

UTILIZATION OF LIME SLUDGE AS A FILLER IN PAPER MAKING- AN INNOVATIVE APPROACH TO COST REDUCTION AND ZERO ENVIRONMENTAL IMPACT



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Abstract :

At Yash papers ltd, about 40 MT/Day of lime sludge is generated from causticizing section with residual NaOH content below 0.4% and CaO content below 0.8%.The physico-chemical analysis of lime sludge shows 86% CaCO₃, 1.6% Sulphate, 82% ISO brightness, 99% particles having particle size less than 25 microns and abrasiveness at 0.23 mg/cm².

The study is aimed at exploring the possibilities of using lime sludge as a filler in paper making by replacing Talc either partially or fully. Experimental work and analysis was done at laboratory scale to compare filler retention, sizing and relevant physical and optical properties of paper by using 100% lime sludge as well as lime sludge & Talc (50:50) and the same were compared with properties obtained using 100% Talc as a filler.

To offset the negative impact of lime sludge on sizing 0.2%, cationic rosin was mixed with lime sludge. Also, 20% starch was added to reduce the porosity.

The study showed that lime sludge could be a low cost substitute for talc as a filler in paper making with dual advantage of zero environmental impact as well as saving integrated paper mills (specially medium sized agro based units) from capital expenditure required for installation of lime kiln.

INTRODUCTION

Lime sludge is a byproduct of soda recovery plant. Generally, it has reprocessed for lime making in lime kiln or been dumped outside as a land fill which causes much environmental nuisance. It enhances leaching, increases the hardness of ground water and decrease the fertility of soil. In agriculture, lime sludge is used in soil amendment to enhance the alkalinity of acidic soil. However, there is a constraint for non-wood pulp mill to reprocess lime sludge for lime making as the impurities and silicon is on higher side than wood based pulp mill.

Filler is the second most used raw material in some grades of paper. Filler

increase the opacity and brightness of paper as well as improves its formation and printing properties. The energy consumption of the papermaking process can also be reduced by the addition of filler since fillers can improve the capacity for water removal during the pressing and drying stages. Also, the addition of filler might reduce the production cost, because mineral fillers are often cheaper than wood fiber. In paper making inorganic fillers (Talc, PCC, GCC, and TiO₂ etc) are used along with fiber to replace a portion of expensive and scarce fiber material.

WHY LIME SLUDGE IS NOT USED AS A FILLER IN PAPER MAKING?

Our study report indicates that lime sludge decreases the sizing property and increases the porosity of paper. This is due to the negative zeta potential because of its lower purities, looser pore structure, non-uniform particle size distribution and larger particle size.

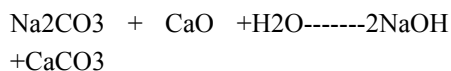
The present work attempts to provide some information on physico-chemical properties of lime sludge and its effect on papers making properties as compared with 100% Talc powder and 50:50 ratio of talc and Lime sludge. By adding cationic rosin and starch in the furnish, we have successfully used Lime sludge as a filler in paper at lab scale while maintaining paper properties.

CAUSTISIZING

Normally the green liquor is converted into white liquor by causticizing reaction. The green liquor composition is 80% Na₂CO₃, 15% NaOH and 5% Na₂S. The Na₂CO₃ reacts with lime (CaO) and convert to NaOH which is again reused

for pulping, While CaCO₃, called lime sludge is either reburnt to get back lime or disposed off as a land fill. .

Reaction of Na₂CO₃ with lime



Complete analysis of lime sludge was done (Table-1) and indicates that it mainly contains 85% CaCO₃, 3% silica, residual NaOH and CaO with Mixed oxides. The particle size test was conducted (Table-2) indicating 99% particles below 25 micron.

