are the sections of the fiber highest in lignin content. These sections are exposed or removed during the pulping process; therefore, sulfonation of the fines as well as the exposed portions of the fiber will predominate.[22] The presence of a higher sulfur and iron content at the fiber surfaces was confirmed by EDS as shown in Figure 6. This higher sulfonic acid content at the surfaces influences ferrite distribution. It is known that by increasing the acid group content of wood pulps, swelling of the pulp is seen to increase.[23] The pulp swells, according to the Donnan theory, as a result of the osmotic pressure difference between the inside of the fiber

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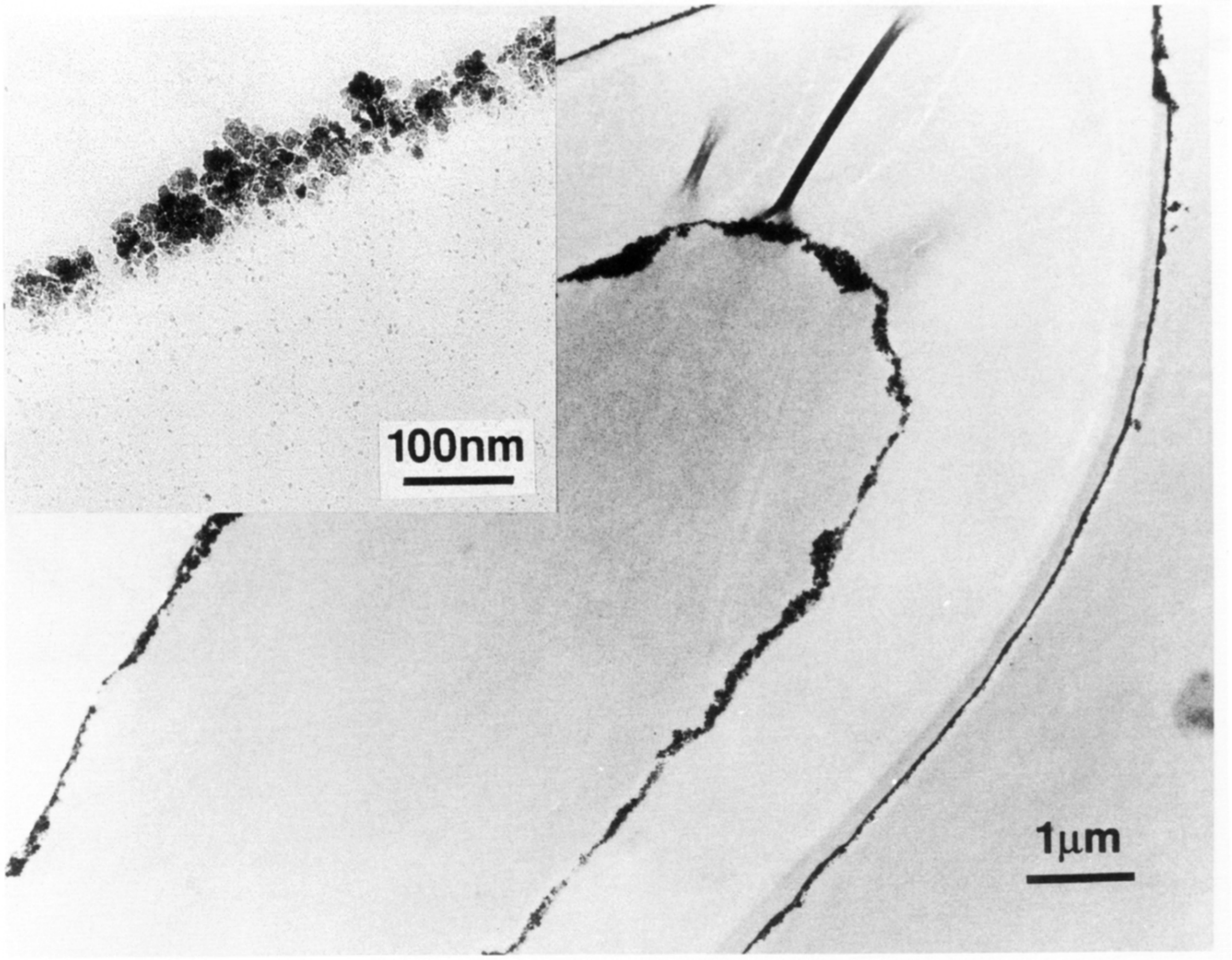

**Figure 5.** TEM micrographs of a section of sulfonated TMP fiber after five cycles of the *in situ* reaction showing a higher concentration of ferrites at the fiber surfaces. Inset: higher magnification of the cell wall showing the presence of small ferrites distributed across the fiber.

and the external solution.[24] Thus, ion exchange with iron in the first step of the *in situ* reaction is enhanced at the fiber surfaces due to swelling. The swelling of the cell wall of highly lignified fibers, however, is known to be restricted due to the three-dimensional cross-linked network of the lignin. Accessibility to the excess ferrous chloride salt solution used for ion-exchange with iron is decreased in the cell wall. The larger concentration of iron ions at the fiber surfaces is therefore a factor in producing the observed ferrite distribution. Since the sulfur content at the surfaces and inside the cell wall are of the same order of magnitude, whereas the iron content is 1–2 orders of magnitude larger in concentration at the surfaces, we concluded that accessibility and space are the two major factors in determining ferrite distribution.

