Background
Bleaching is a whitening process that is used in the paper industry to produce paper with high brightness. Chemicals—such as chlorine gas (C), sodium hypochlorite (H), oxygen (O), hydrogen peroxide (X), ozone (Z), and chlorine dioxide (D)—are used in various combinations to produce pulp with the desired properties. Recent limitations on the use of chlorine (and hypochlorite) have resulted in more extensive use of chlorine dioxide as an alternate bleaching chemical. Chlorine dioxide bleaching is referred to as Elemental Chlorine Free (ECF) and is the process used in over 50% of U.S. mills.

The Process
The chlorine dioxide is mixed with the pulp and contacted in each D (chlorine dioxide) tower (see Figure 1) for about 1 hour per stage. The primary purpose of bleaching is to maximize removal of the lignin binding agents in the pulp without degradation of carbohydrates, which weakens the final product (paper). The pH is maintained at relatively low levels (around 4) to foster rapid chemical reaction. Higher pH levels require more chlorine dioxide for equivalent bleaching action.

Following bleaching in each D tower, the reacted lignin is removed by dissolving the lignin under high pH conditions (typically over 11). Lower pH levels will not dissolve all of the lignin. This caustic extraction (E) stage is preceded by a washing step to reclaim the chlorine dioxide and to minimize carryover of the acidic chemicals. The amount of caustic needed is proportional to the amount of bleach added in the D stage.

Bleach plant sequences vary widely from mill to mill; however, the D-E-D-E stage sequence is quite common. At least 2 bleaching stages are generally required to produce the specified brightness, with additional stages for more specialized uses. Consistency (% solids) is typically maintained at a high level (up to 10%) to minimize water use. Temperature is controlled around 140°F (60°C), and doses of 5% chlorine dioxide are common.

The Measurements
pH is measured in the D tower to control the bleaching reaction conditions. pH is also measured in the E stages to control addition of the caustic used for extraction. ORP can be used in the washer between the D and E stages to verify that rinsing of the chlorine dioxide has been completed. Attempts to use ORP to control chlorine dioxide dosage in the D tower have been mostly unsuccessful due to the nonlinear character of ORP. See Application Data Sheet #43-014 for more information on ORP.

The Products
pH measurements in the D and E stages have historically been among the most difficult applications in the pulp mill. The high pulp consistency of the process stream and harsh bleaching chemicals degrade the performance of most general purpose sensors. Those sensors tend to require cleaning regularly and frequently, and they may not be able to withstand the strongly oxidizing environment.

The TUpH Model 398R pH and ORP sensors are well-suited for this kind of application. The wide-area junction provides resistance to coating, while the patented helical pathway prevents process intrusion into the inner reference chamber. Construction materials of Tefzel and Kalrez are used to withstand the strongly oxidizing environment.

The Models 54e pH/ORP and 5081 pH/ORP are ideal instruments for monitoring and controlling pH and ORP in pulp and paper mills. All configuration and calibration can be conducted remotely using the HART protocol and the AMS PC interface. The combination of the Model 398R with either the AC-powered Model 54e or the DC-powered Model 5081 provides ease of installation, ease of operation, and the lowest maintenance possible.
INSTRUMENTATION

TU\textsc{p}H MODEL 398R RETRACTABLE pH/ORP SENSOR

• Titanium and Tefzel construction with choice of Kalrez or Viton seals allows sensor to be tailored to individual process needs.
• Stands up to chlorine dioxide in pulp bleaching towers.
• Retractable design allows sensor to be removed for calibration and maintenance without process shutdown.
• Patented TU\textsc{p}H reference technology ensures long life in processes that coat.

Model 5081 pH/ORP Smart Transmitter

• Handheld infrared remote control link activates all the transmitter functions.
• NEMA 4X (IP65) weatherproof, corrosion-resistant enclosure.
• Comprehensive pH glass and reference diagnostics.
• HART and AMS compatible.
• FOUNDATION Fieldbus optional

MODEL 54e pH/ORP SMART® ANALYZER

• Comprehensive pH glass diagnostics to warn user of the need for calibration, maintenance or sensor replacement.
• Heavy duty NEMA 4X (IP65) enclosure of epoxy-painted aluminum.
• Fully descriptive diagnostic messages and easy-to-use interface for operation in English, French, German, Italian, or Spanish.
• Automatic calibration with buffer recognition and stabilization check.
• Two independent outputs for primary variable and temperature.
• Three alarms with programmable logic plus one dedicated fault alarm.

FIGURE 1. Bleaching the Pulp Stock