Institute of Paper Science and Technology
Atlanta, Georgia

IPST Technical Paper Series Number 839

Using EXAFS for Problem Solving in the Wood Pulp Mill

G.B. Ow Yang, S. Pattanaik, A.W. Rudie,
D.B. Hunter, and P.M. Bertsch

January 2000

Submitted to
Brookhaven National Laboratory
National Synchrotron Light Source
1999 Activity Report
"Science Highlights"

INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY
PURPOSE AND MISSIONS

The Institute of Paper Science and Technology is an independent graduate school, research organization, and information center for science and technology mainly concerned with manufacture and uses of pulp, paper, paperboard, and other forest products and byproducts. Established in 1929 as the Institute of Paper Chemistry, the Institute provides research and information services to the wood, fiber, and allied industries in a unique partnership between education and business. The Institute is supported by 52 North American companies. The purpose of the Institute is fulfilled through four missions, which are:

- to provide multidisciplinary graduate education to students who advance the science and technology of the industry and who rise into leadership positions within the industry;
- to conduct and foster research that creates knowledge to satisfy the technological needs of the industry;
- to provide the information, expertise, and interactive learning that enables customers to improve job knowledge and business performance;
- to aggressively seek out technological opportunities and facilitate the transfer and implementation of those technologies in collaboration with industry partners.

ACCREDITATION

The Institute of Paper Science and Technology is accredited by the Commission on Colleges of the Southern Association of Colleges and Schools to award the Master of Science and Doctor of Philosophy degrees.

Using EXAFS for Problem Solving in the Wood Pulp Mill

G. B. Ow Yang, S. Pattanaik*, A. W. Rudie
(Institute of Paper Science and Technology, Atlanta, GA);
D. B. Hunter, P. M. Bertsch
(Savannah River Ecology Laboratory, Aiken, SC)

* Pattanaik is now at CFFLS, University of Kentucky.

PARTNERSHIPS IN PAPER SCIENCE

The paper industry has successfully utilized EXAFS spectroscopy capabilities at NSLS to study the structural binding of metals in pulp.[1] These results have enabled researchers to more accurately model material flows in process streams in the on-going effort to achieve total recovery of pulp mill effluents. This incremental step forward has been made possible through an industrial partnership with two government laboratories, an invaluable relationship for the U.S. paper industry.

Pulping and papermaking are water-intensive processes that discharge on average 36 m^3 of water per air dry ton (ADT) of bleached pulp.[2] In the 1990's, cooperation increased between the U.S. pulp and paper industry and the federal government to develop technologies with reduced environmental impact and to help the industry remain competitive in the expanding global market. In 1994, the Department of Energy (DOE) selected the Forest Industry to participate in the DOE program "Industries for the Future". Together, the DOE and the Forest Industry set targets for collaborative research in six key areas, one of those areas being Environmental Performance.[3] Shortly thereafter, in 1998, the Environmental Protection Agency promulgated the "cluster" rules by which mills will be measured for environmental compliance in the areas of air and effluent emissions.[4]

REDUCING WASTEWATER DISCHARGE

One strategy for reducing wastewater discharges is to recycle process water. The pulp and paper industry has already conducted much research for reducing effluent discharge and has succeeded in reducing volumes on average from 200 m^3 of water per ADT of pulp in 1965[5] to 36 m^3 per ADT of bleached pulp in 1996[6]. The configuration of a conventional bleach plant that enables such efficient use of water is made up of acidic stages alternating with alkaline extraction stages (**Figure 1**). Bleaching filtrate is recycled according to "like goes with like", e.g., filtrates from acidic stages are recycled back to the preceding acidic stages. The first acidic stage filtrates are sent to the wastewater treatment plant; this also serves as an outlet for trace metals. The minimum effluent scenario is to recycle bleach plant effluents countercurrently so that the filtrate from one stage is recycled on to the previous stage regardless of its pH. By this method, effluent volumes can be reduced on average to 12 m^3 of water per ADT of pulp.[7]

