Lime Reburning-Problems And Prospects

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ABSTRACT

Silica is known for its adverse effect on operation of lime kiln and its presence in significant quantities can seriously affect the operation and economy of lime reburning plants. Some of the mills have perforce posteponed the installation of lime reburning plants and others which have already installed lime kilns are facing serious problems of high fuel requirement and silica build-up The only possible solution to .these problems is adoption of Desilication process either at black liquor or at green liqour stage. The extensive work carried out at CPPRI clearly indicates that by optimising the slaking conditions and adopting appropriate settling characteristics quality of sludge can be improved satisfactorily.

INTRODUCTION

Bamboo is still one of the important source of long fibre for several pulp & paper mills in India. Also agro residues like wheat straw, rice straw and other grasses are finding increased use in Paper Industry and their processing is restricted due to high silica in black liquors. Specially, Chemical recovery operations are seriously effected and lime sludge is so enriched with silica that it has to be discharged as landfill. In this scenario, the only option for mills is to include desilication at black liquor or green liquor stage so that problems related to silica can be minimised.

Additionally, due to high cost of energy and fuel oil lime sludge quality and moisture are extremely important. The high quality sludge ensures better conversion efficiency and thus reduced dead loads and low moisture in sludge helps to keep fuel consumption within economic limits. To meet both the above requirements, removal of silica is highly essential. Silicates are highly hydrated and they retain significant quantities of moisture which calls for high fuel oil consumption.

Broadly the problems in lime sludge reburning is attributed to presence of silica and other non process elements in lime mud. The buildup of silica in lime sludge in absence of desilication is rapid and in few cycles, the level of silica exceeds the tolerance limit of kiln. To counter this problems, large purge out is necessary and loss is made up with low silica lime which makes the process highly expensive. The silica in green liquor reacts with lime to form calcium silicate which reduces the causticizing efficiency and lime mud settling characteristics and results in lime mud with high moisture contents. Its presence also affects the lime reburning operation where it forms glass like coating on $CaCO_3$ particles which prohibits released of CO_2 and reduces lime availability. Besides silica, lime quality has a great impact on the separation properties of lime mud.

RESULTS AND DISCUSSION

As indicated in Annex-I, the build up of silica in lime sludge in absence of desilication is rapid and in a few cycles, the level of silica exceeds and tolerance

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limit of the kiln. To counter this problem, large purge out of sludge is necessary and the loss is made up with low silica lime which makes the process highly expensive.

EFFECT OF SILICA ON LIME REBURNING

For conservation of resources and environment, it is imperative that lime sludge is reburnt in lime kiln to generate quick lime. As this phenomenon catches on, it is also essential that there is enough background information available on problems expected during reburning of silica rich lime sludge. The melting point of silicate is significantly lower than the calcining temperature of calcium carbonate. As a consequence, the molten silica compounds forms a coating over both the unreacted calcium carbonate and calcium oxide generally known as sintering. This results in poor lime availability for causticization. It was found in our lab studies that available lime index is effected by as much as 13% when silica concentration in lime is raised from 0 to 4%.

Experiment on thermal decomposition carried out in lime sludge containing varying quantities of silica reveal a gradual slope between 375°C and 600°C due to evolution of combined water from the calcium silicate hydrate and the complete decomposition of pure calcium carbonate occurs at 792°C. With the varying amounts of silica, decomposition temperature of calcium carbonate is lowered down to 755°C. It is also observed from the study that calcium carbonate available for conversion to calcium oxide is reduced substantially from 98% to 69% when silica is increased gradully to 5.5%. This highlight the need for removal of silica from the green liquor prior to lime sludge reburning.

TABLE-1

Thermal Decomposition of Lime Sludge in Presence of Silica Using thermal analyser

Sample	Silica Green Liq. %	Silica in Sludge %	$CaCO_3$-------->CaO Conversion: Conversion %	$CaCO_3$-------->CaO Conversion: Conversion Temp., °C
Pure $CaCO_3$	-	-	98	792
A	05.	0.5	93	772
B	1.5	1.3	89	770
C	2.5	N.D	81	767
D	3.5	2.9	76	763
E	5.5	3.2	69	757

In a lime sludge reburning plant, the regulation of temperature in the various zones of the kiln is very important in order to get a product which is completely calcined, porous, light in structure, and which rapidly and completely hydrates.

