Developments in Recausticizing Plant

GKK Menon

Hindustan Dorr-Oliver Ltd., Dorr-Oliver House, Chakala, Andheri (E), Mumbai-400 099

ABSTRACT

Modern recausticizing systems are designed to provide high clarity white liquor of uniform concentration ,while maximising recovery of soda from lime mud and dregs and minimising energy needs and environmental impact.In evaluating recausticizing equipment, it makes sense to choose machines that offer inherent advantages in terms of process efficiency and economic performance. Sizing equipment for recausticizing system depends on a number of parameters which vary from mill to mill . Every kraft or soda pulp mill is unique with its own specific conditions and constraints. Space avaialable, terrain characteristics at the plant site,operating needs,current capacity,existing equipment ,raw material supplies and anticipated future expansion affect a particular mill's requirement to one degree or another. If poor quality lime is used , the causticizing reaction is much slower and many operating problems arise. Contaminates and impurities in the lime require larger processing equipment , special flow sheets and equipment change.

INTRODUCTION

The Recausticizing system is part of the chemical recovery cycle in a kraft pulp mill . It performs a necessary service to make the system economical. As it is a service, the design and operation must be such that the proper quantity and quality of white liquor is supplied to the digester (Fig.1).

Aftor digestion , the spent (black liquor)is concentrated and burned . The combustion air in the recovery furnace is injected at several points so that a reducing atmosphere is maintained at the bottom. The carbon char reduces the Na_2SO_4 to NA_2s , so that one portion of the active cooking chemical is regenerated . The reduction efficiency is between 90 and 95% in a well operated boiler, so there is always some residual Na_2SO_4 in the liquor. In the recovery furnace ,all the rest of the sodium is converted to sodium carbonate (Na_2CO_3) by reaction with CO_2 in the combustion product gases. The sodium carbonate must be regenerated to NaOH before the liquor is ready for reuse in the digester. This is where the recausticizing system comes in.

In Recausticizing, quicklime (CaO) is used to regenerate the liquor:

$CaO + H_2O = Ca(OH)_2$ - Slaking

$Ca(OH)_2 + Na_2CO_3 = 2\ NaOH + CaCO_3$ -Causticizing

When lime is added to water, the reaction with water is called slaking . In this case water is more than the vehicle which carries the chemical around : it is a chemical and it is participating in the chemical reaction. Calcium hydroxide is insoluble under the conditions we practice this reaction. In the causticizing reaction, one mole of Na_2CO_3 converts to two moles of NaOH . For convenience the concentrations are all reported on a common basis to avoid conversion errors. The common unit in North America is the equivalent of each compound as Na_2O. In Europe, South America and Asia, most mills report as NaOH .

Slaked lime or calcium hydroxide , reacts with sodium carbonate in the green liquor to produce sodium hydroxide, the active cooking chemical and calcium carbonate or lime mud. Since both $Ca(OH)_2$ and $CaCO_3$ are insoluble, this reaction takes place by the exchange of OH^- and $CO_3^=$ ions at the interface between the solid particle and the liquid.

The causticizing reaction is reversible and that the amount of conversion is limited. It is an equilibrium reaction and the conversion depends on the liquor concentration. For most kraft mills , the equilibrium conversion efficiency is 85%. Refer to the chemical equilibrium data (Fig.2)

We are fortunate that this reaction proceeds very rapidly at first, but the rate falls off dramatically as the concentration of NaOH increases. Both the equilibrium and the rate must be considered by an engineer designing or operating the system.

After the liquor is regenerated, it must be separated from the lime mud . Experience shows that this separation is very difficult if any residual $Ca(OH)_2$ remains, so we know that we should not try to drive the chemical reaction by adding excess of lime. The free lime is out of control when the causticizing efficiency is above 82%.