Ideally, for minimum environmental impact, the wastewater supply for all of the unit operations in a pulp mill would be integrated as a "closed mill". Bleach plant effluent from the first stage in the bleach plant is recycled back to the washers for unbleached pulp. The washer discharge is recycled back to the pulping reactor (digester) for use in pulping. These spent liquors (black liquor) are sent to the chemical recovery operation where unwanted components would be incinerated in a recovery boiler or a gasifier. Burning of organics provides steam for mill processes, while the bulk of the inorganics are recovered from the smelt to be reused in the pulping process.

For the typical pulp mill, which handles 1500 to 3000 metric tons of wood per day, about 2 metric tons of calcium enters into the pulping process each day. Even without additional recycle of effluent, mills report significant levels of calcium accumulation and scale formation on equipment surfaces throughout the mill.[8] Pipes clog, and screens and washing filters plug up because of scale formation. When these problems persist untreated or undetected, they can literally force production to a halt. During routine maintenance, the cost to mills is the manpower and chemicals required to remove scale deposits. Normal maintenance costs for scale removal run about $800,000 annually. Additional costs are incurred in severe cases because emergency shutdown of the mill causes lost production time and lost output.

BUILDUP OF METALS

Previous mill efforts to recycle effluents have shown that increased recovery of effluent is possible, but only for a limited amount of time. The accumulation of trace metals, e.g., Ca, Ba, and Mn, presents a significant obstacle to overcome before total effluent recovery can be achieved. From 1977 to 1985, the pulp mill at Thunder Bay, Ontario, operated on a continuous basis with partial bleach plant effluent recovery.[9] The mill effort failed due to critical accumulation of chlorides and excessive formation of pitch and scale. A subsequent demonstration in 1997 at a pulp mill in Canton, North Carolina,[10] showed that implementation of new technology had solved the problem with chlorides. However, the problem with the accumulation of trace metals was never clearly resolved because only partial closure of the bleach plant effluent system was achieved.

Results from laboratory studies simulating 100% reuse of the filtrates in the first three stages of bleaching are shown in **Figure 2.**[11] The waste effluent from each bleaching stage was recycled directly back to the preceding stage. As the number of cycles increased, the amount of calcium trapped in the system increased.

SOLVING THE PROBLEM WITH EXAFS

Controlling the accumulation of calcium and preventing the formation of deposits, requires an understanding of the fundamental chemistry that governs calcium throughout the pulping and bleaching process. Calcium enters the mill through the raw material (wood source) and the water source. During pulping, the addition of sodium-based compounds under alkaline conditions favors the displacement of calcium ions in the pulp by sodium ions. Soluble calcium will readily form complexes with carbonate ions and precipitate from solution as calcium carbonate.

It was hypothesized that at the lower pH and sodium ion concentration that exists in the washing step, calcium would readsorb to the ion exchange sites in the fiber. Even after washing, a significant amount of calcium (~1000 ppm) still remains in the pulp, and this residual carries over into the bleach plant. Under closed-loop conditions, calcium ions in acidic stages of the bleach plant form complexes with oxalates and precipitate as calcium oxalate deposits on process equipment and piping. An improved understanding of the binding of the residual calcium in pulp fibers will enable better methods to be devised for the removal of residual calcium prior to pulp bleaching.

In pulp fibers, there are four types of binding sites to which residual calcium may be bound. As a +2 cation, calcium can bind to two adjacent hydroxyl groups, such as those found in sugar molecules or on the alkyl chains off of the aromatic units in lignin. Calcium ions may also bind at the carboxylic acid sites in uronic acids or to 3-methoxy, 4-hydroxy sites of the aromatic units in lignin. Ion exchange experiments on pulp indicate that sodium exchanges for calcium in a ratio of 2:1 and suggests that calcium binds to the carboxylic acid sites.