Table-1 : Chemical Analysis of Lime Sludge

S.NO	Parameters	value
1	Moisture %w/w	50.44
2	Calcium as Ca %w/w	33.76
3	Sodium as Na %w/w	0.43
4	Magnesium as Mg %w/w	0.86
5	Iron as Fe %w/w	0.05
6	Aluminum as Al %w/w	0.10
7	Potassium as K %w/w	0.70
8	Silica as SiO ₂ , %w/w	3.0
9	Calcium carbonate as CaCO ₃ , %w/w	84.4
10	GCV, cal/gm.	Nil
11	Residual CaO %w/w	0.33
12	Residual Na ₂ O %w/w	0.57
13	AOX mg/kg	4.5

Table-2 : Filler Properties Of Talc And Lime Sludge

Parameter	Talc (Soap stone)	Lime sludge
Silica SiO ₂ , %w/w	42.36	4.06
Residual CaO%,w/w	0.23	0.13
Mixed Oxide as R ₂ O ₃ ,%w/w	0.37	2.59
Loss on Ignition,%	4.27	40.10
Acid solubility,%	4.15	90.13
Brightness %ISO	84.0	82.0
Abrasiveness' (mg/m ²)	0.39 (1900 rpm for 24 min)	0.23 (1,70,000 revolution)
Sulfate,%	—	1.62

EXPERIMENTAL

Materials

The lime sludge collected from yash paper mill causticizing plant, had a particle size 99% are below 25 micron and 82% ISO brightness. The talc powder collected from paper machine contained 92% particles below 25 micron, and brightness of 84% ISO brightness. The lime sludge and talc used in this study were analyzed for filler properties at CPPRI & PAPRI. The fiber furnish used in this study was a blend of 97% bleached bagasse pulp and

3% bleached softwood pulp, collected from paper machine with freeness of 24 °SR. AKD, Alum, Cationic starch and Cationic rosin were also collected from mill.

Methods

Stock and Hand sheet making

To the refined pulp slurry containing 30 gm of oven dried pulp in 2 ltrs water, 2% AKD was added with stirring for 3 minutes. Then fillers were added and stirred for 3 minutes. In order to

investigate the lime sludge behavior and its effect on paper making, 10%,20% and 30% filler was added with pulp slurry for comparison with talc powder and 50:50 lime sludge and talc. In the final experiment 20% starch was added to fillers and 0.2% cationic rosin added with lime sludge and stirred for 2 minutes to diminish it negative zeta potential.

Hand sheets were prepared using circular laboratory sheet former. The wet sheets were pressed according to TAPPI test method T-205 sp-95 and then dried at

105±2 °C for 10 min. Before testing, the hand sheets were stored to 24 hr at 25 °C and at 50% relative humidity.

Testing of paper properties

The paper properties, including bulk, tensile index, burst, tear, tensile,

brightness, opacity, gloss, were tested in accordance with the relevant TAPPI test methods. The filler content was determined after the paper samples were ashed 1hr at 750 °C for talc and 900 °C for lime sludge in accordance with TAPPI method. * The ash retention in case of

50:50 lime sludge and talc is reported as such at 900 °C for 1 hr.

RESULTS AND DISCUSSION

Filler properties

The abrasiveness and scaling are the main issues for consideration of filler

Table-3 : Particle Size Distribution of Lime Sludge

Low diameter (µm)	Cumulative mass finer %	Low diameter (µm)	Cumulative mass finer %
25	99.1	3.0	12.9
20	92.5	2.5	12.1
15	50.6	2.0	11.0
10	23.7	1.5	10.3
8	21.1	1.0	10.1
6	18.5	0.6	8.7
5	16.9	0.5	8.4
4	14.7	-	-