The lime mud can be washed to remove the liquor. The chemicals are recovered by using same wash water to dissolve smelt from the recovery boiler, so care must be taken not to use too much water. After washing ,the lime mud can be regenerated to quick lime by heating it to a temperature above 825C°.

$CaCO_3 = CaO + CO_2$

This is also a key step in the recovery cycle. The recycle of lime is necessary to avoid a waste disposal problem which would become unmanageable in a very short time . A 1000 STPD kraft mill produces about 550 tonnes of lime mud every day. Efficient, low cost operation requires skilled analysis of the parameters. We must never lose sight of the fact that this operation exists to serve the pulp mill, so the operation must lend itself to flexibility as well as efficiency.

Recausticizing Operations

Black liquor entering the chemical recovery furnace from the evaporators is at a 55-60% solid concentration . Salt cake (Na_2SO_4) is added at the black liquor furnace to make up for sodium and sulphur losses. The sodium losses average approximately 0.5% for the recausticizing plant and about 8-10% in the black liquor recovery system . The smelt from the recovery furnace is dissolved in the smelt tank with weak white liquor .Weak white liquor is a dilute solution of sodium hydroxide, sulphide and carbonate.

From the smelt dissolving tank the green liquor must be clarified to remove insoluble impurities which are known as dregs. The dregs concentration of the green liquor runs between 800-1200 ppm. Dregs are composed of approximately 50% carbonaceous material (from the recovery furnace) plus silica , metallic sulphides and other salts. The dregs are sent to another settling unit where they are mixed with water and resettled to remove as much soda (sodium chemicals in solution) as possible before they are discharged as wastes. The supernatant liquor from the dregs washer is weak liquor and is used to dilute the lime mud ahead of the mud washer.

Clarified green liquor is then reacted with calcium oxide in the slaker . Here the previously discussed slaking and causticizing reactions take place. The classifying section of the slaker contains a rake mechanism which is used to remove unreacted material called grits. The lime fed into the slaker will run approximately 85% as available CaO. The grits are discharged from the rake classifier as waste.In the slaker the slaking reactions is fully completed and about 90% of the recausticizing reaction is completed. The recausticizing reaction is brought to equilibrium in 2 or 3 retention tanks in series known as causticizers. From the causticizers, the causticized slurry is sent to a clarifier for separation of the lime precipitate from the white liquor. This white liquor clarification stage produces a liquor which normally contains 50-100 ppm suspended solids and caustic content of 80-90 gpl. The clarified white liquor is then sent to the digesters for pulp cooking.

The lime mud slurry from the white liquor clarification stage is sent to a settling tank where water is added for dilution washing . The purpose of this mud washing stage is to remove as much soda from the lime mud as possible prior to the calcining stage.The number of stages of countercurrent washing depends on the purity of lime used. Good quality lime as per ASTM standards will require less number of stages ,since the lime mud produced will be porous in nature and easy to wash. The supernatant solution is known as weak liquor and is sent to the smelt tank (along with the dregs washer overflow) for dissolving the smelt. The washed lime mud is then sent to a vacuum filter for final washing and dewatering. The lime mud cake discharging from the filter range between 65-75% solids. This cake discharge is fed into a calcining unit. Here carbon dioxide is driven off and the calcium carbonate is thus converted to calcium oxide.This reburned lime is then ,fed back into the slaker. Calcium lost with exiting gases from the calciner, with the grits at the slaker ,and also in the form of calcium carbonate in the clarified white liquor, is made up by adding fresh lime (CaO) to the slaker.

In conclusion it should be pointed out that it is the chemical recovery process , which includes recausticizing operations that has made the kraft process economically attractive. Now, in addition to this advantage , the chemical recovery feature of the kraft process greatly reduces the pollution problem.