The impurities such as oxides of aluminium, iron and silica alone with soda prevent proper calcination by forming a non-porous dense coating around the sludge pebbles. When lime stone is fed to the kiln, the individual lumps are preheated by hot stock gases before they enter the calcining zone. It is also reported in the literature that the calcination of lime proceeds inwardly from the outside of the lumps. The heat transfer depends on the temperature drop between the outside and inside of the pumps. The outside temperature of the lump must be higher than the theoretical decomposition temperature of the lime stone. Too high a temperature results in formation of overburnt lime, which is dense non-porous, heavy in weight and which hydrates slowly and incompletely. This is probably due to the atomic rearrangement and closer packing of the molecules. The lime which slakes easily and readily has larger intratomic spacing. Which permits easy and ready penetration of the molecules of water.

The difficulties associated with over and underburnt lime are very frequently met with especially when the sludge fed to the kiln has a high silica content, which forms along with the alkali an easily smelting glasslike compound.

A lime produced from a sludge containing about 10% silica has clay like appearance; it does not hydrate at all at room temperature, but hydrates slowly at 80°C to 100°C although it has an active lime content of 65% to 70% as measured by the acid titration.

The presence of silica causes complications in obtaining a good burnt lime. The impurities like alumina, iron oxide and silica in the lime mud react with the calcium oxide to form glassy compounds, which smelt at the temperature of calcination in the kiln and close the pores of lime lumps by forming a thin coating on the outside of the lumps. Such lumps contain in the inside unburnt cores and in the outside overburnt outer layers. The formation of unburnt cores inside the lumps is explained by the fact that the carbon dioxide has formed at the high temperature cannot find its passage to the outside through the outer dense layer thus the decomposition pressure of calcium carbonate inside the lump is greater than the corresponding to the prevailing temperature outside. The non-uniformity in the lumps reduces as a whole the percentage of available lime in the finished product. In order to obtain an uniformly burnt lime without unburnt ocre, it is usual to maintain a higher temperature in the calcinating zone of the kiln. When this condition prevails, the outside temperature of the lime lumps must be cooled to below 900°C, the decomposition temperature of calcium carbonate, before the product leaves the kiln in order to prevent recarbonation of hot lime during the cooling period.

It is also known that each 1% of silica (SiO_2) in the sludge causes a reduction of about 3% in the available lime. It may be the result of the formation of tricalcium silicate. $3CaO, SiO_2$.

Thus it is nearly impractical and unprofitable to install a lime sludge reburning kiln before finding out some means of removal of silica either from the black liquor or the green liqour.

EFFECT OF OTHER NON-PROCESS ELEMENTS ON LIME REBURNING

The presence of Magnesium and iron hamper the separation of lime mud. Magnesium causes difficulties, especially in filteration because Magnesium hydroxide in gelatinous and plugs up the wire easily. The maximum acceptable content of Mgo in lime is considered to be 2%.

The sodium & potassium are responsible for the ring formation in the lime kilns becuase of the low melting points of sodium and potassium carbonates (852°C and 891 °C). On the other hand, the very low alkali content of the lime mud causes poor pelletizing and thus increases dust formation in the lime kilns. The average concentration of water soluble alkali compounds is in between 0.2 and 0.7% Na_2O in the lime mud.

The increase of inerts in the lime cycle increases the need for lime reburning capacity. It also increases the oil consumption in lime mud reburning . It is estimated that if the causticization efficiency decreases from 90% to 70%, an additional oil consumption of about 9 kg/t of pulp is required.

SETTLING CHARACTERISTICS OF LIME MUD IN PRESENCE OF SILICA

After causticization the settling of lime sludge is an important factor which influences the clarity of the white liquor product and also determines the amount of calcium going back to pulping cycle. A fast and well settled sludge will have better dryness and better quality of white liquor. Calcium silicate is the main component which adversely effect the settling rate. Calcium silicate carries more water and hence the sludge produced without desilication has more moisture. For improved settling, it is necessary to remove silica from the green liqour or black liquor.

Settling characteristics of lime mud were studied in various samples with and without removal of silica and the results are depicted in Fig. 1 and Fig-2. It is clear that there is a remarkable improvement in the settling of lime mud when the silica content in the green liquor is low.

MOISTURE RETENTION BY SILICA RICH SLUDGES

Several mills are facing some problem of high sludge moisture due to presence of silica. This seriously effects the fuel oil consumption which effects the economy of the process. Where as mills based on wood operate with sludges at a moisture levels of 50-55% with additional problem of dead load and low quality lime. This perhaps is the single most important factor which calls for removal of silica from the system. A softwood based mill in comparision has only 25% moisture. The silica free lime sludge having

TABLE-2

COMPOSITION OF LIME SLUDGE GENERATED IN PAPER MILLS

Particulars	Indian Mills raw materials base			Developed countries
	100% wood	100% Bamboo	80% Bamboo + 20% wood.	100% Softwood
Silica from raw material, %w/w	0.5	6	5-6	0.4
Dryness, % w/w	65-70	42-45	50	75
Expected oil requirement in reburning operation litres per ton of lime	150	*	240	110

** No bamboo based mill practices lime reburning.*

a dryness of 75% as in case of softwood baded mills require~ 110 litres of fuel oil per tonne of lime, the oil requirement in case of bamboo/wood based mill it could be 240 litres per ton of lime. Composition of lime sludge generated in paper mill are recorded in Table-2.