**Electron Diffraction.** Electron diffraction patterns were recorded for the sulfonated TMP sections after one and five cycles and compared with X-ray powder diffraction data.[25] Tables 2 and 3 show the *d* spacings obtained for the first and fifth cycle samples, respectively. Table 2 shows that the *d* spacings correspond to those of $\gamma$-$Fe_2O_3$ and in Table 3 the spacings correspond to $Fe_3O_4$. This is in agreement with the TEM micrographs: the first cycle of reaction produces mainly needles ($\gamma$-$Fe_2O_3$), but after five cycles, formation of $Fe_3O_4$ disks predominates, hence the *in situ* reaction produces a mixture of these two oxides.

**Mössbauer Spectroscopy.** The room-temperature Mössbauer spectra are shown in Figure 7. After one cycle, the spectrum shows only a paramagnetic doublet, with parameters consistent with a ferric oxide. We associate this component with the fine ($\sim$10 Å) particles seen within the cell wall. After three cycles, a magnetic sextet is apparent. This component grows on further cycling, and dominates in the five cycle sample. The magnetically ordered component is due to the larger particles (presumably the >100 Å grains seen on the fiber surfaces by TEM). The presence of a static magnetic component in the Mössbauer spectra in contrast with the magnetization measurements which showed contributions only from rapidly relaxing superparamagnetic particles results from a combination of the very different time scales associated with the two techniques and the relaxation rates of the large and small grains. On the seconds scale characteristic of magnetization measurements, both the large and small grains relax rapidly and appear superparamagnetic; however, the large particles relax more slowly and appear static on the Mössbauer time scale of $10^{-7}$ s. Mössbauer spectra recorded at 77 K showed some reduction of the paramag-

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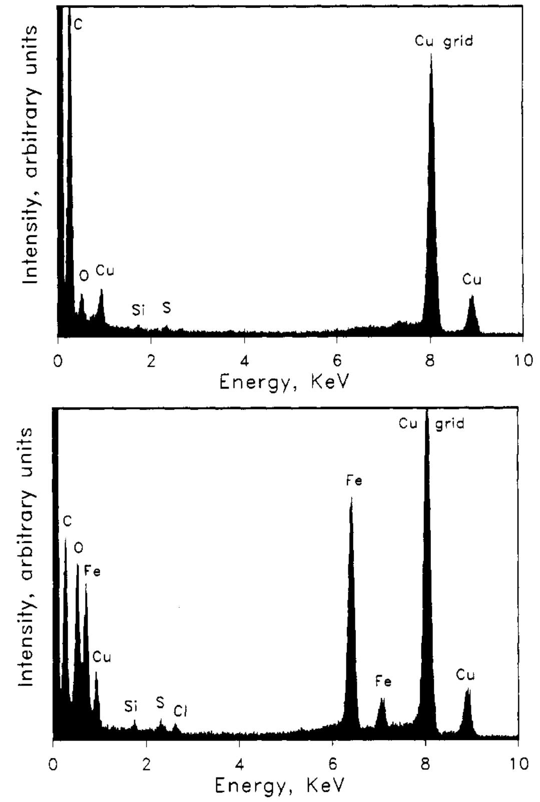

**Figure 6.** Energy-dispersive X-ray spectra of sulfonated TMP after five cycles of *in situ* reaction: (a, top) EDS spectrum for the center of the fiber wall; (b, bottom) EDS spectrum for the exterior fibre surface showing a higher concentration of sulfur and iron at the surface as compared to the fiber centre.

**Table 2. Electron Diffraction Data (*d* Spacings/Å) for Ferrites Synthesized *in Situ* Using Sulfonated TMP after One Cycle of Reaction**

| *in situ* Ferrites | XRD (reference)[a] |
|---|---|
| 3.45 | 3.399 87 |
| 2.61 | 2.514 37 |
| 2.01 | 2.086 58 |
| 1.59 | 1.604 47 |

[a] Powder X-ray diffraction data file for $\gamma$-$Fe_2O_3$.[25]

**Table 3. Electron Diffraction Data (*d* Spacings/Å) for Ferrites Synthesized *in Situ* Using Sulfonated TMP after Five Cycles of Reaction**

| *in situ* Ferrites | XRD (reference)[a] |
|---|---|
| 3.05 | 2.966 14 |
| 2.58 | 2.532 37 |
| 2.15 | 2.099 82 |
| 1.75 | 1.714 33 |
| 1.66 | 1.615 93 |
| 1.52 | 1.484 31 |
| 1.31 | 1.280 27 |
| 1.12 | 1.093 37 |

[a] Powder X-ray diffraction data file for $Fe_3O_4$.[25]

netic component in all samples, but a substantial fraction remained, indicating that some, but not all, of the finer particles are static at 77 K. Thus the division into two distinct particle sizes is an oversimplification.

