Role of Sulphuric Acid in Reduction of Alum Consumption in Small Paper Mills by Controlled Methods.

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ABSTRACT

Authors of the paper feel that alum consumpfion is quite high in small paper mills as compared to big paper mills Factors effecting higher alum consumption have been studied at Shree Vindhya Paper Mills. Experiments were carried out to reduce the alum consumption with the help of sulphuric acid in the laboratory. Plant trials were also taken. From the results it appears that it is possible to reduce the alum consumption with sulphuric acid and sufficient savings can be done.

2. Introduction :

Cost of non-fibrous raw material viz. rosin and alum is increasing day by day. Efforts are being done to find out substitute for rosin as well as alum Experimentation is also going on for alkaline sizing. Experiments are also being conducted in the R&D laboratory of Shree Vindhya Paper Mills, in this direction. The present article is useful for small paper mills who are investing lot of money for procurement of alum.

3. FACTORS EFFECTING HIGHER ALUM CONSUMPTION.

(A) Water Quality.[1]

Water is one of the most important raw material for paper industry. Its characteristics should not be taken lightly as it effects on number of operations of paper making. Hard water causes sizing difficulties by reacting with rosin size, precipitating part of size as insoluble calcium of magnesium soap Another disadvantage of hard water is that by addition of alum, carbonates are decomposed and lot of alum is consumed in this phenomena. Excess alum is required to precipitale the size. The total 'alkalinity and pH are most important properties of water for paper making. Alkalinity may be caused by carbonates and hydroxides although it is more often due to carbonates and bicarbonate and hence it is related to the hardness. pH of the water varies depending upon its source and type of process used for treatment. pH and alkalinity effect on sizing. Characteristics of the water being utilised in small paper mills varies a lot and it is one of the major factor responsible for higher alum consumption.

(B) WASTE PAPER

Most of the small paper mills depend upon waste paper (indegenous and imported) for their furnish. It has been observed that certain types of waste papers, especially coated waste when used in furnish, alum consumption goes up like any thing. The reason is, presence of china clay and other alkaline materials which start consuming more alum, It is our experience, that when certain type of imported pulp and computer wastes are used in the furnish, the size consumption goes high. Investigations are being carried out to find out the cause.

(C) USE OF WHITE WATER[2]

(ii)

In most of the small paper mills the white water is reused in the system due to effluent disposal problem. The use of white water reduces the efficiency of the sizing agents as it is generally acidic and it will precipitate the size before it is thoroughly dispersed in the stock.

(D) FILLERS

Fillers (Soap stone powder) containing calcium salts, especially carbonate offers great sizing difficulties because,c alcium carbonate is decomposed at a pH

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below 6 6 and because of the reaction between calcium and resin, destroys the sizing. As there is no systematic checking of soap stone powder by small paper mills, there is every possibility that soap stone powder may be containing more carbonate.

(E) RETENTION OF CHEMICALS[2,3]

Small paper mills are using different types of imported pulps, but they are not in a position to invest more money on the laboratory equipments and R&D studies. As such it will be difficult for them to study the properties of day to day variable furnish, and hence systematic monitoring of the level of freeness etc., cannot be studied. This is also one of the reason for higher sizing chemical consumption. Added to this, if they are not having good fiber recovery system, the fiber loss and retention of fines and filler will also be poor. Over all the retention is not more than 50% in small paper mills.

4) LABORATORY EXPERIMENTS

A. RAW WATER AND TREATED WATER ANALYSIS

Raw water samples were collected from Hatnoor dam and before entering to our clarifier. Both samples were studied for their different characteristics. From the analysis it appears that our water is not hard but it has excess alkalinity. Chlorides contents and turbidity were observed high in the raw water entering to our clarifier as compared to water available at Hatnoor dam which indicates that water is polluted in the mid way by other streams meeting the river.

Treated water supplied to mill was also collected and analysed in the same way. (Table 1.)

