A CONVERSION GUIDE FOR PULP MILLS

INTRODUCTION

Liquid caustic soda is the historical alkali of choice of the pulp and paper industry; however, during times of high prices or tight supply, this usage can be a problem for the mills. At times such as these the industry looks to soda ash as its source of sodium oxide.

Purchased soda ash can be used to supplement the soda ash generated in the recovery boiler, thereby reducing or eliminating caustic demand for white liquor makeup. As a rule of thumb, a pulp mill should start looking at an ash conversion when caustic pricing in the U.S. Gulf Coast reaches $150.00 per dry ton, FOB Gulf. History tells us that at this point the economics of a switch are worth the investigative effort. The purpose of this guide is to walk you through the economics of such a conversion as well as to introduce you to soda ash so that you may better understand its handling characteristics and how it may work in your application. The following pages will address the questions most often asked regarding a soda ash conversion. Also presented is a total per ton cost analysis for caustic replacement. We would be happy to work more closely with you to determine if soda ash is right for you at this time. Should you wish, we will work with you to design a reliable soda ash slurry system for use at your facility. Our sales department can be reached through our main number at 713-525-6800. Thanks for considering soda ash as well as Solvay Chemicals for your alkali needs.

FREQUENTLY ASKED QUESTIONS

Q: Is caustic conversion to soda ash applicable in all kraft pulp mills?
A: Yes. Any kraft pulp mill that has a recovery boiler for the regeneration of white liquor makeup is actually a producer of soda ash (about 78% of the recovery smelt is soda ash). So, the addition of soda ash solution to the green liquor system is not at all foreign to the process. The recovered sodium makeup from the recovery boiler is routinely causticized into caustic soda via the lime soda reaction.

Q: What costs must be considered in the switch from caustic soda to soda ash?
A: The costs of using soda ash in lieu of caustic soda are the purchase cost of the soda ash on an equivalent alkaline basis, limekiln fuel cost and the capital costs of installing a soda ash handling system.

Q: Is limekiln capacity going to be a limitation?
A: Potentially. The amount of lime recycled by the limekiln will need to increase between 3% and 10% and is determined by total alkalinity and percent makeup as sulfidity used in the cooking liquor.

Q: Are limestone purchase costs added to the cost of soda ash in replacing caustic soda?
A: No. The calcium carbonate is continuously recovered in the lime cycle and converted back to CaO (calcium oxide) in the limekiln. So, the issue really becomes greater kiln throughput. This increased throughput does add to the cost of using soda ash as it increases kiln fuel usage.

Q: How much lime is recycled for every ton of soda ash used?
A: It takes about 0.5 ton of lime (kiln output) combined with a ton of soda ash to produce approximately 0.8 tons of caustic soda.

Q: Assuming a mill purchases 10,000 tons per year of caustic and has a limekiln output of 260 tons per day of lime, how much soda ash and lime will be required to convert from caustic to soda ash and how much additional limekiln output will be needed?
A: Soda Ash Required: (to achieve equal alkalinity value) 10,000 tons of caustic soda X 1.32 = 13,200 tons of soda ash

Lime Required: (as kiln output, not purchased)
13,200 tons of ash X 0.53 (tons of lime/ton of ash) = 6,996 tons of lime
**Additional Kiln Output Required:**
6,996 tons of lime required / 360 days = 19.4 tons per day
(19.4 tpd / 260 tpd) X 100 = 7.5% (required % increase in kiln output)

**Q:** What will typical kiln fuel costs add to the cost of using soda ash?

**A:** Costs vary depending on the mill's choice of fuel, however a good average is $4.00 per MM BTU. Kiln efficiency is also a variable but averages 7.0-8.0 MM BTUs per ton of CaO. $4.00 per MM BTU X 8.0 MM BTU per ton of lime X 0.53 ton lime/ton of soda ash = $16.96 per ton of soda ash.

**Q:** Will soda ash require more labor and handling?

**A:** A simple, reliable system can be constructed to minimize operator attention. Constant monitoring of railcar unloading is not necessary if the system is properly designed. Unlike liquid caustic soda which begins to crystallize at 54° F (12° C) dry bulk soda ash flow is not disrupted by varied weather conditions. As an added plus, soda ash is not corrosive.