Green Liquor Clarification

Raw green liquor is prepared by dissolving smelt from the recovery boiler in weak liquor from the lime mud and dregs washer. The green liquor contains small amount of suspended solids which, if allowed to remain would gradually build up in the lime mud circuit and cause a progressive drop in lime availability. The Dorr-Oliver Green liquor clarifier removes most of the insoluble suspended solids or dregs. It is basically a single compartment thickener, designed so that feed and flow pattern makes maximum use of of overall tank volume. Today's model offers much better retention efficiency than older multi compartment design. It typically provides clarities of 100 ppm or better, with underflow solids ranging from 7.5% to 10 %.

The method of dregs withdrawal from the clarifier is critical. Dregs should not be allowed to build up in the green liquor clarifier for several hours and then pumped at high rates for short periods. This produces an intermittent flow to the dregs washing system and causes poor soda

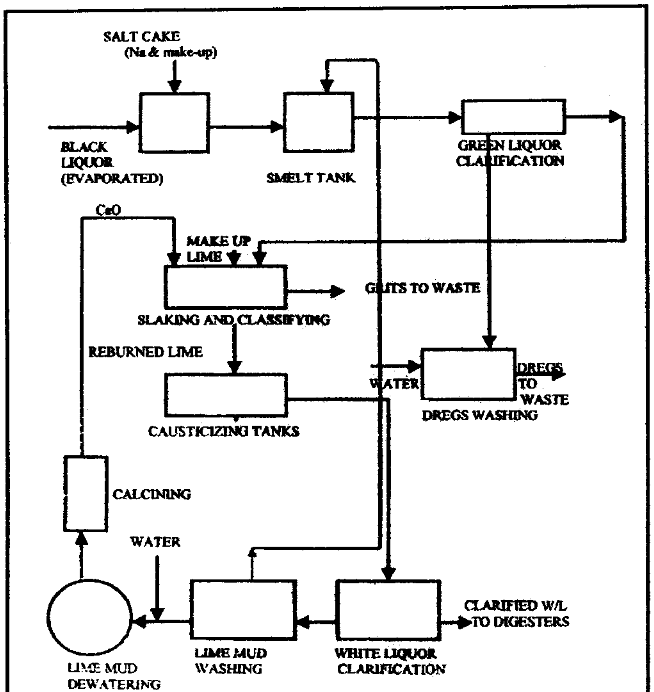

Fig. 1 Recausticizing operations

recovery. In the Dorr-Oliver Clarifier, settled dregs are raked to the central discharge cone where withdrawal is accomplished with an automatically controlled ODS pump that removes a predetermined amount of thickened sludge regularly. The air operated ODS diaphragm pump has an electronic timer to control the operation. This assures that slurry will be pumped at low average flow rates but still avoid settling of suspended particles in the piping due to a sine-wave curve on the pump discharge flow.

Dregs Mixing and Washing

The underflow from the green liquor clarifier is fed to a dregs mixer where it is agitated and diluted with wash water to recover soda before being discarded . The Dregs Mixer is simply a small tank with a top entering agitator. Premixing enhances the efficiency of the washing step and improves recovery. The discharge from the mixer is settled out in the Dregs washer - it recovers 90% of the soda normally discharged with the dregs from a single stage sedimentation washer. The dregs are thickened to a maximum concentration to minimise soda loss . Typically, underflow, containing negligible soda content is discarded. Wash water is returned to weak liquor storage prior to being pumped to the smelt dissolver.

One of the more significant Dorr-Oliver developments in recent years is the growing use of a precoat dregs filter washer to provide a better weak wash balance and to eliminate effluent from the recausticizing system . By using a vacuum drum filter with lime mud precoat and advancing knife discharge, the dregs are picked on the precoat and then doctored off and discharged in a relatively dry state (about 50% solids), ready for landfill disposal. This helps reduce the load on the plant effluent treatment system. Compared to conventional drum or belt filters , the precoat dregs filter offers several distinct advantages. It eliminates the need to admix lime or grits to make the filtered dregs easier to handle. A drier cake is obtained , thus improving soda recovery. Also ,the lime mud precoat dregs filter requires less operator attention and less maintenance than a belt type dregs filter.