Tolerance limits for water used in paper industry for manufacturing bleached soda and kraft papers were studied and characteristics were compared with our raw water. As per ISI and Casey total dissolved solids should not be more than 300 ppm which is around 400 ppm in our water. Casey has mentioned total alkalinity 75 ppm against 230 ppm in our case. Also the free chlorine is nil against prescribed limits of 2 ppm (Table 2)

B. REDUCTION OF pH AND ALKALINITY[4] WITH ALUM

Raw water pH can be brought to 7 and alkalinity can be reduced with addition of alum. The resultant

TABLE—1

S. No.	Characteristics	Hatnoor Dam	Inlet to Clarifier	Treated Water Analysis.
1.	pH	8.6	8.6	8.4
2.	P. Alkalinity (ppm as $CaCO_3$)	8	13	10
3.	M. Alkalinity (ppm as $CaCO_3$)	220	225	220
4.	Total Hardness (ppm as $CaCO_3$)	90	73	80
5.	Excess Alkalinity (ppm as Na_2CO_3)	140	160	150
6.	Turbidity (ppm)	10	20	8
7.	Total Dissolved solids (ppm)	430	430	460
8.	Free Chlorine (ppm)	Nil	Nil	Nil
9.	Dissolved silica (ppm as SiO_2)	20	22	22
10.	Chlorides (ppm as Cl)	30	60	60
11.	Sulphates (ppm as SO_4)	25	26	35
12.	Dissolved oxygen (ppm)	8.5	7.2	7.5

Remarks : Excess alkalinity present in the raw water is responsible for higher alum consumption.

water will be quite clear also. This can be expressed with the following reactions.

(i) $Al_2(SO_4)^3 + 6H_2O = 2Al(OH)_2 + 3H_2SO_4$

(ii) $Al_2(SO_3) + 2Ca(HCO3)^2 = 3CaSO_4 + 2Al(OH)_3 + 6CO_2$

It has been concluded that 100-125 ppm dosing of alum is required to bring PH 7.0—7.2 for our raw water (Table 3.)

TABLE—2

S. No.	Characteristics	IS 2724-1964	J.P. Casey
1.	Colour (Hazen units) (Max.)	10	25
2.	Turbidity (Max.) (scale units.)	15	40
3.	Total dissolved solids (PPM) Max.	300	300
4.	Total Hardness (PPM) Max.	100	100
5.	Free Chlorine as Cl (PPM) Max.	2.0	—
6.	M. Alkalinity as $CaCO_3$, PPM (Max)	—	75

TABLE—3

REDUCTION OF EXCESS ALKALINITY OF RAW WATER

S. No.	Characteristics	Raw Water	Raw water after addition of alum.
1.	pH	8.5	7.04
2.	P. Alkalinity (ppm as $CaCO_3$)	13	nil
3.	M. Alkalinity (ppm as $CaCO_3$)	229	173
4.	Total hardness (ppm as $CaCO_3$)	76	75
5.	Alum dosing. (ppm)	—	125
6.	Reduction in M Alkalinity (%)	—	25
7.	Reduction in P. alkalinity (%)	—	100

C. SOAP STONE POWDER

Poor quality of soap stone powder is one of the major factors responsible for higher alum consumption. This is due to the presence of higher amount of Carbonate content in soap stone powder. Table 4 shows typical analysis of good and bad quality of soap stone powder (SSP).

D. STOCK PREPARATION VARIABLES

Due to reuse of back water at different places, pH of the stock and freeness varies a lot which ultimately effect on retention. (Table. 5)

TABLE—4

S. No.	Characteristics	Specifications	Good Quality	Poor Quality
1.	pH (10% Son)	Max. 9	8.7	9.6
2.	Brightness (%)	78-80	80	76
3.	Residue on 300 mesh (%)	Max. 1.0	1.2	4.5
4.	Loss on ignition (%)	Max. 5.0	4.8	8.5

Remarks :—Higher loss on ignition shows more carbonates. It is experienced while using the above poor quality S.S.P., our alum consumption has gone high.

TABLE—5

S. No.	Pulp Quality	pH	Freeness (CSF)
1.	Wood pulp (refined)	5.24—7.88	170—450
2.	Bagasse pulp	6.58-6.90	415—440
3.	Waste Paper (CPO+Coated +Broke(	4.55-7.51	205—290
4.	Mixed stock (before addition of chemicals.)	4.8—7.4	220—400

Remarks : Variations are responsible for proper size distribution and retention.

E, REDUCTION OF ALUM WITH SULPHURIC ACID

A few experiments were carried out to see the effect of sulphuric acid. Reduction of 2% alum is possible by addition of 10% sulphuric acid on total alum consumption at a certain cobb value. (Table 6A, and 6B.)

