AMETEK®
PROCESS INSTRUMENTS

APPLICATION NOTE

ONLINE MONITORING OF RESIDUAL CHLORINE DIOXIDE

Using an online analyzer that continuously monitors chlorine dioxide residuals benefits paper-making operations.

An aspect of paper-making which is undergoing tremendous change is pulp bleaching. For chemical pulp bleaching there is a definite trend to either eliminate or significantly reduce chlorine use. Increasingly higher substitutions of chlorine dioxide (ClO_2) in the first bleaching stage are common. Because of this increased use of ClO_2, many mills are dioxide-limited.

Additional ClO_2 generating capacity requires capital expenditure. However, more efficient use of the current amount of ClO_2 produced could allow for a higher ClO_2 substitution ratio in the first stage without compromising final pulp brightness.

EQUIPMENT

With online residual ClO_2 analysis using the AMETEK IPS-4 photometric analyzer, it is possible to use the minimum amount of chlorine to achieve the target residual level. It is no longer necessary to use more ClO_2 than required, to ensure that the target residual level is maintained. Lab testing for residual levels is no longer necessary, and the incidence of dips in ClO_2 residual level below the target value is removed.

When the concentrations of bleach chemicals are known, and the minimum amounts are used, there are a number of benefits achieved: reduced environmental impact, reduced effluent load, and lastly, the production of pulp of higher and more consistent quality. Continuous, on-line residual analysis with the IPS-4 provides a means to use ClO_2 most efficiently and to increase the uniformity and overall brightness level of pulp.

IPS-4 ANALYZER

CONTROLLING CHEMICAL DOSAGE DURING BLEACHING

In the interest of pulp quality and bleaching economics, it is important to control the chemical dosage in all bleaching stages. The control strategy for each stage is comprised of both long- and short-term strategies due to the long retention times in the bleaching towers. For the dioxide stages, the long-term strategy has generally been to reach a 75 to 80 brightness in the D1 stage and a brightness above 90 for the D2 stage. Short-term control is then achieved through measurement of the ClO_2 residual in the pre-tower filtrate. Residual targets for the D1 stage, for example, are then updated to reflect the long-term trends in the D1 stage brightness and E1 K number.

Residual control is important for both the D1 and D2 stages. A residual must be maintained throughout the stage to prevent brightness reversion of the pulp caused by the (50 to 70°C) temperature in the tower. In addition, finite residual levels promote pulp cleanliness by improving the bleaching of shives. If the final product is market kraft pulp, for example, cleanliness is especially important for production of the highest quality grades. By maintaining the residual level throughout the stage, to eliminate brightness reversion, and to improve pulp cleanliness, a high-brightness pulp is achieved as a result.

Continuous monitoring of the residual level permits feedback control to compensate for variations in the ClO_2 demand. This eliminates the need to maintain excessively high residual levels to allow for this variability. Control of the ClO_2 bleaching stages based on a continuous residual measurement would, therefore, be of great value. Continuous analysis of the residual in closed-loop control to regulate the ClO_2 injection would permit significant savings in chemicals by allowing the stage to be run at the target residual level rather than above it.

ClO_2 exhibits a strong absorbance in the UV-visible spectrum, which suggests measurement of the residual via spectrophotometry. It is more strongly absorbing in this region than all other bleach plant oxidants. At the measuring wavelength selected for the IPS-4, the absorbance of ClO_2 is not affected by either chlorine or sodium chlorite which may be present.

Chlorite might be expected in the D1 stage if the pH rises above 4.0. Under these conditions, significant concentrations of chlorite can develop, since the ClO_2 only partially reacts with the pulp while the chlorite formed is unreactive. Neither typical mill titrimetric methods nor polarographic sensors can differentiate chlorine dioxide and chlorite under the high-pH conditions. Even with a high ratio of chlorite to ClO_2 (1/1 molar ratio), the IPS-4 measures only the absorbance due to ClO_2.

In addition to providing an accurate measurement of ClO_2 at a high pH, the residual measurement should be insensitive to changes in pH. Variations in pH are common during pulp bleaching due to fluctuations in the washing efficiency of the extraction stage directly before it. The absorbance of ClO_2 is independent of pH, since it is a free radical. Measurement of the residual with the IPS-4 is thus independent of pH.

PHOTOMETRIC ANALYZER RESULTS

A model 4000 – the predecessor of the IPS-4 – was installed to monitor and control ClO_2 residual on a D2 stage. During that time the incidence of off-grade low-brightness pulp was reduced from 1.9 percent of the total production down to 0.4 percent. The D2 stage brightness levels increased and the monthly average standard deviations of the final pulp brightness levels decreased. Improved control of the D2 stage residual decreased the incidence of over-bleaching. Not only does over-bleaching waste ClO_2 but it also causes high washer and vat residuals which off-gas into the work environment. The analyzer has proved reliable and has contributed to significant savings. The mill has subsequently installed two more analyzers to control residuals, one on a D1 stage and another on a D2 stage.

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