Table-4 : Particle Size Distribution of Talc Powder

Low Diameter (µm)	Cumulative Mass Finer (%)	Low Diameter (µm)	Cumulative Mass Finer (%)
25.0	92.9	3.0	22.6
20.0	88.9	2.5	18.6
15.0	80.5	2.0	14.3
10.0	64.4	1.5	10.3
8.0	55.0	1.0	6.9
6.0	43.2	0.6	3.3
5.0	37.2	0.5	2.2
4.0	30.5	-	-

for paper making. However, we get low abrasiveness value of lime sludge than talc powder while the particle size distribution analysis report indicate that particles below 3 micron are 22% in talc and 12% in lime sludge. Both have almost same brightness level of about 80% ISO but the acid insolubility is much lower incase of lime sludge. The sulfate content of lime sludge is reported 1.6%. Analysis reports are given. (Table 2, 3 & 4)

Effect of fillers loading on paper properties

Bulk, Sizing and Porosity

The filler particle size, particle size distribution and particle shape determine the bulk of paper. Lime sludge has the

advantage of higher bulk when used as filler in comparison with talc powder. The bulk density improve by 12%, mainly on account of large particle size of lime sludge. The larger particles are able to open larger inter-fiber spaces with in paper which contributes to the bulk of paper.

The porosity of lime sludge- filled paper was much higher than talc powder-filled paper. Filler shape and particle size play an important role on the porosity. The larger particle size of lime sludge opens up pores in paper more easily, resulting in higher porosity (Table-5, 6). To reduce the porosity, we decided to fill the porousness of sheet and air voids that exist in the lime sludge with cationic starch. (Table 7, 8)

Sizing chemicals provide paper and paper board with resistance to liquid wetting, penetration and absorption. Cellulose is hydrophilic polysaccharides with a high surface energy. The porous structure of paper acts like a sponge in the presence of liquid. The purpose of internal sizing agents is to make cellulosic fibers hydrophobic and thus control the wettability of paper and operation of paper machine. The sizing process comprises retention, distribution, spreading and anchoring of the sizing agent to fiber.

The water resistance of paper filled with lime sludge is lower than talc filled paper. The negative surface charge is present in lime sludge because of residual CaO and

Table-5 : Experiment-I

Parameter	Talc powder used as a filler (30% addition)	Lime sludge used as a filler (30% addition)
GSM of lab pulp sheet (g/m ²)	82	77
Thickness (mm)	0.19	0.19
Bulk (cc/g)	2.3	2.46
Smoothness (ml/min)	65	65
Porosity (ml/min)	500	1000
Gloss (%)	20	17
Opacity (%)	86	86
Brightness (%)	84	85
Burst Factor	7.62	7.84
Tear Factor	53.01	51.28
Cobb (g/m²)	53	150
Tensile strength (kg/15 mm)	0.94	0.99
Ash (%)	10.1	12.7

Table-6 : Experiment-II

Properties	B/G-97% S/W-3% Soap Stone -30% AKD-2%	B/G-97% S/W-3% AKD-2% Lime Sludge 30% Cationic Rosin 2-3 Drops	B/G-97% S/W-3% AKD-2%, Cationic rosin 2-3 Drops LimeSludge(15%)+Soap Stone (15%)
Gsm (g/m ²)	57	65	65
Thickness (mm)	0.147	0.174	0.195
Bulk (cc/g)	2.16	2.53	2.5
Burst Factor	12.38	9.02	8.97
Tear Factor	37.68	36.29	35.89
Tensile strength (kg/15 mm)	1.25	0.8	0.94
Brightness (%)	84.5	82.7	84.3
Opacity (%)	72.7	73	73
Glass (%)	21.4	18.4	21.9
Cobb-60 (g/m²)	18	15	13
Porosity (ml/min)	750	1800	1100
Ash (%)	10.15	* 8.76	12.04

Table-7 : Experiment-III

Parameter	Bagasse+ 30 % lime sludge	Bagasse+ 30% lime sludge+20% starch
cy%	3.97	4.55
⁰ SR	15	17
Burst Factor	11.69	14.81
Tear Factor	46.67	48.27
Porosity (ml/min)	1975	1650

