OXIDIZED WHITE LIQUOR USE IN EOP STAGE*

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APPLICATION AND BENEFITS IN PULP BLEACHING

HYDROGEN PEROXIDE BLEACHING TECHNOLOGY WAS initially developed for the production of totally chlorine free (TCF) pulps. Even a few years ago, advances in hydrogen peroxide bleaching technology were most often dependent on the development of TCF technology. The improved efficiency and performance of these technologies, however, are applicable to modern elemental chlorine free (ECF) sequences, as well.

Probably the most important goal of the use of oxygen-based chemicals, such as oxygen and hydrogen peroxide, is to close the bleach plant and recycle the filtrates. Alkaline effluents, for example, from the oxygen delignification or hydrogen peroxide stages can be recovered. In an ECF bleaching sequence, however, the most beneficial effect of using oxygen-based chemicals is a corresponding decrease in chlorinated organic byproducts in effluents. As a result of today's increased environmental awareness, oxygen delignification has become standard in a modern kraft mill.

The majority of mills practicing oxygen delignification use oxidized white liquor (OWL) as the source of alkali due to the need to maintain the chemical balance of the mill. When OWL is used in other bleaching stages, such as an EOP stage, where it may not be returned to the recovery cycle, it offers an opportunity for purging sulfur or non-process elements that build up in the system. In addition to that, OWL usually can be made available at significantly lower cost than purchased sodium hydroxide. According to previous studies, OWL had a significant (*1*) positive effect on selectivity in oxygen delignification when compared to sodium hydroxide. Unoxidized white liquor (WL) also can be used as alkali in the oxygen system, but there is a significant adverse effect on selectivity due to the presence of sulfide ions. The use of OWL in other oxygen-based chemical stages, such as an EOP stage, is not a standard practice because of the unfavorable composition of OWL for hydrogen peroxide. Some impurities in the OWL, such as transition metal ions, decompose hydrogen peroxide. Besides, if OWL is not fully oxidized, part of the hydrogen peroxide will be consumed to the further oxidation of OWL instead of delignification and bleaching of pulp. Therefore, in the bleaching stages that involve the use of hydrogen peroxide, fresh sodium hydroxide normally is used as alkali.

As WL is oxidized, it is important to consider the reaction products. The basic components of WL are sodium hydroxide and sodium sulfide. While laboratory liquors are prepared with relatively pure caustic and sulfide, mill WL contains significant amounts of other inorganic ions, such as carbonate, sulfate, and thiosulfate. Often WL also contains significant amounts of impurities and non-process elements that likely originate in the wood, such as calcium, magnesium, potassium, silicate, and iron. Part of the calcium also results from carryover from the causticizing plant. When WL is used as an alkali for oxygen delignification, sulfide is oxidized in a complex process where several intermediates can be detected. The most important of these intermediates are polysulfides, sulfate and thiosulfate. If WL is oxidized completely, thiosulfate and polysulfides also eventually will be oxidized to sulfate. In addition to these sulfur ions, OWL contains significant amounts of carbonate.

Because thiosulfate reacts with hydrogen peroxide, it would be more beneficial to use fully oxidized white liquor (FOWL) in any bleaching stage where it may come in contact with hydrogen peroxide. According to previ-

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Alkali type	$\Delta\eta/\Delta\kappa$, mL/g (1% H_2O_2 in EOP)	$\Delta\eta/\Delta\kappa$, mL/g (2% H_2O_2 in EOP)
NaOH	23.8	24.5
NaOH+Mg^{2+}	19.1	18.7
OWL	22.0	21.7
NaOH+$Na_2S_2O_3$	25.4	24.9
NaOH+Na_2SO_4	25.6	26.5
NaOH+Na_2CO_3	21.8	21.5

I. The effect of alkali type on selectivity in a two-stage oxygen delignification (O-EOP) measured as overall specific viscosity drop, Δviscosity/Δkappa number, mL/g (3)

ous studies (*2*), FOWL appeared to be the preferred alkali over NaOH or OWL due to the resulting higher brightness and viscosity. According to another study (*3*), OWL or sodium hydroxide solution containing sodium carbonate had a slight positive effect on the selectivity when compared to pure NaOH (**Table I**).

As with all hydrogen peroxide bleaching, an optimal metal profile in the pulp is essential to obtain a good bleaching result. Hydrogen peroxide decomposition is catalyzed by transition metals normally present in the pulp as well as bleaching solution. Therefore, if the mill uses FOWL as alkali in the EOP stage, the contents of the impurities and non-process elements in both pulp and FOWL also must be monitored.

It apparently is possible to extend the delignification in the EOP stage by the use of FOWL without an excessive loss in viscosity, and, therefore, the EOP stage has immense commercial implications in terms of good pulp quality, improved economics, and decreased environmental load. TJ

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