CellGuard® OP Magnesium Hydroxide Slurry as a Replacement for Magnesium Sulfate and Caustic Soda in Chemical Pulp Bleaching

CellGuard® OP Magnesium Hydroxide Slurry is a high purity, aqueous suspension that functions as an alkali and cellulose protector in chemical pulp bleaching. Since CellGuard OP contains both hydroxyl ions (OH\(^-\)) and magnesium ions (Mg\(^{2+}\)), replacement of magnesium sulfate (MgSO\(_4\)) and partial substitution of caustic soda (NaOH) in chemical pulp bleaching stages are feasible.

Although magnesium hydroxide has a relatively low solubility in water, under dynamic conditions such as those found in chemical pulp bleaching, magnesium hydroxide is readily available. In the presence of hydrogen peroxide, magnesium hydroxide dissociation is facilitated by the activation of peroxide. As the reaction for peroxide activation consumes hydroxyl ions, the dissociation of magnesium hydroxide shifts continuously to the right making both magnesium ions and hydroxyl ions available for cellulose protection and alkalinity requirements (see reactions below).

\[
\text{Mg(OH)}_2 \leftrightarrow \text{Mg}^{2+} + 2 \text{OH}^- \quad (\text{Magnesium Hydroxide Dissociation})
\]

The above reaction shifts to the right due to peroxide activation.

\[
2 \text{OH}^- + 2 \text{HOOH} \leftrightarrow 2 \text{H}_2\text{O} + 2 \text{OOH}^- \quad (\text{Peroxide Activation})
\]

CellGuard OP Magnesium Hydroxide Slurry has been proven in laboratory studies and mill trials to be cost effective in replacing magnesium sulfate and in reducing caustic soda in chemical pulp bleaching. As shown in the following examples, CellGuard OP can be used in the Eop stage to reduce overall bleach costs while maintaining or improving pulp properties.

**Case Study #1**

A laboratory study was conducted on Kraft softwood pulp that is typically bleached to 88%-89% ISO in a sequence containing an Eop stage. CellGuardOP was evaluated at an equivalent weight basis to MgSO\(_4\) and at 25% substitution for NaOH on a hydroxyl molar basis. Base case conditions for the Eop stage employed 0.1% MgSO\(_4\) on pulp.

As shown in the graphs, when substituting CellGuard OP for MgSO\(_4\) on an equiweight basis (0.1% Mg(OH)\(_2\) on pulp) and reducing the NaOH charge by the amount of alkalinity contributed by CellGuard OP in the Eop stage, equivalent brightness and viscosity are achieved.
Similarly, when CellGuard OP is substituted at 25% molar basis for NaOH and MgSO₄ is eliminated, equivalent brightness and slightly higher viscosity values result.

Based on this lab study, the mill conducted a plant trial using CellGuard OP as a replacement for MgSO₄ in the Eop stage. CellGuard OP was added on a Mg²⁺ equivalent weight basis (0.048% Mg(OH)₂ on pulp) and the NaOH charge was reduced by the equivalent amount of hydroxyl ions contributed by CellGuard OP.

Once the bleach process achieved steady state, final pulp brightness and viscosity were measured. Substituting CellGuard OP for MgSO₄ and a portion of the NaOH charge yielded comparable pulp brightness and viscosity. The mill estimated a bleach cost reduction of at least 10% by eliminating MgSO₄ and using CellGuard OP Magnesium Hydroxide Slurry. The mill anticipates additional cost savings as caustic soda prices increase and the demand for an alternate alkali such as CellGuard OP is considered as a partial substitute for NaOH.

Case Study #2

A Kraft mill bleaches hardwood pulp to 85% ISO using a bleach sequence containing an Eop stage. The mill currently does not add MgSO₄ to the Eop stage as they found it to be cost prohibitive. However, a mill trial was conducted with CellGuard OP Magnesium Hydroxide Slurry as a cellulose protector. CellGuard OP was added to the Eop stage at a dosage rate of 0.25% - 0.35% on pulp to determine if final pulp brightness can be increased at a lower cost per ton of chemical compared to MgSO₄.

The results of the mill trial showed that final pulp brightness in the final D stage increased by 3.5 points from 85.1% ISO with no additive to 88.6% ISO with CellGuard OP demonstrating that solubilization of magnesium hydroxide provided sufficient magnesium ions for cellulose protection during the bleach process.

The significant increase in pulp brightness prompted the mill to evaluate other potential benefits of using CellGuard OP such as decreasing hydrogen peroxide and chlorine dioxide for significant cost savings. Additional savings are also anticipated when CellGuard OP is utilized as a partial substitute for NaOH as caustic prices increase.
**CellGuard® OP Benefits**

Compared to bleaching processes that do not utilize a cellulose protector or use magnesium sulfate, and employ caustic soda as an alkali, the CellGuard process provides the following benefits:

- **CellGuard OP Magnesium Hydroxide Slurry** serves a dual function by supplying both magnesium ions and hydroxyl ions to provide cellulose protection and to promote peroxide activation.
- Bleach costs are improved at equivalent pulp brightness and viscosity by eliminating or reducing the amount of magnesium sulfate and caustic soda required in an Eop or Ep bleaching stage. Since CellGuard OP is about one-third the cost of epsom salt (i.e. magnesium sulfate), typical bleach cost savings of over $100,000 annually can be achieved.
- Increased pulp brightness can result when using CellGuard OP in an Eop or Ep stage that previously did not employ a cellulose protector. As a result of higher brightness, the potential to achieve significant cost savings by decreasing hydrogen peroxide or chlorine dioxide exists.
- Pulp bleached by the CellGuard process has the same properties as pulp bleached by the conventional process.
- CellGuard OP Magnesium Hydroxide Slurry is safe to handle since it is non-hazardous and noncorrosive.
- The CellGuard process requires minimal capital changes to the conventional bleaching system.

Since bleaching conditions and quality goals are specific for each mill, Martin Marietta Magnesia Specialties can conduct laboratory tests using the mill’s pulp and process conditions to determine the optimum CellGuard formula while meeting the mill’s objectives.

Martin Marietta’s Application Group can design and supply handling and metering equipment for trials and permanent installations for CellGuard® OP Magnesium Hydroxide Slurry, CellGuard® 35 Magnesium Oxide Powder, and CellGuard® MH Magnesium Hydroxide Powder.

To learn how the CellGuard process can reduce bleach costs in your pulp mill, give us a call at (800) 648-7400 or (410) 780-5500, or e-mail us at: Magchem@martinmarietta.com.