Online monitoring of inorganic cooking chemicals in white liquor by pulse voltammetry

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ABSTRACT: White liquor parameters in the recovery area of a kraft pulp mill were monitored for a 1-year period using rhodium as an electrode material in a sensor system based on pulse voltammetry. Shift personnel performed offline titration analysis of the liquor every 4 hours. The results for effective alkali, sulfidity, and total titratable alkali were used to train and validate the sensor for online monitoring. Partial least square regression models developed from 150 reference titration results for each parameter from the first month of the study predicted concentrations for the following 11 months. Validation of the models using titration results indicated that overall relative root mean squared errors for prediction of the parameters were 3.7% for effective alkali, 3.4% for sulfidity, and 5.1% for total titratable alkali. Process stops that exposed the sensor to temperature excursions or acid washings resulted in temporary periods of poor prediction.

Application: A nonspecific sensor based on multivariate techniques has the potential to predict cooking chemical concentration parameters on the time scale of minutes.

Chemical pulp is predominately produced by the kraft process, and environmental and economic demands necessitate that the chemicals in the liquor be recycled. The optimum weight ratio of wood chips to concentrations of the chemicals requires continuous analysis of the recycled liquor. The offline ABC titration method [1] is the most widely used analysis method. Titration of the liquor with strong acid results in three inflection points in titration curves. Calculations based on these values yield a number of important processing parameters such as effective alkali (expressed as g/L sodium hydroxide [NaOH] or sodium oxide [Na_2O]), sulfidity (percentage ratio of sodium sulphide (Na_2S) to active alkali), and total titratable alkali (sum of all bases titratable by strong acid).

Online monitoring of the liquor composition enhances the capability for process control. The commercial online robotic titrator has the ability to continuously sample the process stream at a number of locations and perform analyses on the time scale of minutes [2]. Several nontitration-based systems have also been developed for rapid kraft liquor analysis. These include conductivity [3–6], UV-VIS [7], and UV-ATR [8–10], near infrared (NIR) [11–13], and multisensor approaches [14, 15]. In the latter, the researchers used a combination of conductivity, ion chromatography, refractive index, and ultraviolet (UV) absorbance to determine nonspecific properties that were used to predict concentrations of alkali, sulfide, solids, and lignin.

We previously described applications of a multielectrode sensor for voltammetric monitoring of wet-end [16] and effluent [17] process streams for pH, cationic demand, chemical oxygen demand, and turbidity, among other parameters. In this paper we report the use of a rhodium-based sensor for monitoring recovered white liquor prior to its introduction to the digester.

White liquor is a strong electrolyte having conductivity on the order of 35 S/m. Alkali concentration is directly related to conductivity [3–6]. Sulfur is an element that can have several oxidation states; thus, the sulfur compounds present in white liquor can be electrochemically oxidized and reduced. Processes developed to produce polysulfides in white liquor by electrochemical oxidation use this property of sulfur compounds to increase pulp yield [18, 19]. The pulse voltammetry technique makes it possible to register both conductivity-related charging/discharging currents of ionized species and the reduction-oxidation reaction (redox) currents at longer times resulting from oxidizable compounds present in the liquor. Although the sensor was not sensitive to specific compounds, information contained in the measured currents could be incorporated in models using multivariate methods to predict the effective alkali, sulfidity, and total titratable alkali parameters.

EXPERIMENTAL

On the basis of information from preliminary experiments, we constructed a corrosion-resistant probe with two 1-mm-diam rhodium electrodes embedded in a housing of the thermoplastic polyetheretherketone (PEEK). Electrical contact to the external cables was via copper rods pressed against the electrodes. A tank located in the recovery area of a pulping facility served as measurement site; the PEEK housing was fastened in a flange that put the electrodes in contact with a slipstream flow of white liquor. A proprietary potentiostat generated voltage sequences for the measurements. The wall of the measure-

ment tank served as auxiliary electrode and the potentiostat was galvanically isolated from ground and the PC used for data storage. Because the corrosive environment ruled out the use of a standard reference electrode, there was uncertainty about the exact potentials of the working electrodes. However, this was not a significant problem with respect to generating current patterns for multivariate analysis. The area of the auxiliary electrode was large and thus did not limit the currents flowing at any of the applied potentials. In addition, the conductivity of the liquor was sufficiently high to make it a suitable electrolyte for a two-electrode cell configuration [20].