**Q:** What equipment is needed to use soda ash instead of caustic?

**A:** A system to convey soda ash to a storage silo or tank will be required. A heating system to keep a slurry warm (100° F) is also necessary. Once in solution the soda ash can be added directly to the green liquor clarifier.

**Q:** Will more storage capacity be needed?

**A:** A soda ash slurry system will allow the storage of approximately 250 dry tons of soda ash (30% solution) in a 158,000-gallon tank (30’ high x 30’ in diameter). A tank of the same size would hold approximately 500 dry tons of 50% liquid caustic soda.

**THE LIME SODA REACTION – NORMAL RECOVERY OPERATION**

A caustic soda conversion to soda ash in the kraft mill recovery cycle is predicated on the operation of the recovery boiler with excess capacity available in the limekiln and causticizing unit. In normal operation 78% of the recovery boiler smelt is soda ash. This smelt is solubilized in the green liquor-dissolving tank, clarified, and reacted with slaked lime to generate caustic. To increase caustic generation from the process, it is necessary to add soda ash to the green liquor at the dissolving tank or clarifier. As would be expected, soda ash increases the load on the limekiln and causticizing unit.

Theoretically for every 100 pounds of calcium carbonate that is put into the limekiln, 100 pounds remain available after the lime soda reaction. Detailed below is the lime soda reaction, which converts the soda ash from the recovery smelt back into white liquor in the recausticizing system.

**The Limekiln:**

<table>
<thead>
<tr>
<th>Molecular Weight</th>
<th>Reaction</th>
<th>heat</th>
<th>(from white liquor clarifier)</th>
<th>(to lime slaker)</th>
<th>(vent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCO₃</td>
<td>100.09</td>
<td>56.08</td>
<td>44.01</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**The Lime Slaker:**

<table>
<thead>
<tr>
<th>Molecular Weight</th>
<th>Reaction</th>
<th>(from kiln product)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>56.08</td>
<td>18.01</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Molecular Weight</th>
<th>Reaction</th>
<th>(from lime slaker)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂CO₃</td>
<td>105.99</td>
<td>74.09</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Molecular Weight</th>
<th>Reaction</th>
<th>(from white liquor)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2NaOH</td>
<td>100.09</td>
<td>40.00</td>
</tr>
</tbody>
</table>

The lime soda reaction can be summarized as follows:

\[ CaCO_3 + \text{lime slaker} \rightarrow CaO + CO_2 \]

\[ CaO + H_2O \rightarrow Ca(OH)_2 \]

\[ Na_2CO_3 + Ca(OH)_2 \rightarrow 2NaOH + CaCO_3 \]
ALKALINITY VALUES

Alkalinity (active sodium oxide) is expressed as a percent of the molecular weights of the alkali relative to sodium oxide. An alkalinity conversion factor of 1.32 tons of soda ash for each dry ton of caustic soda is established from this comparison of percent Na₂O.

Soda Ash:
61.98 (molecular weight Na₂O)  
105.99 (molecular weight Na₂CO₃)  = 58.5% Na₂O

Caustic Soda:
61.98 (molecular weight Na₂O)  
79.99 (molecular weight 2NaOH)  = 77.5% Na₂O

ECONOMICS OF CONVERSION

The economic issues in a conversion that need to be considered are listed below:
1. The delivered purchase cost of soda ash on an equivalent alkalinity basis
2. Limekiln fuel cost
3. Capital costs of installing a soda ash handling system

Use of the worksheets shown below will help facilitate your analysis:

Calculating Additional Limekiln Fuel Expense

Kiln Fuel Costs ($ per MM BTU)  
x Kiln Efficiency (MM BTU per ton of lime)  
x Conversion Factor (tons of lime per ton of ash) 0.53  
= Total Cost of Additional Limekiln Fuel (A)

Calculating a Direct Cost Comparison

Delivered Alkali Cost  
+Additional Limekiln Fuel Cost (A)  
Subtotal:  
x 1.32 (soda ash only)  
Direct Comparison  

Once the direct per-ton savings are determined, the mill should evaluate the capital costs of installing a soda ash handling system. Solvay Chemicals will be happy to work with your mill engineers to determine this capital cost.

SODA ASH HANDLING

Soda ash is a free-flowing white crystal that is normally transported in 100-ton covered hopper cars. To make the most effective use of product storage, soda ash should be stored as a slurry. A slurry storage system consists of a storage tank, a means for slurrying the bulk soda ash and transferring it to storage and a means to replenish the saturated solution by adding steam or water to the slurry bed.