Lime Slaking and Causticizing

With the dual compartment Dorr-Oliver Slaker-Classifier, continuous slaking, classification and grit washing and removal takes place in a single piece of equipment. Lime from the calciner plus make -up lime is added to clarified green liquor. In the slaking compartment. Calcium Oxide (Lime) is converted to calcium hydroxide (Slaked Lime) in an exothermic reaction . As calcium hydroxide is formed, it begins to react with sodium carbonate in the green liquor. This causticizing reaction produces sodium hydroxide, the primary cooking chemical and precipitates calcium carbonate (Lime mud). The slurry then flows to the classifier compartment where the grits are continuously washed and removed via an inclined ramp and mechanically driven rakes. The Dorr-Oliver Slaker, constructed of abrasion and corrosion resistant materials, employs an impeller type mixer to promote rapid intimate contact of lime and green liquor. The machine has recently been improved with an internal shower to reduce scrubber loadings and minimise lime losses. Also, an improved rake drive system has been developed to lessen classifier maintenance. Lime with lumps from a rotary kiln can be broken down in a water cooled Dorr-Oliver Hot Lime Crusher preceding the slaker.

The causticizing reaction begins in the slaker and is allowed to reach equilibrium in a series of causticizers tanks. Mechanical agitation continually blends the lime and green liquor. The Dorr-Oliver Causticizers are equipped with a high speed stainless steel impeller type mixer. Multiple tanks are used to minimise short circuiting and flow is by gravity.

White Liquor Clarification

In this step, the calcium carbonate formed in the slakers and causticizers is separated from the white liquor. Dorr-Oliver offers single compartment unit clarifier and multi comparment or tray types, depending on mill preference. Tray units are used where space is at an extreme premium. Generally they cost more than unit clarifiers and somewhat more difficult to operate. In most cases, the unit clarifier with storage above the clarification zone is recommended for several reasons. In addition to lower first cost, this eliminates the need to pump the liquor to a separate storage tank . Thus additional savings are realized in tank cost,floor space, piping and the foundations required for separate storage tanks. The straight bustle overflow design simplifies pipe cleaning and costs less to install than circular bustle piping or launders.

Dorr-Oliver White Liquor Clarifiers are constructed for maximum resistance to corrosion and to assure long equipment life. The feedwell, provided for optimum clarification , is made from stainless steel and critical components are heavy steel plates. The white liquor clarification stage normally produces a liquor which contains 40 -60 ppm suspended solids. The clarified white liquor is sent to the digesters for pulp cooking. The thickened lime mud having approximately 40 -45% solids, is pumped to the washing and dewatering stages.

Lime Mud Washing

To recover soda withdrawn with the lime mud before calcining, the mud is united with wash water in a lime mud mixer and then washed by dilution and rethickened in a Lime Mud Washer . In some cases, two stages of lime mud washing are needed. The Dorr-Oliver Lime Mud Washer is the same as the green liquor and white liquor clarifiers- essentially a unit thickener with storage capacity for weak liquor located over the thickener section. The rake action within the settled mud moves the lime mud to a central discharge point. This raking action also produces particle reorientation with an upward release of liquor from the mud. Washed lime mud is stored in an agitated tank to keep solids in suspension and maintain slurry uniformly. The storage of slurry ensures an uninterrupted flow of of material to the lime mud filter which is necessary for good soda recovery. After dilution water has been added, the filter dewaters the mud. Water spray controls the final soda content in the calciner feed to a low soda level of 0.5% or less.

The simplified unit compartment lime mud washer design substantially reduces installed costs. It is considered as the most economical arrangement in most applications. However there are special situations in very large plants where two compartment designs could be considered. Dorr-Oliver provides appropriate designs to meet any specific requirement.