(4) PLANT TRIALS

Sulphuric acid trials were taken for about ten days in a month. Acid was added in alum dissolving tank and alum solution mixed with acid was used in stock preparation to maintain the pH and precipitate the rosin size. Alum solution, stock (after addition of chemicals) and back water water were checked at different intervals for their respective characteristics.

Regular paper testing reports show that strength properties and cobb values are not effected adversely. It was also observed that consumption of whitening agent and rosin was also low during the trial but no conclusion can be drawn due to variation in furnish.

By addition of 6% of sulphuric acid (on alum) 3% alum saving was achieved, which may result saviug of about 40 rupees per ton of paper. (Table 7A, 7B and 8A, 8B.)

6. RESULTS AND DISCUSSIONS.[3]

Major reasons for higher alum consumption in small paper mills are raw water quality, poor quality of loading materials and assorted variety of waste paper. Raw water should be treated properly with alum to neutralize the alkalinity and and bring down pH to 7.0.

TABLE—6A

REDUCTION OF ALUM WITH SULPHURIC ACID

	(a)	(b)
A. Furnish		
i) Bagasse pulp (unrefined.)(%)	50.0	50 0
ii) CPO + Broke (%)	40.0	40.0
iii) Wood Pulp (%)	10.0	10.0
B. Chemicals and other conditions.		
i) Initial pH of mixedpulp.	7.3	7 3
ii) Initial freeness of mixed pulp	350	350
iii) Temperature °C	Ambient	Ambient
iv) Rosin added (%)	1.0	1 0
v) Alum added (%)	6.0	4.0
vi) Final pH	4.33	4 31
vii) Consistency (%)	3.0	3 0
C. Sheet Testing (50 gms.)		
i) One minute cobb (gsm)	22	23

Remarks : I) 3% consistency was maintained by addition of Raw Water.

ii) Hand sheets were made with back water (pH 4.5)

iii) In case of (a)pH of alum solution was 3.1

iv) In case of (b) pH of alum solution was reduced to 1.5 by addition of 10.78% sulphuric acid on alum.

TABLE—6B

REDUCTION OF ALUM WITH SULPHURIC ACID

	(a)	(b)
A. Furnish		
i) Bagasse pulp (Un refined) (%)	50.0	50 0
ii) CPO + Coated mixed (%)	40 0	40.0
iii) Imported wood pulp (%)	10.0	10 0
B. Chemicals and other conditions		
i) Initial pH of mixed pulp.	7.2	7.2
ii) Consistency (%)	3.0	3.0
iii) Temperature °C	Ambient	Ambient
iv) Rosin added (%)	1.0	1.0
v) Alum added (%)	6.0	4.0
vi) Final pH	4.34	4.38
C. Sheet Testing (60 gsm)		
i) 1 minutes cobb (gsm)	21	24
ii) Sizing (sec)	12-15	10-12

Remarks :— i) 3% Consistency was maintained by addition of raw warer.

ii) Hand sheets were made with back water (pH 4.7)

iii) In case of (a) pH of alum solution was 3.1

iv) In case of (b) pH of alum solution was reduced to 1.5 by addition of 10.7% sulphuric acid on alum.

This will reduce alum consumption in the stock perparation area. Excessive use of back water will save fines and fillers, however use of white water in all the places of paper machine and stock preparation tends to increase the Calcium hardness which consumes more alum. To decompose the calcium hardness, cheap and best alternative is sulphuric acid. However, excess use of sulphuric acid should also be avoided otherwise increase of sulphate ions (acidity) will result low sizing in paper.

pH, consistency and freeness are the major variables of stock preparation area which not only effect on chemical consumption but also effect on overall quality of paper. These parameters should be studied for different furnishes to achieve optimum results. Construction of stock chests with its thorough agitation for good mixing is one of the most important criteria. In addition, even though the mills are very small, it is essential to have good consistency regulators atleast in the mixing chest and the machine chest along with level indicators which helps for keeping up proper proportion of the furnish.

To optimise on addition of chemicals and to reduce the chance of error of addition in places where sophisticated instruments are not available the easiest method is to metre the chemical in dilution form. By this a better mixing of chemicals with stock is achieved and control is easier as errors are minimised. By reducing the concentration of alum solution from 100gpl to 75gpl it is possible to bring down overall consumption by 5 kgs/ ton of paper. Similar results may be obtained by reducing rosin concentration from 30 to 20 gpl.

TABEE—7 A

Characteristics of Alum Solution, Stock & Back Water (Without Sulphuric Acid.)