Extended absorption fine structure (EXAFS) spectroscopy was used to probe the local atomic environment around calcium in wood pulp that had been taken from the last stage of the washers after pulping. Calcium K EXAFS was conducted at beamline X19A. A plot of the EXAFS chi data for calcium in pulp appears in **Figure 3**. Calcium was expected to dissolve and readsorb to the pulp in the washing operation; this did not happen. EXAFS analysis indicated that the calcium in the pulp sample was predominately in the form of calcium carbonate (calcite). These results confirm that during the alkaline pulping process, calcium is displaced from the carboxylic acid binding sites on the fibers and reprecipitates within the fibers as an entrapped calcite phase. This knowledge has already been used to improve equilibrium models of metals in the bleach plant and the washers preceding the bleach plant.

The next phase of the project is to employ EXAFS to determine the chemistry of calcium in wood fibers within the bleach plant. One possibility is that calcium in bleached and partially bleached pulp exists physically bound or at least associated with carboxylic acid functional groups in the fiber. The alternative here is that calcium in bleached and partially bleached pulps exists as precipitates of calcium oxalate. These two hypotheses will be tested in the next series of experiments.

Acknowledgements This research was supported by the Georgia Traditional Industries Program in Pulp and Paper under grant MP4-FY99 and the member companies of the Institute of Paper Science and Technology (IPST), Atlanta, GA. The authors wish to thank S. Khalid for technical support at the X19A beamline. This work was used by G. Ow Yang in partial fulfillment of the requirements for the Ph.D. degree at IPST.

---

[1] Ow Yang, G.B.; Kemner, K.; Hunter, D.B.; Bertsch, P.M. Metal binding sites in wood pulp. TAPPI Proc. Intl. Eng. Conf. Poster Book, Miami, FL; TAPPI, Atlanta, 1998, pp. 76-80.
[2] Histed, J.; McCubbin, N.; Gleadow, P.L. Section VI: Bleach Plant Operations, Equipment and Engineering, Chapter 6: Water Reuse and Recycle in Pulp Bleaching: Principles and Practice. (eds. C.W. Dence and D.W. Reeve) TAPPI, Atlanta, 1996, p. 649.
[3] Agenda 2020: A Technology Vision and Research Agenda for America's Forest, Wood, and Paper Industry; American Forest & Paper Association, New York, 1994, p. 4.
[4] Final Pulp and Paper Cluster Rule. U.S. Environmental Protection Agency, Office of Water, Washington D.C., 1998, Fed. Regist. 63 Notice 18504-18751, 42238-42240.
[5] Rydholm, S.A. Pulping Processes, Interscience, New York, 1965, p. 1082.
[6] Histed, J.; McCubbin, N.; Gleadow, P.L. *Op. cit.*

[7] D.N. Carter, P. L. Gleadow Water use reduction in chemical pulp mills in Water Use Reduction in the Pulp and Paper Industry 1994. (ed. by P. Turner, P. Williamson and K. Wadham) CPPA, Montreal, 1994, p. 60.
[8] Ulmgren, P.; Radestrom, R. Calcium oxalate in bleach plant filtrates. TAPPI Proc. Minimum Effluent Mill Symposium, San Francisco, CA; TAPPI Press, Atlanta, 1997, pp. 51-62.
[9] Donovan, D. A. A review of the closed-cycle mill operating experience at Great Lakes Forest Products Limited: 1997-1985. Presented at the TAPPI Annual Meeting, Atlanta, GA, 1994.
[10] Caron, J.R.; Delaney, G. Initial learnings from the BFR demonstration. TAPPI Proc. Minimum Effluent Mill Symposium, San Francisco, CA; TAPPI, Atlanta, 1997, pp. 73-78.
[11] Rudie, A.W.; Puckett, A.; Rorrer, G. NPE Modeling of a Laboratory Bleach Filtrate Recycle Experiment. Presented at the AICHE Forest Products Division Joint TAPPI Sessions, Orlando, FL, November 1999.