Lime Mud Dewatering

The Dorr-Oliver Lime Mud Filter is a rugged revolving drum continuous vacuum unit, with improved capacity and designed for flow maintenance. Construction is of mild steel with a stainless wire or polypropylene cloth filter medium. Maintenance requirements have been greatly reduced because of our heavier duty agitator and agitator drive system.

Lime mud cake is formed continuously on the surface of the drum as it rotates and submerges . The cake is subjected to hot water wash where the caustic in the lime mud is replaced by water. After passing the washing nozzles, the cake is further dewatered before it is discharged and fed to the calciner or kiln.

Improvements in filter design through the years have resulted in increased hydraulic capacity, lower maintenace cost, reduced spare parts requirement and the ready availability of units in various materials of construction. A higher capacity open valve has been incorporated for exceptional filtration throughputs.Consequently, filter cake solids have been increased to higher levels . A unique automated cake doctoring system results in higher discharge consistencies and longer operating time between precoating and acid washing. The modern Dorr-Oliver Precoat Filter, with new doctoring system can yield 75% solids depending on lime mud quality.

Proper filter sizing is important. In addition to more efficient soda recovery , the properly sized filter can result in sizeable energy saving. To recover 1 tonne of of lime which is 75% dry, rather than 60%,will save 1.7 million BTU, and provide better pelletization in the calciner. Also a drier cake to the calciner reduces the total TRS emissions in flue gases.

Improvements in Technology Available

Overall improvement desired by various mills are with regard to better efficiency on the recovery which would maximize the quality of cooking liquor and minimize the power and utility consunption.

Some of the innovations are listed below:

The clarifil pressure filter is a cylindrical vertical pressure filter manufactured from Stainless steel, type AISI 316 OR 304. A tube plate supporting a number of perforated tube filter elements is welded into the top section of the cylinder. Each of the perforated tube filter elements is equipped with a replaceable needled felt sock made of reinforced polypropylene. The area above the tube plate is equally divided into sections . Each section contains a filtrate outlet which directs the clarified liquor to a head box. The filtrate outlets are positioned to allow a pressurised air cushion to be formed under the filter head.

The mud and liquor slurry is pumped into the filter. The liquor is forced through the felt covered perforated tube elements while the lime mud forms a cake on each tube sock. The clarified liquor is forced to an overhead level box and then flows by gravity to storage. After 4-6 minutes of filtering time, cake discharge from the tube socks is initiated by the automatic opening of a bypass valve for reciculation of liquor slurry to the pump sump. For a short period of time , the liquor located in the upper portion of the vessel flows back through the filter socks and discharges the cake. The automatic valve opening causes a rapid fall of pressure in the lower portion of the vessel, permitting the pressurised air cushion in the upper portion of the vessel to expand and force liquid back through the socks. This high flow provides for efficient cake discharge.

The discharged lime mud settles in the conical bottom of the filter where it is homogenized by an agitator. The homogenized lime mud is then pressed out through a bottom discharge connection.

White Liquor Clarification

The clarifier is fed from the causticizers by means of a pump. The clear filtrate obtained is sent to the liquor storage and the concentrated lime mud is delivered to the mud washing station.

Lime Mud Washing

After dilution with hot water , the lime mud slurry is pumped to a second clarifil. The filtered weak liquor is sent to storage and the washed underflow mud is pumped to a storqage silo.

Features

- High filtrate clarity
- Totally enclosed operation
- Compact design
- Fully automated operation
- White liquor clarifier and lime mud washer of same design
- Pressure feed
- All stainless steel construction
- Storage tank is separate
- Liquor discharged under pressure.