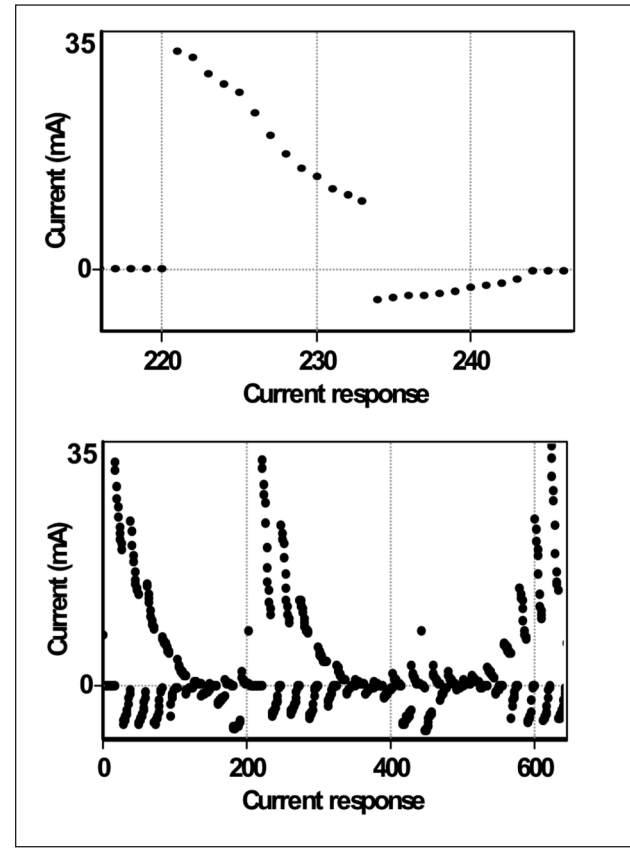
The potentials chosen covered a range of liquor properties. Two of the voltage sequences started at +1.2 V and decreased at 0.2-V intervals to -0.6 V with 0.0 V applied between each interval. These sequences had interval times (duration of each applied potential) of 25 and 250 ms, respectively. The third voltage sequence started at –0.6 V and increased at 0.2-V intervals to +1.2 V (again with 0.0 V applied between intervals), with an interval time of 125 ms for each applied voltage. Clean electrode surfaces are important for reliable measurements, so we used a cleaning step before each voltage sequence consisting of 1 s at +1 V, 1 s at -1 V, and 3 s at 0 V. Each measurement recorded a total of 640 currents from each electrode and took about 90 s. Measurements were continuous, but data were only stored at 5-min intervals. A Pt100 element recorded the white liquor temperature, which was normally 95°C –97°C.

The shift personnel collected white liquor samples at 4-h intervals from a location near the probe. A Mettler DL53 automatic titrator (Mettler-Toledo International Inc., Columbus, OH) performed the titrations using 1.0 N hydrogen chloride (HCl) to obtain the ABC values used to calculate the reference parameters (SCAN-test Method SCAN-N 30:85, "Total, active, and effective alkalai").

Sensor data evaluation was accomplished using DXE software from Proxedra (Linköping, Sweden) [21]. From 150 measurements obtained during the second month of operation, we developed partial least square models for effective alkali, sulfidity, and total titratable alkali. The procedure was to place sensor currents recorded at the titration sampling times in an X-matrix with 150 rows and up to 2 x 640 columns [22]. The liquor reference parameters filled a corresponding Y-matrix. After principal component analyses on both matrices, a linear regression for each principal component between the scores for the matrices yielded models that could be used to predict the individual parameters. To validate the models, we used the results of titration analysis that continued at 4-h intervals for 11 additional months.