Table-8 : Experiment-IV

Parameter	UOM	Exp 1	Exp 2	Exp 3	Exp 4
Cationic starch	%	Nil	2.00	2.00	2.00
Soap stone	%	Nil	20.0	10.0	Nil
Cationic rosin	%	Nil	Nil	0.2	0.2
Lime sludge	%	Nil	Nil	10.0	20.0
AKD	%	2.0	2.0	2.0	2.0
Burst Factor		10.9	10.5	10.4	11.3
Tear Factor		60.0	57.1	53.9	64.0
Tensile Strength	kg/15mm	0.8	1.1	0.8	1.0
Brightness	%	83.9	84.7	85.2	85.4
Thickness	mm	0.158	0.144	0.154	0.149
Opacity	%	68.5	73.7	76.4	77.2
Smoothness	ml/min	900	1300	800	600
Porosity	ml/min	2500	2000	2400	2200
Ash	%	1.2	* 8.54	6.95	8.12
Glass Cobb	% g/m ²	18.2 25	14.4 22	13.2 24	14.6 23

Table-9 : Filler Retention

Filler	10% Addition		20% Addition		30% Addition	
	Ash %	% Ash Retention	Ash %	% Ash Retention	Ash %	% Ash Retention
Talc	5.1	51	8.54	42.7	10.15	33.83
Lime Sludge	5.1	51	8.12	40.60	12.04	40.13

NaOH and its large sized particles while consuming more of the sizing agent, also are not sized, themselves. This results in poor sizing of paper (Table-5). Cationic rosin addition in lime sludge improves the sizing in paper. (Table -6, 8).

Strength properties

There is no major difference noticed in strength with these two types of fillers. The results obtained show slightly lower properties in case of lime sludge filled paper. This is due to more filler retention in sheet as well as larger particle size of lime sludge. (Table 5,6 and 8). While lime sludge with starch gives better strength than only lime sludge-filled paper. Tear, tensile, burst increased marginally, reported (Table-7).

Ash retention and optical properties

With increasing dose of lime sludge % ash retention in paper increases (Table-9). The larger particle size distribution is also helping in increased % ash retention in case of lime sludge. The optical properties are more or less equal in all experiments. (Table 5,6 and 8)

CONCLUSION :

Laboratory scale trials have proved that the lime sludge can be definitely used as a filler in paper making either exclusively or in combination with soap stone without any adverse effect on paper properties.

Encouraged by positive findings, Yash papers Ltd proposes to conduct a plant scale trial very soon.

If successful this application will help industry to achieve twin objective of getting a low cost substitute for fillers in paper and avoiding solid waste disposal problem which poses a great challenge at present.

ACKNOWLEDGMENTS

The authors are thankful to Yash paper ltd management for giving permission to present and publish this research work. Also express thanks to Mr Vinod Srivastava, Mr Naveen Srivastava, Mr Pradeep Viswakarma and Mr Pradeep Srivastava for their valuable help in laboratory analysis work.

REFERENCES CITED

1. Using a novel fly ash based calcium silicate as a potential paper filler- *BioResources*8(2),2768-2779. Zhang et al.(2013)
2. Lindstrom,T and Larsson,P.T (2008). Alkyl kettendimer(AKD) sizing- A review- *Nordic pulp pap. Res.J.* 23(2), 202-209.
3. Fairchild, G.H. (1992).- Increasing the filler content of PCC-filled alkaline papers. *TAPPI J.* 75(8), 85-90.
4. Chauhan, Bhardwaj and Chakrabarti (2011a)- Inorganic filler- modification and retention during paper making: A review, *IPPTA J.*23(2), 93-100.
5. The effect of dead load chemicals in the Kraft pulping and recovery system-TAPPI July 2009,pg-18,23
6. Non process element control in the liquor cycle using ash leaching system TAPPI July 2010 pg -7
7. Desilication of green liquor by two stage causticizing. *IPPTA J.* Apr-Jun 2009 (Pg 103-105)
8. Effect of particle size distribution of lime sludge on the hydrophobicity of paper, *Bio Resources* 9(1),1361-1372 He et al. (2014)