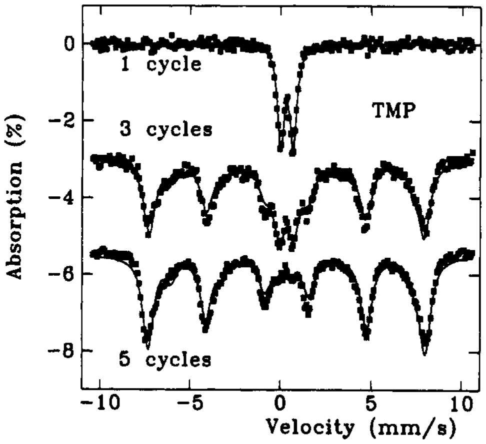

**Figure 7.** Room-temperature Mössbauer spectra of samples of sulfonated TMP after one, three, and five cycles of the *in situ* reaction.

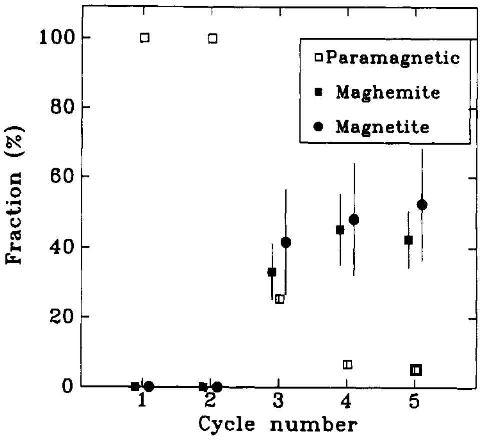

**Figure 8.** Fraction percentages of magnetite ($Fe_3O_4$) and maghemite ($\gamma$-$Fe_2O_3$) as a function of the number of *in situ* reaction cycles.

The Mössbauer spectrum of $Fe_3O_4$ consists of two magnetic sextets in the ratio 2:1, corresponding to iron in the A and B sites of the structure respectively. That of $\gamma$-$Fe_2O_3$ shows a single sextet. Unfortunately, the maghemite spectrum overlaps the A-site component of the $Fe_3O_4$ spectrum so that the two compounds are not readily distinguishable in mixed samples. Furthermore the line-broadening apparent in Figure 7, due both to some residual relaxation effects and chemical disorder in the material, also reduces the resolution of the measurement. The magnetic components of the spectra can be fitted with two subspectra approximating the A- and B-site contributions of $Fe_3O_4$; however, the A:B ratio is always above the 2:1 expected for pure $Fe_3O_4$. If we associate the excess A-site intensity with the presence of $\gamma$-$Fe_2O_3$, we can obtain estimates shown in Figure 8 for the amounts of iron present as each oxide. The morphology of the fine particles seen by TEM would suggest that the paramagnetic component is mainly $Fe_3O_4$; however, it is not possible to reliably distinguish the two oxides in the paramagnetic state and so this component is given separately in Figure 8.

## Conclusions

It has been shown that by an *in situ* synthesis method, cellulosics can be used to produce ferrites in the nanoscale size range, producing a "cellulosic nanocomposite". Of the materials studied, a sulfonated thermomechanical wood pulp sample showed the highest potential for magnetic fiber. Because it is a mechanical wood pulp, it is able to withstand the reaction conditions of the *in situ* method with cycling. Following five cycles of the *in situ* reaction, the material exhibited a high saturation magnetization (~25 J/T/kg). Aggregation of small paramagnetic ferrites of approximately 20 Å in size was inhibited by the three-dimensional cross-linked nature of the highly lignified wood fiber cell wall. We conclude that accessibility and space factors determine ferrite distribution.

The continuous filament material is in the preliminary phase of study.[12] The desirability of extending the technology to the field of textiles has recently led to experimentation with continuous filaments such as rayon fibers, poly(vinyl alcohol), alginate, and lightly cross-linked chitosan, all of which possess the required functional groups for the creation of superparamagnetic ferrites via *in situ* chemistry.

Both the lumen-loading and *in situ* methods of conversion to magnetic cellulose fibers are straightforward from a process viewpoint. However, lumen-loading is limited to natural wood fibers with a pit morphology. The advantage of the *in situ* method is that it can be practiced with many kinds of materials, natural and artificial, producing nanocomposites which are materials of growing interest.

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