RESULTS AND DISCUSSION

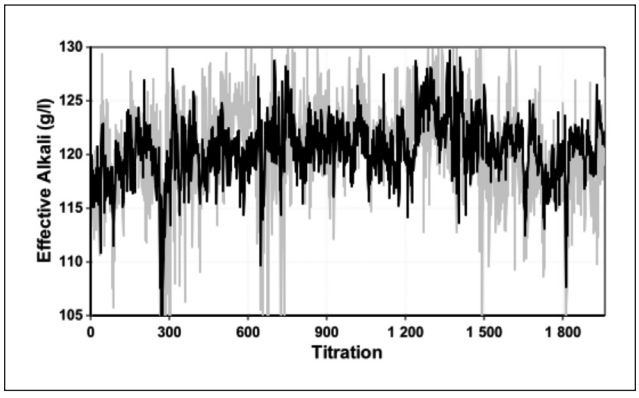
The voltage sequences generated a current pattern for each electrode. **Figure 1** shows charging/discharging currents and a complete pattern recorded during one measurement. Individual currents (for example, response 221 in Fig. 1) were stable in a narrow range during the study, indicating that the rhodium electrodes maintained an electrochemically stable surface in the white liquor process stream. A platinum electrode in an earlier probe slowly dissolved in the liquor, losing about 0.5 mm in depth during a 6-month period.



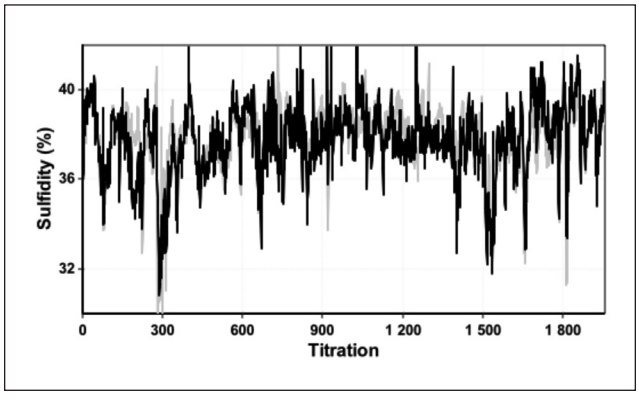
1. (Upper) measured current at +1.2 V (responses 221–233) and 0.0 V (234–246), and (lower) complete current pattern from the three voltage sequences having interval times of 25 ms (responses 1–210), 250 ms (211–420), and 125 ms (421–640), applied to one electrode. X-axes were not scaled after time.

We developed models to predict white liquor parameters using the DXE software. It was necessary to vary the currents used, their scaling, and the number of principal components to obtain the best prediction for each parameter, defined as the lowest overall relative root mean squared error (RMSE) for model validation. The best prediction models were different for each electrode and for the combination of both electrodes. Although the two electrodes were nominally identical, they did not yield exactly the same measured currents and did not identically predict the white liquor parameters. For clarity, we describe only the models using one electrode.

The model for the effective alkali parameter contained currents from only the 125-ms voltage sequence with no scaling and five principal components. **Figure 2** shows the prediction resulting from this model. Prediction was good over the entire period, with significantly low prediction for titration 400–600 and high prediction after 1800. The overall relative RMSE for model validation after titration 150 was 3.7%. For sulfidity, the model included currents from all the voltage sequences, variance scaling, and five principal components. **Figure 3** shows that prediction was excellent except for short intervals at titrations 200, 600, 1300, and 1700. Overall, relative RMSE was 3.4%. The model for total titratable alkali



2. Effective alkali values from ABC titrations (gray curve) and predicted values from the model described in the text (black curve) during the 1-year period of the study. Values from titrations 1–150 were used for training the model.