DESILICATION TECHNOLOGIES

CPPRI has been involved in development of Desilication Technology for the last 15 years and has conducted research on black liquor as green liquor desilication.

BLACK LIQUOR DESILICATION

It is recommended for black liquor having silica more than 2 gpl. The desilication process, developed & patented by CPPRI is based on the principle of submerse buble technology where the liquor to be desilicated is circular loop. The pH is reduced by introducing CO_2 gas from the recovery boiler at the upper limb of the circulation loop. The flow of the liquor works the gas in a kneading fashion exposing new gas liquid interfaces and size of the gas bubles is reduced into discreet particles. This ensure slow & gentle carbonation resulting in precipitation of silica without coprecipitation of lignin. More than 80% of easily filtrable silica mass is removed from the black liquor. The mills size demo plant based on this technology is already in operation at Hindustan Newsprint Ltd, Kerala. The process has successfully tested for agro residues black liquors. The silica sludge is a value added by product.

GREEN LIQUOR DESILICATION

Green liquor desilication is mainly recommended when the silica levels in corresponding black liquors are lower than 2 gpl and can be accomplished by-

Carbonation method

Two stage lime treatment

Green liquor carbonation can be done by using the submerse buble or any other techique involving high gas liquid mass transfer rates. The silica is precipitated as white colored easily filterable sludge. However loss of sulphur as H_2S occur in case of sulfate liquors.

TWO STAGE CAUSTICIZATION

Two stage lime treatment method has been tested in CPPRI which involves addition of lime in smaller dosage to remove silica as silica reacts preferentially with lime. The sludge is separated and discarded and the second stage causticization is carried out in normal fashion to generate alkali. It is noted that silica lime react better at a lower temperature, whereas Na_2CO_3-lime react faster at high temperature.

CONCLUSION

In the present context although the mills have gone for installation of lime reburning plant to reduce the cost of production & environmental implications. It has been experienced even the silica below 2% also

Annexure-1

SILICA BUILD UP WITH & WITHOUT DESILICATION

Silica in black liquor g/l on solids	3.0	4.5	6.0	7.5
Silica build-up in product lime after 5% purge, of lime sludge, in Ist cycle	9.0	10.9	12.3	14.1
Silica build-up in product lime after 5% purge, in 2nd cycle	11.5	14.4	16.9	19.6
SILICA BUILDUP AFTER BLACK LIQUOR DESILICATION				
Silica in black liquor, g/l	3.0	4.5	6.0	7.5
Silica in desilicated black liquor, g/l	0.5	0.5	0.5	0.5
Silica Build-up in Ist cycle, %	5.4	5.4	5.4	5.4
Silica Build-up in IInd Cycle, %	5.8			
Silica build-up in Vth cycle, %	6.7			
Silica Build-up in VIIth cycle, %	7.0			

Annexure-1I

ENERGY SAVINGS WITH BLACK LIQUOR DESILICATION

Particulars	With Desilication	Without Desilicaton
ENERGY IMPACTS		
Steam economy in evaporation	4.0	3.5
Saving in steam, t/d	100	--
Lime sludge dryness, %	65	40
Fuel oil requirement in lime kiln, kg/t of lime	150	200
ENVIRONMENTAL IMPACTS		
Solid waste generation kg/tonne of pulp	130	900
Environmental hazards	Low ground water contamination	Severe ground water contamination

causing problems in lime reburning plant due to silica buildup. The studies carried out at CPPRI clearly indicates that silica can be effectively removed from black liquor or green liquor and a dinstinct advantage in fuel savings in lime kiln can be accomplished. Please see Annex-2. Further, possibility of use of biogas, Natural gas, Producer gas and hog fuels should be expressed to reduce the operational cost of lime kiln as in future lime sludge reburing will become an integral part of chemical recovery operation due to environmental concerns.

REFERENCES

1. Terry. N. Adams; Lime reburning, Kraft Recovery Operation TAPPI Short Notes, 1990.
2. Dorris, G.M. The physical characterisation of hydrated lime and lime mud particles. J of Pulp and Paper Science 19 (6)- 1993.
3. Keitaanniemi. O. Virkla. F; Undesirable elements in causticizing systems Tappi 65 (7)-1982.
4. Panda A, Indian Pulp & Paper, 1962 p-470
5. Boniface et al; Pulp & Paper 42 (44) : 287, 1982