Desilication of Black/Green Liquor From Paper Mills A New Approach

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INTRODUCTION

Paper and paper products are playing increasingly important role in modern society and their demands are regularly increasing. Paper mill occupy unique position in the economy of the country. The cost of paper and paper products depends very much on the recovery of the chemicals used in the process. The alkali used in pulping process is recovered from green liquor by lime treatment, whereby lime sludge is produced. The requirement of lime per ton of paper is around 0.4 ton. In soft wood based paper mills, the lime sludge is calcined to recover the lime for reuse in causticization of green liquor. The cost of such reburnt lime is much lower than fresh lime and therefore recycling of lime sludge bring substantial economy to the paper mills.[1]

Lime sludge generated in paper mills using silica rich pulping material like bamboo as in most of the Indian paper plants including those of N.E. region are however rich in silica (5-15%) and alkali (0.5-2%). The silica exists in the sludge as calcium silicic acid, sodium silicate etc. Calcination of such silica and alkali rich sludge leads to formation of clinkers and rings in rotary calcinators and cause operational difficulties. The impurities also form low melting compounds which cover the grains of calcium carbonate and resist its decomposition. The low melting silicates form a glassy layer at high temperature and thus seal off the pores of the burnt lime. The available lime from such reburnt sludge is therefore low. Lime with low available lime content also hinders the settling in clarifiers during use. Therefore, the bamboo based paper mills so far could not avail the economic advantages of using lime recovered from sludge. The sludge in these mills remains as waste. Normally, sludge to the extent of 0.3–0.7 ton per ton of pulp is produced. Sludge generated even in a small mill is enormous, its cumulative deposits is a matter of much concern because of its disposal and associated pollution problems. The alkali and silica in the sludge from silica rich pulping materials restrict reuse of the sludge for generating paper grade lime. The alkali may be brought down to the permissible limit by introducing efficient washing technique to the sludge, but the lowering of silica in the sludge requires bringing down the silica content from either black or green liquor stage. Adoptation of suitable desilication technique to the green liquor may be adequate for recycling of lime sludge. Desilication from black liquor however leads to some additional advantages. It reduces the scale formation in multiple effect evaporator as well as in spray burners of the paper mill. The formation of scale lowers the heat transfer efficiency and increases the maintainance cost and frequent down time losses. The handling volume of black liquor is enormous in comparison to green liquor and therefore capital cost for introducing suitable desilication technique from black liquor will be much higher than from green liquor.

EARLY DEVELOPMENTS

Extensive research has been done on developing suitable methods for desilication of black/green liquor and a good number of processes have been developed[2-6]. All the methods are concentrated at laboratory stage only. The processes mostly involve precipitation of silica as metal (Ca, Mg or Al) silicates or as silicic acid by addition of appropriate cation or through pH reduction. Precipitation of silica using lime has been studied by many workers. However, by using 100-200% excess lime than theoretical requirement could not bring down the silica content to desired level. Moreover, the calcium silicates formed is voluminous and slow

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settling and therefore filtration becomes difficult. Desilication through pH reduction using CO_2 or mineral acid produces colloidial form or silica which require several treatments like centrifugation, boiling under pressure etc. for separation.

NEW APPROACH

Regional Research Laboratory, Jorhat (RRL-Jt) undertook process development work for desilication of black/green liquor from paper mills with financial support from NEC, Shillong. The efforts led to development of a suitable process applicable to both black/green liquor[7-9]. The process is also based on pH reduction with CO_2 or mineral acid as in silicic acid precipitation method, but the precipitate is not obtained as silicic acid but modified with aluminium. The advantage being that the precipitates are not colloidial but easily coagulate and settle. The desilicated liquor for chemical recovery may be collected even by decantation and the precipitates may be washed easily.

The process consists in addition of small amount of aluminium salt solutions like aluminium sulphate, aluminium chloride, sodium aluminate etc to the reaction vessel containing the black/green liquor and equipped with stirrer. The amount of aluminium salt depends upon the concentration of the silica present in the liquor and usually it amounts to about 10-20% of the silica. The pH of the system is then slowly lowered to 13-9 pH depending on silica concentration by addition of mineral acid or carbondioxide to the agitated solution, maintained at room to around 90°C temperature. The precipitates obtained may be filtered immediately or may be allowed to age. The aging period may vary from few minutes to several hours depending on the temperature. The silica containing preceipitates forms a sediment, the supernatant desililicated liquor may be pumped out and the precipitate washed with water.