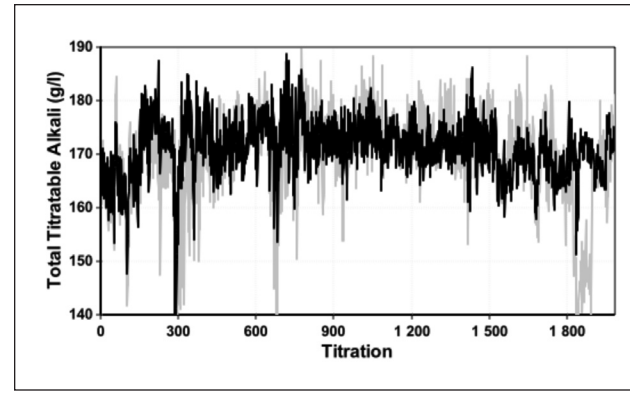
3. Sulfidity values from ABC titration (gray curve) and predicted values from the model described in the text (black curve) during the 1-year period of the study. Titrations 1–150 were used for training the model.

contained currents from all the voltage sequences, normalization scaling, and three principal components. **Figure 4** shows there were a few minor misses in prediction at titrations 200 and 1200 and a substantial deviation after 1800. The overall relative RMSE for validation was 5.1%.

As shown in Figs. 2–4, the prediction capability of models generated from 1 month of reference titrations was reliable over a 1-year period. However, in order to be able to better quantitatively evaluate the technique, we determined relative RMSE for model validation relative to the titration results over shorter time periods. **Table I** shows the relative RMSE for each parameter during 1-week intervals for the final 5 weeks of the study (starting at about titration 1760). As shown in the table, the effective alkali and sulfidity predictions scored the lowest relative RMSE and the total titratable alkali prediction was considerably off during weeks 2 and 3. **Figure 5** shows the correlation between the model prediction and the titration results for sulfidity during week 1 where the relative RMSE for the week was 3%.

Week	Effective Alkali	Sulfidity	Total Titratable Alkali
1	2	3	3
2	4	5	18
3	3	3	17
4	3	2	7
5	5	3	4

I . Weekly relative RMSE (%) for the final weeks of the study.



4. Total titratable alkali values from ABC titration (gray curve) and predicted values from the model described in the text (black curve) during the 1-year period of the study. Titrations 1–150 were used for training the model.

5. Sulfidity values from ABC titration (gray curve) and predicted values from the model described in the text (black curve) during week 1. Titrations 1–150 from the first month were used for training the model and 151–191 are shown to validate the model for week 1 (defined in Table I).

Models for prediction are no better than the reference values that they are built upon. Validation of models by comparison of predicted values with results obtained by the reference method is also dependent on the accuracy of the reference values. The titration method used to obtain the reference data has a number of possible error sources. One possible error source was operator related because a number of different individuals collected the samples and introduced them into the titration vessel by pipette. There was thus a risk for variation in volume delivered on the basis of time after sample collection because of temperature variations. To minimize operator-related error, shift supervisors made quality control evaluations during the course of the study to ensure standardization of procedures among the different shift personnel.

There is an additional possible error source for the SCAN titration method because inflection points in the generated

pH curve can vary with deadload concentrations of sulfite, thiosulfate, and polysulfides. These ions are all electrochemically active in alkaline media [18, 19, 23, 24] and will thus influence the sensor signal. Evaluating the magnitude of this error source would require analysis of the liquor using additional techniques specific for the deadload species, such as capillary ion electrophoresis [25, 26] and gas chromatography [27]. This information could be incorporated into models to determine how deadload species affect model predictions.

The periods of obvious discrepancies between the predicted and titration values shown in Figs. 2–4 were critical for evaluating the utility of the sensor for monitoring white liquor parameters. The most significant periods were around titration 500 for effective alkali (Fig. 2) and 1900 for total titratable alkali (Fig. 4). One difficulty was that the pulping process did not operate continuously without incident; temperature fluctuations, process stops, and acid washings of the lines occurred. While the overall stability of the electrode was good, we would have preferred a stable, continuous white liquor flow at constant temperature throughout the study.