Fig. 1 Typical configuration of a conventional bleach plant.

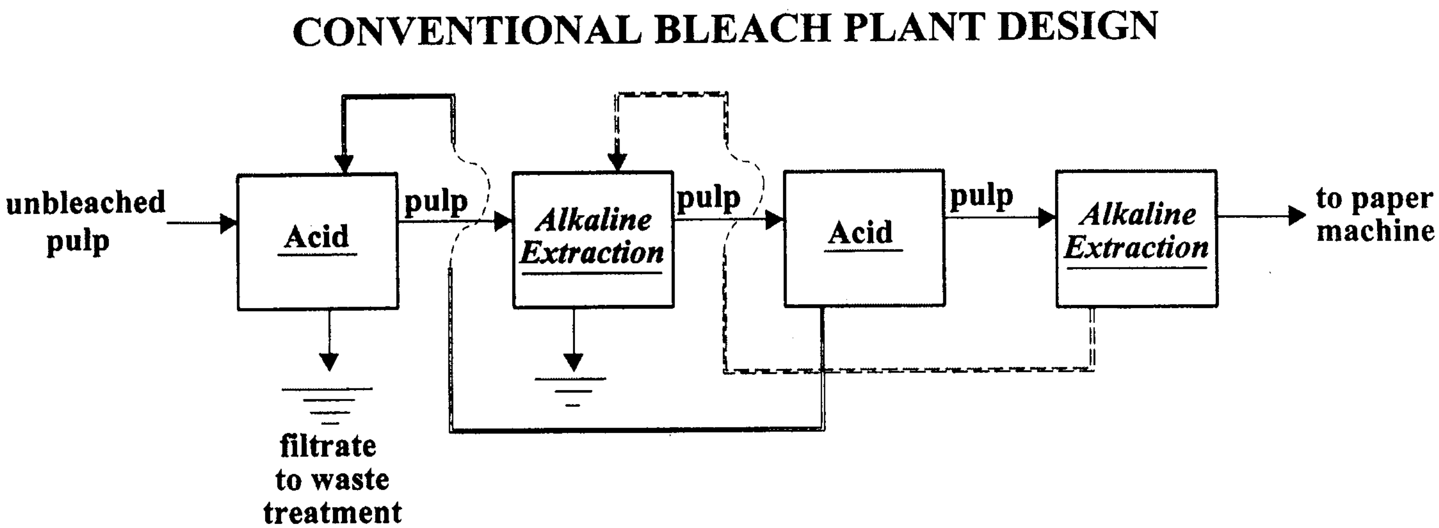

Fig. 2 Accumulation of calcium in a three-stage, laboratory simulation of water recycle in a bleach plant.

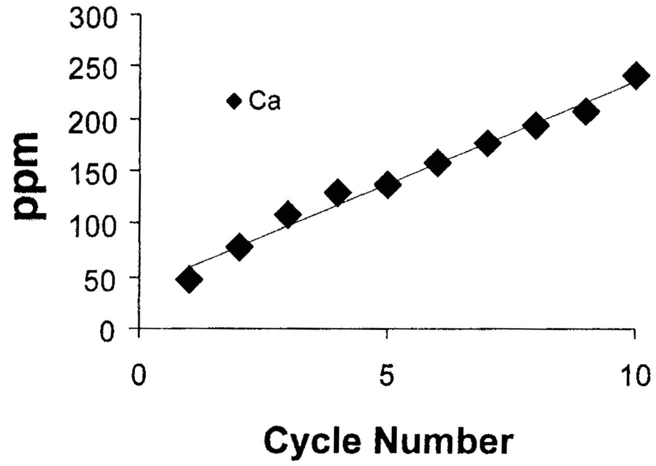

Fig. 3 EXAFS chi plot in k-space of calcium in pulp compared to calcite.