Benefits

- High capacity due to higher differential pressure
- Reduced scaling of piping and digester heat exchanger
- Liquor oxidisation minimised and clean environment
- Minimum space required
- Reduced operating costs
- High operating flexibility
- Can push out thickest mud concentration
- Corrosion resistant
- Less chance of pulp mill downtime
- No liquor transfer pump to storage required

Lime Mud Filter

For the Reacausticizing plant especially with lime mud reburning system, Dorr-Oliver have developed for dewatering of lime sludge, a new design filter incorporating the state of art technology. This is a proven equipment and operating in many paper mills in India and abroad. This new technology for lime mud filtration is a major process development for this application with the following as the main objective.

- The filter hydraulic design contributes practically no resistance to vapour flows involved in vaccum drying and particularly during the air blow cycle.
- The oxidation of sulphur compounds present on the filter cake, prior to calcination , which is the very important parameter in limiting TRS emission from the kiln stack, i.e. producing mud with minimum moisture content and the quantum of sulphur components going to the kiln which are considerably minimised.
- The design feature permits operation of the filter with thin precoat , which results in improved dryness of the mud fed to the kiln.
- The filter unit per-se is designed for operation at a faster speed between 3-5.5 rpm as against 1-4 rpm of conventional filters. Thus the faster speed operation results in improved throughput capacity. Besides, only a very thin cut from the extreme outside of the filter cake is removed with it's well washed and low moisture characteristics .
- The snap blow lime mud filter incorporates autoprecoat removal system. This design affords unique process advantage during continuous operation of the filter; namely almost constant quantity of cake with improved dryness getting discharged.This results in stable economic operation of lime kiln with better fuel efficiency.
- The filter valve is of special design for high capacity flow ideally suited for snap blow features and including mechanism to ensure that each section of the drum surface is blown in it's specific order and cycle- one of the features to discharge the cake at uniform rate wihout any surge condition to the kiln operation.
- We wish to highlight the improved design features and the accrued benefits to mill operation as under.

• Design features	Benefits
• Snap blow discharge	• Online automatic reprecoating
	• Increased kiln capacity
	• Less fuel consumption
	• Less shock load to the kiln
	• Shaft mounted Gear reducer
	• Easy maintenance
	• Greater variability in speed for

optimal discharge of solids

- Large stream line drum pipe with friction losses
- Improved hydraulics
- Increased evacuation capacity maximize sulphur oxidation.
- Discharge scraper with micrometer screw advance mechanism
- Reduced maintenance
- Better discharge of solids
- Heavy duty discharger Agitator
- Low maitenance
- Uniform suspension of particles in the feed slurry.

Continuous Cleaner

The latest development in Lime mud filter is Dorr-Oliver Continuous Cleaning (DOCC) system, which involves the state-of-the-art technology. This equipment could be retrofitted in any of your existing Dorr-Oliver Lime Mud Filter or Dregs filter. This unit will continuously remove small amount of lime mud pre-coat(heel cake) and clean the filter cloth, when the unit is in continuous operation. DOCC is mounted on brackets welded to the filter vat on the opposite side of the discharge, which allows easy access for maintenance. The drive motor of the unit shall be mounted outside the end panel of the filter. DOCC shall be provided with nozzle assembly over the face of the filter with header. A hydra cell shall be included to provide adequate high pressure water for the nozzles. The additional unique feature of DOCC is provision of nozzle reversal system, which does not require any electrical controls.

- Dorr-Oliver Continuous Cleaning System suitable for assembly on to Lime Mud Filter:
- Inbuilt housing in SS 304 construction mounted on the vat supported with mild steel bracket.
- 3 nos. nozzle assembly in SS 304 MOC attached to a common header.
- Oscillator with automatic reversing screw and shaft, which shall be enclosed in a heavy duty rubber bellows.
- Reversing screw drive complete with proximity switch and motor mounted outside the filter end panels. A torque limit coupling shall be fixed between the screw and the reducer.
- Skid mounted "hydra-cell" high pressure pump with strainer complete with motor and pressure relief valve.
- Control panel with interlock and push buttons.
- Continuous cleaning technology offers the following benefits to the operation of the recausticizing plant:
- More lime production due to virtual elimination of blinded precoats
- More stable kiln operation , again due to minimal blinded precoats.
- Potential for higher lime mud solids and lower soda in the feed to the kiln due to filtration through a thinner precoat "heel".