The precipitate obtalned during desilication, on drying is a light free flowing white powder. The I. R. spectra of the precipitate does not indicate any absorption associated with lignin structures indicating that no organic matter is lost during desilication of black/green liquor. The precipitate essentially consit of fine particles, 10 micron or below sized particles constitute around 40% (Fig. 1). The particles possesses cation exchange capacity as high as high as 93.5 m.eq./100 gms may be converted to molecular sieve zeolites. The precipitate may therefore find industrial application as ion exchanger, filler or coating material or as starting material for making crystalline zeolites. As filler or coating material, it may find application in paper and speciality paper industries also.

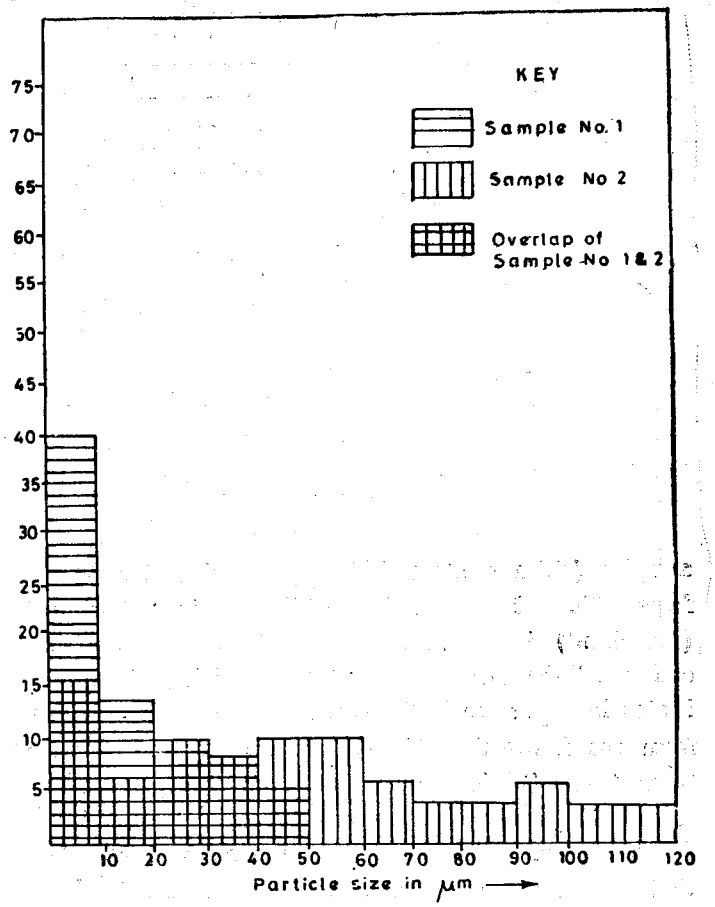

Fig 1 PARTICLE SIZE DISTRIBUTION OF SOME PRECIPITATES

The flow sheet of the 'RRL-Jt desilication process" along with recovery of byproducts is shown in fig. 2. It appears that the process is simple and may be easily adopted for desilication of green liquor of an existing paper plant without much change in the layout of the plant. However, the process is developed at laboratory scale and needs optimization at scale up level to work out the equipment sizes and cost economics.

The RRL-Jt process of desilication was verified with liquors collecied from paper mills. Results of desilication experiments conducted with black liquor

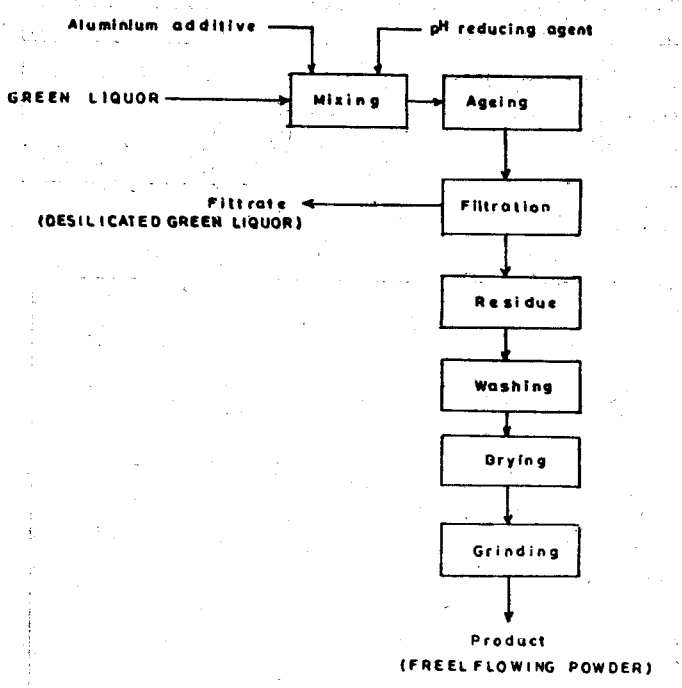

Fig. 2. FLOW SHEET DESILICATION OF GREEN LIQUOR AND RECOVERY OF BYPRODUCT (RRL-J PROCESS)