Deviations in process conditions affected parameter predictions to different degrees. The period following titration 280 was during the process restart after the mill's annual stop for maintenance. Despite the interruption in the sensor's operation during the stop, the predictions of effective alkali and sulfidity were quite good during the restart period. A sudden decrease in measured late interval (redox) currents was observed for the voltage sequence having 250-ms intervals at about titration 1300. This coincided with the sulfidity prediction miss seen in Fig. 3. This correlation was probably due to the fact that sulfur compounds contributed to redox currents, but it was not clear how the temporary high- sulfidity predictions observed were related to the sharp current decreases.

Toward the end of the study there was a temporary temperature drop in the white liquor to 80°C at about titration 1800. This may have had an effect on the predictions that followed, most notably for total titratable alkali (Fig. 4). Clearly, an important consideration for sensor operation is employment of a measurement chamber having automatic isolation capability in the event of process interruptions and auxiliary heating to avoid precipitation of liquor components.

The prediction capability of the sensor is based on titration results, so it can only have the potential to partially replace the titration procedure. Once in operation, it would permit white liquor parameters to be determined on the time scale of minutes without labor-intensive sample taking. The occasional titration analyses necessary to continuously confirm the sensor predictions could possibly be used to update the models to take account of any slow changes occurring in the white liquor process composition, such as the build-up of nonprocess elements [28].

SUMMARY AND CONCLUSIONS

The widely used offline ABC titration analysis method for active pulping chemicals is labor intensive and cannot be used for process control because of the time involved. Commercial at-line robotic titrators are faster but require considerable maintenance. Online electrochemical sensors are an attractive alternative to titration, and commercial conductivity probes are available to monitor charged species in the liquor. Since pulse voltammetry is a technique which can collect data about both charged and redox active compounds, we investigated if such non-specific information, coupled with multivariate analysis methods, could be used to monitor concentrations of hydroxide and sulfide components in white liquor.

Rhodium is well known for its corrosion resistance and eventually proved to have the best stability in the liquor. Our machinist devised a simple construction method to insert electrodes with reliable electrical contacts in the PEEK probe housing. Since it was unknown how many reference titration values were required to train the sensor, we started the study in a mill equipped with an at-line robotic titrator. Results there indicated that as few as 100 training values were sufficient and we moved operations to a mill where shift personnel take manual samples. One month training time yielded 11 months of parameter predictions.

Halfway through the study, we discovered that the sensor was not always isolated from the system during process stops. This fact explained several of the prediction misses observed and made clear that, for stability, an automatic isolation system is important to maintain the sensor in the preferred warm white liquor environment.

We continued development of the sensor by monitoring green liquor parameters during a short trial. In addition, Senset AB tested a system in the recovery area control room for real time evaluation of the data, providing white liquor concentration parameters at about 2- min intervals.

In our study, rhodium exhibited stable electrode properties during use for voltammetric measurements on white liquor in a kraft pulp mill. Predicted values of the liquor parameters effective alkali, sulfidity, and total titratable alkali by partial least squares models agreed well with results from titration during an 11- month validation period. Sensor performance was best during periods of continuous process operation. Process interruptions were sometimes followed by periods of poor prediction performance, but these were normally corrected by continued exposure to the flowing white liquor. **TJ**

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LITERATURE CITED

1. MacDonald, R.G., (Ed.) *Pulp and Paper Manufacture*, 2nd edn., vol. 1, McGraw-Hill, New York, 1969, p. 563.
2. Laitinen, M., Kemppainen, A., and Rinne, R., *ABTCP-TAPPI 2000 Pulp and Paper International Congress Proceedings*, TAPPI PRESS, Atlanta, p. 1.