Desilication of Green Liquor

Removal of silica from green liquor requires a two stage causticization of green liquor.This method proposes to remove silica in the first stage using about 25% of the total lime addition to give silica rich lime sludge for disposal . In the second stage , causticization is completed with balance of the total lime requirement; the resulting lime sludge should be low in silica and suitable for satisfactory calcination in a rotary kiln. This method seeks to reduce the lime sludge solid waste disposal problem by recycling reburned lime for causticization . A block diagram illustrating the principle of desilication during causticization is given in Figure - 1

Probable Reactions During Desilication

It is generally believed that the silica /silicic acid in bamboo or bagasse is solubilised in alkali during kraft pulping according to reaction (1) and will be present as sodium silicate in the process liquors-black luiquors and green liquor.

$$H_2SiO_3 + 2NaOH = Na_2SiO_3 + 2H_2O \qquad (1)$$

Sodium silicate would probably combine with lime during lime treatment of green liquor according to reaction (2)

$$Na_2\,SiO_3 + Ca\,(OH)_2 = CaO.SiO_3 + 2NaOH \qquad (2)$$

Reaction (2) would contribute to an increase in concentration of sodium hydroxide depending upon the extent of desilication accomplished. However ,analysis of desilicated green liquor from first stage showed that the observed increase in concentration of sodium hydroxide was in accordance with causticizing reaction (3) only.

$$Na_2\,CO_2 + Ca\,(OH)_2 = CaCO_3 + 2NaOH \qquad (3)$$

Other possible reactions involving hydroxyl ion include hydrolysis of sodium sulphide, sodium carbonate and sodium silicate, reactions (4) to (9)

Hydrolysis of sulphide : (pk value at 25^{0}C)