samples (silica content 1620 ppm, Table 1) collected from Tuli Paper Mill, (HPC), Mokok-chung (Nagaland) is presented in Fig. 3. Results of desilication of the same liquid following silicic acid method is also incorporated in the same figure. It is obvious from the figure that RRL-Jt process may lead to more than (+96%) desilication at even 9.5 pH against around 90% achieved at a much lower pH of 8.5 by following the silicic acid precipitation method. The desilicated black liquor obtained by following RRL-Jt method contain only 50-65ppm silica against 180-360ppm silica as obtained in the other method. Results of dsilication experiments conducted with green liquor (silica content 5000 ppm, Table 2) collected from Naogaon Paper mill (HPC), Jagi road as shown in fig. 4 indicate that the liquor can be desilicated to the extent of plus 98% even at a pH as high as 13.0 The residual silica in the solution is in the range of 43-91 ppm. The silica content of green liquor sample after desilication following RRL-Jt method is much lower than those in green liquor from soft wood based paper industries (about 200 ppm).

The characteristics of the desilicated black/green liquor samples along with original as presented in Table 1 and 2 indicate that removal of silica does not lead to

Table—I.

CHARACTERISTICS OF BLACK LIQUOR SMPLES BEFORE AND AFTER DESILICATION.

(1) Before desilication	Samples I	Samples II
pH (at 27°C)	11.79	11.82
Specific gravity (grams/cc.)	1.082	1.062
Total dissolved solid (% wt./vol.)	14.592	14.468
Silica (ppm)	1620	1842
Total titrable alkali as Na_2O (gpl)	50.57	50.65
(II) After desilication		
pH (at 27°C)	9.4	9.4
Speeific gravity (grams/cc.)	1.078	1,060
Total dissolved solid (% wt./vol.)	14.580	14.312
Silica (ppm)	38	40
Residual titrable alkali as Na_2O (gpl)	38.34	38.63

Table—II

CHARACTERISTICS OF GREEN LIQUOR BEFORE AND AFTER DESILICATION.

(I) Before desilication			
pH (ar 30°C)	13.75		
Specific gravity (grams/cc)	1.288		
Total dissolved solid (% wt /vol.)	24.42		
Silica (ppm.)	5028		
Total titrable alkali as Na_2O (gpl.)	110.04		
(II) After desilication (at different pH)			
pH (at 30°C)	11.0	12.0	13.0
Specific gravity (gms/cc.)	1.242	1.256	1.261
Total dissolved solid (% wt./vol.)	20.84	21.52	21 97
Residual silica (ppm.)	43 45	76.0	90.93
Residual titrable alkali as Na_2O (gpl)	70 51	72 26	86 33