		(1)	(2)	(3)	(4)	(5)	(6)	Avg.
Furnish								
Bagasse. (%)		40	50	40	35	35	35	39
Imported Wood Pulp (%)		20	20	10	12	12	12	14
CPO + Coated · Broke (%)		40	30	50	53	53	53	47
Alum Solution								
pH	(Range)	2.39–2.92	2.80-2.96	2.6-3.05	2.69–2.78	2.6–2.86	2.63–3.35	
	(Avg.)	2.6	2.92	2.65	2.73	2.74	2.95	2.7
°TWD	(Range)	10–26	12–17	6–20	13–15	9.5–20	8.5–24	
	(Avg.)	15.4	13.5	15.0	13.5	12	13.4	14
Stock Characteristics After Chemical Addition								
pH	(Range)	3.9—4.2	3.97–4.37	3.88–4.6	3.9–4.25	3.95–5.22	3 88–4.29	
	(Avg)	4 01	4.14	4.22	4.08	4.3	4.06	4·09
Consistency	(Range)	3 7–4.5	3.26-3.75	3.25–3.76	3.0–4.08	3.18–4.0	3.2–3.9	
	(Avg)	4.09	3.51	3.84	3.71	3 57	3 62	3.6
Freeness (CSF)	(Range)	305–368	300–360	240–320	250–310	290–330	290–350	
	(Avg)	337	339	274	282	303	314	316
Back Water Characteristics								
pH	(Range)	4.06–5.36	4.15–4.9	4.28–6 25	4.15–5 9	4.1–6 49	3.45–4 66	
	(Avg.)	4.52	4.45	4.7	4.84	4.77	4.18	4.5
Acidity (PPM)	(Range)	29–185	40–196	9.8–100	8.8–170	7.8–111	117–133	
(as H_2SO_4)	(Avg.)	84	96	65	76	77	127	111
Hardness (PPM)	(Range)	175–350	195–230	179–290	174–310	180–356	165–400	
(as $CaCO_3$)	(Avg.)	233	220	225	247	265	228	243

TABLE—7B

CHARACTERISTICS OF ALUM SOLUTION STOCK & BACK WATER (WITH SULPHURIC ACID)

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	Avg.
Furnish										
Bagasse (%)	45	35	35	40	40	35	35	35	40	38
Imported wood Pulp (%)	25	35	35	30	20	5	10	10	30	22
(CPO + Coated + Broke.) (%)	30	30	30	30	40	60	55	55	30	40
Alum Solution										
pH (Range)	1.26–1.55	1.33–1.78	1.36–1.64	1.34–1.5	1.42–2.18	1.33-1.69	1.4-1.55	1.17—1 65	1.34—1.70	
(Avg.)	1.43	1.55	1.53	1.41	1.63	1.47	1.48	1.47	1 51	1 49
°TWD (Range)	12–17	9.5–14	13–16.5	10.5–16.5	8.5–13	14–26	12–20	12-20	12-21	
(Avg.)	15	11.2	14.2	13.1	11.2	18	15 6	14	14.9	13 7
Stock Characteristics after chemical addition										
pH (Range)	4.03–4.23	3.7–4.3	3.75–4.21	4.08–4.96	3.88–4.33	3.9–4.21	4.02–4.25	3 8—4.14	3.7—4 1	
(Avg.)	4.31	4.08	3.93	4.36	4.06	4.08	4.12	3 96	3 95	4.07
Consistency (Range)	3.05–3.75	2 85–3.47	3.42–4.42	3.5–4.4	3.1–3.75	3.33–3.83	3.74–4 02	3.64—4 3	3 62—4.43	
(Avg.)	3.39	3.43	3.81	3.96	3.44	3.62	3.85	3 99	4 09	3.73
Freeness (CSF) (Range)	325–411	277–416	319–395	280–380	265–333	205–330	280–340	280—340	250—334	
Avg.	359	323	355	311	291	283	311	309	295	326
Back Water Characteristics										
pH (Range)	4.16–5.91	4.14–4.4	4.2–4.3	5.0–6.95	3.99–5 3	4.16-5.4	4.23–4.62	4.0–4.5	4.07–4.93	
(Avg.)	4.57	4.28	4.25	5.65	4.53	4.63	4.4	4.29	4.44	4.56
Acidity (ppm) (as H_2SO_4) (Range)	15–162	78–137	68–90	3.4–24.5	14.7–392	29–166	49–95	26–300	14.7–300	
(Avg.)	96	108	75	9.7	210	93	93	216	133	116
Hardness (ppm) (as $CaCo_3$) (Range)	250–300	240–300	240–300	275–340	172–354	250–340	230–310	235–340	175–310	
(Avg.)	283	283	265	302	266	276	265	302	253	277

TABLE – 8 A.

