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Evaluation of Trace Barium in Wood Pulps

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Introduction: Barium is typically found in wood at about 20 ppm [1]. Although a very low level, a typical paper mill handles 2000-4000 tons of wood each day, an input of about 60 kg of barium daily. In many mills, this accumulates in the process resulting in barium sulfate mineral scale that interferes with the mill operation by clogging pipes, mixers and other process instruments and equipment [1,2]. The barium in the wood probably precipitates in the lumens of the wood fibers during the pulping process, either as barium carbonate, or barium sulfate. Chemical equilibrium models suggest the precipitate should be as barium carbonate after the pulping process. This is the pulp entering the bleach plant where barite scale problems are most serious. The difference between barium sulfate and barium carbonate is critical to improving the operation of the mill. Barium sulfate is largely insoluble until the pH drops below 3, whereas barium carbonate begins to dissolve at a pH around 6. The barium must first dissolve somewhere in the bleach plant in order to reprecipitate as mineral scale. Mills currently operate the initial stage of the bleach plant at a pH between 2 and 4, largely to optimize the efficiency of the bleaching chemicals. But if the Barium is present as the sulfate, it should be possible to run the first bleach stage at the higher pH and minimize the amount of barium that dissolves in this stage [2]. As carbonate, the mill would be better off to run at the lower pH, driving all the barium into solution, and optimize the amount of filtrate discharged to the wastewater treatment plant to control the barium concentration. Knowing whether the barium in the unbleached pulp is present as sulfate or carbonate can help mills make proper decisions on how to address this type of scale problem.

Methods and Materials: Several samples of commercial unbleached pulps have been prepared into sheets and pressed into 1 cm pellets. EXAFS spectra have been recorded on these samples using the L(III) edge with scans carried out from -100 eV below, to 400 eV above the barium edge (5147 eV to 5647 eV).

Results: Because of:

1. the low natural concentration of barium in wood (20 – 60 mg/kg)
2. the compressed scan region (5247-5624 eV) between the L(III) and L(II) edge
3. a relatively small difference between the EXAFS spectra of BaCO₃ and BaSO₄,

Many scans are required to obtain sufficient signal to noise for a definitive result. A final group of scans is currently being collected and should allow a determination of whether the barium is in the form of the carbonate or sulfate.

Conclusions: EXAFS spectra have been collected for the barium in unbleached wood pulp and for barium sulfate and barium carbonate reference standards. At this point, the signal to noise ratio of the wood pulp samples is not sufficient to distinguish between the two mineral forms and additional spectra are being collected in an effort to make a definitive determination.

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References:

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