3. Bertelsen, P.M. and Svensson, J.-O., *Tappi J.* 69(8): 72(1986).
4. Paulonis, M.A. and Krishnagopalan, A., *Tappi J.* 73(6): 205(1990).
5. Courchene, C.E., Suh, S., and McDonough, T.J., *Tappi J.* 77(7): 101(1994).
6. Petersen, D.E., *TAPPI J.* 81(3): 147(1998).
7. Romppainen, P., Savolainen, M., Keski-Ruismäki, K., et al., *Process Control Qual.* 11(4): 255(1999).
8. Chai, X.S., Li, J., and Zhu, J.Y., *J. Pulp Pap. Sci.* 28(4): 110(2002).
9. Chai, X.S., Zhu, J.Y., Luo, Q., et al., *J. Pulp Pap. Sci.* 29(6): 204(2003).
10. Chai, X.S., Hou, Q., Zhu, J.Y., et al., *Ind. Eng. Chem. Res.* 42(2): 254(2003).
11. Hodges, R.E. and Krishnagopalan, G.A., *TAPPI J.* 82(9): 101(1999).
12. Kester, M., Trung, T., Leclerc, D., et al., *J. Pulp Pap. Sci.* 30(5): 121(2004).
13. Hodges, R., Cullinan, H., and Krishnagopalan, G.A., *TAPPI J.* 5(11): 3(2006).
14. Paulonis, M. A. and Krishnagopalan, G.A., *J. Pulp Pap. Sci.* 20(10): J296(1994).
15. Vanchinathan, S. and Krishnagopalan, G.A., *TAPPI J.* 78(3): 127(1995).
16. Carlsson, A., Krantz-Rülcker, C., and Winquist, F., *Nord. Pulp Pap. Res. J.* 16(4): 319(2001).
17. Gutés, A., Cespedes, F., del Valle, M., et al., *Sens. Actuators, B* 115: 390(2006).
18. Behm, M. and Simonsson, D., *J. Appl. Electrochem.* 27(5): 519(1997).
19. Miller, B. and Chen, A.C., *Electrochim. Acta* 50(11): 2203(2005).
20. Bard, A.J. and Zoski, C.G., *Anal. Chem.* 72(9): 346A(2000).
21. Proxedra, Universitetsvägen 14, SE-583 30, Linköping, Sweden.
22. Esbensen, K.H., *Multivariate Data Analysis in Practice*, Camo Process AS, Oslo, 2001.
23. Loućka, T., *Collect. Czech. Chem. Commun.* 65 (1): 1(2000).
24. Westbroek, P., De Strycker, J., Van Uytfanghe, K., et al., *J. Electroanal. Chem.* 516(1–2): 83(2001).
25. Salomon, D.R. and Romano, J., *J. Chromatogr., A* 602(1–2): 219(1992).
26. Jones, C.Y., Chen, G., Dai, S., et al., *Ind. Eng. Chem. Res.* 42(18): 4228(2003).
27. Borchardt, L.G. and Easty, D.B., *J. Chromatogr., A* 299(C): 471(1984).
28. Wannenmacher, N., Kimura, S., and Frederick, W.J., *Ind. Eng. Chem. Res.* 44(24): 9316(2005).

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White liquor recovery was identified as an area of research for sensor development. Electrochemical sensors based on conductivity have been employed for monitoring cooking chemicals. The pulse voltammetry technique extends that type of sensor by including the redox properties of the liquor in addition to the ionic charges of the chemicals present.

We had no control over the process stream past the sensor when process stops and maintenance occurred, which was the biggest challenge to our research. Exposure to cooling liquor and acid washing caused temporary prediction errors. In addition, automatic isolation was unfeasible and mill personnel had difficulty remembering to close isolation valves when events occurred.

As a result of our work, we discovered that platinum and even alloys with well-known corrosion resistance such as Pt90Ir10 (international kilogram standard) are relatively quickly dissolved in white liquor at 97°C. Rhodium proved to be a very stable electrode material.

If properly installed and maintained, this sensor could deliver cooking chemical parameters on a time scale of minutes. Because it is a non-specific sensor, it could possibly be adapted to follow product quality parameters such as kappa number directly.

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