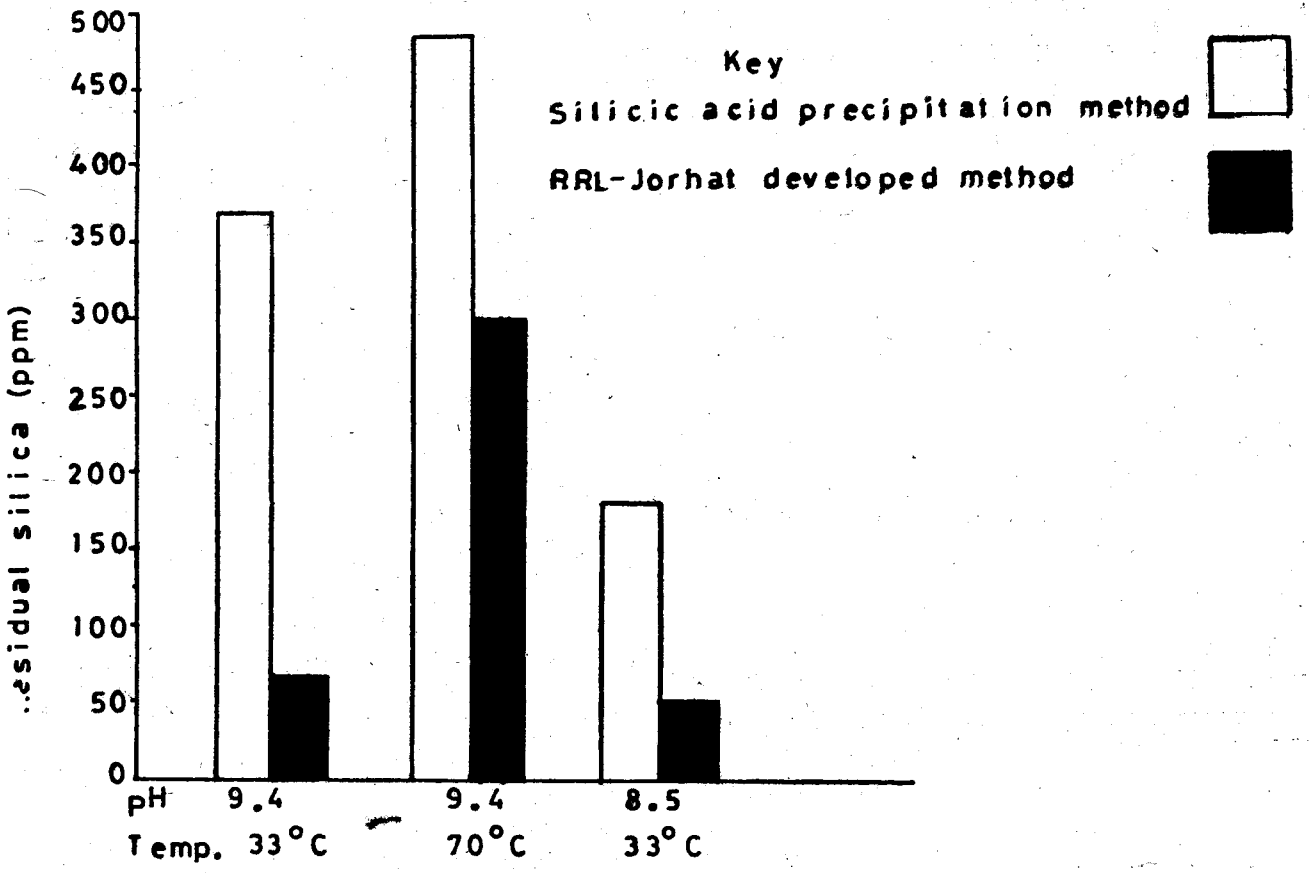

Fig. 3. Desilication of black liquor (from Tuli paper Mill, Nagaland).

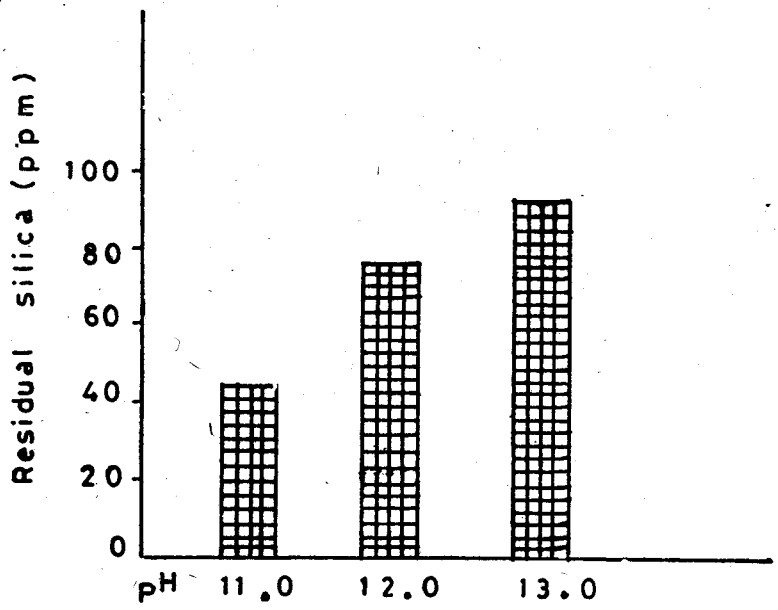

Fig. 4. Desilication of green liquor (from Naogaon Paper Mill, Assam) at 33°C.

much change in the characteristics of the original liquors except slight loss of alkali (Na_2O). It may however be indicated that the actual alkali loss will be mueh lower if alkali recovered from washing of the precipitate is also taken into account.

RECOMMENDATION

It is expected that adoption of RRL-Jt process for desilication of green liquor in paper mills will pave way for utilization of limc sludge for recovering paper grade lime. Besides, the process will generate a by product having potentiality of various industrial applications. RRL-Jt will welcome veriffcation of the process with black/green liquor samples from other paper plants and may take up optimization study of the process at scale up level in conjuction with paper mills.

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