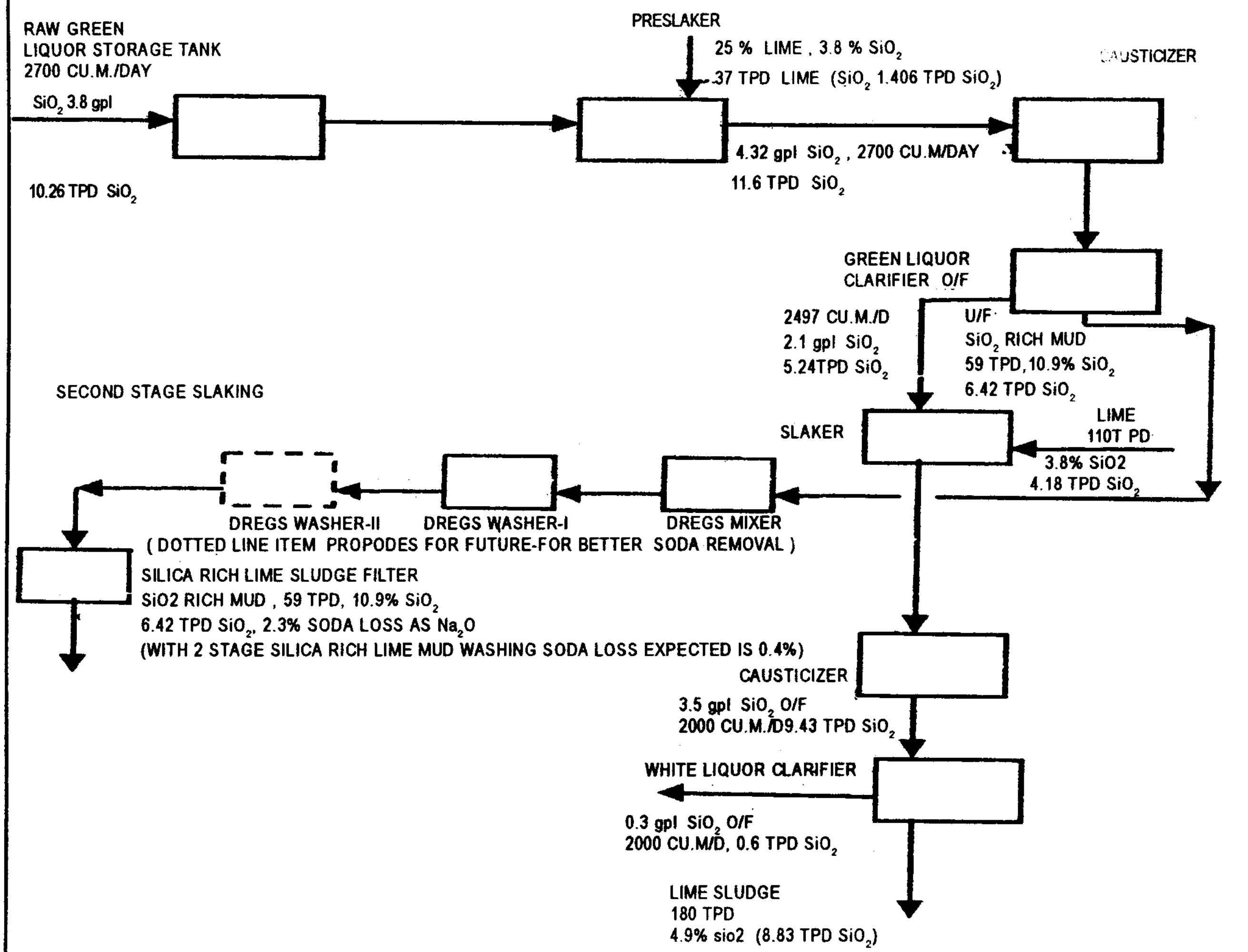

Fig. 2 Mass balance for silica in 400 tonnes per day bagasse pulp mill first stage slaking.

$$Na_2S + H_2O \; pk = 14.2 \rightleftharpoons NaOH + NaHS \qquad (4)$$

$$NaHS + H_2O \; pk = 6.9 \rightleftharpoons NaOH + H_2S \qquad (5)$$

Hydrolysis of carbonates :

$$Na_2CO_3 + H_2O \; pk = 10.3 \rightleftharpoons NaOH + NaHS \qquad (6)$$

$$NaHCO_3 + H_2O \; pk = 6.4 \rightleftharpoons NaOH + H_2CO_3 \qquad (7)$$

Hydrolysis of silicate:

$$Na_2SiO_3 + H_2O \; pk = 11.8 \rightleftharpoons NaOH + NaHSiO_3 \qquad (8)$$

$$NaHSiO_3 + H_2O \; pk = 9.8 \rightleftharpoons NaOH + H_2SiO_3 \qquad (9)$$

Alkalinity of white liquor would correspond to PH above 14 and green liquor with PH=12-14 is buffered by the high concentration of carbonate ions. Sulphur will be present as sulphide in white liquor and hydrosulphide in green liquor, reaction (4). The degree of hydrolysis of carbonate will be small, reaction (6). Reactions (5) and (7) will be significant only at lower PH levels. Hydrolysis of silicate would be significant , reaction(8) in green liquor.Under the influence of the electrolyte (ionic strength 5-6 g ion /l) and temperature (80-1000°C), reaction (9) also can be assumed to be significant. Desilication could then proceed according to reaction (10) rather than reaction (2) as postulated earlier

$$Ca(OH)_2 + H_2SiO_3 == CaSiO_3 + {}_2H_2O \qquad (10)$$

Reaction (10) will also be compatible with the observed increase in concentration of hydroxide conforming to reaction (3)alone. Silica will be separated from the system as calcium silicate through reactions (8), (9) and 10 .