Tanks and piping can be made from mild steel. Dilution water should be softened as a carbonate sludge can form requiring periodic tank cleanouts.
When a quantity of soda ash is mixed with water, part of the soda ash will dissolve to form a saturated solution. The part that is not dissolved will settle to the bottom of the tank as a fluid non-hardening slurry. The slurrying device must wet each particle of soda ash because the ash can lump and cake, impairing its conversion to monohydrate. Slurry volume should not occupy more than 85% of the storage tank volume.

The saturated solution must be kept above 97° F (36° C) to prevent the formation of hepta and decahydrates. We recommend that the slurry storage tank be insulated and equipped with heating coils to maintain an operating temperature between 115-130° F (46-54° C).

Heat is evolved during the formation of the saturated solution and monohydrate. Mixing dry soda ash with recirculated saturated solution to produce settled slurry will generate enough heat to raise the temperature of the mixture about 35° F (19.4° C).

Saturated soda ash solution is continuously drawn from the slurry storage tank by decanting from the clear liquid layer at the top of the slurry. Water addition to the bottom of the slurry needs to be warmed and must equal the volume of saturated solution withdrawn. The process liquor is formed by adding water or steam through a network of nozzles located at the bottom of the tank. The water dissolves the solids as it percolates up through the crystal bed. Saturated solution above the monohydrate crystals remains uniform in strength at the above noted operating temperatures. Transfer of the saturated solution to the process or the slurrying device must be conducted without heat loss, as it is susceptible to crystallization below 97° F (36° C).

Typically a 100-ton hopper car can be unloaded at the rate of about 12 to 15 tons per hour.

**TECHNICAL DATA**

<table>
<thead>
<tr>
<th>Chemical Name</th>
<th>Sodium carbonate, anhydrous</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAS Name, Number</td>
<td>Disodium carbonate (497-19-8)</td>
</tr>
<tr>
<td>Chemical Formula</td>
<td>Na₂CO₃</td>
</tr>
<tr>
<td>Molecular Weight</td>
<td>105.99</td>
</tr>
</tbody>
</table>

**PHYSICAL PROPERTIES**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td>Odorless, white granular crystal</td>
</tr>
<tr>
<td>Density</td>
<td>60-63 lb/ft³</td>
</tr>
<tr>
<td>Solubility</td>
<td>33% maximum by weight in water</td>
</tr>
<tr>
<td>pH</td>
<td>11.6 (1% solution)</td>
</tr>
<tr>
<td>Hazard Class</td>
<td>Not listed</td>
</tr>
</tbody>
</table>

**TYPICAL CHEMICAL ANALYSIS**

<table>
<thead>
<tr>
<th>Component</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂O</td>
<td>58.4</td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td>99.8</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>0.01</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.03</td>
</tr>
<tr>
<td>Fe (ppm)</td>
<td>2.0</td>
</tr>
<tr>
<td>Moisture (%)</td>
<td>0.15</td>
</tr>
</tbody>
</table>
Solubility of Soda Ash in Water

- Unsaturated Solutions
- $\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$
- $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$
- $\text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + \text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$
- Based on data from Int. Crit. Tables and Solubilities of Inorganic & Metal Organic Compounds by A. Seidell

Weight Percent Soda Ash vs Temperature of Solution

SODIUM CARBONATE
SODA ASH
Technical Data Sheet

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Soda_Ash_Conversion_Guide 3306 1/2015
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1-800-765-8292
www.solvaychemicals.us

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Percent Concentrations and Specific Gravity of Soda Ash Solutions

Based on data by Robert R. Mangold, Ind. & Eng. Chem. (1936)
Specific Heat of Soda Ash Solutions

Based on data from Int. Crit. Tables, Vol. 5, Page 124
**Soda Ash Slurry Concentrations**

- Approximate Total Pounds of Slurry per Gallon of Mixture
- Approximate Total Pounds of Na₂CO₃ per Gallon of Mixture

Data experimentally derived for typical Soda Ash.
Before using, read Safety Data Sheet (SDS) for this chemical.
Solvay Chemicals, Inc.
24-hour Emergency Phone Number – 800-424-9300 (CHEMTREC®)

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