PAPER PROPERTISES (WITH SULPHURIC ACID.)

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	AVG
Quality	C.W.60	C.W.60	C.W.60	C.W.60	C.W.60	C.W.60	C.W.60	C.W.90	C.W.60	C.W.60
Basis Weight (gsm)	59.7	59.8	60.2	59.7	59.1	57.9	60.1	59.7	58.9	59.6
Caliper(Microns)	89.2	91 5	88 5	90.1	85.8	91.5	90.4	91	96	90.4
Bulk (cc/g)	1.49	1.53	1.47	1.51	1.45	1.53	1.50	1.50	1.54	1.50
Breaking Length (M) MD	4590	4440	4000	3740	4380	4180	4320	4000	4530	4240
CD	2470	2490	2730	2225	2480	2390	2690	2460	2790	2550
Burst Factor (L&W)	15.5	15.7	14.9	13.0	14.0	13.7	13.1	13.0	13.8	14.0
Tear Factor MD	60	60	60	62	61	55	60	62	58	60
(L&W) CD	70	70	66	69	68	62	70	69	64	67
Double Folds MD	10	13	9	8	9	9	10	9	14	10
(L&W) CD	6	10	7	5	6	5	6	6	10	7
Brightness % (Lasserphot)	76	76	75	74	75	75	75	75	75	75
Opacity % (Tappi)	86	86	84	85	85	85	85	85	85	85
Porosity (sec/100 ml)	18	17	21	20	29	19	20	23	29	21
Smoothness (sec/50 ml)	50	46	52	52	49	57	51	47	61	52
Ash content. %	6.3	5.7	7.1	9.0	7.3	6.5	8.0	9.0	6.7	7.3
1 Min cobb(gsm) (top/bottom)	22/24	20/24	21/25	22/25	20/24	20/23	21/24	21/24	21/24	21/24

TABLE—8 B

PAPER PROPERTIES (WITHOUT SULPHURIC ACID.)

	(1)	(2)	(3)	(4)	(5)	(6)	Avg.
Quality	C.W.60	C.W.60	C.W.60	C.W.60	C.W 60	C.W.60	C.W.60
Basis weight (gsm)	60.1	59.8	59.0	59 4	59.0	59.4	59.4
Caliper (Microns)	90.1	91.6	94.9	92.5	94	92 1	92.5
Bulk (cc/g)	1.50	1 53	1.61	1.56	1.61	1.55	1.56
Breaking length (M) MD	4410	4690	4350	3860	3875	3800	4160
CD	2900	2840	2580	2460	2490	2470	2620
Burst Factor. (L&W)	12 2	15.4	15.1	13.9	13.9	12.0	13 6
Tear Factor MD	63	60	61	59	58	61	60
(L&W) CD	73	68	68	66	64	66	67
Brightness% (Lasserphot)	75	75	75	76	76	74	75
Double folds MD	8	9	8	8	8	8	8
(L&W) CD	5	6	6	5	6	6	6
Opacity % (Tappi)	84	85	85	85	86	84	85
Porosity (sec/100 ml)	21	16	20	23	19	19	20
Smoothness (Sec/50 ml)	52	41	60	42	44	50	48
Ash content (%)	7.1	6 2	6.9	8.4	7.1	6.8	7.0
1 Min. cobb (gsm) (top/bottom)	22/25	22/25	21/23	21/24	20/22	19/21	21/23

Concentration of gums, dyes whitening agents should also be reduced which will result in savings as well as uniform product.

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8. LITERATURE CITED

1. Pulp and paper Technology by casey (Vol. IInd).

2. Pulp and Paper Manufacturing by Stephonson (Vol. IInd).

3. Viswanathan, S.A., Subba Rao G., Trikannand, P.M., Rangan S.G. "Effective utilization of Chemicals in stock preparation" (IPPTA, March, 1982.)

4. Tappi August 1986, Page 160.

5. Unpublished data of sulphuric acid trials in different papers mills by the author.